Ontario

Protocol for Analytical Methods Used in the Assessment of Properties under Part XV.1 of the *Environmental Protection Act* and Excess Soil Quality

Laboratory Services Branch

Ministry of the Environment, Conservation and Parks

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ACRONYMS

AAS	atomic absorption spectrophotometry
ABN	acid base neutral compounds
ASTM	ASTM International (formerly the American Society for Testing and Materials)
B[a]P	benzo[a]pyrene
BTEX	benzene/toluene/ethylbenzene/xylene
CALA	Canadian Association for Laboratory Accreditation (formerly the Canadian Association for Environmental Analytical Laboratories, CAEAL)
CAS	Chemical Abstracts Service of the American Chemical Society
CCME	Canadian Council of Ministers of the Environment
CCV	continuing calibration verification
CP	chlorophenols
CRM	Certified Reference Material
C of A	Certificate of Analysis
CVAAS	cold vapour atomic absorption spectrophotometry
CVAFS	cold vapour atomic fluorescence spectrophotometry
DF	dilution factor
DLPCB	dioxin-like polychlorinated biphenyl
DNP	2,4-dinitrophenol
ECCC	Environment and Climate Change Canada
ECD	electron capture detector
EDL	estimated detection limit
EPA	*Environmental Protection Act*, R.S.O. 1990, c. E.19
FID	flame ionization detector
FOC	fraction organic carbon
GC	gas chromatography (or GLC, gas liquid chromatography)
GCxGC (or 2DGC)	two-dimensional gas chromatography
GC-ECD	gas chromatography-electron capture detector
GC-FID	gas chromatography-flame ionization detector
GC-HRMS	gas chromatography-high resolution mass spectrometry
GC-MS	gas chromatography-mass spectrometry
GC-MS/MS	gas chromatography-tandem mass spectrometry
GFAAS	graphite furnace atomic absorption spectrophotometry
HDPE	high density polyethylene
HGAAS	hydride generation atomic absorption spectrophotometry
HPLC-UV	high performance liquid chromatography with ultraviolet detector
HPLC-UV/FLU	high performance liquid chromatography with ultraviolet and fluorescence detectors
HRGC-HRMS	high resolution gas chromatography-high resolution mass spectrometry
HWSB	hot water-soluble boron
ICP	inductively coupled plasma spectroscopy
ICP-OES	inductively coupled plasma-optical emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectrometry includes single quadrupole, multiple quadrupoles, sector and multichannel instruments

ISO/IEC	International Organization for Standardization/International Electrotechnical Commission
IUPAC	International Union of Pure and Applied Chemistry
LCS	laboratory control sample
LSB, LaSB	Laboratory Services Branch
MDL	method detection limit
MECP	Ontario Ministry of the Environment, Conservation and Parks
MS	mass spectrometry
mSPLP	ministry Synthetic Precipitation Leaching Procedure or referred to as MECP method E9003
OC	organochlorine pesticide
O. Reg. 153/04	Ontario Regulation 153/04: Records of Site Condition - Part XV.1, under the *Environmental Protection Act*, R.S.O. 1990, c. E. 19
O. Reg. 406/19	Ontario Regulation 406/19: On-Site and Excess Soil Management, under the *Environmental Protection Act*, R.S.O. 1990, c. E.19
ORP	other regulated parameters
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzofuran
PET	polyethylene terephthalate
PHC	petroleum hydrocarbon
PT	proficiency testing (refers to performance testing sample)
QA	quality assurance
QC	quality control
QMS	quality management section
QP	qualified person
RL	reporting limit
RPD	relative percent difference
RSC	Record of Site Condition
SAR	sodium adsorption ratio
SIM	selected ion monitoring
SCC	Standards Council of Canada
SM	Standard Methods (American Public Health Association/American Water Works Association/Water Environment Federation)
SVOC	semi-volatile organic compound
TEF	toxic equivalency factor
TEQ	toxic equivalency
USDA	United States Department of Agriculture
U.S. EPA	United States Environmental Protection Agency
USGS-NWQL	United States Geological Survey-National Water Quality Laboratory
VOC	volatile organic compound
WHO	World Health Organization

GLOSSARY

Accreditation: Formal recognition that a testing laboratory is competent (as audited to most current IS0/IEC 17025 standard by a recognized body) to carry out specific tests or specific types of tests.

Analyte: A substance or chemical constituent that is determined in an analytical procedure, such as a titration.

Analytical Run: A group of samples processed together through each step of an analytical procedure.

Analytical Standards: A series of chemical standards of the target analytes, used to set the relationship between instrument response and concentration or qualitative verification of instrument output.

Blank: Pure Water or other type of blank (i.e., acid or solvent) used to monitor for contaminated reagents, glassware and method processes.

Composite Sample: A sample that is made up of a number of laboratory grab samples from a single sample container that have been thoroughly mixed together.

Contaminant: Any solid, liquid, gas, odour, heat, sound, vibration, radiation or combination of any of them resulting directly or indirectly from human activities that may cause an adverse effect.

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 and ISO/IEC GUIDE 33:2015).

Duplicate Sample: One of two samples taken from the same population and carried through all steps of sampling and analytical procedures in an identical manner.

Estimated Detection Limit (EDL): The estimated detection limit is based on sample signal-to-noise ratio and is typically determined on a per sample basis where the sample signal is at least 2.5-fold higher than the noise. This approach is acceptable for dioxin isotope dilution methods and where dictated by the reference methods.

Excess soil quality standards: For the purpose of this protocol, the prescribed contaminants and the quality standards for those contaminants are those set out in Tables 1 through 9 of the “Rules for Soil Management and Excess Soil Quality Standards,” which is adopted by reference in O. Reg. 406/19 (as amended from time to time).

Extractable Organic Compound: An organic compound which has a boiling point higher than water and which may vaporize when exposed to temperatures above room temperature, also known as a semi-volatile organic compound (SVOC).

Field Filter: Where required, ground water samples must be filtered using a 0.45 µm membrane filter as soon as possible after sampling and immediately preserved (if preservation is required). A 0.45 µm pore size is the default filter pore size used to separate dissolved species, unless otherwise specified in the method for a given parameter.

Field Preserve: Where required, samples must be preserved with the specified preservative for that parameter group (within 24 hours of sampling) or immediately following filtration (if filtration is required).

Hermetic Sampler: A commercially available, U.S. EPA accepted device for sampling soil for VOC analysis. The device is inserted into the soil where it collects and seals a soil core (with no headspace). The device is transported to the laboratory where the entire sample is extracted and analysed.

Holding Time: Elapsed time between sample collection and commencement of sample preparation or analysis, as appropriate.

Internal Standard: A standard that has chemical characteristics similar to those of the analyte(s) and provides an analytical response that is distinct from the analyte and not subject to interference. Internal standards are usually added to the sample or sample extract just prior to sample analysis in order to correct for variations in sample matrix, injection volume, etc.

ISO/IEC 17025 Standard: The requirements of the International Organization for Standardization/ International Electrotechnical Commission , as amended from time to time, for testing laboratories to demonstrate that they are technically competent, maintain a quality system appropriate to the scope of their activities, and are able to generate technically valid calibration or test results.

Laboratory Control Sample: A sample of known concentration used as a basis for comparison with test samples, and which undergoes sample processing identical to that carried out for test samples. This sample may also be referred to as a blank spike.

Laboratory Duplicate Sample: One of two sample aliquots obtained from the same sample container and carried through the entire analytical process. This sample may also be referred to as a split sample.

Matrix: The environment from which a given sample is taken (analytical chemistry), usually air, soil/sediment, ground water or surface water for the purposes of this document.

Method Detection Limit (MDL): The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero; it is determined from data produced by analysing a sample in a given matrix containing the analyte (CAN-P-1585-November 2006).

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.

Method of Standard Additions: The determination of analyte concentration by adding known analyte amounts (spikes) to sample aliquots. Determination is based on the slope and intercept of the standard additions curve (recovery). The analytical response must be linear. The technique is used to correct for matrix effects.

Parameter: A parameter to be tested, synonymous with other terminology such as “contaminant”, “target analyte”, or “analyte” which may be used in the regulation or other documents related to O. Reg. 153/04 or O. Reg. 406/19.

Qualified Person(s) (QP): A person as defined by O. Reg. 153/04, or O. Reg. 406/19 (as amended from time to time).

Quality Assurance (QA): Quality assurance is a system of planned activities intended to provide adequate confidence that quality requirements are being met. Quality assurance is one element of the quality system.

Quality Control (QC): Quality control is a set of operational techniques and activities intended to ensure that quality requirements are being met within known probability limits. Quality control is one part of the quality system.

Quality Control Sample: A sample (e.g., test sample or laboratory control sample/standard) used either singly or in replicate, as appropriate, to monitor performance characteristics (ISO 3534-1, 2.30).

Quality System: A set of interrelated elements (e.g., policies and objectives) that direct and control the way a facility operates with regard to quality.

Replicate Analyses: Natural samples may be split in the laboratory and analysed together in the same run. Replicates are taken through the entire method process. This data can be used to assess the within-run precision of the analysis or sample matrix homogeneity.

Replicate Sample: An additional or second aliquot (portion) of a randomly selected sample in the analytical run.

Representative Sample: A subsample of material that has been taken so that it has essentially the same composition and characteristics of the sample in the container.

Reporting Limit (RL): The concentration at which a single analysis using the methods and matrices listed in this document will consistently detect target analytes when present. The RL must be equal to or greater than the MDL.

Reference Material (RM): A material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for calibration of an apparatus, the assessment of a measurement method, or for assigning values to the materials (ISO/IEC Guide 35:2017 or more recent version). The RM should be matrix matched to the samples and carried through the entire analytical process.

Relative Percent Difference (RPD): The absolute difference between two results expressed as a percentage of the average result:

$$RPD = \left| \frac{(x_1 - x_2)}{(x_1 + x_2)/2} \right| \times 100$$

Significant Figures: The number of figures required to express a numerical determination such that only the last figure is uncertain. The number of significant figures, usually one or two for environmental tests is dependent upon method precision at the measured value.

Site Condition Standards: For the purpose of this protocol the prescribed contaminants and the site condition standards for those contaminants are those set out in Tables 1 through 9 of the Soil, Ground Water and Sediment Standards in O. Reg. 153/04, s. 34 to 39 (as amended from time to time).

Surrogate: Has chemical characteristics similar to that of the analyte and provides an analytical response which is distinct from the analyte. The surrogate(s) is normally added to the sample prior to sample preparation and is used to assess the recovery of analyte(s) carried through the analytical process.

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

Travel Blank: A clean sample of a matrix that is transported to and from the sampling site unopened and submitted to the laboratory for analysis without having been exposed to sampling procedures. A travel blank is used to document contamination attributable to preparation, shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organic compound (VOC) samples (U.S. EPA 530-D-02-002; Appendix A).

Uncertainty: A non-negative parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand (International vocabulary of metrology – Basic and general concepts and associated terms; ISO/IEC Guide 99:2007 (VIM 2007) and ISO/IEC Guide 98-1:2009 Uncertainty of measurement – Part 1: Introduction to the expression of uncertainty in measurements, as amended from time to time).

Volatile Organic Compound (VOC): Any organic compound having, at 20 °C, a vapour pressure of 0.01 kPa or more or having a corresponding volatility under the particular conditions of use, which is released into the atmosphere.

SECTION 1: INTRODUCTION

This protocol document is incorporated in **Ontario Regulation 153/04: Records of Site Condition – Part XV.1 of the *Environmental Protection Act* (O. Reg. 153/04)**. It provides specific requirements for laboratory sample submission, analysis and data reporting. As well this protocol document is referenced in **Ontario Regulation 406/19 under the *Environmental Protection Act* (O. Reg. 406/19), titled "On-Site and Excess Soil Management"** to support improved management of excess soil.

Samples must be submitted to a laboratory that is accredited by an internationally recognized accreditation body (e.g., Standards Council of Canada (SCC), or Canadian Association for Laboratory Accreditation (CALA)) in accordance with the International Standard ISO/IEC 17025:2017 – General Requirements for the Competence of Testing and Calibration Laboratories (as amended from time to time). Accreditation ensures that laboratories maintain a comprehensive documented quality system consistent with good analytical practice. Accreditation establishes a consistent basis for acceptable quality among analytical laboratories and ensures they adopt a satisfactory quality system to carry out sample analysis.

This protocol sets out the sample handling and storage requirements, analytical methods and method specific quality control and assurance procedures for laboratories established by recognized organizations: United States Environmental Protection Agency (U.S. EPA), U.S. Department of Agriculture (USDA), Ontario Ministry of the Environment, Conservation and Parks (MECP) Laboratory Services Branch (LaSB), ASTM International (formerly American Society for Testing and Materials), Standard Methods: American Public Health Association (APHA)/American Water Works Association (AWWA)/Water Environment Federation (WEF), U.S. Geological Survey (USGS) of the U.S. Department of the Interior, and the National Water Quality Laboratory (USGS-NWQL), Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup, Environment and Climate Change Canada (ECCC), and the Canadian Council of Ministers of the Environment (CCME).

The information in this protocol is provided to ensure that appropriate samples are submitted to laboratories, the samples are analysed with methods that are fit for purpose and that the results of laboratory analyses are reported with sufficient quality upon which to base decisions required for **O. Reg. 153/04** or **O. Reg. 406/19.**

Unless the wording of this protocol explicitly indicates that a statement is describing options, the words of the protocol are requirements which must be followed, subject to **O. Reg. 153/04, O. Reg. 406/19** and other applicable laws. Wording in this protocol which is explicitly mandatory, as well as wording in it which is simply descriptive, both serve to set out requirements which must be followed.

Sample processing and analysis depends largely on the chemical and physical properties of the parameter to be measured. Parameters with similar chemical and physical properties can be grouped and processed together. Section 1 contains the parameters that can be grouped and processed together.

Chemical Abstracts Service Registry Numbers (CAS RNs) for individual chemical parameters (where applicable) are listed in Table 4.1.1 (Required Reporting Limits).

1.1 Organic Parameter Groups

1.1.1 Acid/Base/Neutral Compounds (ABNs)

Parameters*

Biphenyl, 1,1-
Bis(2-chloroethyl) ether
Bis(2-chloro-1-methylethyl) ether[#]
Bis(2-ethylhexyl) phthalate
Chloroaniline, p
Dichlorobenzidine, 3,3'-
Diethyl phthalate
Dimethyl phthalate
Dimethylphenol, 2,4-
Dinitrophenol, 2,4-
Dinitrotoluene, 2,4-(2,6-)[^]
Phenol
Trichlorobenzene, 1,2,4-

*Selected ABN parameters contained within **O. Reg. 153/04 or O. Reg. 406/19**
[#]Erroneously known as bis(2-chloroisopropylether)
[^]The sum of 2,4- and 2,6-dinitrotoluene is compared to the standard

1.1.2 Chlorophenols (CPs)

Parameters*

Chlorophenol, 2-
Dichlorophenol, 2,4-
Trichlorophenol, 2,4,6-
Trichlorophenol, 2,4,5-
Pentachlorophenol

*may also be determined with ABNs

1.1.3 1,4-Dioxane

Parameters*

Dioxane, 1,4-

*may also be determined with ABNs or VOCs

1.1.4 Dibenzo-p-Dioxins/Dibenzofurans (Dioxins/Furans, PCDDs/PCDFs)

Parameters

Congener group	2,3,7,8-Substituted Isomers
total tetrachlorodibenzo-p-dioxins (T4CDDs)	2,3,7,8-T4CDD
total pentachlorodibenzo-p-dioxins (P5CDDs)	1,2,3,7,8-P5CDD
total hexachlorodibenzo-p-dioxins (H6CDDs)	1,2,3,4,7,8-H6CDD
	1,2,3,6,7,8-H6CDD
	1,2,3,7,8,9-H6CDD
total heptachlorodibenzo-p-dioxins (H7CDDs)	1,2,3,4,6,7,8-H7CDD
octachlorodibenzo-p-dioxin (O8CDD)	1,2,3,4,6,7,8,9-O8CDD
total tetrachlorodibenzofurans (T4CDFs)	2,3,7,8-T4CDF
total pentachlorodibenzofurans (P5CDFs)	1,2,3,7,8-P5CDF
	2,3,4,7,8-P5CDF
total hexachlorodibenzofurans (H6CDFs)	1,2,3,4,7,8-H6CDF
	1,2,3,6,7,8-H6CDF
	1,2,3,7,8,9-H6CDF
	2,3,4,6,7,8-H6CDF
total heptachlorodibenzofurans (H7CDFs)	1,2,3,4,6,7,8-H7CDF
	1,2,3,4,7,8,9-H7CDF
octachlorodibenzofuran (O8CDF)	1,2,3,4,6,7,8,9-O8CDF

1.1.5 Organochlorine Pesticides (OCs)

Parameters (Synonym)

Aldrin
Chlordane, *alpha*- (α-chlordane)[1]
Chlordane, *gamma*- (γ-chlordane)[1]
DDD[3]
DDE[3]
DDT[3]
Dieldrin
Hexachlorocyclohexane, *gamma*- (γ-HCH, lindane, γ-BHC[#])
Endosulfan I (thiodan sulphate I)[2]
Endosulfan II (thiodan sulphate II)[2]
Endrin
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Hexachlorobutadiene
Hexachloroethane
Methoxychlor (DMDT)

[#]erroneously known as benzene hexachloride (BHC)

[1]the sum of *alpha*- and *gamma*-chlordane is compared to the standard

[2]the sum of endosulfan I and II is compared to the standard

[3]DDT standard applies to the total DDT (i.e., sum of the DDT isomers), the DDE standard applies to total DDE (i.e., sum of the DDE isomers), and the DDD standard applies to the total DDD (i.e., sum of the DDD isomers).

1.1.6 Petroleum Hydrocarbons (PHCs)

Parameters

Petroleum hydrocarbons (PHCs) (C_6–C_{10} Fraction)
F1 (C_6 to C_{10})
Petroleum hydrocarbons (PHCs) (C_{10}–C_{50} Fraction)
F2 (C_{10} to C_{16}),
F3 (C_{16} to C_{34}),
F4† (C_{34} to C_{50}),
F4G† (gravimetric)

†the larger result obtained for F4 and F4G is compared to the standard

1.1.7 Polychlorinated Biphenyls (PCBs)

Parameters

Aroclor 1242
Aroclor 1248
Aroclor 1254
Aroclor 1260
polychlorinated biphenyls (PCBs), total

1.1.8 Polycyclic Aromatic Hydrocarbons (PAHs)

Parameters (Synonym)

Acenaphthene
Acenaphthylene
Anthracene
Benz[a]anthracene
Benzo[a]pyrene (B[a]P)
Benzo[b]fluoranthene
Benzo[g,h,i]perylene
Benzo[k]fluoranthene
Chrysene
Dibenz[a,h]anthracene
Fluoranthene
Fluorene
Indeno[1,2,3-cd]pyrene
Methylnaphthalene, 2-(1-)†
Naphthalene
Phenanthrene
Pyrene

†the sum of 1- and 2-methylnapthalene is compared to the standard

1.1.9 Trihalomethanes (THMs)

Parameters* (Synonyms)

Bromodichloromethane (dichlorobromomethane)

Bromoform (tribromomethane)

Chloroform (trichloromethane)

Dibromochloromethane (chlorodibromomethane)

*may also be determined with VOCs

Note that the compounds in the list above are commonly detected as a result of chlorination of drinking water and, therefore, are included as a separate group from the volatile organic compounds (Section 1.1.10).

1.1.10 Volatile Organic Compounds I: (VOCs)

Parameters (Synonyms)

Acetone (propanone)

Carbon tetrachloride (tetrachloromethane)

Chlorobenzene

Dichlorobenzene, 1,2-

Dichlorobenzene, 1,3-

Dichlorobenzene, 1,4-

Dichlorodifluoromethane

Dichloroethane, 1,1-

Dichloroethane, 1,2-

Dichloroethylene, 1,1- (dichloroethene)

Dichloroethylene, *trans*-1,2- (dichloroethene)

Dichloroethylene, *cis*-1,2- (dichloroethene)

Dichloropropane, 1,2-

Dichloropropene, *cis*-1,3-† (dichloropropylene)

Dichloropropene, *trans*-1,3-† (dichloropropylene)

Ethylene dibromide (dibromoethane, 1,2-)

Hexane, n-**

Methyl ethyl ketone (MEK)**

Methyl isobutyl ketone (MIBK)**

Methyl *tert*-butyl ether (MTBE)**

Methylene chloride (dichloromethane)

Styrene

Tetrachloroethylene (tetrachloroethene, perchloroethylene)

Tetrachloroethane, 1,1,1,2-

Tetrachloroethane, 1,1,2,2-

Trichloroethane, 1,1,1-

Trichloroethane, 1,1,2-

Trichloroethylene (trichloroethene)

Trichlorofluoromethane

Vinyl chloride (chloroethene)

†the sum of *cis*- and *trans*-dichloropropene is compared to the standard

**may also be determined with BTEX

1.1.11 Volatile Organic Compounds II: Benzene, Toluene, Ethylbenzene, Xylene (BTEX)

Parameters* (Synonyms)

Benzene

Ethylbenzene

Toluene (methylbenzene)

Xylenes, total (o-xylene; m- & p-xylene)

*may also be determined with VOCs

Note that the above BTEX compounds (benzene, toluene, ethylbenzene, xylenes) are a subset of volatile organic compounds (VOCs), are often requested as a discrete analysis and, therefore, are included as a separate group from the VOCs (Section 1.1.10).

1.1.12 Volatile Organic Compounds III: Bromomethane

Parameters* (Synonyms)

Bromomethane[†] (methyl bromide)

*may also be determined with VOCs

[†]methanol-preserved samples may elevate the detection limit for bromomethane; a separate bisulphate-preserved sample or hermetically sealed sample may be submitted at the time of sampling if bromomethane is a chemical of concern.

