

Volume 4 of the 2016 CCME Guidance Documents: Compendium of Analytical Methods for Contaminated Sites

TECHNICAL
BULLETIN

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At the beginning of 2016, the Canadian Council of Ministers of the Environment (CCME) published new guidance documents for "Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment at Contaminated Sites". The goal of these guidance documents is to provide consistency to sampling and analysis procedures, as well as to the quality of analytical data. The 2016 CCME guidance documents were greatly anticipated and adoption across Canada is being registered:

- **British Columbia** Ministry of Environment is adopting the Data Quality Objectives, however local regulations and guidelines are to be followed;
- **Alberta Environment** is in the process of fully adopting the guidance; Mar 1 2017
- **Saskatchewan** and **Manitoba Environment** have already adopted the guidance;
- **Quebec** MDDELCC is in the process of partially adopting the guidance. Jan 2017
- **Atlantic Canada** adopted the Guidance in Sept 2016.
- Volume 4 is based on the **Ontario** Analytical Protocol and thus Ontario protocols are essentially the same as Volume 4

The purpose of this technical bulletin is to provide a summary of key methods and practices and the changes from previous guidance, as specifically detailed in **Volume 4: Compendium of Analytical Methods for Contaminated Sites**.

The guidelines included in this document are largely based on current reference methodologies and approved practices in Canada and the US, specifically the Ontario Ministry of Environment and Climate Change (OMOECC), Environmental Protection Agency (EPA) and British Columbia (BC) Guidelines. The document is comprehensive, providing detailed information on **(1) Parameter Groups, (2) Sample Handling, Storage Requirements & Analytical Methods** and **(3) Required QA/QC**. For the purpose of simplicity, the summaries following have been organized to follow the structure identified Below. Protocols are provided for all elements and compounds with CCME Guidelines.

1. Parameter Groups

Parameters have been consolidated and grouped in accordance with classes of contaminants, such as *Petroleum Hydrocarbons and Volatile Organic Compounds*. This is in contrast to the previously published CCME guidance documents (1993) which classified parameters based on applicable instrumentation or analytical methodologies. Recommendation is provided towards analysis and reporting of the full list of parameters, regardless of suite, rather than individual parameters, to account for possible associated contaminants or degradation products. In addition, the guidance document recommends the QP use **Open Characterization** analyses when anthropogenic sources of impact are identified.

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A notable addition to the list of parameters includes Perfluoro Alkyl Substances (PFASs) with 13 of the most commonly identified contaminants. It should be noted that no actual concentration guidelines are yet developed for the majority of these compounds, however this class of contaminants continues to receive attention due to their persistent and recalcitrant nature. Please note that Maxxam has packaged PFC parameters to offer standard (2 or 17 parameters), extended (23 parameters) or full (25 parameters) lists.

2. Sample Handling, Storage Requirements and Analytical Methods

The 2016 Guidance document has adopted the use of sample collection methodologies that increase the ease of field procedures and improve parameter stability. On a general basis, samples should be submitted $\leq 10^{\circ}\text{C}$; for samples submitted to the laboratory the same day as collected, temperatures above 10°C are acceptable so long as cooling media has been added. This guideline is in specific reference to organic and other parameters that may be affected by volatilization or biodegradation.

- **Sample collection procedures for BTEX, F1, VOCs and THMs in soils:** the new guidance document specifies the use of either **field preservation with Methanol / Sodium Bisulphate** or the use of **hermetic sampling devices** as the only suitable methods for the collection of volatile organic contaminants. A coring device may be used to extrude (approx.) 5g of soil into a methanol pre-charged 40mL vial; alternatively, the coring device may be a hermetic sampler which only requires capping and submission to the laboratory.

Depending on the method, care must be taken with regards to the applicable holding times. **Methanol extracts are considered stable for 40 days from sample collection** (*please note that CCME guidance recommends separating the methanol extract from the soil material for prolonged storage*). Hermetic sampling devices **must be processed at the laboratory within 48 hours** (i.e. extrusion in methanol, for extraction); alternatively, hermetic devices may be frozen within 48 hours from collection to extend the holding time to **14 days**.