Note that bromomethane is a subset of volatile organic compounds (VOCs), and is often analysed as a discrete analysis and, therefore, is included as a separate group from the VOCs (Section 1.1.10).

1.2 Inorganic Parameter Groups

1.2.1 Calcium and Magnesium (Ca, Mg)

Parameters

Calcium (Ca)
Magnesium (Mg)

1.2.2 Metals

Parameters

Barium (Ba)
Beryllium (Be)
Boron (B)
Cadmium (Cd)
Chromium (Cr)
Cobalt (Co)
Copper (Cu)
Lead (Pb)
Molybdenum (Mo)
Nickel (Ni)
Silver (Ag)
Thallium (Tl)
Uranium (U)
Vanadium (V)
Zinc (Zn)

1.2.3 Metals, Hydride-Forming (As, Se and Sb)

Parameters*

Antimony (Sb)
Arsenic (As)
Selenium (Se)

*may also be determined with the other metals by ICP-MS, or ICP-OES

1.2.4 Sodium (Na)

Parameters

Sodium (Na)

1.3 Other Regulated Parameters (ORPs)

Parameters*

Boron, hot water soluble (HWS)
Chloride
Cyanide
Electrical conductivity
Fraction of organic carbon (FOC)
Hexavalent chromium
Nitrate
Nitrite
Nitrogen (total)
Mercury
Methyl mercury
Particle size
pH
Sodium adsorption ratio (SAR)

*The ORPs listed above are single parameter tests

Fraction organic carbon (FOC) is calculated from total organic carbon.

1.4 Leachates

Parameters

Leachates for volatile organics and cyanide parameters

Leachates for Metals and Semi-volatile Organics (exclusive of VOC and cyanide)

To support O. Reg. 406/19, a leachate test has been introduced to protect ground and surface water from contaminants that may be leached from soil by rainwater. This leachate test is a modified version of the U.S. EPA's Synthetic Precipitation Leaching Procedure (SPLP). Leachates will be generated using two leaching fluids prescribed in the ministry Synthetic Precipitation Leaching Procedure (mSPLP)[1], based on test parameters requiring analysis.

[1] Until January 1, 2022, when a sample of *soil* is submitted for leachate analysis, the leachate extraction shall be completed using either the ministry Synthetic Precipitation Leaching Procedure (E9003 or mSPLP), the Synthetic Precipitation Leaching Procedure (U.S. EPA, SW-846 Method 1312), the Toxicity Characterization Leaching Procedure (U.S. EPA, SW-846 Method 1311) or another method approved by the Director. After January 1, 2022 the ministry Synthetic Precipitation Leaching Procedure (E9003 or mSPLP) or another method approved by the Director must be used.

SECTION 2: SAMPLE HANDLING AND STORAGE REQUIREMENTS

This section provides details on the procedures for sample handling and storage, including sample container, volume, preservation and storage requirements, and maximum holding times for all regulated analytes.

It is especially important for samples requiring organic analysis, that samples be placed in the appropriate containers and the cooling begun as soon as possible after sampling. Sufficient ice or other coolants should be added to produce a temperature less than (<) 10 °C. Note that samples arriving at the laboratory on the day of sampling may not have had time to achieve a temperature of < 10 °C. This is acceptable if the cooling process has begun.

Ground Water Sample Containers

Extractable organics testing in ground water samples is “whole bottle” analysis where the entire sample is extracted, and the bottle rinsed with solvent. This is necessary to prevent analyte losses due to adsorption on the container walls. Thus, additional containers are required for laboratory QC (duplicates and matrix spikes). Similarly, for volatile organics testing, additional vials are required for laboratory QC and possible repeats because once a vial has been sampled it is not suitable for further testing. Consult the laboratory for the correct number of sample vials.

Most inorganic tests have differing container and preservative requirements. Chloride and electrical conductivity can be determined from a single unpreserved sample.

Ground Water Samples Requiring Hexavalent Chromium Analysis

Samples requiring analysis for hexavalent chromium in ground water are field filtered, immediately followed by field preservation. The samples are field filtered through a 0.45 µm membrane filter and within 24 hours of sampling the pH is adjusted within the recommended range with the addition of a buffer solution (please refer to Section 3.1.2.10 for specific details). Unpreserved samples must be preserved by the laboratory within 24 hours of sampling. Unfiltered, preserved samples are not suitable for laboratory filtration. The filter media must be proven clean (i.e., analyte of interest is below the method detection limit).

Soil and Sediment Sample Containers

For organic compound testing, each analysis requires about 10 grams of sample, thus, multiple tests can be conducted on a full 125 mL or 250 mL soil container. A separate container, usually 40 – 60 mL, is required for volatile organics testing. A single container will normally suffice for inorganic tests.

Soil and sediments samples requiring analysis for VOCs, BTEX, PHC (F1), THMs, bromomethane and 1,4-dioxane[#] are preserved in the field with methanol or collected using hermitically sealed sampling devices. For BTEX and PHC (F1), this is an accepted deviation from the CCME method. An additional sample collected in a glass jar is required for moisture content determination. Each batch of methanol-preserved soil samples requires an additional vial pre-charged with methanol for the travel blank.

[#]**Note:** 1,4-dioxane can be treated as either an ABN or as a VOC; please use the appropriate sample handling based on how its analysis will be conducted.

Note: Tables A and B and the notations below them provide the requirements for sample containers, sample preservation, sample storage and sample holding times. The specified information on the number of sample containers and container sizes is a guide. Always consult the laboratory prior to sampling. The laboratory will provide sufficient appropriate containers for the required scope of testing. Collection of multiple sample containers is encouraged to avoid the need for resampling if the sample is consumed or compromised during shipping and/or analysis.

Soil and Sediment Samples for Leachates:

Soil and sediment samples which will require leachate analysis should be submitted in appropriate containers (See Table A). Multiple sampling containers may be submitted and a minimum sample size of 125 grams (metal/semi-volatile organics and VOC/cyanide analysis) is required, although a 500 gram sample will allow for all compounds to be analysed and for duplicate analysis.

TABLE A: SOIL AND SEDIMENT Sample Handling and Storage Requirements

SOIL Inorganic Parameters	Container[1]	Field Preservation	Storage Temp.[2]	Preserved Holding Time[3]	Unpreserved Holding Time[3]
Chloride, Electrical conductivity (EC)	glass, HDPE, PP or PET	none	5 ± 3 °C		30 days as received (without lab drying); indefinite when dried at the lab
Cyanide (CN^-)	glass jar (Teflon™ lined lid) or PP	protect from light	5 ± 3 °C		14 days
Fraction organic carbon (FOC), Nitrogen (total)	glass, HDPE, PP or PET	none	5 ± 3 °C		28 days as received (without lab drying); indefinite storage time when dried
Hexavalent chromium	glass, HDPE or PP	protect from light	5 ± 3 °C		30 days as received
Metals (includes hydride-forming metals, SAR, HWS boron, Calcium, Magnesium, Sodium)	glass, HDPE or PP	none	5 ± 3 °C		180 days as received (without lab drying); indefinite when dried at the lab
Mercury, Methyl mercury	glass, HDPE, PP or PET	none	5 ± 3 °C		28 days
pH	glass, HDPE, PP or PET	none	5 ± 3 °C		30 days as received
SOIL Organic Parameters	**Container**[1,5,6,7,19]	**Field Preservation**	**Storage Temp.**[2]	**Preserved Holding Time**[3]	**Unpreserved Holding Time**[3]
BTEX[8], PHCs (F1)[8], THMs, VOCs[7], Bromomethane	40–60 mL glass vial (charged with methanol preservative, pre-weighed)[6] AND glass jar (for moisture content) (hermetic samplers are an acceptable alternative)[5, 18]	methanol (aqueous $NaHSO_4$ is an acceptable alternative for bromomethane)[6, 7, 18]	5 ± 3 °C	14 days[3]	hermetic samples: stabilize with methanol preservative within 48 hours of sampling[18]

SOIL Organic Parameters	Container[1,5,6,7, 19]	Field Preservation	Storage Temp.[2]	Preserved Holding Time[3]	Unpreserved Holding Time[3]
1,4-Dioxane[9, 15]	glass jar (Teflon™ lined lid)[9, 15, 18]		5 ± 3 °C		when processed as a VOC sample: same as per VOCs above; when processed as an extractable: same as per ABNs below; (consult laboratory)[18]
PHCs (F2–F4)	glass jar (Teflon™ lined lid)	none	5 ± 3 °C		14 days
ABNs, CPs, OCs, PAHs	glass jar (Teflon™ lined lid)	none	5 ± 3 °C		60 days
Dioxins and furans, PCBs	glass jar (Teflon™ lined lid)	none	5 ± 3 °C		indefinite storage time
SOIL Sample for LEACHATE Preparation	**Container** [1,5,6,7]	**Field Preservation**	**Storage Temp.**[2]	**Preserved Holding Time**[3]	**Unpreserved Holding Time**[3]
VOC, cyanide, metals and semi-volatiles	glass jar, Teflon or PET	none	5 ± 3 °C		14 days
Metals	glass jar, Teflon, PET or PP	none	5 ± 3 °C		180 days
LEACHATE Extracts	**Container** [1,5,6,7]	**Field Preservation**	**Storage Temp.**[2]	**Preserved Holding Time**[3]	**Unpreserved Holding Time**[3]
Volatile organics	40–60 mL glass vials (no headspace)	protect from light	5 ± 3 °C		14 days
Semi volatile organics, and Cyanide	glass jar	protect from light	5 ± 3 °C		14 days
Mercury	glass jar, Teflon or PET	none	5 ± 3 °C		28 days
Metals	HDPE or PET	none	5 ± 3 °C		180 days

HDPE = high density polyethylene; PET = polyethylene terephthalate; PP = polypropylene (bags acceptable) HWS = hot water-soluble boron; THM = trihalomethanes; VOC = volatile organic compounds; BTEX = benzene, toluene, ethylbenzene, xylenes; PHCs = petroleum hydrocarbons; CPs = chlorophenols; PCBs = polychlorinated biphenyls; OCs = organochlorine pesticides

Semi-volatiles organics = 1,4-Dioxane, PHCs (F2–F4), ABNs, CPs, OCs, PAHs, Dioxins and furans, PCBs

[1–19] footnotes immediately follow Table B

Table B: Ground Water Sample Handling and Storage Requirements

GROUND WATER Inorganic Parameters	Container[10]	Field Preservation	Storage Temperature[2]	Preserved Holding Time[3]	Unpreserved Holding Time[3]
Chloride, Electrical conductivity (EC)	HDPE, PET or glass	None	5 ± 3 °C		28 days
Nitrate, Nitrite and Nitrogen (total)	HDPE, PET or glass	None	5 ± 3 °C		7 days
Cyanide (CN^-)	HDPE, PET or glass	NaOH to pH > 12	5 ± 3 °C	14 days	must be field preserved
Hexavalent chromium	HDPE or glass	field filter followed by buffer solution designed to reach the specified pH[17]	5 ± 3 °C	28 days[17]	24 hours[17]
Metals (includes Hydride-forming Metals, Calcium, Magnesium, Sodium)	HDPE, PET[4] or Teflon™ [10]	field filter followed by HNO_3 to pH < 2 [11]	room temperature when preserved	60 days	must be field preserved
Mercury	glass or Teflon™ [10]	field filter followed by HCl to pH < 2 [11]	room temperature when preserved	28 days	must be field preserved
Methyl mercury	glass or Teflon™	HCl or H_2SO_4 to pH < 2 [12]	5 ± 3 °C	28 days	must be field preserved[12]
GROUND WATER Organic Parameters[10, 13, 14]	**Container[10, 13, 14]**	**Field Preservation**	**Storage Temperature[2]**	**Preserved Holding Time[3]**	**Unpreserved Holding Time[3]**
BTEX, PHCs (F1), THMs, VOCs, Bromomethane	40–60 mL glass vials (minimum of 2)[14] (no headspace)	$NaHSO_4$ or HCl to a pH < 2[16]	5 ± 3 °C	14 days	7 days (must preserve for BTEX)
1,4-Dioxane[9, 15]	same as per VOCs above or; as per ABNs below; (consult laboratory)[9, 15]		5 ± 3 °C	14 days	14 days
PHCs (F2–F4)	glass, Teflon™ lined lid	$NaHSO_4$ or HCl to a pH < 2[16]	5 ± 3 °C	40 days	7 days
ABNs, CP, OCs, PAHs, PCBs	glass, Teflon™ lined lid	none	5 ± 3 °C		14 days

GROUND WATER Organic Parameters[10, 13, 14]	Container[10, 13, 14]	Field Preservation	Storage Temperature[2]	Preserved Holding Time[3]	Unpreserved Holding Time[3]
Dioxins and furans	glass, Teflon™ lined lid	none	5 ± 3 °C		indefinite storage time

HDPE = high density polyethylene; THM = trihalomethanes; VOC = volatile organic compounds; BTEX = benzene, toluene, ethylbenzene, xylenes; PHCs = petroleum hydrocarbons; CPs = chlorophenols; PCBs = polychlorinated biphenyls; OCs = organochlorine pesticides: PET = Polyethylene Terephthalate, PP = polypropylene (bag acceptable)

1. One soil container is generally sufficient for inorganic analysis and another for extractable organics. A separate container is required for BTEX, THM, VOC, bromomethane and PHC (F1) moisture analysis.
2. Storage temperature refers to storage at the laboratory. Samples should be cooled and transported as soon as possible after collection.
3. Holding time refers to the time delay between time of sample collection and time stabilization/analysis is initiated. For samples stabilized with methanol, the holding time for the recovered methanol extract is up to 40 days from the date of methanol recovery which must occur within 14 days of sampling.
4. For PET containers, preservatives are known to leach antimony under certain circumstances.
5. As an alternative, the U.S. EPA has investigated hermetic sample devices that take and seal a single core sample. The sample is submitted “as is” to the laboratory where it is extruded into an extracting solvent. Samples must be received at the laboratory within 48 hours of sampling. Consult the laboratory for the number of samples required.
6. The U.S. EPA has approved field preservation. Pre-weighed vials containing known weights of methanol preservative (or aqueous sodium bisulphate if used for bromomethane) are sent to the field. Sample cores (approximately 5 grams) are extruded directly into the vial. The vials are sealed and submitted directly to the laboratory. In practice, this technique requires great care to prevent losses of methanol due to leaking vials or through splashing. Consult the laboratory for the number of containers required.
7. Methanol-preserved samples may elevate the detection limit for bromomethane (VOC); a separate bisulphate-preserved sample or hermetically sealed sample may be submitted at the time of sampling if bromomethane is a chemical of concern – contact the laboratory to determine if a separate sample should be collected.
8. For BTEX and PHC (F1) pre-charging the soil sampling container with methanol preservative is an accepted deviation from the CCME method.
9. 1,4-Dioxane may be analysed with the ABNs or VOCs; sample container requirements used for ABNs or VOCs are both acceptable. Consult the laboratory for the container type and the total number required (see also footnote #15).
10. Samples containing visual sediment at the time of analysis should be documented and noted on the Certificate of Analysis or written report as results may be biased high due to the inclusion of sediment in the extraction.
11. Field filter with 0.45 µm immediately prior to adding preservative or filling pre-charged container.
12. Sample directly into a HCl or H_2SO_4 preserved container or add acid to an unfiltered sample immediately after sample collection in the field

13. Aqueous organic samples should be protected from light. If amber bottles are not available, glass should be wrapped in foil.
14. Separate containers are required for each organic water analysis. Consult the laboratory for required volumes. Chloride and electrical conductivity can be taken from the same container.
15. For 1,4-dioxane in soil and sediment, no preservative is required if processed as an ABN; however, methanol is an acceptable alternative if processed as a VOC. For 1,4-dioxane in ground water, no preservative is required, however, $NaHSO_4$ or HCl are acceptable alternatives.
16. Preserved to reduce biodegradation, however, effervescence/degassing may occur in some ground water samples. In this case, rinse preservative out three times with sample and submit to the laboratory as unpreserved.
17. To achieve the 28-day holding time, use the ammonium sulfate buffer solution (i.e., $(NH_4)_2SO_4/NH_4OH$) or $(NH_4)_2SO_4/NH_4OH/NaOH + NaOH$) as specified in U.S. EPA Method 218.6 (revision 3.3, 1994) or Standard Methods 3500-Cr Chromium (2009). Ground water samples must be preserved with ultra-pure concentrated NH_4OH to pH > 9 for analysis by ion chromatography coupled to an ICP-MS. Using only NaOH without the ammonium sulfate buffer to adjust the pH would require analysis within 24 hours of sampling.
18. Alternatively, to achieve a longer hold time, hermetic samples may be frozen within 48 hours of sampling as per ASTM method D6418 – 09; however, storage stability must be validated by the laboratory with no more than 10% losses.
19. Special care must be used when sampling for VOC, BTEX, bromomethane and PHC (F1) in soil and sediment. Studies have shown that substantial losses can occur through volatilization and bacterial degradation. There are several allowable options for field collection of samples. Each is discussed below. Consult SW846, Method 5035A for additional detail. The laboratory is required to stabilize the sample on the day of receipt, either by extraction or freezing.

2.1 Subsampling

The procedures described cover common situations when subsampling solid and liquid samples in the laboratory. When such situations arise, these procedures shall be followed. All actions taken to obtain representative samples other than those described below must be included in the Certificate of Analysis or written report so that the Qualified Person (QP) will be able to properly assess the data and be able to determine if the data are of sufficient quality upon which to base decisions required for **O. Reg. 153/04** or **O. Reg. 406/19**. It should be noted that no drying is required for excess soil samples that are intended for leachate analysis.

Note: For samples submitted for laboratory analyses outlined in this protocol, the laboratory is not expected to perform milling and/or crushing of rocks and stones for size reduction.

2.1.1 Procedure: Soil and Sediment – Inorganic/Other Regulated Parameters

1. Prior to homogenization or drying, samples are to be inspected in the laboratory for multiphase conditions (free water, petroleum product, etc.) or other anomalies. Small amounts of free water or petroleum product may be mixed with the sample, but large amounts of free water or petroleum product should be separated. The QP should be contacted and an agreement reached on how to proceed. All such anomalies and the actions taken must be noted in the Certificate of Analysis or analytical report.

   Drying may change the pH of the soil; therefore, pH is conducted on the sample as received. Also, because of potential volatilization losses for cyanide and possible redox reactions for hexavalent chromium, aliquots for these tests are also taken from the sample as received. To determine moisture content, a separate aliquot is taken and dried at 105 °C overnight or until a constant weight is achieved.

   The sample is mixed as well as possible and several aliquots are taken to obtain the desired weight. Hard clay samples that cannot be mixed are “cored”, using a spatula in different spots or sections of the jar. Stones, twigs and other foreign materials are excluded. To ensure a representative subsample is obtained, a minimum 10 grams aliquot is taken.

2. For other inorganic soil and sediment tests, the entire sample (or representative sub-sample) is air or oven dried at a temperature of ≤ 60 °C to prevent the potential loss of volatile analytes, for a minimum of 48 hours, or less if no visible moisture remains.

   Stones, twigs and other foreign materials are excluded from the subsamples.

   Physical reduction of large clay aggregates is required.

   Samples are then passed through a 2 mm sieve. Any portion that does not pass through this sieve is discarded. Minimum 5 grams aliquots of the 2 mm portion of the sample are then used in the analysis of chloride, electrical conductivity, sodium absorption ratio and hot water-soluble boron.

3. A subsample of the 2 mm portion is then taken and ground to pass through a 355 µm sieve in its entirety. This portion is then used in the analysis of all metal parameters including hydride-forming metals, mercury and fraction organic carbon.

Fraction Organic Carbon (FOC):

A minimum of three 5 grams subsamples are required for each soil sample requiring FOC analysis; samples are analysed and reported in triplicate.

2.1.2 Subsampling of excess soils for leachate analysis

Excess soil samples received by the laboratory for mSPLP leachate analysis are not subjected to drying prior to leachate extraction. A sample is evaluated if physical reduction or milling of large clay aggregates is required. Stones, twigs and other foreign materials are excluded to ensure a representative subsample is obtained (milling or crushing of this material is not expected to occur in the laboratory). Samples are then passed through a 9.5 mm sieve and a minimum 100 grams aliquot is taken for mSPLP extraction as described in section 1.4. To avoid volatilization losses, for VOC and cyanide, there should be minimal sample manipulation apart from removal of stones, twigs and other foreign objects.

2.1.3 Procedure: Soil and Sediment – Organic Parameters

1. Prior to subsampling, samples are inspected for multiphase conditions (free water, petroleum product, etc.) or other anomalies. Small amounts of free water or petroleum product may be mixed with the sample, but large amounts of free water or petroleum product should be separated. The QP should be contacted and asked how to proceed. All such anomalies and the actions taken must be noted in the Certificate of Analysis.

2. Samples requiring organic analysis for ABNs, dioxins, CPs, OC pesticides, PAHs, PCBs and 1,4-dioxane[#] are air dried for a minimum of 48 hours, or until no visible moisture remains, ground, and homogenized. Alternately to drying, samples can be mixed with equal amounts of anhydrous sodium sulphate, or until the sample resembles a free-flowing powder. Stones, twigs and other foreign materials are excluded from the subsamples.

3. Field preserved samples requiring analysis for volatile analytes (VOC; BTEX; PHC (F1), THM, bromomethane and 1,4-dioxane[#]) are processed as received. Samples collected in hermetic sampling devices are extruded directly into the extraction solvent.

4. Samples requiring analysis for PHC (F2, F3, F4 and F4G) are not field preserved. The use of sodium sulphate as a drying agent could lead to an exothermic reaction and thus should not be used. A minimum of 5 grams dry weight of the soil is taken for analysis. The extraction fluid is added immediately after weighing to minimize volatilization losses.

5. For all other organic analyses, the sample is mixed as well as possible and several aliquots are taken to obtain the desired weight. Hard clay samples that cannot be mixed are "cored", using a spatula in different spots or sections of the jar. Stones, twigs and other foreign materials are excluded. The extraction fluid should be added as soon as possible after weighing to minimize sample degradation.

[#]**Note:** 1,4-dioxane can be treated as either an ABN or as a VOC; please use the appropriate sample handling based on how its analysis will be conducted.

2.1.4 Procedure: Ground Water Samples – Inorganic/Other Regulated Parameters

Prior to subsampling, samples are inspected for particulate and the approximate amount of visible particulate (v/v) noted. If particulate is > 5% v/v, the QP is contacted. It may be necessary to separate the solids and treat as separate samples. If multiphase samples are encountered, (usually petroleum product on the surface), the non-aqueous phase is excluded from any subsamples. This is also noted and reported.

Chloride, Cyanide

Shake and pour the sample. Alternatively, an aliquot may be syringe filtered or decanted to prevent instrument problems.

Electrical Conductivity

Do not shake, dilute or alter the samples in any way as this can alter the result. Pour the sample into the sample cup or measurement vessel.

Hexavalent Chromium

Samples requiring analysis for hexavalent chromium in ground water are field filtered through a 0.45 µm filter immediately followed by field preservation as described under "Ground Water Samples Requiring Hexavalent Chromium Analysis" at the beginning of Section 2. Unpreserved samples must be preserved by the laboratory within 24 hours of sampling. Unfiltered, preserved samples are not suitable for laboratory filtration. The filter media must be proven clean (i.e., analyte of interest is below the method detection limit).

Nitrate, Nitrite and Nitrogen (total)

Nitrogen (total) is the sum of total Kjeldahl nitrogen (the sum of ammonia-nitrogen and organic nitrogen) and nitrate/nitrite nitrogen and can be derived by monitoring for organic nitrogen compounds, free-ammonia, and nitrate-nitrite individually and adding the components together.

Metals, Including Hydride-Forming Metals

Ground water sample analysis for metals must be carried out on the dissolved fraction.

Dissolved Metals, Including Mercury

Samples requiring analysis for dissolved metals and mercury in ground water are field filtered through a 0.45 µm filter immediately followed by field preservation. Unfiltered, preserved samples are not suitable for laboratory filtration. The filter media must be proven clean.

2.1.5 Ground Water Samples – Organic Parameters

Volatile Organic Compounds

Volatile organic compound samples (e.g., VOC; BTEX; PHC (F1); THM and bromomethane) are treated differently than extractable organic samples. Samples should be received in replicate VOC vials. 1,4-dioxane would be included here if treated as a VOC.

1. When sampling, the vials or bottles should be filled slowly to the top rim of the container so that a dome or convex meniscus is present. A slight loss of sample may occur when the cap is applied. When capped, the cap or septum should be in contact with the sample so that no air is trapped in the sample container and when the vial or bottle is turned upside down, any air bubble present should not cover the bottom of the vial. The Teflon™ liner, not the silicone or rubber backing of the septum, must be in contact with the sample.

2. Prior to analysis, samples are inspected for particulate and the approximate amount of visible particulate (v/v) noted. They are also examined for headspace and if on inversion, there is an air bubble present that covers the bottom of the vial, the sample is compromised and should not be analysed. If the client requires analysis, the data must be reported qualified.

3. If the sample contains a non-aqueous layer, it is generally unsuitable for analysis. If the client requires analysis, an aliquot may be removed with a syringe from below the non-aqueous layer, analysed and the data qualified.

Extractable Organic Compounds

Extractable organic analytes tend to be hydrophobic and will adsorb to both the sample bottle and any particulate in the sample. As such, the default method of analysis is “whole sample” analysis in which the entire contents of the sample are extracted, the sample bottle rinsed with solvent and the combined extract used for analysis. Inclusion of particulates will tend to produce a high bias.

1. Prior to extraction, the sample is inspected for particulate and a non-aqueous phase. If there is no non-aqueous phase, the amount of particulate (if any) is noted and reported on the Certificate of Analysis or analytical report, the entire sample is extracted, the sample bottle rinsed with solvent and the combined extract used for analysis.

2. If a surface “sheen” is observed, it is noted and reported but the sample is treated as in number 1 above.

3. If a substantial (separable) non-aqueous layer is observed, the QP is contacted for instructions as to how to proceed. If instructions are not received, the non-aqueous layer is separated from the aqueous layer, its volume estimated, and it is retained for possible analysis. The aqueous layer is extracted as in number 1 above.

SECTION 3: ANALYTICAL METHODS

The analytical methods described in this section derive from the following sources:

ASTM International (formerly American Society for Testing and Materials) (www.astm.org)

Canadian Council of Ministers of the Environment (CCME) (www.ccme.ca)

Environment and Climate Change Canada (www.ec.gc.ca)

Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup (www.mass.gov/orgs/bureau-of-waste-site-cleanup-massdep)

Ontario Ministry of the Environment, Conservation and Parks (MECP) Laboratory Services Branch (LaSB); email requests for these methods can be sent to LaboratoryServicesBranch@ontario.ca

Standard Methods for the Examination of Water and Wastewater: American Public Health Association (APHA)/American Water Works Association (AWWA)/Water Environment Federation (WEF) (www.standardmethods.org)

United States Environmental Protection Agency (U.S. EPA; www.epa.gov)

United States Geological Survey (USGS) of the United States Department of the Interior, (www.usgs.gov) and the National Water Quality Laboratory (USGS-NWQL) (http://nwql.usgs.gov)

Laboratories are required to verify that all procedures in the analytical method are documented and based on the latest valid edition of the reference method. Modifications to the analytical method are limited to the instructions provided in the method principle outlined below. All modifications to the analytical method must be documented; the method must be validated and must contain a statement that the method is fit for the intended use with respect to the sensitivity, selectivity, analytical range, and the method precision and bias.

All the method validation, quality assurance and quality control requirements in Section 5 must be met.

3.1 Analytical Method Summaries

The methods are organized according to the type of parameter for which each method may be used.

There are several cases below where it is stated that test groups can be analysed together. Combining test groups may compromise analytical conditions. Such combinations are permitted only when all the required performance standards in Tables 5-1 through to 5-15 are met.

3.1.1 Organic Parameters

3.1.1.1 Acid/Base/Neutral Compounds (ABNs)

Parameters*

Biphenyl, 1,1-
Bis(2-chloroethyl) ether
Bis(2-chloro-1-methylethyl) ether[#]
Bis(2-ethylhexyl) phthalate
Chloroaniline, p-
Dichlorobenzidine, 3,3'-
Diethyl phthalate
Dimethyl phthalate
Dimethylphenol, 2,4-
Dinitrophenol, 2,4-
Dinitrotoluene, 2,4-(2,6-)[^]
Phenol
Trichlorobenzene, 1,2,4-

* Selected ABN parameters contained within **O. Reg. 153/04 or O. Reg. 406/19**

[#] Erroneously known as bis(2-chloroisopropylether)

[^] The sum of 2,4- and 2,6-dinitrotoluene is compared to the standard

Table 3.1.1.1 Acid/Base/Neutral Compounds (ABNs)*

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Preparation** SW-846, Method 3540C SW-846, Method 3541 SW-846 Method 3546 SW-846, Method 3550C SW-846, Method 3570 **Sample Cleanup** SW 846 Method 3610B SW846 Method 3630C **Analysis** SW-846, Method 8270E EPA Method 1625C	**Sample Preparation** SW-846, Method 3510C SW-846, Method 3520C SW-846, Method 3535A **Analysis** SW-846, Method 8270E EPA Method 1625C
Standard Methods		Method 6410B
MECP-LaSB		E3265

Method principle

Aqueous or soil samples, as received, are fortified with surrogates and extracted with a solvent or solvent mix (Table 3.1.1.1).

Soil and sediment samples are to be air dried or can be mixed with anhydrous sodium sulphate prior to extraction. Ground water sample extraction must be carried out at pH <2 (acid extractables) and >11 (base neutral extractables). Extracts are dried, concentrated and exchanged

into a solvent compatible with the cleanup (if necessary) or determinative technique being employed.

Internal standards are added after all preparation and cleanup steps are completed. Extracts can be kept for up to 40 days. Analysis is by gas chromatography-mass spectrometry (GC-MS) operated in either the full scan or selected ion monitoring (SIM) mode. The SIM mode provides lower detection limits while the full scan mode provides diagnostic capability and permits investigation of non-target analytes.

Derivatization when required involves a chemical reaction that converts the phenol and chlorophenol analytes of interest to their corresponding esters resulting in improved chromatography and detection limits. Cleanup techniques remove interferences that may impact quantitation and degrade column performance. In general, derivatization will not be required to achieve the required reporting limits (RLs) for phenols and chlorophenols. Cleanup may be required for difficult samples and laboratories may elect to perform cleanups routinely to extend column life.

Quantitation is by the internal standard method.

3.1.1.2 Chlorophenols (CPs)

Parameters*

Chlorophenol, 2-
Dichlorophenol, 2,4-
Trichlorophenol, 2,4,6-
Trichlorophenol, 2,4,5-
Pentachlorophenol

*may also be determined with ABNs

Table 3.1.1.2 Chlorophenols (CPs)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Preparation** SW-846, Method 3540C SW-846, Method 3541 SW-846, Method 3546 SW-846, Method 3550C SW-846, Method 3570 **Analysis** SW-846, Method 8270E	**Sample Preparation** SW-846, Method 3510C SW-846, Method 3520C SW-846, Method 3535A **Analysis** SW-846, Method 8270E
Standard Methods		Method 6410B Method 6420C 6410B
MECP-LaSB	E3504	E3265 E3552

Method principle

Reference methods in Table 3.1.1.2 shall be followed with the following addition: ground water samples must be acidified to pH < 2 prior to liquid/liquid extraction in order to achieve adequate recoveries. Solid phase extraction procedures (Method 3535A) may not require acidification.

3.1.1.3 1,4-Dioxane

Parameters*

Dioxane, 1,4

*may also be determined with ABNs or VOCs

Table 3.1.1.3 1,4-Dioxane

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Introduction** SW-846 Method 5021A SW-846 Method 5035A **Sample Preparation** SW-846, Method 3540C SW-846, Method 3541 SW-846 Method 3546 SW-846, Method 3550C **Analysis** SW-846, Method 8270E EPA 1624C EPA 1625C	**Sample Introduction** SW-846 Method 5000 SW-846 Method 5030C **Sample Preparation** SW-846, Method 3510C SW-846, Method 3520C SW-846, Method 3535A **Analysis** SW-846, Method 8270E EPA 1624C EPA 1625C EPA 522
MECP-LaSB		E3534

Method principle

1,4-Dioxane is a water-soluble organic compound which can be analysed either as an extractable organic or volatile organic compound (Reference methods are included in Table 3.1.1.3)

Because 1,4-dioxane recovers (or purges) poorly, isotope dilution, where the native analyte is quantitated using the deuterated analog (EPA1624C, EPA 1625C) is required. Other than quantitation by isotope dilution, all other facets of the preparation and analysis are similar to the analysis of VOCs (Table 3.1.1.10) or ABNs (Table 3.1.1.1).

3.1.1.4 Dibenzo-p-Dioxins/Dibenzofurans (Dioxins/Furans, PCDDs/PCDFs)

Parameters

Congener Groups	2,3,7,8-Substituted Isomers
total tetrachlorodibenzo-p-dioxins (T4CDDs)	2,3,7,8-T4CDD
total pentachlorodibenzo-p-dioxins (P5CDDs)	1,2,3,7,8-P5CDD
total hexachlorodibenzo-p-dioxins (H6CDDs)	1,2,3,4,7,8-H6CDD
	1,2,3,6,7,8-H6CDD
	1,2,3,7,8,9-H6CDD
total heptachlorodibenzo-p-dioxins (H7CDDs	1,2,3,4,6,7,8-H7CDD
octachlorodibenzo-p-dioxin (O8CDD)	1,2,3,4,6,7,8,9-O8CDD
total tetrachlorodibenzofurans (T4CDFs)	2,3,7,8-T4CDF
total pentachlorodibenzofurans (P5CDFs)	1,2,3,7,8-P5CDF
	2,3,4,7,8-P5CDF
total hexachlorodibenzofurans (H6CDFs)	1,2,3,4,7,8-H6CDF
	1,2,3,6,7,8-H6CDF
	1,2,3,7,8,9-H6CDF
	2,3,4,6,7,8-H6CDF
total heptachlorodibenzofurans (H7CDFs)	1,2,3,4,6,7,8-H7CDF
	1,2,3,4,7,8,9-H7CDF
octachlorodibenzo-p-furan (O8CDF)	1,2,3,4,6,7,8,9-O8CDF

Table 3.1.1.4.A Dibenzo-p-Dioxins/Dibenzofurans (Dioxins/Furans, PCDDs/PCDFs)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	SW-846, Method 3545A SW-846, Method 3546 SW-846, Method 8290A Method 1613B	Method 1613B SW-846, Method 8290A
Environment Canada	EPSI/RM/19	EPSI/RM/19
MECP-LaSB	E3572	E3418

Method principle

This analytical method is used to determine the concentrations of dioxins (PCDDs) and furans (PCDFs) in a variety of matrices using isotope dilution with high resolution mass spectrometric detection (HRMS).

Solid samples are dried, ground and homogenized. All samples are fortified prior to sample extraction, digestion, or elution, with known amounts of ($^{13}C_{12}$-) isotopically labelled PCDDs and PCDFs. All analytes are quantified using isotope dilution against labelled standards. Solid samples are extracted using Soxhlet, microwave or pressurized liquid extraction (PLE) with solvent (Table 3.1.1.4), followed by a chromatographic cleanup procedure to remove any potential chemical interference.

Aqueous samples are extracted with solvent (Table 3.1.1.4), followed by a chromatographic cleanup procedure to remove potential chemical interferences. Extracts are stable indefinitely. The final extracts are analysed using high resolution gas chromatography-high resolution mass spectrometry (HRGC-HRMS).

Calculation of toxic equivalents (TEQ)

There are a total of 210 dioxins and furans. Only 17 are toxic (2,3,7,8-substituted congeners) and their toxicity is normalized to 2,3,7,8-TCDD (the most toxic). The TEQ is determined (as shown in the following example) by multiplying the concentration of each detected 2,3,7,8-substituted congener by its respective toxic equivalency factor (TEF) to determine its toxic equivalence (TEQ). The TEFs in the following table are those provided by the World Health Organization (WHO), 2005, as amended from time to time. For any 2,3,7,8-substituted congeners that are not detected, half of the estimated detection limit (EDL) is multiplied by the TEF to determine the TEQ for that congener. This converts each of the congeners to 2,3,7,8-TCDD toxic equivalents. The sum of the 17 toxic equivalents gives the TEQ (toxic equivalent) for the sample normalized to 2,3,7,8-TCDD. The result in this example is 1.65 pg/L.

Table 3.1.1.4.B TEQ Example

Compound	CAS Number	Conc. pg/L	EDL pg/L	TEF WHO2005	TEQ / congener pg/L
2,3,7,8-T4CDD	1746-01-6	ND	1.1	1	0.550
1,2,3,7,8-P5CDD	40321-76-4	ND	1.0	1	0.500
1,2,3,4,7,8-H6CDD	39227-28-6	ND	1.2	0.1	0.0600
1,2,3,6,7,8-H6CDD	57653-85-7	ND	0.89	0.1	0.0445
1,2,3,7,8,9-H6CDD	19408-74-3	ND	1.0	0.1	0.0500
1,2,3,4,6,7,8-H7CDD	35822-46-9	ND	1.1	0.01	0.00550
OCDD	3268-87-9	3.4		0.0003	0.00102
2,3,7,8-T4CDF	51207-31-9	ND	1.0	0.1	0.0500
1,2,3,7,8-P5CDF	57117-41-6	ND	1.0	0.03	0.0150
2,3,4,7,8-P5CDF	57117-31-4	ND	1.0	0.3	0.150
1,2,3,4,7,8-H6CDF	70648-26-9	ND	0.82	0.1	0.0410
1,2,3,6,7,8-H6CDF	57117-44-9	ND	1.1	0.1	0.0550
2,3,4,6,7,8-H6CDF	60851-34-5	ND	1.1	0.1	0.0550
1,2,3,7,8,9-H6CDF	72918-21-9	ND	1.2	0.1	0.0600

Compound	CAS Number	Conc. pg/L	EDL pg/L	TEF WHO2005	TEQ / congener pg/L
1,2,3,4,6,7,8-H7CDF	67562-39-4	ND	0.95	0.01	0.00475
1,2,3,4,7,8,9-H7CDF	5567-89-7	ND	1.0	0.01	0.00500
OCDF	39001-02-0	1.8		0.0003	0.000540
TOTAL TEQ 2,3,7,8-TCDD (0.5 DL) (Sum of the TEQ/congener for each compound listed above					1.65 pg/L

TEQ = toxic equivalents = sum of individual TEQ/congener

EDL = estimated detection limit (sample specific detection limit based on sample signal-to-noise ratio

TEF = toxic equivalency factor based on WHO 2005

Report format

The source and year of the TEF values used to calculate the TEQ must be identified.

3.1.1.5 Organochlorine Pesticides (OCs)

Parameters (Synonym)

Aldrin

Chlordane, *alpha*–(α-chlordane)[1]

Chlordane, *gamma*–(γ-chlordane)[1]

DDD[3]

DDE[3]

DDT[3]

Dieldrin

Hexachlorocyclohexane, *gamma*-(γ-HCH, lindane, γ-BHC[#])

Endosulfan I (thiodan sulphate I)[2]

Endosulfan II (thiodan sulphate II)[2]

Endrin

Heptachlor

Heptachlor epoxide

Hexachlorobenzene

Hexachlorobutadiene

Hexachloroethane

Methoxychlor (DMDT)

[#] erroneously known as benzene hexachloride (BHC)

[1] the sum of *alpha*- and *gamma*-chlordane is compared to the standard

[2] the sum of endosulfan I and II is compared to the standard

[3] DDT standard applies to the total DDT (i.e., sum of the DDT isomers), the DDE standard applies to total DDE (i.e., sum of the DDE isomers), and the DDD standard applies to the total DDD (i.e., sum of the DDD isomers.)

Table 3.1.1.5 Organochlorine Pesticides (OCs)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Preparation** SW-846, Method 3540C SW-846, Method 3541 SW-846, Method 3545A SW-846, Method 3546 SW-846, Method 3550C SW-846, Method 3570 **Sample Cleanup** SW-846 Method 3610B SW-846, Method 3620C SW-846, Method 3630C SW-846, Method 3660B **Analysis** SW-846, Method 8081B SW-846, Method 8270E	**Sample Preparation** SW-846, Method 3510C SW-846, Method 3520C SW-846, Method 3535A **Sample Cleanup** SW-846, Method 3610B SW-846, Method 3620C SW-846, Method 3630C SW-846, Method 3660B **Analysis** SW-846, Method 8081B SW-846, Method 8270E
Standard Methods		Method 6410B Method 6630B Method 6630C Method 6630D
MECP-LaSB	E3487	E3488

Method principle

Each soil sample is extracted in a solvent or solvent mix (Table 3.1.1.5). Extraction methods include using Soxhlet extraction or ultrasonic bath followed by vortex shaker. Alternatively, pressurized fluid extraction may be used for soil or sediment samples.

Each aqueous sample is extracted with a solvent or solvent mix (Table 3.1.1.5). After extraction, a number of cleanup techniques may be applied, depending on the sample matrix and the determinative analytical method.

Soil and ground water extracts can be kept for 40 days.

Samples are analysed using dual-column gas chromatography with electron capture detector (GC-ECD) or gas chromatography-mass spectrometer (GC-MS). The GC-ECD is more sensitive than the GC-MS for highly chlorinated compounds but the ECD is nonspecific and more subject to interferences. Thus, sample cleanup is required, and second column confirmation of target analyte is required. Alternatively, samples may be analysed by comprehensive two-dimensional gas chromatography with electron capture detector (GCxGC-ECD).

3.1.1.6 Petroleum Hydrocarbons (PHCs)

Parameters (Synonym)

Petroleum hydrocarbons (PHCs) (C_6–C_{10} Fraction)
F1 (C_6 to C_{10})
Petroleum hydrocarbons (PHCs) (C_{10}–C_{50} Fraction)
F2 (C_{10} to C_{16}),
F3 (C_{16} to C_{34}),
F4† (C_{34} to C_{50}),
F4G† (gravimetric)

†the larger result obtained for F4 and F4G is compared to the standard

Table 3.1.1.6 Petroleum Hydrocarbons (PHCs)

Method Reference Source	Soil & Sediment	Ground Water
CCME	**Sample Preparation and Analysis** Reference Method for the Canada-wide Standard for Petroleum Hydrocarbons (CWS-PHC) in Soil – Tier 1 Method, 2001 Reference Method for the Canada-wide Standard for Petroleum Hydrocarbons (CWS-PHC) in Soil – Tier 1 Method – Addendum 1, 2002	**Analysis** Reference Method for the Canada-wide Standard for Petroleum Hydrocarbons (CWS-PHC) in Soil – Tier 1 Method, 2001 Reference Method for the Canada-wide Standard for Petroleum Hydrocarbons (CWS-PHC) in Soil – Tier 1 Method – Addendum 1, 2002
U.S. EPA		SW 846 Method 5030C (F1) SW 846 Method 5021A (F1) SW 846 Method 8015M (F1–F4)
MECP-LaSB	E3398	E3421

PHCs in soil and sediment

Note: The analysis of petroleum hydrocarbons (PHCs) must be in accordance with the Canadian Council of Ministers of the Environment (CCME) method[2], which is composed of both “prescriptive” and “performance based” elements. The method also contains mandatory chromatography performance elements. For BTEX and PHC (F1) pre-charging the soil sampling container with methanol preservative is an accepted deviation from the CCME method.