- **Physical Parameters & Inorganics in soil:** For stable parameters and physical testing of soil samples, such as chloride, pH, conductivity, particle size, fraction organic carbon (FOC), total nitrogen, metals, sodium absorption ratio (SAR) and hot water soluble boron (HWSB) samples may be collected in **polyethylene terephthalate (PET) or polypropylene (PP) plastic bags**. *Please note that minimum volume requirements still apply, depending on type or number of analyses performed from a bag.*

- **Analysis of PFASs:** The use of Teflon lining for sample collection of PFAS parameters is prohibited; polyethylene (PE) lined lids must be used instead. Soil samples **must be extracted at the laboratory within 14 days** and the extracts are **stable for an additional 40 days** from collection; water samples **must be analyzed within 14 days if preserved** at the time of collection or **within 7 days if unpreserved**.

- **Analysis of Hydrocarbons:** The 2016 CCME guidance documents prescribe the use of silica gel in soil samples to remove polar materials that would contribute to quantified concentrations of hydrocarbons in the F2 to F4 (C10-C50) range. However, the guidance indicates that the use of silica **is a single step performed either in-situ or ex-situ**; the use of silica gel for water samples is optional.

For samples that are identified to contain high concentrations of organic matter and, consequently, saturate the silica gel used in the clean-up step, the guidance document provides the following acceptable strategies:

- (1) A second aliquot of the extract to be treated with a larger weight (than normally or originally performed) of silica;
- (2) Employ the use of GC/MS analysis to identify non-petrogenic components that may be contributing to the extractable PHC concentrations;
- (3) Comparison to background samples from quantitative and qualitative perspectives, for confirmation.

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In addition, corrected concentrations values for hydrocarbons in the F1, F2 and F3 ranges must be reported whenever BTEX and PAH compounds are also analyzed on the same sample: F1-BTEX, F2-naphthalene and F3-PAHs¹.

- **Analysis of Phenolic Compounds:** The 2016 guidance document no longer identifies the 4-Aminoantipyrine (4-AAP) reagent (colorimetry) as an acceptable method. Due to the fact that the method only provides a total result and is inefficient at capturing / low specificity for many phenolic species, this has been replaced with a parameter-specific method by GC/MS. The list includes 8 individual phenol parameters, as well as 2 summation parameters: (1) mono- & dihydric- Phenols and (2) non-chlorinated Phenols.

3. Required QA/QC

The 2016 CCME guidance document clearly defines the reporting limits to eliminate confusion and promote consistency in terminology used across the industry. The **Laboratory Reporting Limit (LRL)** is the limit at which analytes in all matrices are **consistently and confidently quantified**. In contrast, the **Method Detection Limit (MDL)** is the limit at which the laboratory can **consistently and confidently identify the presence** of the analyte. The LRL must be greater than or equal to the MDL and typically, the LRL is 3 to 10 times larger than the MDL.

Several other QC related elements are prescribed in the 2016 guidance document, as indicated below.

- **Minimum reporting:** laboratories must provide, in the standard Certificates of Analysis, information on (1) Time markers, (2) Data reportable, (3) QC reportables, (4) Analysis reportables, (5) Remarks and comments and (6) Subcontracted analyses.

- **Uncertainty of Measurement:** Laboratories are required to calculate the estimated uncertainty of measurement for all analytes. Although this information must be available upon request, this information does not have to be reported with the standard Certificate of Analysis.

- **QC Alert Limits:** guidance is provided for field and laboratory QC samples. Specific alert limits are provided for each laboratory QC parameter and specific to the various groups of parameters. The 2016 guidance document indicates that it is generally accepted **for the field QC alert limits to be 1.5 to 2 times broader than the laboratory QC alert limits**.

With specific regard to **laboratory duplicates**, as the measured result approached the LRL, the uncertainty associated with the Relative Percent Difference (RPD) increases dramatically. To account for this, **duplicate acceptance criteria are either the tabulated RPD acceptance limits or within 2 x LRL** (for low level data). For example, if the LRL is 10, duplicates of 15 and 30 are acceptable (difference of 15, acceptance 2 x LRL = 20).

It should be noted that, although many jurisdictions have adopted the new 2016 CCME guidance documents, deviations from the specifics outlined in Volume 4 may still be employed. As such, it is advisable that a review of the applicable provincial regulation and guidance is also performed.

(1) Note that PAHs in this context only refers to the following: **phenanthrene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, fluoranthene, dibenz[a]anthracene, indeno[1,2,3-c,d]pyrene and pyrene**.