[2] Canadian Council of Ministers of the Environment (CCME) “Reference Method for the Canada-wide Standard for Petroleum Hydrocarbons (CWS-PHC) in Soil – Tier 1 Method.”

Method principle

Fraction F1 is determined by processing a field-preserved soil or sediment sample as received (approximately 5 grams) within 14 days from sampling, then analysing by purge & trap or headspace gas chromatography with a flame ionization detector (GC-FID). Hermetic samplers and freezing are additional sample handling options that require modified preparation techniques–see Section 3.1.1.10 (VOCs) for details. Methanol must be removed from the soil/sediment sample within 14 days of sampling to give recovered methanol.

Recovered methanol extracts must be analysed within 40 days from date of methanol removal.

Fractions F2, F3, F4 are determined by extracting a minimum of 5 grams dry weight soil sample with 50:50 hexane/acetone in a Soxhlet apparatus or equivalent. The solvent recovered from the extracted soil sample is back extracted with water to remove and/or minimize the acetone content in the organic extract. The organic extract is dried using sodium sulphate and treated either *in situ* or by column chromatography with silica gel to remove polar material (50:50 dichloromethane/ hexane). Recovered solvent extracts are analysed within 40 days from extraction. The extract is analysed by GC-FID.

Moisture content is determined as described in Section 2.1.1 (1).

For F1, the sample is analysed by gas chromatography with a 100% polydimethylsiloxane (DB-1 or equivalent) column and a flame ionization detector. All area counts are integrated from the beginning of the nC_6 peak to the apex of the nC_{10} peak to give F1. Standards containing nC_6, nC_{10} and toluene are run. Toluene is used as a calibration standard. The nC_6 and nC_{10} response factors must be within 30% of the response factor for toluene.

For F2, F3, F4, the sample is analysed by gas chromatography with a 100% polydimethylsiloxane (DB-1 or equivalent) column and a flame ionization detector. It must be demonstrated daily that the average response factors for nC_{10}, nC_{16} and nC_{34} must be within 10% and the response factor of nC_{50} must be within 30% of the average response factor for nC_{10} nC_{16} and nC_{34}. The hydrocarbon concentrations are calculated in the following three ranges.

F2 result, nC_{10} to nC_{16} hydrocarbons, is determined by integration of all area counts from the apex of the nC_{10} peak to the apex of the nC_{16} peak. The average response factor for nC_{10}, nC_{16} and nC_{34} hydrocarbons is used for primary calibration.

F3 result, nC_{16} to nC_{34} hydrocarbons, is determined by integration of all area counts from the apex of the nC_{16} peak to the apex of the nC_{34} peak. The average response factor for nC_{10}, nC_{16} and nC_{34} hydrocarbons is used for primary calibration.

F4 result, nC_{34} to nC_{50} hydrocarbons, is determined by integration of all area counts from the apex of the nC_{34} peak to the apex of the nC_{50} peak. The average response factor for nC_{10}, nC_{16} and nC_{34} hydrocarbons is used for primary calibration. The GC response factor of the nC_{50} must be within 30% of the average response factor of the $nC_{10,}$ nC_{16} and nC_{34} hydrocarbons. This result gives fraction F4 provided that the chromatogram descends to baseline by the retention time of nC_{50}.

F4G, gravimetric analysis is determined if the chromatogram does not return to baseline at or before C_{50}. A 5 grams or greater soil sample is extracted with 50:50 hexane/acetone. The solvent is evaporated, and the weight of residue determined. If the result is less than 50% of the applicable standard specified for the soil texture and proposed use, stop the analysis and report this result. If the result is higher than 50% of the applicable site condition standard, the sample is reconstituted in 50:50 dichloromethane/hexane, treated with silica gel one time only, re-evaporated and the weight of residue determined. Both the F4 (GC) result and the F4G (gravimetric) result are reported, but the greater result is reported as Fraction F4 and used for purposes of comparison to the applicable site condition standard in **O. Reg. 153/04 or O. Reg. 406/19.**

F2–F4 analysis of high organic carbon soils

Soils and sediment with high organic content, such as peat, may exceed the capacity of the silica gel to remove non petroleum hydrocarbons. If it is suspected that a sample extract may overload the silica gel a pre-dilution of the extract is allowed; however, any dilution will result in a higher reporting limit as such the dilution should be limited to ensure the modified reporting limit is lower than any standard that will used to compare with sample results. Gas chromatography-mass spectrometric (GC-MS) analysis may also be used to identify non-petroleum hydrocarbons. The reference method also suggests comparison to background samples. See the Reference Method for the Canada-wide Standard for Petroleum Hydrocarbons (CWS-PHC) in Soil – Tier 1 Method for additional detail.

PHCs in ground water

Note: A national method has not been approved for water samples. However, analysis of petroleum hydrocarbons (PHCs) in ground water must be in accordance with performance requirements in Table 3.1.1.6.

Method principle

Fraction F1 is determined by purging a volume of a ground water sample, then analysing by gas chromatography with a flame ionization detector (GC-FID).

Fractions F2, F3 and F4 are determined by extraction with hexane. Recovered extracts may be kept for up to 40 days from extraction. The solvent recovered from the extracted sample is dried using sodium sulphate and can be treated either *in situ* or by column chromatography with silica gel to remove polar material (50:50 dichloromethane/hexane). The extract is then analysed by GC-FID.

For F1, the sample is analysed by gas chromatography with a 100% polydimethylsiloxane (DB-1 or equivalent) column and a flame ionization detector. All area counts are integrated from the beginning of the nC_6 peak to the apex of the nC_{10} peak to give F1. Standards containing nC_6, nC_{10} and toluene are run. Toluene is used as the calibration standard. The nC_6 and nC_{10} response factors must be within 30% of the response factor for toluene.

For F2, F3, F4, the sample is analysed by gas chromatography with a 100% polydimethylsiloxane (DB-1 or equivalent) column and a flame ionization detector as shown in method principle for petroleum hydrocarbons in soil and sediment.

Calculations:

For F1 in soil and sediment, the result is corrected for the soil moisture extracted into the methanol. The total solvent/water volume (Vt) is calculated using the following equation:

$$Vt\ (mL) = methanol\ volume\ (mL) + \left(\frac{\%\ moisture \times sample\ wet\ weight\ (g)}{100}\right)$$

The results of PHC analysis need not include either benzene/toluene/ethylbenzene/xylenes (BTEX) or polycyclic aromatic hydrocarbons (PAHs). If concentrations of BTEX and/or PAHs are determined, both corrected and uncorrected results must be reported as follows:

F1, $F1_{-BTEX}$

F2, $F2_{-napthalene}$

F3, $F3_{-PAH}$[3]

F4, $F4_{-PAH}$[3] F4G

3.1.1.7 Polychlorinated Biphenyls (PCBs)

Parameters

Aroclor 1242

Aroclor 1248

Aroclor 1254

Aroclor 1260

Polychlorinated biphenyls, total (PCBs)

Table 3.1.1.7 Polychlorinated Biphenyls (PCBs)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Preparation** SW-846, Method 3540C SW-846, Method 3541 SW-846, Method 3545A SW-846, Method 3546 SW-846, Method 3550C SW-846, Method 3570	**Sample Preparation** SW-846, Method 3510C SW-846, Method 3520C SW-846, Method 3535A

[3] PAH = subtract appropriate PAH, phenanthrene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, fluoranthene, dibenz[a,h]anthracene, indeno[1,2,3-c,d] pyrene, pyrene, or any other determined PAH from appropriate fraction

Method Reference Source	Soil & Sediment	Ground Water
	Sample Cleanup SW-846, Method 3610B SW-846, Method 3620C SW-846, Method 3630C SW-846, Method 3640A SW-846, Method 3660B SW-846, Method 3665A **Analysis** SW-846, Method 8082A SW-846, Method 8270E	**Sample Cleanup** SW-846, Method 3610B SW-846, Method 3620C SW-846, Method 3630C SW-846, Method 3640A SW-846, Method 3660B SW-846, Method 3665A **Analysis** SW-846, Method 8082A SW-846, Method 8270E
Standard Methods		Method 6630B Method 6630C Method 6630D Method 6431
ASTM		Method D5175-91 (2017)e1
USGS	O-5129-95	
MECP-LaSB	E3487	E3488

Method principle

An aliquot of a solid sample is extracted with a solvent or solvent mix (Table 3.1.1.7). Extracts may be kept for up to 40 days. The extract is cleaned up using an approved reference method (Table 3.1.1.7) technique.

After sample cleanup, the extract is analysed by injecting an aliquot of the sample into a gas chromatograph with an electron capture detector (GC-ECD). Analysis may be performed using single or dual column. Alternatively, samples may be analysed by comprehensive two-dimensional gas chromatography with electron capture detector (GCxGC-ECD).

Aqueous samples are extracted, then concentrated, reconstituted, and analysed by GC-ECD. Typical extraction solvents are methylene chloride or methylene chloride:hexane.

Alternatively, gas chromatography-mass spectrometry (GC-MS) or comprehensive two-dimensional gas chromatography with electron capture detector (GCxGC-ECD) may be used, provided the reporting limits (RLs) in Table 4 can be achieved and the quantitation protocol described below is used.

PCB Identification and Quantitation:

The concentrations of PCBs may be determined by either an Aroclor or a congener approach.

An Aroclor approach generally involves the quantitation of four Aroclors: 1242, 1248, 1254 and 1260. Each Aroclor contains a mixture of individual PCB congeners that form a distinctive recognizable pattern in the chromatogram. Identification is accomplished by comparing the sample chromatogram to reference chromatograms of the individual Aroclors. Retention times and relative intensities of at least three and preferably five major peaks must match the reference

spectrum within specified limits for positive identification. A concentration for each of the identified peaks and the average concentration of all identified peaks are calculated. Acceptance limits are retention times ± 6 seconds relative to a standard of that Aroclor and ratios within ±20% of the reference Aroclor.

If the sample contains a single Aroclor, compare the response of the major peaks in the identified Aroclor to the reference Aroclor chromatogram and calculate the concentration of each. The average of the major peak concentrations is the concentration of the Aroclor (after including appropriate dilution factors).

If more than one Aroclor is identified and quantified, "total PCB" is the sum of the identified and quantitated Aroclors. If an Aroclor other than 1242, 1248, 1254 or 1260 (e.g., 1016) is identified in the sample, a reference spectrum must be obtained and included in the quantification.

In cases where chromatographic patterns indicate the presence of PCBs, but it is difficult to assign a specific Aroclor(s), analyst judgement is used to best select the best fit. If a mixture or extreme weathering is evident, such that individual Aroclor identification is not possible, quantitate using a total area sum (excluding any "non-PCB" peaks) and comparing the sum against the Aroclor or Aroclor mixture that most closely resembles the sample. In this case "total PCB" is the result obtained using the total area sum.

The Aroclors in the environment may have been subjected to degradation ("weathering") or affected by other factors. Such weathered PCB mixtures may have significant differences in peak patterns compared to those of Aroclor standards.

A congener approach provides another means to determine "Total PCBs" by measuring a selected group of the 209 possible PCB congeners. The congener approach can potentially provide better quantitative accuracy. Congener analysis is routinely completed by GC-HRMS, GC-MSMS and GCxGC-ECD.

3.1.1.8 Polycyclic Aromatic Hydrocarbons (PAHs) (may be analysed with ABNs)

Parameters (Synonyms)

Acenaphthene	Benzo[g,h,i]perylene	Indeno[1,2,3-cd]pyrene
Acenaphthylene	Benzo[k]fluoranthene	Methylnaphthalene, 2-(1-)[†]
Anthracene	Chrysene	Naphthalene
Benz[a]anthracene	Dibenz[a,h]anthracene	Phenanthrene
Benzo[a]pyrene (B[a]P)	Fluoranthene	Pyrene
Benzo[b]fluoranthene	Fluorene	

[†]the sum of 1- and 2-methylnapthalene is compared to the standard

Table 3.1.1.8 Polycyclic Aromatic Hydrocarbons (PAHs)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Preparation** SW-846, Method 3540C SW-846, Method 3541 SW-846 Method 3546 SW-846, Method 3550C SW-846, Method 3570 **Sample Cleanup** SW-846, Method 3610B SW-846, Method 3630C **Analysis** SW-846, Method 8270E	**Sample Preparation** SW-846, Method 3510C SW-846, Method 3520C SW-846, Method 3535A **Sample Cleanup** SW-846, Method 3611B **Analysis** SW-846, Method 8270E
Standard Methods		Method 6440C
MECP-LaSB	E3425	E3480

Method principle

Soil samples fortified with deuterium-labelled surrogates are extracted using a solvent or solvent mix (Table 3.1.1.8). Cleanup of the extract is optional.

Aqueous samples, fortified with surrogates, are extracted with solvent (Table 3.1.1.8). If only PAHs are being determined, extraction may be at neutral or basic pH.

Extracts may be kept for up to 40 days. The sample extract is concentrated and then analysed by means of gas chromatography-mass spectrometry (GC-MS), with or without using selected ion monitoring (SIM) mode.

See Section 3.1.1.1 (ABNs) for additional detail.

3.1.1.9 Trihalomethanes (THMs)

Parameters* (Synonyms)

Bromodichloromethane (dichlorobromomethane)

Bromoform (tribromomethane)

Chloroform (trichloromethane)

Dibromochloromethane (chlorodibromomethane)

*may also be determined with ABNs or VOCs

Note that the above list of compounds are commonly detected as a result of chlorination of drinking water and, therefore, are included as a separate group from the volatile organic compounds (VOCs). The method principle for THMs is identical to the VOCs as outlined in Section 3.1.1.10 and Table 3.1.1.10.

3.1.1.10 Volatile Organic Compounds I: (VOCs)

Parameters (Synonym)

Acetone
Carbon tetrachloride (tetrachloromethane)
Chlorobenzene
Dichlorobenzene, 1,2-
Dichlorobenzene, 1,3-
Dichlorobenzene, 1,4-
Dichlorodifluoromethane
Dichloroethane, 1,1-
Dichloroethane, 1,2-
Dichloroethylene, 1,1- (dichloroethene)
Dichloroethylene, *cis*-1,2- (dichloroethene)
Dichloroethylene, *trans*-1,2- (dichloroethene)
Dichloropropane, 1,2-
Dichloropropene, *cis*-1,3-† (dichloropropylene)
Dichloropropene, *trans*-1,3-† (dichloropropylene)
Ethylene dibromide (dibromoethane, 1,2-)
Hexane, n-**
Methyl ethyl ketone (MEK)**
Methyl isobutyl ketone (MIBK)**
Methyl *tert*-butyl ether (MTBE)**
Methylene chloride (dichloromethane)
Styrene
Tetrachloroethylene (tetrachloroethene, perchloroethylene)
Tetrachloroethane, 1,1,1,2-
Tetrachloroethane, 1,1,2,2-
Trichloroethane, 1,1,1-
Trichloroethane, 1,1,2-
Trichloroethene (trichloroethylene, TCE)
Trichlorofluoromethane
Vinyl chloride (chloroethene)

†the sum of *cis*- and *trans*-dichloropropene is compared to the standard

**may also be determined with BTEX

Table 3.1.1.10 Volatile Organic Compounds I: (VOCs)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Introduction** SW-846, Method 5021A SW-846, Method 5035A Reference Method for the Canada-wide Standard for Petroleum Hydrocarbons (CWS-PHC) in Soil – Tier 1 Method **Analysis** SW-846, Method 8260D	**Sample Introduction** SW-846, Method 5000 SW-846, Method 5030C **Analysis** SW-846, Method 8260D EPA Method 624
Standard Methods		Method 6200B
MECP-LaSB	E3490	E3132

VOCs in Soil and Sediment

Method principle

Volatile organic compounds (VOCs) present in field-preserved soil and sediment samples (approximately 5 grams) are processed in the laboratory as received (Table 3.1.1.10) within 14 days from sampling. If required for bromomethane, duplicate samples preserved with aqueous sodium bisulphate can be analysed as received.

Alternatively, unpreserved samples collected in hermetic sampling devices are extracted in the laboratory with methanol within 48 hours of sampling, to achieve a longer hold time, hermetic samples may be frozen within 48 hours of sampling as per ASTM method D6418 – 09; however, storage stability must be validated by the laboratory with no more than 10% losses.

Methanol must be removed from the soil/sediment sample within 14 days of sampling to give recovered methanol. The recovered methanol must be analysed within 40 days from date of recovery. Moisture content is determined as described in Section 2.1.1 (2).

Samples containing compounds exceeding the calibration range of the instrument are diluted by taking an aliquot of the extract diluted into volatile-free water and analysed. Samples may be pre-screened by headspace gas chromatography-mass spectrometry (GC-MS) or other appropriate instrumentation to determine appropriate dilutions.

The volatile compounds present in the methanol or bisulphate solution are introduced by purge & trap or headspace into the gas chromatograph where they are separated by a capillary column and then detected by a mass spectrometer operating in either full scan or selected ion monitoring (SIM) mode.

Identification of target analytes is accomplished by comparing sample mass spectra with the mass spectra of analytical standards. Quantitation is accomplished by using the response of a major (quantitation) ion relative to an internal standard and a response factor generated from a calibration curve.

Calculations

When reporting data based on a methanol extraction, concentrations must be corrected for the moisture extracted into the methanol (Table 3.1.1.10)

VOCs in ground water

Method principle

Aqueous samples are analysed as received by purge & trap or headspace GC-MS (Table 3.1.1.10).

3.1.1.11 Volatile Organic Compounds II: Benzene, Ethylbenzene, Toluene, Xylenes (BTEX)

Parameter* (Synonyms)

Benzene

Ethylbenzene

Toluene (methylbenzene)

Xylenes, total (o-xylene; m- & p-xylene)

*may also be determined with VOCs

Note that the above BTEX compounds (benzene, toluene, ethylbenzene, xylenes) are a subset of volatile organic compounds (VOCs), are often analysed as a discrete analysis and, therefore, are included as a separate group from the VOCs. The method principle for BTEX is identical to the VOC I as outlined in Section 3.1.1.10 and Table 3.1.1.10.

3.1.1.12 Volatile Organic Compounds III: Bromomethane

Parameters* (Synonyms)

Bromomethane[†] (methyl bromide)

*may also be determined with VOCs

[†]methanol-preserved samples may elevate the detection limit for bromomethane; a separate bisulphate-preserved sample or hermetically sealed sample may be submitted at the time of sampling if bromomethane is a chemical of concern.

Note that bromomethane is a subset of volatile organic compounds (VOCs), and is often analysed as a discrete analysis and, therefore, is included as a separate group from the VOCs. The method principle for bromomethane is identical to the VOC I as outlined in Section 3.1.1.10 and Table 3.1.1.10.

3.1.2 Inorganic Chemical/Physical and Other Regulated Parameters

3.1.2.1 Calcium and Magnesium

Parameters (Synonyms)

Calcium (Ca)

Magnesium (Mg)

Soil and sediment

Calcium and magnesium are determined for the calculation of sodium adsorption ratio (SAR) in soil and sediment samples. The method principle is outlined in Section 3.1.2.17 and Table 3.1.2.17 for SAR.

3.1.2.2 Metals

Parameters (Synonym)

Barium (Ba)
Beryllium (Be)
Boron (B)[#]
Cadmium (Cd)
Chromium (Cr)
Cobalt (Co)
Copper (Cu)
Lead (Pb)
Molybdenum (Mo)
Nickel (Ni)
Silver (Ag)
Thallium (Tl)
Uranium (U)
Vanadium (V)
Zinc (Zn)

[#] strong acid extractable boron

Table 3.1.2.2 Metals

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Preparation** SW-846, Method 3050B SW-846, Method 3051A EPA 200.2 **Analysis** SW-846, Method 6010D SW-846, Method 6020A SW-846, Method 6800 SW-846, Method 7000B SW-846, Method 7010	**Sample Preparation** SW-846, Method 3005A SW-846, Method 3010A SW-846, Method 3015A SW-846, Method 3020A **Analysis** SW-846, Method 601, Rev 4.2 Method 200.7, Rev 4.4 Method 200.8, Rev 5.4 Method 200.9, Rev 2.2 Method 200.15, Rev 1.2
Standard Methods		Method 3111 B Method 3111 D Method 3113 B Method 3120 B Method 3125 B
MECP-LaSB	E3470	E3497 E3537 E3566

Method principle

For soils, a previously dried, ground (<0.355 mm) sample is subjected to digestion with a heated, hydrochloric:nitric acid solution (Table 3.1.2.2). The digestate is separated from the soil residue and brought to volume with deionized water. This method provides environmentally available metals, not total metals.

Ground water samples requiring analysis for “dissolved” metals must be previously field filtered (0.45 µm) and field preserved to pH < 2. Unpreserved and unfiltered samples can be filtered and preserved at the laboratory provided that analysis does not commence for at least 16 hours after preservation. This deviation must be noted on the Certificate of Analysis.

Analysis is performed with inductively coupled plasma-optical emission spectroscopy (ICP-OES) or inductively coupled plasma-mass spectrometry (ICP-MS) or atomic absorption spectrophotometry (AAS) (Table 3.1.2.2).

The analytical standards must be matrix matched to the samples.

3.1.2.3 Metals, Hydride-Forming (As, Se and Sb)

Parameters*

Antimony (Sb)

Arsenic (As)

Selenium (Se)

*may also be determined with metals by ICP-MS or ICP-OES

Table 3.1.2.3 Metals, Hydride-Forming (As, Se and Sb)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Preparation** SW-846, Method 3050B SW-846, Method 3051A **Analysis** SW-846, Method 6020B SW-846, Method 7010 SW-846, Method 7061A SW-846, Method 7062 SW 846, Method 7742	**Sample Preparation** SW-846, Method 3005A SW-846, Method 3010A SW-846, Method 3015A SW-846, Method 3020A **Analysis** SW-846, Method 6020B SW-846, Method 7010 SW-846, Method 7061A SW-846, Method 7062 SW 846, Method 7742 Method 200.5, Rev 4.2 Method 200.8, Rev 5.4 Method 200.9, Rev 2.2
Standard Methods		Method 3113 B Method 3114 B Method 3114 C Method 3125 B
MECP-LaSB	E3245 E3470	E3089 E3302 E3566

Method principle

Previously dried and ground (<0.355 mm) soil samples are extracted with a heated, mixed acid solution (Table 3.1.2.3). Filtered and preserved water samples may be acid digested or analysed as received.

Samples are analysed using graphite furnace atomic absorption spectrophotometry (GFAAS), inductively coupled plasma-mass spectrometry (ICP-MS) or hydride generation atomic absorption spectrophotometry (HGAAS). Alternatively, for elevated levels of arsenic, selenium and antimony, analysis can be performed with inductively coupled plasma-optical emission spectroscopy (ICP-OES) and reported for each individual parameter five times above the ICP-OES method detection limit.

3.1.2.4 Sodium (Na)

Parameters

Sodium (Na)

Table 3.1.2.4 Sodium (Na)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Preparation** SW-846, Method 3050B SW-846, Method 3051A **Analysis** SW-846, Method 6010D SW-846, Method 6020B SW-846, Method 7000B	**Sample Preparation** SW-846, Method 3005A SW-846, Method 3010A SW-846, Method 3015A SW-846, Method 3020A **Analysis** SW-846, Method 6010D SW-846, Method 6020B SW-846, Method 7000B SW-846, Method 7010 Method 200.5, Rev 4.2 Method 200.7, Rev 4.4 Method 200.9, Rev 2.2 Method 200.15, Rev 1.2
Standard Methods		Method 3111 B Method 3111 D Method 3113 B Method 3120 B Method 3125 B
MECP-LaSB	E3470	E3171 E3497 E3509 E3537

Method principle

For soils and sediment samples, sodium (calcium and magnesium) is used to calculate the sodium adsorption ration (SAR). The method principle is outlined in Section 3.1.2.17 for SAR.

For sodium in ground water the method principle is outlined in Section 3.1.2.4 for metals.

3.1.2.5 Boron (B-HWS) (Hot Water Soluble)

Parameters (Synonym)

Boron, hot water soluble

Table 3.1.2.5 Boron (B-HWS)

Method Reference Source	Soil & Sediment	Ground Water
	Sample Preparation Gupta, 1967, Soil Science 103: 424-428	Not applicable
MECP-LaSB	E3537	

Boron in soil or sediment

Method principle

A minimum 5 gram portion of a dried, disaggregated (<2 mm) solid sample is extracted with 10 mL 0.01M calcium chloride (used to ensure a clear filtrate) through a 0.45 µm filter. The sample is heated and must boil for five minutes followed by cooling and filtration. The sample is then analysed using the spectrometric technique listed in Table 3.1.2.5.

Note: 5 grams is the minimum weight for a representative sample. Larger weights may be used but the 2:1 ratio v/w of aqueous calcium chloride to soil must be maintained.

Calculations and Reporting

All results are reported as µg/g dry weight.

3.1.2.6 Chloride (Cl^-) (water extractable)

Parameters

Chloride (Cl^-)

Table 3.1.2.6 Chloride (Cl^-)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	SW-846, Method 9056A Method 300.1	SW-846, Method 6500 SW-846, Method 9056A SW-846, Method 9250 SW-846, Method 9251 SW-846, Method 9253 Method 300.1
Standard Methods		Method 4110 B Method 4110 C Method 4500-Cl^-C Method 4500-Cl^-D Method 4500-Cl^-E
MECP-LaSB	E3013	E3016

Chloride in soil or sediment

Method principle

A minimum 5 grams portion of the previously dried, disaggregated (< 2mm) solid sample is extracted with 50 mL deionized water by shaking for a minimum of 30 minutes, then filtered and analysed using ion chromatography or colourimetry. Note: 5 grams is considered the minimum size for a representative sample. Larger weights may be used but the 10:1 ratio water to soil ratio must be maintained.

In the colourimetric procedure, the chloride ions combine with mercuric thiocyanate to form an undissociated salt, mercuric chloride, and release thiocyanate ions which then complex ferric ions to produce a coloured solution. The absorbance of the coloured solution measured at the appropriate wavelength is proportional to the original concentration of chloride ion in the sample. The analysis is usually carried out using an automated continuous flow, flow injection or discrete analysis system.

Alternatively, ion chromatography can be used. Ion chromatography is a form of liquid chromatography that uses ion-exchange resins to separate atomic or molecular ions based on their interaction with the resin.

Chloride in ground water

Method principle

Samples can be analysed directly or filtered in the laboratory prior to analysis using colourimetry or ion chromatography (Table 3.1.2.6).

3.1.2.7 Cyanide (CN^-)

Parameters

Cyanide (CN^-)

Table 3.1.2.7 Cyanide (CN^-)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Analysis** SW-846, Method 9012B SW-846, Method 9014 SW-846, Method 9016	**Analysis** SW-846, Method 9012B SW-846, Method 9014 SW-846, Method 9016 Method 335.4 Method OIA-1677-09
Standard Methods	**Sample Preparation** Method 4500-CN-A **Analysis** Method 4500-CN-I Method 4500-CN-N Method 4500-CN-O	Method 4500-CN-I Method 4500-CN-N Method 4500-CN-O
MECP-LaSB	E3015	E3015

Weak acid dissociable (WAD) cyanide provides a conservative estimate as it recovers both free and weak acid dissociable cyanide from complexes and must be compared to the standard.

Soils and sediment

Method principle

A minimum 5 grams sample as received is extracted with 50 mL of 0.01M aqueous sodium hydroxide. The sample is shaken for minimum one hour, followed by centrifuging and decanting. Larger weights may be used but the 10:1 ratio v/w of aqueous sodium hydroxide to soil must be maintained–see section 3.1.2.7 for cyanide analysis in excess soil leachates.

Ground water

Method principle

Water samples are analysed as received (Table 3.1.2.7). Particulates should not be included. Centrifugation or filtration in the laboratory may be required to remove particulate.

A portion of the aqueous sample or leachate is introduced directly to the autoanalyser system from an autosampler. Cyanide is separated from water by auto acid distillation without UV oxidation at controlled pH and then analysed colourimetrically or by means of a gas permeable membrane. Care must be taken in the analysis conditions to prevent thiocyanate interference. Offline distillation prior to analysis is an acceptable option.

3.1.2.8 Electrical Conductivity

Parameters

Electrical Conductivity (EC)

Table 3.1.2.8 Electrical Conductivity

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	SW-846, Method 9050A	
USDA	Handbook #60, Chapter 6	
Standard Methods		Method 2510
MECP-LaSB	E3530	E3218

Soil and Sediment

Method principle

A minimum 5 grams sample of a previously dried, disaggregated (< 2 mm), sample is extracted with 10 mL pure water (20 mL for organic soils) by shaking for at least 30 minutes. The sample is then analysed using a conductivity meter (Table 3.1.2.8). Note: 5 grams is considered the minimum size for a representative sample. Larger weights may be used but the 2:1 ratio v/w of water to soil must be maintained.

Certain soil types may require a higher water:soil ratio in order to have sufficient liquid for measurement. In this case, a 5:1 water to soil ratio must be used and this ratio must be documented on the Certificate of Analysis or analytical report along with possible reasons why the use of higher ratio is necessary.

Only if either a 2:1 or 5:1 water:soil ratio is not adequate for a measurement, the saturated extracts can be used. In this case, a water saturated soil paste is made with approximately 100 cc (cubic centimeter) volume soil. After intermittent stirring and equilibration for 2 hours, the free water is extracted by filtration or centrifugation. The filtrate/supernatant is measured for electrical conductance and expressed as $\mu S\ cm^{-1}$.

Note that soil standards for electrical conductivities are based on a 2:1 water to soil ratio. If other analytical methods are used, the following adjustment factors must be applied to the analytical results and the resultant numbers can be compared to the applicable standards:

Identified water to soil ratio	Adjustment Factor[#]
5:1 water to soil ratio	2.0
Saturated Paste	0.35 or 0.2 [if organic matter is measured and greater than 30% (or greater than 17% organic carbon)]

[#]electrical conductivity measurements multiplied by an appropriate adjustment factor before comparing to the applicable standard.

All aqueous solutions conduct electricity to various degrees. Conductivity is measured by an electronic meter or controller that applies an alternating voltage on the conductivity sensor and measures the resulting signal. The conductivity sensor consists of two or more electrodes of a certain area (A) separated by a predetermined distance (d). The sensor's cell constant (expressed in units of cm) is defined by:

$$K = d/A$$

The conductivity in µS/cm is determined by multiplying the measured conductivity by the cell constant.

Report Format

The conductivity as measured in the extract multiplied by the appropriate adjustment factor, if applicable, is reported.

3.1.2.9 Fraction of Organic Carbon (FOC)

Parameters

Fraction of Organic Carbon

Table 3.1.2.9 Fraction of Organic Carbon (FOC)

Method Reference Source	Soil & Sediment	Ground Water
ASTM	Method D2974-20e1 Method E1915-07	n/a
MECP-LaSB	E3529	n/a

Method principle

Fraction of organic carbon (FOC) in soil is measure of the ratio of the organic carbon in the soil relative to the mass of sample ($g_{(carbon)}/g_{(soil)}$). Total organic carbon (TOC) is calculated as the difference from analysis for total carbon (TC) and total inorganic carbon (TIC). The measurement of total carbon in soils and sediments requires the destruction of both carbonate minerals (primarily calcite and dolomite) as well as organic carbon.

Oxygen is purged through the system, as the samples are combusted, oxidizing carbon to carbon dioxide (CO_2). The CO_2 is collected, passed through two traps to remove moisture and dust, and then measured by an infrared detector (TC in mg/g carbon). Inorganic carbon (carbonate carbon) is determined by the measurement of CO_2 evolved by the reaction of carbonate with strong acid solution swept by purified nitrogen through a potassium iodide scrubber into the cathode compartment of a coulometer (Table 3.1.2.9). The evolved CO_2 is quantitatively absorbed by the cathode solution and converted to a strong acid causing the indicator colour to fade. Base is electrically generated to titrate the solution back to the starting point (TIC in mg/g carbon).

Alternatively, approved wet chemical reference methods can be used (Table 3.1.2.9). In these procedures, soil, after carbonate removal using acid, is treated with excess acidic dichromate, which reacts with the organic carbon, oxidizing it to CO_2. The residual dichromate is titrated with ferrous ammonium sulphate and TOC calculated by difference.

Results are reported in triplicate; separately and as an average.

3.1.2.10 Hexavalent Chromium (Chromium VI, Cr (VI), Cr^{+6})

Parameters (Synonyms)

Hexavalent chromium (chromium VI, Cr (VI), Cr^{+6})

Table 3.1.2.10 Hexavalent Chromium (Chromium VI, Cr (VI), Cr^{+6})

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Preparation** SW-846, Method 3060A **Analysis** SW-846, Method 6800 SW-846, Method 7196A SW-846, Method 7199	**Sample Preparation** **Analysis** Method 1636 SW-846, Method 7196A SW-846, Method 7199
Standard Methods		Method 3500-Cr
USGS	I-1232-85	I-1232-85
MECP-LaSB	E3519	E3056 E3510

Method principle

For soil and sediment samples, a minimum 2.5 grams sample as received is subjected to an alkaline digestion with continuous stirring prior to analysis (Table 3.1.2.10). The extract must be analysed within seven days of extraction.

For the determination of dissolved hexavalent chromium, aqueous samples are field filtered and preserved at pH 9 – 9.5 with ammonium sulfate buffer solution specified in U.S. EPA Methods 218.6, 1636, or 7199 or at pH 9.3 to 9.7 specified in Standard Methods 3500-Cr Chromium to achieve the 28 day[4] holding time, or alternatively with sodium hydroxide with a holding time of 24 hours.

[4] U.S. EPA Federal Register Part III. March 12, 2007. 40 CFR Part 122, 136, et al. Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations; Analysis and Sampling Procedures; Final Rule, pages 11218, 11236, 11239 (footnote #20). Footnote 20 states: To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed.

The most common analytical procedure is manual or automated colourimetry. The alkaline digestate (or base preserved aqueous sample) is acidified and treated with 1,5-diphenylcarbazide (DPC) which reacts with chromium VI to give a reddish-purple colour, the absorption of which is measured spectrophotometrically at a wavelength of 540 nm.

Alternatively, ion chromatography may be used for the analysis employing post column derivatization with DPC and measurement at 540 nm. A method based on ion chromatography coupled to an ICP-MS can also be used for ground water samples preserved with ultra-pure concentrated NH_4OH to pH > 9. Samples preserved at pH > 9 are injected directly into an anion exchange column to separate Cr(VI) from other possible Cr species and other metals by the anion exchange functioning group inside the column. The column eluent is introduced directly into the sample introduction interface and the ionization source of the ICP-MS. The resulting chromatographic peak of chromium (VI) is identified and quantified by the mass spectrometer with external calibration.

3.1.2.11 Nitrate/Nitrite

Parameters

Nitrate

Nitrite

Table 3.1.2.11 Nitrate/Nitrite

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA		A**nalysis** Method 300.0 Rev 2.1 Method 300.1 Rev 1.0
Standard Methods		Method 4110B Method 4500 NO2 Method 4500 NO3
MECP		E3364

Method Principle

Nitrate plus nitrite may be determined colourimetrically or by ion chromatography. Samples are analysed as received or after filtration, if necessary to remove particulate. Nitrate/Nitrate are analysed using the analytical techniques described in Section 3.1.2.11.

The automated colourimetric method incorporates a split manifold used to determine both nitrite singly and nitrite and nitrate combined. On one channel, the nitrate is quantitatively reduced to nitrite in a reductor column containing amalgamated copperised cadmium filings. The nitrite yielded by the reduction plus the nitrite already present in the sample is then determined. The nitrite (that was originally present, plus reduced nitrate) is determined by diazotizing with sulphanilamide and coupling with N-(1-naphthyl)-ethylenediamine to form an azo dye, measured colourimetrically at 520 nm, yielding a value for nitrate + nitrite.

In the second channel, nitrite alone is determined by using the same chemistry without the cadmium reduction step, yielding a value for nitrite only.

Nitrate is determined by subtraction of the nitrite result from the nitrate + nitrite value–refer to Section 5.3.1 regarding detection limits for subtracted parameters.

The ion chromatography method determines nitrate and nitrite individually. Either conductivity or UV detection may be employed. Nitrate + nitrite is the sum of the individual results.

Calculations and Reporting

Nitrate is expressed in units of µg/L as NO_3.

Nitrate + nitrite is expressed in units of µg/L as N.

Nitrite is expressed in units of µg/L as N.

For nitrate, to convert from units of µg/L as NO_3 to µg/L as N, multiply by 14/62.

For nitrite, to convert from units of µg/L as N to µg/L as NO_2, multiply by 46/14.

3.1.2.12 Nitrogen (total)

Parameters (Synonyms)

Nitrogen (total)

Table 3.1.2.12 Nitrogen (total)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA		Method 351.2, Rev. 2.0
Standard Methods		Method 4500 N
MECP	E3529	E3567

Method Principle

Alkaline oxidation at 100°C to 110°C converts organic and inorganic nitrogen to nitrate. Total nitrogen is determined by analysing the nitrate in the digestate using the analytical techniques described in Section 3.1.2.12. Automated digestions using UV radiation and persulphate may also be used.

Automated combustion techniques that detect evolved nitrogen oxides may also be used.

Alternatively, total Kjeldahl nitrogen (TKN), nitrite, and nitrate (all expressed as Nitrogen) may be determined separately and summed to provide a Nitrogen (total) value. Since not all forms of organic nitrogen are determined by TKN, the Nitrogen (total) value determined in this way may be biased low relative to the alkaline oxidation or combustion procedures. For most environmental samples, however, the bias is not significant.

Reporting

Results are reported in units of µg/L as Nitrogen (total).

3.1.2.13 Mercury (Hg)

Parameters

Mercury (Hg)

Table 3.1.2.13 Mercury (Hg)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	**Sample Preparation** EPA 200.2 BCSALM SW-846, Method 3050B SW-846, Method 3051A SW-846, Method 7471B **Analysis** SW-846, Method 7470A SW-846, Method 7473 SW-846, Method 7474 SW-846, Method 6800 SW-846, Method 6020B EPA 200.2	**Sample Preparation** EPA 200.2 SW-846, Method 7470A Method 245.1, Rev 3.1 Method 245.2 Method 245.7, Rev 2.0 Method 200.8, Rev 5.4 Method 1631E **Analysis** SW-846, Method 6800
Standard Methods		Method 3112 B
ASTM		Method D3223-17
USGS	I-16463-86	I-3462-85
MECP-LaSB	E3059	E3526

Method principle for mercury in soil, sediment and ground water soil

Previously dried and ground (<0.355 mm) soil samples or aqueous samples are digested with a heated, strong, mixed acid solution to convert all forms of mercury to divalent mercury (Table 3.1.2.13). Excess oxidizing agents are removed by the addition of hydroxylamine. The divalent mercury is then reduced to elemental mercury, sparged from solution and analysed in one of the following ways: manual or automated cold vapour atomic absorption spectrophotometry (CVAAS), or cold vapour atomic fluorescence spectrophotometry (CVAFS).

3.1.2.14 Methyl Mercury (Monomethyl Mercury, CH_3Hg^+, $MeHg^+$)

Parameters (Synonyms)

Methyl mercury (monomethyl mercury, CH_3Hg^+, $MeHg^+$)

Table 3.1.2.14 Methyl Mercury (Monomethyl Mercury, CH_3Hg^+, $MeHg^+$)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	SW-846, Method 3200	Method 1630

Soils and sediment

Method Principle

Extractable organomercury and inorganic mercury compounds are extracted from the soil matrix with acid using microwave or ultrasonic extraction. The organomercury compounds are separated using solid phase extraction or distillation and determined using a method for total mercury analysis (Table 3.1.2.14). Extracts/distillates must be analysed within 48 hours of preparation.

Ground water

Method principle

Aqueous samples are acidified with hydrochloric acid forming organomercuric chloride (RHgCl) which is separated by distillation (Method 1630). The distillate is ethylated forming RHgEt. The volatile RHgEt complexes are purged onto a carbon trap, subsequently thermally desorbed, reduced to elemental mercury and detected by cold vapour atomic fluorescence spectrophotometry (CVAFS).

3.1.2.15 Particle Size

Parameters

Particle size

Table 3.1.2.15 Particle Size

Method Reference Source	Soil & Sediment	Ground Water
Soil Sampling and Methods of Analysis, 2nd Edition, Carter and Gregorich, Editors	Sample Preparation and Analysis Chapter 55, Particle Size Distribution	n/a
ASTM	D422-63(2007)e2	n/a
MECP-LaSB	E3328	n/a

Method principle

Particle Size Determination: Fine and Coarse

As-received soil samples are sieved using a #200 mesh (0.075 mm) sieve with the aid of water; care is taken not to break larger particles. The material passing through the sieve is collected in a pan. The sieve and pan are dried and weighed. The percentage of soil retained on and passing through the #200 sieve is calculated. If > 50% passes through the sieve the soil is classified as "fine", otherwise it is classified as "coarse".

O. Reg. 153/04 requires that all particles > 2 mm (#10 mesh) be removed prior to applying the procedure described above. Other jurisdictions may require that fine or coarse determination be based on the entire sample.

Particle Size Determination: Sand, Silt and Clay

As-received soil samples are passed through a series of sieves ranging from #4 mesh (4.75 mm) to #200 mesh (0.075 mm) or finer. The sieves must include #10 mesh (2 mm). In addition, a second aliquot is subjected to hydrometer analysis where the soil is suspended in water by agitation/ inversion with the aid of a dispersing agent. The cylinder is placed upright, and a series of hydrometer readings are taken over time.

The sand, silt, clay measurement is always determined on the < 2 mm fraction only. A semilogarithmic curve of percent passing vs. particle size is constructed from the measurements and used to calculate the percent sand:silt:clay. The ranges are in accord with the USDA and Canadian Soil Classifications and may be used with the USDA and Canadian Soil Triangles.

They are:

Soil Classification	Particle Size Range
Sand	2 – 0.05 mm
Silt	0.05 – 0.002 mm
Clay	< 0.002 mm

Report Format

The proportions retained and passing the #200 sieve are reported in percent. The soil classification as "fine" or "coarse" is also reported.

3.1.2.16 pH by Potentiometry

Parameters

pH

Table 3.1.2.16 pH by Potentiometry

Method Reference Source	Soil & Sediment	Ground Water
ASTM	D4972-19	n/a
MECP-LaSB	E3530	n/a

Method principle

A minimum 10 grams portion of the sample, as received, is extracted with 20 mL of 0.01M calcium chloride solution by shaking for at least 30 minutes. The aqueous layer is separated from the soil by centrifuging, settling or decanting and then analysed using a pH meter and electrode (Table 3.1.2.16). Note: 10 grams is considered the minimum size for a representative sample. Larger weights may be used but the 2:1 ratio v/w of aqueous calcium chloride to soil must be maintained.

The pH of a solution is defined as the negative logarithm of the hydrogen ion activity and in dilute solutions the activity is approximately equal to the concentration of the hydrogen ion:

$$pH = -\log_{10}[H^+]$$

Since the activity of the hydrogen ion cannot be measured directly, it is measured potentiometrically with a glass electrode in combination with a reference electrode.

Report Format

The pH as measured in the extract is reported in pH units.

3.1.2.17 Sodium Adsorption Ratio (SAR)

Parameters (Synonym)

Sodium Adsorption Ration (SAR)

Table 3.1.2.17 Sodium Adsorption Ratio (SAR)

Method Reference Source	Soil & Sediment	Ground Water
U.S. EPA	SW-846, Method 6010D SW-846, Method 6020B SW-846, Method 7000B	

Method principle

A 5 grams portion of previously dried, disaggregated sample (< 2 mm) is extracted with 10 mL deionized water by shaking for 30 minutes. For some soil types, a higher water:soil ratio may be required to obtain sufficient liquid for measurement. The aqueous extract is separated from the solid, acidified and then analysed using a spectrometric technique. Inductively coupled plasma-

optical emission spectroscopy (ICP-OES) is recommended, and alternatives are atomic absorption spectroscopy (AAS) and inductively coupled plasma-mass spectrometry (ICP-MS) (Table 3.1.2.17).

Report format

The concentrations of sodium, calcium and magnesium are in units of milliequivalents per liter. SAR is determined from the equation below. Since SAR is a ratio, it is unitless.

$$SAR = \frac{[Na^{+}]}{\sqrt{\frac{1}{2}\left([Ca^{2+}] + [Mg^{2+}] \right)}}$$

If any of the values are below the reporting limit (RL), zero is used in the calculation for those parameters.

3.1.2.18 Leachates

Parameters

Leachates, from Soil and Sediment

Table 3.1.2.18 Leachates

Method Reference Source	Soil & Sediment	Ground Water
MECP-LaSB	E9003	n/a

Method principle

Since improper management of excess soils could negatively affect soil, sediment, or ground water quality, a modified version of the U.S. EPA's Synthetic Precipitation Leaching Procedure (U.S. EPA method 1312, SPLP) is used to leach the regulated parameters (under O. Reg. 406/19) when leachate analysis is required. U.S. EPA SPLP method was designed to characterize soils based on the ability of contaminants to partition, or leach, into a simulated precipitation. The modifications include the use of extraction fluid #2 (pH = 5) for all analytes except for VOC and cyanide. Extraction fluid #3 (water) is used for VOC and cyanide analytes. All samples are filtered (0.6–0.8 µm glass fiber) prior to analysis except for leachates for metal analysis which are filtered through 0.45 µm metal free filters. Leachate are prepared according to method outlined in table 3.1.2.18. The resulting leachate is analysed by the appropriate analytical methodologies described in section 3.1.

Leachates – VOC and cyanide

For the extraction of VOCs and/or cyanide in excess soil samples, the mSPLP is followed. The excess soil sample (25 grams) is leached in a Zero Headspace Extractor (ZHE) with 500 mL extraction fluid #3 (water) for 18 ± 2 hours. Use TEDLAR bag to collect the filtered extract (0.6 – 0.8 µm glass fiber) from the ZHE device. The sample in the TEDLAR bag is transferred into PTFE-lined septum-capped glass vials (with no headspace) for analysis of VOCs. A minimum of 50 mL leachate is collected in glass or plastic container, preserved with sodium hydroxide to a pH >12 at the time of collection and submitted for cyanide analysis.

Note: If less than 25 grams of material is available, the leaching solution must maintain the 20:1 leaching ratio. If less than 25 grams of sample is used, a note must accompany the analytical result noting that the sample size does not comply to the sample size requirements due to insufficient sample.

Leachates – Metals and semi-volatile organics (exclusive of VOC and cyanide)

A soil sample (100 grams) is leached (18 ± 2 hours) with 2.0 liters of leaching fluid #2 (pH 5, 60:40 weight mixture of H_2SO_4:HNO_3). The resulting slurry is filtered, and the resulting leachate is analysed for various parameters by the appropriated analytical method. For semi-volatile organics analysis, leachate is filtered through a 0.6 – 0.8 µm glass fiber filter. For metals analysis, the leachate is filtered through a 0.45 µm metal-free filter. This filtrate is submitted for the analysis of metals.

Note: If less than 100 grams of material is available, the leaching solution must maintain the 20:1 leaching ratio. If less than 100 grams of sample is used, a note must accompany the analytical result noting that the sample size does not comply to the sample size requirements due to insufficient sample.

SECTION 4: REPORTING

4.1 Required Reporting Limits (RLs)

Reporting limit is the concentration at which a single analysis using the methods and matrices listed in this document will consistently detect target analytes when present. The RL must be equal to or greater than the method detection limit (MDL).

TABLE 4.1.1 Required Reporting Limits

Chemical Name (Inorganic chemicals in bold)	CAS RN	Parameter Group	Soil Required RL µg/g (=mg/kg)	Ground Water/ Leachate Required RL µg/L
Acenaphthene	83-32-9	PAHs or ABNs	0.05	1
Acenaphthylene	208-96-8	PAHs or ABNs	0.05	1
Acetone	67-64-1	VOCs	0.5	30
Aldrin	309-00-2	OC pesticides	0.05	0.01
Anthracene	120-12-7	PAHs or ABNs	0.05	0.1
Antimony	**7440-36-0**	**hydride metals**	**1**	**0.5**
Arsenic	**7440-38-2**	**hydride metals**	**1**	**1**
Barium	**7440-39-3**	**metals**	**5**	**2**
Benzene	71-43-2	VOCs	0.02	0.5
Benz[a]anthracene	56-55-3	PAHs or ABNs	0.05	0.2
Benzo[a]pyrene	50-32-8	PAHs or ABNs	0.05	0.01
Benzo[b]fluoranthene	205-99-2	PAHs or ABNs	0.05	0.1
Benzo[g,h,i]perylene	191-24-2	PAHs or ABNs	0.1	0.2
Benzo[k]fluoranthene	207-08-9	PAHs or ABNs	0.05	0.1
Beryllium	**7440-41-7**	**metals**	**2**	**0.5**
Biphenyl, 1,1'-	92-52-4	ABNs	0.05	0.5
Bis(2-chloroethyl) ether	111-44-4	ABNs	0.5	5
Bis(2-chloro-1-methylethyl) ether^†	108-60-1	ABNs	0.5	4
Bis(2-ethylhexyl) phthalate	117-81-7	ABNs	5	10
Boron HWS (hot water soluble)	**n/a**	**ORP**	**0.5**	
Boron (Total)	**7440-42-8**	**metals**	**5**	**10**
Bromodichloromethane	75-27-4	THMs or VOCs	0.05	2
Bromoform	75-25-2	THMs or VOCs	0.05	5
Bromomethane	74-83-9	VOCs	0.05	0.5
Cadmium	**7440-43-9**	**metals**	**1**	**0.5**

Chemical Name (Inorganic chemicals in bold)	CAS RN	Parameter Group	Soil Required RL µg/g (=mg/kg)	Ground Water/ Leachate Required RL µg/L
Carbon tetrachloride	56-23-5	VOCs	0.05	0.2
Chlordane	57-74-9	OC pesticides	0.05	0.06
Chloride	**16877-00-6**	**ORP**	**5**	**1000**
Chloroaniline, p-	106-47-8	ABNs	0.5	10
Chlorobenzene	108-90-7	VOCs	0.05	0.5
Chloroform	67-66-3	VOCs	0.05	1
Chlorophenol, 2-	95-57-8	CPs or ABNs	0.1	2
Chromium Total	**7440-47-3**	**metals**	**5**	**10**
Chromium VI	**18540-29-9**	**ORP**	**0.2**	**10**
Chrysene	218-01-9	PAHs or ABNs	0.05	0.1
Cobalt	**7440-48-4**	**metals**	**2**	**1**
Copper	**7440-50-8**	**metals**	**5**	**5**
Cyanide (CN^-)	**57-12-5**	**ORP**	**0.05**	**5**
Dibenz[a,h]anthracene	53-70-3	PAHs or ABNs	0.1	0.2
Dibromochloromethane	124-48-1	THMs or VOCs	0.05	2
Dichlorobenzene, 1,2-	95-50-1	VOCs	0.05	0.5
Dichlorobenzene, 1,3-	541-73-1	VOCs	0.05	0.5
Dichlorobenzene, 1,4-	106-46-7	VOCs	0.05	0.5
Dichlorobenzidine, 3,3'-	91-94-1	ABNs	1	0.5
Dichlorodifluoromethane	75-71-8	VOCs	0.05	2
DDD	72-54-8	OC pesticides	0.05	0.05
DDE	72-55-9	OC pesticides	0.05	0.01
DDT	50-29-3	OC pesticides	0.05	0.05
Dichloroethane, 1,1-	75-34-3	VOCs	0.05	0.5
Dichloroethane, 1,2-	107-06-2	VOCs	0.05	0.5
Dichloroethylene, 1,1-	75-35-4	VOCs	0.05	0.5
Dichloroethylene, 1,2-*cis*-	156-59-2	VOCs	0.05	0.5
Dichloroethylene, 1,2-*trans*-	156-60-5	VOCs	0.05	0.5
Dichlorophenol, 2,4-	120-83-2	CPs or ABNs	0.1	20
Dichloropropane, 1,2-	78-87-5	VOCs	0.05	0.5
Dichloropropene, 1,3- (*cis*- + *trans*-)	542-75-6	VOCs	0.05	0.5
Dieldrin	60-57-1	OC pesticides	0.05	0.05
Diethyl phthalate	84-66-2	ABNs	0.5	2
Dimethylphthalate	131-11-3	ABNs	0.5	2

Chemical Name (Inorganic chemicals in bold)	CAS RN	Parameter Group	Soil Required RL µg/g (=mg/kg)	Ground Water/ Leachate Required RL µg/L
Dimethylphenol, 2,4-	105-67-9	ABNs	0.2	10
Dinitrophenol, 2,4-	51-28-5	ABNs	2	10
Dinitrotoluene, 2,4-(2,6-)	121-14-2	ABNs	0.5	5
Dioxane,1,4-	123-91-1	ABNs or VOCs	0.2	20
Dioxin/furan (TEQ)	n/a	dioxins/furans		
Electrical Conductivity (mS/cm)	**n/a**	**ORP**	**0.005**	
Endosulfan I/II	115-29-7/ 959-98-8/ 33213-65-9	OC pesticides	0.04	0.05
Endrin	72-20-8	OC pesticides	0.04	0.05
Ethylbenzene	100-41-4	VOCs	0.05	0.5
Ethylene dibromide (dibromoethane, 1,2-)	106-93-4	VOCs	0.05	0.2
Fluoranthene	206-44-0	PAHs or ABNs	0.05	0.4
Fluorene	86-73-7	PAHs or ABNs	0.05	0.5
Fraction Organic Carbon		**ORP**		
Heptachlor	76-44-8	OC pesticides	0.05	0.01
Heptachlor epoxide	1024-57-3	OC pesticides	0.05	0.01
Hexachlorobenzene	118-74-1	OC pesticides	0.01	0.01
Hexachlorobutadiene	87-68-3	OC pesticides	0.01	0.01
Hexachlorocyclohexane, *gamma*-	58-89-9	OC pesticides	0.01	0.01
Hexachloroethane	67-72-1	OC pesticides	0.01	0.01
Hexane, n-	110-54-3	VOCs	0.05	5
Indeno[1,2,3-c,d]pyrene	193-39-5	PAHs or ABNs	0.1	0.2
Lead	**7439-92-1**	**metals**	**10**	**1**
Mercury	**7439-97-6**	**ORP**	**0.1**	**0.1**
Methoxychlor	72-43-5	OC pesticides	0.05	0.05
Methyl ethyl ketone	78-93-3	VOCs	0.5	20
Methyl isobutyl ketone	108-10-1	VOCs	0.5	20
Methyl mercury	**22967-92-6**	**ORP**		
Methyl *tert*-butyl ether (MTBE)	1634-04-4	VOCs	0.05	2
Methylene chloride	75-09-2	VOCs	0.05	5
Methlynaphthalene, 2- (1-)	91-57-6/ 90-12-0	PAHs or ABNs	0.05	2
Molybdenum	**7439-98-7**	**metals**	**2**	**0.5**

Chemical Name (Inorganic chemicals in bold)	CAS RN	Parameter Group	Soil Required RL µg/g (=mg/kg)	Ground Water/ Leachate Required RL µg/L
Naphthalene	91-20-3	PAHs or ABNs	0.05	2
Nickel	**7440-02-0**	**metals**	**5**	**1**
Nitrate	**84145-82-4**	**ORP**	**5**	**100**
Nitrite	**14797-65-0**	**ORP**	**5**	**100**
Nitrogen (total)	**7727-37-9**	**ORP**	**500**	**250**
Pentachlorophenol	87-86-5	CPs or ABNs	0.1	0.5
Petroleum hydrocarbons F1	n/a	PHCs	10	25
Petroleum hydrocarbons F2	n/a	PHCs	10	100
Petroleum hydrocarbons F3	n/a	PHCs	50	500
Petroleum hydrocarbons F4[#]	n/a	PHCs	50	500
Phenanthrene	85-01-8	PAHs or ABNs	0.05	0.1
Phenol	108-95-2	ABNs	0.5	1
Polychlorinated biphenyls (total)	1336-36-3	PCBs	0.3	0.2
Pyrene	129-00-0	PAHs or ABNs	0.05	0.2
Selenium	**7782-49-2**	**hydride metals**	**1**	**5**
Silver	**7440-22-4**	**metals**	**0.5**	**0.3**
Sodium Adsorption Ratio		**ORP**		
Sodium	**7440-23-5**	**metals and ORP**	**50**	**5000**
Styrene	100-42-5	VOCs	0.05	0.5
Tetrachloroethane, 1,1,1,2-	630-20-6	VOCs	0.05	0.5
Tetrachloroethane, 1,1,2,2-	79-34-6	VOCs	0.05	0.5
Tetrachloroethylene	127-18-4	VOCs	0.05	0.5
Thallium	**7440-28-0**	**metals**	**1**	**0.5**
Toluene	108-88-3	VOCs	0.2	0.5
Trichlorobenzene, 1,2,4-	120-82-1	ABNs	0.05	0.5
Trichloroethane, 1,1,1-	71-55-6	VOCs	0.05	0.5
Trichloroethane, 1,1,2-	79-00-5	VOCs	0.05	0.5
Trichloroethylene	79-01-6	VOCs	0.05	0.5
Trichlorofluoromethane	75-69-4	VOCs	0.05	5
Trichlorophenol, 2,4,5-	95-95-4	CPs or ABNs	0.1	0.2
Trichlorophenol, 2,4,6-	88-06-2	CPs or ABNs	0.1	0.2
Uranium	**7440-61-1**	**metals**	**1**	**2**
Vanadium	**7440-62-2**	**metals**	**10**	**0.5**
Vinyl chloride	75-01-4	VOCs	0.02	0.5
Xylene mixture	1330-20-7	VOCs	0.05	0.5

Chemical Name (Inorganic chemicals in bold)	CAS RN	Parameter Group	Soil Required RL µg/g (=mg/kg)	Ground Water/ Leachate Required RL µg/L
Zinc	**7440-66-6**	**metals**	**30**	**5**

CAS RN = Chemical Abstracts Service Registry Number

ORP = other regulated parameters (listed in Section 1.2.3)

[#]the larger result obtained for F4 and F4G is compared to the RL

[^] Erroneously known as bis(2-chloroisopropylether)

[†] For comparing this chemical to the site condition standards and excess soil standards, refer to either bis(2-chloroisopropylether) or bis(2-chloro-1-methylethyl) ether.

4.2 Reporting Requirements

As required by **O. Reg. 153/04,** each laboratory must adhere to the reporting requirements of Section 47 (3)(5)(6).

IMPORTANT For **O. Reg. 153/04,** a laboratory is required to analyse and report all parameters listed within a parameter group (Section 1.1 and 1.2) when a parameter or parameters from that group are requested. Laboratories are allowed to combine parameter groups (e.g., parameter group 1.1.1 with 1.1.2 or parameter group 1.1.9 with 1.1.10 and 1.1.11) when processing samples, if the method in use has been accredited for those parameters and those parameters are listed in the reference method cited by the laboratory. Other regulated parameters (ORPs) listed in Section 1.3 can be reported individually. For **O. Reg. 406/19** leachate analysis do not require analysis of the full parameter group, therefore it is acceptable to analyse and report individual parameter from any parameter group.

Certificates of Analysis or analytical reports shall include at least the following:

Submitted site and client information, including sample identifiers, location, etc.

Time Markers:

- Date and time sampled (for each sample) (if provided)
- Date extracted or digested (for each sample/test)
- Date analysed (for each sample/test)
- Date reported (for each sample/test)

Comment that report supersedes previous reports when corrected reports are generated and differences identified

Data Reportables:

- Temperature of samples upon receipt including whether the samples are frozen
- Presence of custody seals and whether intact
- Any other issues impacting sample integrity

Chain of custody for samples submitted to the laboratory or shipped between laboratories

QC Reportables:

- For the QP to be able to properly assess the quality of the analytical data, all associated QC must be reported as follows:
- Laboratory duplicate analyses (including relative percent difference (RPD) for each parameter)
- Travel blank(s) (where applicable)
- Method blank(s)
- Laboratory control sample analyses
- Matrix spike analyses (where applicable) (including % recovery)
- Reference materials (where applicable)
- Surrogate recoveries (where applicable)

QC reportables must include flags of QC exceedances

Analysis Reportables:

- Analytical data
- Reporting limits (RLs)
- Units
  - all data to be reported in the same units as in the regulation
  - all soil/sediment data to be reported as dry weight
- Data qualifiers (interference, dry weight, etc.)
  - visible particulate in ground water samples must be noted in the Certificate of Analysis or analytical report
- If requested the analytical uncertainty associated with each measurement

The title of the analytical method as described in the scope of accreditation including the reference method upon which the analytical method is based

Remarks/Comments:

- Report any unusual behavior noted in any step of the analytical process (such as sample inhomogeneity, headspace in a volatile organic compound (VOC) etc.)

Any other regulatory required comments (e.g., CCME performance criteria compliance)

Subcontract Analyses:

- Analysis conducted in third party laboratories, including sister laboratories, must be indicated

4.3 Sample Dilution

When the concentration of one or more parameters in a multicomponent scan (or the single analyte in a one component test) exceeds the concentration of their respective highest calibration standard, sample dilution is required to more accurately quantify the parameter. When this is required, the reporting limit (RL) for each target analyte must be adjusted (increased) in direct proportion to the dilution factor (DF).

The dilution factor is determined as follows:

$$DF = \frac{\textbf{\textit{Final Volume of Diluted Sample}}\ (\textbf{\textit{mL}})}{\textbf{\textit{Sample Aliquot Volume}}\ (\textbf{\textit{mL}})}$$

RL_d (the revised RL for the diluted sample) is determined as follows:

$$RL_d = DF \times RL$$

Situations that require reporting RL_d (as a result of dilution) may not satisfy RL reporting limits. Such increases in RL are acceptable, as long as all parameter results are at or below the applicable standard. Each laboratory must fully document all sample dilutions and appropriately qualify the data.

> Analytical note: the post-dilution concentration of the highest reported parameter must be no less than 20% of the highest calibration standard in the method. This will avoid losses of precision and accuracy and unnecessarily high reporting limits for other parameters that did not require dilution.

In multicomponent analytical scans it is also permissible to report results of the undiluted sample for analytes within the calibration range (if review shows the data to be valid).

4.3.1 Elevated non-target analyte or matrix interferences resulting in RLs above the standard

Where matrix interferences or elevated target/non-target compounds are present, sample dilution is required. The dilution may result in some target analytes being reported with adjusted RLs (as per the above calculation), above the pertinent **O. Reg. 153/04** or **O. Reg. 406/19** limits.

In these cases, results are reported as “less than (<)” with a raised RL, corresponding to the level of interference, which may result in an RL above the standard.

In these cases, the QP must review the analytes where the RLs exceed the standard and establish if the results reported are contaminants of concern identified in the Phase I Environmental Site Assessment (ESA). The QP must submit multiple lines of evidence to support that the compound(s) above the standard are not contaminants of concern. If they are contaminants of concern, consult with the laboratory. Additional effort or non-routine testing may be required to achieve the required RLs. Note, however, that in cases involving very “dirty” samples it may not be possible to accurately quantify some analytes at the regulatory standard levels.

SECTION 5: REQUIRED QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

This section provides the method specific quality assurance and quality control (QA/QC) requirements with respect to the sample processing, analysis and reporting of analytical data submitted for the purpose of **O. Reg. 153/04** and **O. Reg. 406/19**.

5.1 Accreditation

Laboratories must be accredited by an internationally recognized accreditation body (e.g., Standards Council of Canada (SCC), or Canadian Association for Laboratory Accreditation (CALA) in accordance with the International Standard ISO/IEC 17025:2017 – General Requirements for the Competence of Testing and Calibration Laboratories (as amended from time to time).

5.2 Method Validation

All analytical methods providing data in support of **O. Reg. 153/04** and **O. Reg. 406/19** must be properly validated and proven fit for purpose. The validation data must be available for inspection on request.

In the event that the technique employed has been in place for a significant period of time, ongoing method performance data may be used to demonstrate the method is valid and fit for purpose. Method blanks, laboratory duplicates, laboratory control samples and matrix spikes must all meet the performance criteria outlined in Tables 5-1 to 5-15. A minimum of 30 data points for each measure is required. Method detection limits (MDLs) and uncertainty data must be current and fit for purpose. The MDLs must be less than or equal to (≤) the reporting limits (RLs) in Table 4.1.1 as determined as per section 5.3.

In addition, single blind proficiency testing (PT) samples (if available) must demonstrate ongoing acceptable performance.

At a minimum, initial validation must include the following items. Further guidance is provided in the “Ontario Ministry of the Environment Protocol for the Acceptance of Alternate Methods (PAAM) Version 1.4 January 2005” (as amended from time to time).

5.2.1 Demonstration of Acceptable Precision, Accuracy, Selectivity and Specificity

Ground Water

A minimum of two sets of eight aliquots of real or synthetic ground water (not containing the analytes of interest) are spiked with the analytes of interest in the routinely used sample containers. One set is spiked at 5–10 times the RL, the other set at or above midrange. The samples are carried through the entire analytical process.

Soil and Sediment

A minimum of two different soil types must be analysed. One must be a clay matrix, the other an organic matrix (containing more than three percent total organic carbon, > 3% TOC). Well homogenized composite samples are prepared and a minimum of five aliquots of each soil type is spiked with all the analytes of interest at 5–10 times the RL and at or above the midrange (20 samples total). If suitable reference materials are available, they may be used. The samples are carried through the entire analytical process.

Analysis and Acceptability Criteria

If possible, the analyses should be split between two analysts. The precision and accuracy of the two analysts should be within a factor of 1.5 to demonstrate acceptable method ruggedness.

The relative percent difference (RPD) of the replicates, and matrix spike recovery are calculated. Electrical conductivity and pH are exempt from requiring matrix spikes. The RPD and recoveries must meet the limits specified in Tables 5-1 to 5-15 as appropriate. If the native concentration of some analytes are greater than the matrix spike concentration for some parameters, the matrix spike limits do not apply. If certified reference materials (CRMs) are used, the acceptance limits associated with the CRM must be met.

5.3 Method Detection Limits

Method detection limits (MDLs) must be determined for every regulated parameter analysed (except pH or other parameters where MDL may be irrelevant). If more than one instrument is used for a test, MDLs must be established for each instrument or must be evaluated in a way that considers all instruments that are used for the test. The MDLs are redetermined at a minimum every two years or whenever major changes are made to the method or instrumentation.

The MDLs must be less than or equal to (≤) the required reporting limit (RL) for each parameter.

The minimum standard for MDL determination (should only be used for new methods with limited available data) is described as follows:

Prepare a sample (usually reagent water or blank soil) fortified at a level 1–10 times the expected MDL for the analytes of interest. If the resultant calculated MDL is not within this range the determination must be repeated until the calculated MDL concentration is 1–10 times the spike concentration.

Take a minimum of seven aliquots of the sample and process each through the entire analytical method. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analysed.

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

It is widely accepted that MDL determined by approach described above are typically lower than those that are achievable on a day-to-day basis. A more robust approach would include the assessment of method blank contributions, as such this approach is recommended for mature methods. This alternative MDL approach was adopted by U.S. EPA in 2016 and MECP (LSBSOP026, v. 5, 2019, as amended from time to time) in 2019 and is described below; It is estimated using blanks and low-level spikes as the resulting MDL is the higher of the two estimates.

The key elements of this protocol are that a 99% confidence MDL is calculated based on standard deviation assessments derived from long term method blanks (minimum 8 method blanks from multiple calendar dates) and/or long-term low-level spikes (Laboratory Control Samples), rather than using single-batch MDL spike studies. Please note that this approach can also combine/pool data from multiple instruments. Use of between run data provides a more realistic estimate of method detection capabilities under routine operating conditions.

If more than one instrument is used for a method, two options are possible: MDLs must be established for each instrument and the final MDL will be the largest of several MDLs or analyse the replicate samples on each instrument used for the analytical procedure and calculate a single MDL using all the values from each instrument. A minimum of five values are required from each instrument. For example, if two instruments are used, there would be a minimum of ten values (2x5) to be used to calculate the MDL. Make sure to use the appropriate Student's t-statistic that corresponds to the correct degree of freedom. In the above example, the df = 9 (10-1) and the corresponding t-statistic is: t (n-1, 0.99) = 2.821.

Calculate the conventional standard deviation (S_1) of the replicate measurements as follows:

$$S_1 = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}$$

where:

x_i = analytical results in the final method reporting units for the n replicate aliquots (i = 1 to n)

$\bar{x}$ = average of the "*n*" replicate measurements

Outliers identified using Grubb's test or Dixon's Q test may be deleted if proven, but a minimum of seven data points must remain.

An alternative is to use previously determined within run replicate analysis data and calculate the standard deviation (S_2) of the replicate measurements as follows.

$$S_2 = \sqrt{\frac{\sum_{i=1}^{n}(x_1 - x_2)_i^2}{2n}}$$

where:

x_1, x_2 = the two replicate results for each of the n replicate pairs

Compute the MDL as follows:

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

Or if blank component is assessed

$$MDL = X_{blk} + t_{(n-1,\ \alpha=0.01)} S_{blk}$$

where:

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

α = traditionally called the level of significance of the test and is a measure of the maximum probability of a Type I error for all distributions consistent with the null hypothesis.

S = standard deviation as determined above.

X_{blk} = mean of the method blank results (use zero in place of the mean if the mean is negative)

Table 5.3 Single-Tailed 99th Percentile t-Statistic

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1,\ 0.99)}$
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
32	31	2.453
48	47	2.408
50	49	2.405
61	60	2.390
64	63	2.387
80	79	2.374
96	95	2.366
100	99	2.365
∞	∞	2.326

5.3.1 Determination of MDL for Summed Parameters

For summed parameters such as total xylenes, the MDL is the square root of the sum of the squares of the individual component MDLs. For example, if the MDL for o-xylene is 0.02 and m/p-xylene is 0.03, the total xylene MDL will be 0.04:

$$MDL_{total\ xylenes} = \sqrt{\left(MDL^2_{o-xylene}\right) + MDL^2_{m/p-xylene}} = \sqrt{0.0004 + 0.0009} = 0.04$$

5.3.2 Determination of MDL for Subtracted Parameters

Because of measurement uncertainty considerations, special circumstances for detection limit treatment apply when a parameter is determined by subtraction of one result from another. If parameter C_3 is defined as $C_1 - C_2$, the MDL and RL (reporting limit), for parameter C_1 are normally used for C_3.

However, when the magnitude of C_2 approaches C_1 (i.e., if C_2 is ≥ 1/3 of C_1), the uncertainty of C_3 increases significantly. When the uncertainty of a test result exceeds the magnitude of the result itself, the confidence of detection becomes uncertain. Therefore, in this circumstance, the detection limit should be increased to the value of the uncertainty of the subtracted parameter, as follows:

$$RL\ for\ C_3 = \sqrt{\left[\left(U_{C_1}\right)^2 + \left(U_{C_2}\right)^2\right]}$$

Where

U_{C1} = The laboratory's 95% confidence Measurement Uncertainty (MU) estimate for C_1

U_{C2} = The laboratory's 95% confidence Measurement Uncertainty (MU) estimate for C_2

5.3.3 Determination of MDL for Sodium Adsorption Ratio (SAR)

For calculated parameters such as SAR, the MDL is determined as in every other case by multiplying the standard deviation of SAR (S_{SAR}) by three. The MDL of SAR (MDL_{SAR}) is estimated using the following four equations.

EQUATION 1:

$$\overline{SAR} = \frac{[\overline{Na}]}{\sqrt{\frac{1}{2}\left([\overline{Ca}] + [\overline{Mg}]\right)}}$$

EQUATION 2:

$$R_{SAR} = \sqrt{\left[\left(\frac{S_{Na}}{\overline{Na}}\right)^2\right] + \left[\frac{{S_{Ca}}^2}{\frac{1}{\overline{Ca}^2}\left[\overline{Ca}^2 + \overline{Mg}^2\right]^2}\right] + \left[\frac{{S_{Mg}}^2}{\frac{1}{\overline{Mg}^2}\left[\overline{Ca}^2 + \overline{Mg}^2\right]^2}\right]}$$

EQUATION 3:

$$S_{SAR} = R_{SAR}\ x\ \overline{SAR}$$

EQUATION 4: $MDL_{SAR} = S_{SAR} \times 3$

Where:

R_{SAR} = relative standard deviation of sodium adsorption ratio

S_{SAR} = standard deviation sodium adsorption ratio

S_{Na} = standard deviation of sodium ion

S_{Ca} = standard deviation of calcium ion

S_{Mg} = standard deviation of magnesium ion

$\overline{SAR}$ = average value of sodium adsorption ratio

$\overline{Na}$ = average value of sodium ion

$\overline{Ca}$ = average value of calcium ion

$\overline{Mg}$ = average value of magnesium ion

5.3.4 Calculation of Toxic Equivalence MDL

The toxic dioxin and furan isomer concentrations are used to calculate a toxic equivalence factor. The same principle described in 5.3.1 is used except the MDL is multiplied by the toxic equivalency factor (TEF), then squared. The TEF MDL is the square root of the sum of squares of the individual MDL times the TEF values. An example is given below.

Table 5.3.4 Example: Calculation of Toxic Equivalence MDL

CONGENER	TEF WHO 2005[a]	MDL[b] (pg/g)	MDL x TEF (pg/g)	(MDL x TEF)^2 (pg/g)
2,3,7,8-T4CDD	1	1.8	1.80	3.24
1,2,3,7,8-P5CDD	1	5.7	5.70	32.5
1,2,3,4,7,8-H6CDD	0.1	3.7	0.370	0.137
1,2,3,6,7,8-H6CDD	0.1	6.2	0.620	0.384
1,2,3,7,8,9-H6CDD	0.1	23	2.30	5.29
1,2,3,4,6,7,8-H7CDD	0.01	9.5	0.0950	0.00903
OCDD	0.0003	46	0.0138	0.000190
2,3,7,8-T4CDF	0.1	8.9	0.890	0.792
1,2,3,7,8-P5CDF	0.03	9.3	0.279	0.0778
2,3,4,7,8-P5CDF	0.03	7.8	0.234	0.0548
1,2,3,4,7,8-H6CDF	0.1	8.5	0.850	0.723

CONGENER	TEF WHO 2005[a]	MDL[b] (pg/g)	MDL x TEF (pg/g)	(MDL x TEF)^2 (pg/g)
1,2,3,6,7,8-H6CDF	0.1	7.2	0.720	0.518
2,3,4,6,7,8-H6CDF	0.1	8.6	0.860	0.740
1,2,3,7,8,9-H6CDF	0.1	8.6	0.860	0.740
1,2,3,4,6,7,8-H7CDF	0.01	12	0.120	0.0144
1,2,3,4,7,8,9-H7CDF	0.01	8.4	0.0840	0.00706
OCDF	0.0003	15	0.00450	0.0000203
			(Sum of squares)	45.2 pg/g
			TEQ (2,3,7,8-TCDD) MDL = square root of sum of squares	6.7 pg/g

The MDL for each of the 17 “toxic congeners” is determined from eight spiked samples. The standard deviation of the mean is multiplied by Student *t* value (2.998 if eight samples are analysed).

The MDL for each of the 17 congeners is multiplied by its TEF to convert its value to equivalents of 2,3,7,8-TCDD.

These values are then squared and summed. The square root of the sum of squares is the MDL value for the 2,3,7,8-TCDD toxic equivalent quantity (TEQ).

[a]TEF = international toxic equivalency factor based on WHO, 2005

[b]MDL = method detection limit for each individual congener

5.4 Measurement Uncertainty

Uncertainty of measurement must be estimated and documented. There are several guidelines for the estimation of measurement uncertainty including those published by MECP, the International Organization for Standardization (ISO) and EURACHEM/Cooperation on International Traceability in Analytical Chemistry (CITAC). Every possible source of uncertainty must be evaluated, but only those exceeding one-third of 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.

Uncertainty of measurement must be estimated for all analytes and expressed as expanded uncertainty (U) at 95% confidence (k=2).

Measurand: The specific quantity subject to measurement, such as the concentration of an analyte.

Uncertainty: A non-negative parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

Uncertainty Component: Uncertainty of a result may rise from many possible sources. Each of the separate contributions to uncertainty is referred to as an uncertainty component.

Standard Uncertainty: Uncertainty components are evaluated by the appropriate method and each is expressed as a standard deviation and is referred to as a standard uncertainty.

Combined Standard Uncertainty: Standard uncertainty components are combined to produce an overall value of uncertainty known as the combined standard uncertainty. It is an estimated standard deviation equal to the positive square root of the sum of variances of all uncertainty components.

$$\mu_c = \sqrt{\sum \mu_i^2}$$

where:

μ_c = combined uncertainty of the result

μ_i = uncertainty of the individual component

Expanded Uncertainty: Expanded uncertainty (U) is obtained by multiplying the combined standard uncertainty by a coverage factor "**k**" to provide an interval within which the value of the measurand is believed to lie, with a specified level of confidence (e.g. 95%).

$$U = \mu_c \times k$$

where:

μ_c = combined uncertainty of the result

k = 2 (for 95% confidence level)

5.5 Quality Control Samples

The laboratory quality control (QC) samples routinely analysed are method blanks, laboratory control samples, sample duplicates and matrix spikes. In addition, surrogate standards are employed for organic analysis. The acceptance limits for these QC samples are the metrics by which the quality of the associated laboratory data is demonstrated.

Note that all applicable QC samples as tabulated below must be analysed when sufficient sample is available. Extractable organic tests on ground water require multiple containers and the containers cannot be subsampled. The QP is responsible for the submission of multiple samples. If multiple containers are not submitted, matrix spike and duplicate samples cannot be provided.

Laboratory QC may be supplemented by various field QC samples such as blind field duplicates, travel blanks, equipment rinse blanks and travel spikes. In general, acceptance limits for field QC are broader than laboratory QC.

As well as these QC samples, there are additional data quality related requirements associated with all analytical methods such as: number of calibration standards, calibration curve frequency and acceptance criteria, continuing calibration frequency and acceptance criteria and gas chromatography-mass spectrometry (GC-MS) tuning criteria.

The acceptance criteria specified in the reference method for these elements should be met. If there are deviations from the reference, they must be documented, and valid reasons given.

Blanks are defined as matrices that have negligible or unmeasurable amounts of the analytes of interest.

Travel Blank: is a sample of methanol preservative, reagent water or blank soil transported unopened to and from the sampling location carried through the entire sampling and analytical process including all sample preparation steps. It is recommended that a travel blank be submitted with each batch of pre-weighed methanol or bisulphate vials to verify that no VOCs were introduced during the vial preparation process.

Method Blank: is a sample of reagent water or blank soil carried through the entire analytical process including all sample preparation steps.

Laboratory Control Sample (LCS): is a sample of reagent water or blank soil spiked with the analytes of interest and carried through the entire analytical process including all sample preparation steps. In general, the LCS will be a second source standard and have a concentration near the midpoint of the calibration range.

LCS Recovery = [measured concentration] / [design concentration]

Sample Duplicate: is a second aliquot of a soil or water sample carried through the entire analytical process including all sample preparation steps. Note that since most water sample tests for extractable organic analytes consume the entire sample, duplicates are actually field duplicates, and are only possible if sufficient additional sample bottles are provided to the laboratory.

Duplicate RPD = {([sample] – [sample duplicate]) / ([sample] + [sample duplicate])/2} x 100

For organic analysis, soils are analysed as received. As such, duplicates are primarily a measure of sample homogeneity. Similarly, because water analyses are “whole bottle” tests, sample duplicates are field duplicates, subject to sampling variability. The duplicate acceptance limits contained in the following tables are based on homogeneous samples. If samples are visibly non-homogeneous, repeat analysis is not required. Data are reported flagged as “exceedance due to sample heterogeneity”. For most inorganic tests, samples are taken from the original container and processed with the documented method that will be used for the real samples, so the above stipulations do not apply.

Matrix Spike is a second aliquot of a soil or water sample spiked, usually about mid-range, with all analytes determined in the analysis and carried through the entire analytical process including all sample preparation steps. Note that for soil tests where the extraction is not intended to recover all the native analyte (chloride, cyanide, HWS boron), the spike is added post extraction. In general, the matrix spike will be a second source standard and have a concentration near the midpoint of the calibration range. Reference materials (RMs) may be used in place of matrix spikes where appropriate, provided the matrix is similar to the samples and they contain all analytes in the test.

Matrix Spike Recovery = {([spiked sample] – [un-spiked sample]) / [spike]} x 100

Because matrix spikes are also impacted by sample heterogeneity, the issues discussed in sample duplicates above may apply.

Surrogates are used for organic tests. All samples are spiked with compounds (usually deuterated analogs) representative of the analytes being determined but not found in environmental samples. The surrogates are spiked into the sample prior to any sample preparation steps and carried through the entire analytical process.

Surrogate Recovery = ([measured concentration] / [theoretical concentration]) x 100

Internal Standards are used for some organic tests (i.e., ABNs, VOCs). A known amount of compound(s) (not present in the samples, but closely matching the chemical behavior of the compound(s) of interest) are added to every sample (including all QC samples) prior to analysis to quantitate by comparing the response of a major (quantitation) ion relative to an internal standard.

Continuing Calibration Verifications: (CCVs) are evaluated to determine whether the instrument was within acceptable calibration throughout the period in which samples were analysed (i.e., to verify that the initial calibration was applicable during the sample analyses). In general, failure of the CCV indicates that the initial calibration is no longer valid and should trigger recalibration and the reanalysis of the associated samples in the analytical sequence.

5.5.1 Acceptance Limits and Qualifiers

The pre-established ranges of acceptability tabulated below are in accord with the reference methods outlined in Section 3 of this document.

Multi-element Scan Qualifier: as the number of analytes in a scan increases, so does the chance of a limit exceedance by random chance as opposed to a real method problem. Thus, in multi-element scans, for the LCS and matrix spike, up to 10% of the analytes may exceed the quoted limits by up to 10% absolute and the spike is considered acceptable. For example, in a polycyclic aromatic hydrocarbon (PAH) scan of 17 analytes with matrix spike acceptance limits of 50–140%, 10% or one analyte may have a recovery outside of 50–140% by 10% absolute, i.e., a recovery of 40–150%.

Duplicate Qualifier: for duplicates as the measured result approaches the RL, the uncertainty associated with the value increases dramatically, thus duplicate acceptance limits apply only where the average of the two duplicates is greater than five times the RL.

Matrix Spike Qualifier: for matrix spikes, as the concentration of the native analyte increases, the uncertainty of the matrix spike recovery increases. (It is not possible to accurately quantitate a small difference between two large numbers). Thus, the matrix spike acceptance limits apply only when the concentration of the matrix spike is greater than or equal to the concentration of the native analyte.

Calculated Parameters: for calculated parameters, acceptance limits should reflect the uncertainty (μ_i) in each measurement (see section 5.4). This is especially important for parameters calculated by difference such as $F1_{-BTEX}$.

For example, in a sample with a summed BTEX concentration of 10 mg/L and an F1 concentration of 11 mg/L, each with an μ_i of 20% or about 2 mg/L, the μ_i of the $F1_{-BTEX}$ reported result is 1 mg/L ± 2.8, a component uncertainty of 280%:

$$\mu_{F1_{-BTEX}} = \sqrt{(2^2 + 2^2)} = 2.8 = 280\%$$

In this example the routine QC acceptance limits for BTEX and F1 obviously cannot apply. For additive parameters, the impact is much less. Thus, for parameters calculated by subtraction, QC acceptance limits are only applied to the individual components.

TABLE 5-1: Performance Criteria – Acid/Base Neutral Extractable Organic Compounds (ABNs), Chlorophenols (CPs), Polycyclic Aromatic Hydrocarbons (PAHs)

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method Blank	Laboratory contamination evaluation	• Extracted with every batch or every 20 samples, whichever is more frequent • Matrix-specific (e.g., water, soil) • Target analytes should be less than the reporting limit (RL)	**YES:** If an analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis), the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard • LCS percent recovery should be between 50–140% for all compounds except 30–130% for p-chloroaniline, 3,3-dichlorobenzidene, phenol, 2,4-dimethylphenol, DNP	**YES:** Re-extract/re-analyse all associated samples, if possible. If not, report the data flagged for all failing analytes.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Extracted with every batch or every 20 samples, whichever is more frequent • Separate-source standard • Percent recoveries should be between 50–140% for all compounds except 30–130% for p-chloroaniline, 3,3-dichlorobenzidene, phenol, 2,4-dimethylphenol, DNP, soil and water	**YES**: If recovery is outside of specified limits, repeat if necessary, see 5.5 Matrix Spike. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • RPD should be ≤30% for waters and ≤40% for solids	**YES**: If RPD is within method specifications no action is required. If RPD fails, repeat analysis may be required, see 5.5 Sample Duplicate.

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Surrogates	Accuracy in sample matrix	• Surrogates should represent analytes of interest and be representative of compound class of target analytes (e.g., use deuterated PAH if analysing for PAHs, use phenolic surrogates if analysing for pentachlorophenol) • Percent recoveries in soil and water should be between 50–140% for compounds. Surrogates are optional for isotope dilution methods	**YES**: If recovery is outside of specified limits, laboratory must report recovery and qualify the result.
Internal Standards (IS)	Laboratory accuracy, method accuracy in sample matrix	• Minimum of 3 at retention times across GC run • Area counts in samples must be between 50–200% of the area counts in associated continuing calibration standard (CCV) (Section 5.10 of 8260B). Retention times of internal standards should be within ±6 seconds of retention times in the associated CCV	**NO:** If one or more internal standards are outside limits, reanalyse sample unless obvious interference present.
Quantitation	N/A	• Quantitation must be based on IS calibration • Laboratory must use the average response factor or regression curve generated from the associated initial calibration for quantitation of each analyte • At least 1 qualifier ion (recommend 2) must be used and meet ratio requirements. See SW-846 for guidance. At low concentrations ratios may be expanded but the qualifier must be present for positive identification	**NO**

TABLE 5-2: Performance Criteria – 1,4-Dioxane

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method Blanks	Laboratory contamination evaluation	• Prepared with every batch or every 20 samples, whichever is more frequent • Matrix-specific (e.g., water, soil) • Target analytes should be less than the reporting limit (RL)	**YES:** If an analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis) the data is reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard • LCS percent recovery should be between 50–140%	**YES:** Re-prepare/reanalyse all associated samples, if possible. If not, report the data flagged for all failing analytes.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Extracted with every batch or every 20 samples, whichever is more frequent • Separate-source standard • Percent recoveries should be between 50–140% soil and water	**YES:** If recovery is outside of specified limits, repeat if necessary, see 5.5 Matrix Spike. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • RPD should be ≤30% for waters and ≤50% for solids	**YES:** If RPD is within method specifications, no action is required. If RPD fails, repeat analysis may be required, see 5.5 Sample Duplicate.
Surrogates	Accuracy in sample matrix	• Surrogates should represent analytes of interest and be representative of compound class of target analytes • Percent recoveries in soil should be between 50–140%, soil and water	**YES:** If recovery is outside of specified limits, laboratory must report recovery and qualify the result.

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Quantitation	N/A	• Quantitation must be based on isotope dilution method • Laboratory must use the average response factor or regression curve generated from the associated initial calibration for quantitation of each analyte • At least 1 qualifier ion must be used and meet ratio requirements. See SW846 for guidance. At low concentrations ratios may be expanded but the qualifier must be present for positive identification	**NO**

TABLE 5-3: Performance Criteria – Dioxins/Furans

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method Blanks	Laboratory contamination evaluation	• Extracted with every batch or every 20 samples, whichever is more frequent • Matrix-specific (e.g., water, soil) • Target analytes should be less than the reporting limit (RL)	**YES:** If an analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis), the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard • LCS percent recovery should be between 50–150% for soil and water	**YES:** Re-extract/re-analyse all associated samples, if possible. If not, report the data flagged for all failing analytes.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Extracted with every batch or every 20 samples, whichever is more frequent • Separate-source standard • Percent recoveries should be between 50–150% for soil and water	**YES:** If recovery is outside of specified limits, repeat if necessary, see 5.5 Matrix Spike. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • RPD should be ≤30% for waters and ≤40% for solids	**YES:** If RPD is within method specifications, no action is required. If RPD fails, repeat analysis may be required, see 5.5 Sample Duplicate.
Surrogates	Accuracy in sample matrix	• Surrogates should represent analytes of interest and be representative of compound class of target analytes • Percent recoveries should be between 40–140% for soil and water	**YES:** If recovery is outside of specified limits, laboratory must report recovery and qualify the result.

TABLE 5-4: Performance Criteria – Organochlorine (OC) Pesticides

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method Blanks	Laboratory contamination evaluation	• Extracted with every batch or every 20 samples, whichever is more frequent • Matrix-specific (e.g., water, soil) • Target analytes should be less than the reporting limit (RL)	**YES:** If an analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis) the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard • LCS percent recovery should be between 50–140% for soil and water	**YES:** Re-extract/re-analyse all associated samples, if possible. If not, report the data flagged for all failing analytes.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Extracted with every batch or every 20 samples, whichever is more frequent • Separate-source standard • Percent recoveries should be between 50–140% for soil and water	**YES:** If recovery is outside of specified limits, repeat if necessary, see 5.5 Matrix Spike. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • RPD should be ≤30% for waters and ≤40% for solids	**YES:** If RPD is within method specifications, no action is required. If RPD fails, repeat analysis may be required, see 5.5 Sample Duplicate.
Surrogates	Accuracy in sample matrix	• Surrogates should represent analytes of interest and be representative of compound class of target analytes • Percent recoveries should be between 50–140% for soil and water on both columns	**YES:** If recovery is outside of specified limits, laboratory must report recovery and qualify the result.

TABLE 5-5: Performance Criteria – Polychlorinated Biphenyls (PCBs)

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method Blanks	Laboratory contamination evaluation	• Extracted with every batch or every 20 samples, whichever is more frequent • Matrix-specific (e.g., water, soil) • Target analytes should be less than the reporting limit (RL)	**YES:** If an analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis) the data is reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard • LCS percent recovery should be between 60–140% for soil and water	**YES:** Re-extract/re-analyse all associated samples, if possible. If not, report the data flagged for all failing analytes.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Extracted with every batch or every 20 samples, whichever is more frequent • Separate-source standard • Percent recoveries should be between 60–140% for soil and water	**YES:** If recovery is outside of specified limits, repeat if necessary, see 5.5 Matrix Spike. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • RPD should be ≤30% for waters and ≤40% for solids	**YES:** If RPD is within method specifications, no action is required. If RPD fails, repeat analysis may be required, see 5.5 Sample Duplicate.
Surrogates	Accuracy in sample matrix	• Surrogates should represent analytes of interest and be representative of compound class of target analytes • Percent recoveries should be between 60–140% for soil and water	**YES:** If recovery is outside of specified limits, laboratory must report recovery and qualify the result.

TABLE 5-6: Performance Criteria – Petroleum Hydrocarbons (PHCs)

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method Blanks	Laboratory contamination evaluation	• Extracted with every batch or every 20 samples, whichever is more frequent • Matrix-specific (e.g., water, soil) • Target analytes should be less than the reporting limit (RL)	**YES:** If an analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis) the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard • LCS percent recovery should be between 80–120% for soil and 60–140% for water	**YES:** Re-extract/re-analyse all associated samples, if possible. If not, report the data flagged for all failing analytes.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Extracted with every batch or every 20 samples, whichever is more frequent • Separate-source standard prepared from gasoline or diesel/motor oil as appropriate • Percent recoveries should be between 60–140% soil and water	**YES:** If recovery is outside of specified limits, repeat if necessary, see 5.5 Matrix Spike. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • RPD should be ≤30% for waters and ≤30% for solids	**YES:** If RPD is within method specifications, no action is required. If RPD fails, repeat analysis may be required, see 5.5 Sample Duplicate.
Surrogates	Accuracy in sample matrix	• Surrogates should represent analytes of interest and be representative of compound class of target analytes • Percent recoveries in soil should be between 60–140% for soil and water	**YES:** If recovery is outside of specified limits laboratory must report recovery and qualify the result.

TABLE 5-7: Performance Criteria – Volatile Organic Compounds (VOCs)

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Travel Blanks	Field contamination evaluation and methanol vial integrity	• Prepared with every batch of methanol-preserved soil samples • Travel blank is reweighed at the lab and compared to tarred weight to determine any loss of methanol and methanol is analysed. Loss of up to 4% methanol is acceptable, • Target analytes should be less than the reporting limit (RL). Note: acetone, methylene chloride, toluene and hexane are common laboratory artefacts. If any are > RL the laboratory must comment on the impact on data quality.	**YES:** If an analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis) the data are reported flagged.
Method Blanks	Laboratory contamination evaluation	• Prepared with every batch or every 20 samples, whichever is more frequent • Matrix-specific (e.g., water, soil) • Target analytes should be less than the reporting limit (RL). Note: acetone, methylene chloride, toluene and hexane are common laboratory artefacts. If any are > RL the laboratory must comment on the impact on data quality.	**YES:** If an analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis) the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard • LCS percent recovery should be between 50–140% for compounds that are gaseous at 20C and ketones, 60–130% for all others, soil and water	**YES:** Re-prepare/re-analyse all associated samples, if possible. If not, report the data flagged for all failing analytes.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Extracted with every batch or every 20 samples, whichever is more frequent • Separate-source standard • Percent recoveries should be between 50–140% soil and water	**YES:** If recovery is outside of specified limits, repeat if necessary, see 5.5 Matrix Spike. If not or if the repeat also fails, report recovery and qualify the result.

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • RPD should be ≤30% for waters and ≤50% for solids	**YES:** If RPD is within method specifications – no action is required. If RPD fails, repeat analysis may be required, see 5.5 Sample Duplicate.
Surrogates	Accuracy in sample matrix	• Surrogates should represent analytes of interest and be representative of compound class of target analytes. At least one surrogate is added to the soil/sediment sample in methanol prior to analytical processing • Percent recoveries in soil should be between 50–140%, soil and water	**YES:** If recovery is outside of specified limits, laboratory must report recovery and qualify the result.
Internal Standards (IS)	Laboratory analytical accuracy land method accuracy in sample matrix	• Minimum of 3 at retention times across GC run • Area counts in samples should be between 50–200% of the area counts in associated continuing calibration standard (Section 5.10 of 8260B) • Retention times of internal standards should be within ±6 seconds of retention times in associated continuing calibration standard	**NO:** If one or more internal standards are outside limits, reanalyse sample unless obvious interference present.
Quantitation	N/A	• Quantitation must be based on IS calibration • Laboratory must use the average response factor or regression curve generated from the associated initial calibration for quantitation of each analyte • At least 1 qualifier ion (recommend 2) must be used and meet ratio requirements. See SW846 for guidance. At low concentrations ratios may be expanded but the qualifier must be present for positive identification	**N/A**

TABLE 5-8: Performance Criteria – Cyanide (CN^-)

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method Blanks	Laboratory contamination evaluation	• Every batch or every 20 samples whichever is more frequent • Should be matrix-matched (same concentration of reagents as calibration and QC standards) and distilled with samples in batch • Target analytes should be less than the reporting limit (RL)	**YES:** If the analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis), the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard (soil or water) spiked post extraction for soil • LCS percent recovery should be between 80–120%	**YES:** Re-prepare/re-analyse all associated samples, if possible. If not, report the data flagged.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Analysed with every batch or every 20 samples, whichever is more frequent • Separate-source standard, spiked post extraction for soil • Percent recoveries should be between 70–130% soil and water	**YES:** If recovery is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • Percent difference should be ≤ 20% for water and ≤ 35% for soils	**YES:** If RPD is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.

TABLE 5-9: Performance Criteria – Electrical Conductivity (EC)

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method (Preparation) Blank	Laboratory contamination evaluation	• Every batch or every 20 samples whichever is more frequent • Target analytes should be less than the reporting limit (RL)	**YES:** If the analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis), the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard (soil or water) • LCS percent recovery should be between 90–110%	**YES:** Re-extract/re-analyse all associated samples, if possible. If not, report the data flagged.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	**N/A**	**N/A**
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • RPD should be ≤ 10%	**YES:** If RPD is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.

TABLE 5-10: Performance Criteria – Fraction Organic Carbon (FOC), Chloride

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method (Preparation) Blank	Laboratory contamination evaluation	• Every batch or every 20 samples whichever is more frequent • Should be matrix-matched (same concentration of reagents as calibration and QC standards) and prepared with samples in batch • Target analytes should be less than the reporting limit (RL)	**YES:** If the analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis) the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard (soil or water) spiked post extraction for chloride in soil • LCS percent recovery should be between 70–130%	**YES:** Re-prepare/re-analyse all associated samples, if possible. If not, report the data flagged.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Analysed with every batch or every 20 samples, whichever is more frequent • Separate-source standard spiked post extraction for chloride in soil • Percent recoveries should be between 70–130% in soil and water	**YES:** If recovery is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	• For chloride samples: analysed with every batch or every 20 samples, whichever is more frequent • For FOC samples: all samples are taken and analysed in triplicate, therefore, additional duplicates are not required • RPD should be ≤ 20% for water and ≤ 35% for soils	**YES:** If RPD is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.

TABLE 5-11: Performance Criteria – Hexavalent Chromium, Cr(VI)

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method (Preparation) Blank	Laboratory contamination evaluation	• Every batch or every 20 samples whichever is more frequent • Should be matrix-matched (same concentration of reagents as calibration and QC standards) and prepared with samples in batch • Target analytes should be less than the reporting limit (RL)	**YES:** If the analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis), the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard (soil or water) • LCS percent recovery should be between 80–120%	**YES:** Re-prepare/re-analyse all associated samples, if possible. If not, report the data flagged.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Analysed with every batch or every 20 samples, whichever is more frequent • Separate-source standard • Percent recoveries should be between 70–130% soil[#] and water	**YES:** If recovery is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • RPD should be ≤ 20% for water and ≤ 35% for soils	**YES:** If RPD is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.

[#] Some soil samples may react with the Cr(VI) spike reducing it to Cr(III). These samples are highly unlikely to contain native hexavalent chromium. Thus, a failed spike recovery does not invalidate a negative result on the native sample.

TABLE 5-12: Performance Criteria – Mercury

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method (Preparation) Blank	Laboratory contamination evaluation	• Every batch or every 20 samples whichever is more frequent • Should be matrix-matched (same concentration of reagents as calibration and QC standards) and prepared with samples in batch • Target analytes should be less than the reporting limit (RL)	**YES:** If the analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis), the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard (soil or water) • LCS percent recovery should be between 80–120%	**YES:** Re-digest/re-analyse all associated samples, if possible. If not, report the data flagged.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Analysed with every batch or every 20 samples, whichever is more frequent • Separate-source standard • Percent recoveries should be between 70–130% soil and water	**YES:** If recovery is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • RPD should be ≤ 20% for water and ≤ 30% for soils	**YES:** If RPD is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.

TABLE 5-13: Performance Criteria – Methyl Mercury

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method (Preparation) Blank	Laboratory contamination evaluation	Every batch or every 20 samples whichever is more frequent Should be matrix-matched (same concentration of reagents as calibration and QC standards) and prepared with samples in batch Target analytes should be less than the reporting limit (RL)	**YES:** If the analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis), the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	Every batch or every 20 samples whichever is more frequent Separate-source standard (soil or water) LCS percent recovery should be between 70–130%	**YES:** Re-prepare/re-analyse all associated samples, if possible. If not, report the data flagged
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	Analysed with every batch or every 20 samples, whichever is more frequent Separate-source standard Percent recoveries should be between 60–140% soil and water	**YES:** If recovery is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	Analysed with every batch or every 20 samples, whichever is more frequent RPD should be ≤ 30% for water and ≤ 40% for soils	**YES:** If RPD is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.

TABLE 5-14: Performance Criteria – Boron, Hot Water Soluble (HWS); Calcium, Nitrate, Nitrite, Nitrogen (total), Magnesium; Sodium; Metals (Including Hydride-Forming Metals)

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method (Preparation) Blank	Laboratory contamination evaluation	• Every batch or every 20 samples whichever is more frequent • Should be matrix-matched (same concentration of reagents as calibration and QC standards) and prepared with samples in batch • Target analytes should be less than the reporting limit (RL)	**YES:** If the analyte fails, corrective action is required. If it cannot be corrected (reinjection, reanalysis), the data are reported flagged.
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard (soil or water), spiked post extraction for HWSB • LCS percent recovery should be between 80–120%. HWBS 70–130%	**YES:** Re-extract/re-analyse all associated samples, if possible. If not, report the data flagged.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	• Analysed with every batch or every 20 samples, whichever is more frequent • Separate-source standard, spiked post extraction for HWSB • Percent recoveries should be between 70–130% soil and water. HWSB 60–140% (soil)	**YES:** If recovery is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • RPD should be ≤ 20% for water and ≤ 30% for soils. HWSB ≤ 40% for soil	**YES:** If RPD is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.

TABLE 5-15 Performance Criteria – pH in Soil

Required QA/ QC Parameter	Data Quality Objective	Required Performance Standard	Included in Analytical Report/ Certificate of Analysis
Method (Preparation) Blank	Laboratory contamination evaluation	N/A	**N/A**
Laboratory Control Sample (LCS)	Laboratory method accuracy without matrix effects	• Every batch or every 20 samples whichever is more frequent • Separate-source standard (soil or water) • LCS percent recovery should be between ± 0.2 pH units	**YES:** Re-analyse all associated samples, if possible. If not, report the data flagged.
Matrix Spike (or Reference Material as per Section 5.5)	Laboratory method accuracy with matrix effects, sample homogeneity	N/A	**N/A**
Sample Duplicate	Sample homogeneity, laboratory method precision	• Analysed with every batch or every 20 samples, whichever is more frequent • within 0.3 pH units	**YES:** If RPD is outside of specified limits, repeat if possible. If not or if the repeat also fails, report recovery and qualify the result.

SECTION 6: REFERENCES

- American Society for Testing and Materials (ASTM), 2010 Annual Book of Standards
- American Society for Testing and Materials (ASTM) Method D6418 – 09: Standard Practice for Using the Disposable EnCore Sampler for Sampling and Storing Soil for Volatile Organic Analysis, Annual Book of Standards 2010, Volume 11.04
- Canadian Council of Ministers of the Environment (CCME). Guidance Manual for Environmental Characterisation in Support of Environmental and Human Health Risk; Volume IV: Compendium of Analytical Methods for Contaminated Sites (2015 *release date TBD)*
- Canadian Council of Ministers of the Environment (CCME). Reference Method for the Canada-wide Standard for Petroleum Hydrocarbons (CWS-PHC) in Soil – Tier 1 Method. 2001
- EURACHEM/Cooperation on International Traceability in Analytical Chemistry (CITAC), Quantifying Uncertainty in Analytical Measurement, (Second Edition, 2000)
- Gupta, UC 1967: A simplified method for determining hot water-soluble boron in podzol soils, Soil Science 103: 424-428
- Handbook of Quality Assurance for the Analytical Chemistry Laboratory. Dux, James P. 1986. Van Nostrand Reinhold Company Inc
- International vocabulary of metrology – Basic and general concepts and associated terms; ISO/IEC Guide 99:2007 (VIM 2007)
- International Standard ISO/IEC 17025:2017 – General Requirements for the Competence of Testing and Calibration Laboratories
- International Standard ISO/IEC Guide 33.2015 – Reference materials – Good practice in using reference materials
- International Standard ISO/IEC Guide 99.2007 – International vocabulary of metrology – Basic and general concepts and associated terms (VIM)
- Massachusetts Department of Environmental Protection Bureau of Waste Site Cleanup, Quality Assurance and Quality Control Requirements for SW-846 Method 7196A, Hexavalent Chromium by UV-Visible Spectrophotometry for the Massachusetts Contingency Plan (MCP)
- Quality Assurance and Quality Control Requirements for SW-846 Method 8081B, Chlorinated Pesticides by Gas Chromatography (GC) for the Massachusetts Contingency Plan (MCP)
- Quality Assurance and Quality Control Requirements for SW-846 Method 8082, Polychlorinated Biphenyls (PCBs) by Gas Chromatography (GC) for the Massachusetts Contingency Plan (MCP)

- Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 8151A, Chlorinated Herbicides by Gas Chromatography Using Methylation or Pentafluorobenzylation Derivatization, for the Massachusetts Contingency Plan (MCP)

- Quality Assurance and Quality Control Requirements for SW-846 Method 8270E, Semi-volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) for the Massachusetts Contingency Plan (MCP)

- Quality Assurance and Quality Control Requirements and Performance Standards for SW-846 Method 9014, Total Cyanide and the MADEP Physiologically Available Cyanide (PAC) Protocol, for the Massachusetts Contingency Plan (MCP)

- Quality Assurance and Quality Control Requirements for SW-846 Method 8260B, Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS) for the Massachusetts Contingency Plan (MCP)

- Ontario Ministry of the Environment (MOE) Practices for the Collection and Handling of Drinking Water Samples, Version 2.0, April 1, 2009

- Ontario Ministry of the Environment (MOE) Protocol for Analytical Methods Used in the Assessment of Properties under Part XV.1 of the *Environmental Protection Act,* March 9, 2004

- Ontario Ministry of the Environment (MOE) Protocol for Analytical Methods Used in the Assessment of Properties under Part XV.1 of the *Environmental Protection Act,* March 9, 2011, amended as of July 1, 2011.

- Ontario Ministry of the Environment (MOE) Protocol for the Acceptance of Alternate Methods (PAAM) Version 1.4 January 2005

- Ontario Ministry of the Environment, Protocol of Accepted Drinking Water Testing Methods, Version 2.0, May 2010

- Ontario Ministry of the Environment, Protocol for Sampling and Analysis of Industrial/ Municipal Waste Water, Version 2.0, January 2016

- Ontario Ministry of the Environment Conservation and Parks (MECP), Laboratory Services Branch, Quality Management Section, LaSB Procedures Manual, LSBSOP.030, Laboratory Services Branch (LaSB) Guidelines for the Determination and Documentation of Uncertainty of Chemical Measurements

- Ontario Ministry of the Environment Conservation and Parks (MECP), Laboratory Service Branch, Assistant-Director Office, LSBSOP026, Standard Operating Procedure for the Determination of Method Detection Limit, v. 5, November 2019.

- Standard Methods, APHA-AWWA-WEF, Standard Methods for the Examination of Water and Wastewater (23rd Edition)

- Standard Methods for the Examination of Water and Wastewater (23rd Edition): Volatile Organic Compounds – Purge & trap Capillary-Column Gas Chromatographic/Mass Spectrometric Method

- Standard Methods, Standard Methods News, Revised sections in Part 3000. 3500-Cr Chromium (2009), November 11, 2010 (www.standardmethods.org)

- United States Department of Agriculture (USDA) Agriculture Handbook No. 60; Chapter 6: Methods for Soil Characterization, February 1954

- United States Environmental Protection Agency (U.S. EPA) Definition and Procedure for the Determination of the Method Detection Limit, Revision 2, Dec. 2016. https://www.epa.gov/sites/production/files/2016-12/documents/mdl-procedure_rev2_12-13-2016.pdf

- United States Environmental Protection Agency (U.S. EPA) Federal Register Part III. March 12, 2007. 40 CFR Part 122, 136, et al. Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; and National Secondary Drinking Water Regulations; Analysis and Sampling Procedures; Final Rule (page 11218, 11236, 11239)

- United States Environmental Protection Agency (U.S. EPA) SW846. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

- United States Environmental Protection Agency (U.S. EPA) Contract Laboratory Program, Office of Superfund Remediation and Technology Innovation. Multi-Media, Multi-concentration Organics Analysis, OLM04.3

- United States Environmental Protection Agency (U.S. EPA) National Exposure Research Laboratory. Method 524.2: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry

- United States Geological Survey (USGS), United States Department of the Interior

- United States Geological Survey (USGS) – National Water Quality Laboratory (NWQL)