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CCME Volume IV

Guidance Manual for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment – Volume IV Analytical Methods

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Background

Maxxam Contracted by CCME Jan 2012

- Mandate to develop a methods compendium covering all parameters with CCME Guidelines
- Format / style based on OMOE Analytical Protocol
- Previous Guidance 1993

"This compendium was prepared for CCME by Maxxam Analytics, Mississauga, Ontario, Canada, with Dr. Barry Loescher acting as Project Lead and Elizabeth Walsh as Technical Editor. The compendium was developed through a series of twelve webinars held in 2012 with technical analytical methods experts from provincial, territorial and federal environment agencies, as well as private environmental laboratories across Canada, and was extensively reviewed by CCME's Soil Quality Guidelines Task Group".

Background

- V IV 180 pages
- 3 Companion Sampling Documents
  - V1 Guidance Manual 330 pages
  - V2 Checklists
  - V3 Sampling SOPs
  - Additional Maxxam contract to ensure V I consistent with V IV

Background

- Good acceptance
  - Accepted Federally and Provincially
  - Regulator focus on Field Methanol preservation
  - Not certain of the awareness of all the other stuff

Background

"The goal of the environmental site characterization guidance is to provide Canadians with a **consistent approach** to sampling and analyzing complex environmental matrices, such that the data obtained will be representative and of known quality. The guidance provides a summary of key elements that should be performed, and reported, during site investigations. The guidance also recommends sample handling and storage requirements, analytical methods, and method specific quality control and assurance procedures to ensure that the results of laboratory analyses are reported for Canadian Environmental Quality Guidelines with sufficient quality upon which to base decisions".

"The primary authors of the four volume Site Characterization guidance were: Dr. Ian Hers, Mr. Guy Patrick, Dr. Reidar Zapf-Gilje (Golder Associates Ltd) for volume 1 (chapters 1-8), volume 2, and volume 3, and SOPs 1-6; Ms. Miranda Henning, Ms. Andrea Fogg, Ms. Katrina Leigh (Environ International Corp.) for volume 1 (chapters 9-11) and sections of chapter 4, media specific material in volume 2, volume 3, and SOPs 7-17;"

CCME Volume IV Principles

- Reasonableness
- Best Science
- Specific Data Quality Objectives (DQOs) – all tests
- Specific Laboratory Reporting Limits (LRLs)
- Consensus (i.e. I didn't always get my way)
- Method Principles provided , alternates allowed if DQOs are met.
- Consistency with OMOECC Analytical Protocol

Highlights Section 3 Sampling

- Water Hold Times
  - pH, DO, Cl2 - 15 min
    - Comment on report.
  - Colour, NO3, NO2, o-P, turbidity – 3 days
- “Whole bottle” analysis for semivolatile organics in water”
  - Requires extra containers for QC

Highlights Section 3 Sampling

Hold Time Disclaimer

- “Three day hold times may not be practically achievable, particularly for samples from remote locations. Laboratories should commence analysis as soon as possible but within 48 hours of receipt. Exceedance of hold time increases the uncertainty of test results, but does not necessarily imply that results are compromised”.

Highlights Section 3 Sampling

- Temperature

"Sufficient ice or other coolant should be added to produce a temperature less than or equal to (≤) 10°C in transit (but not frozen). 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 as long as the cooling process has begun"

Highlights Section 3 Sampling

- PAH in Groundwater

- Polycyclic aromatic hydrocarbons adsorb strongly to particulate matter. Thus, analysis of a water sample containing particulate may be biased high relative to the PAH actually dissolved in the water. This will also be true for other hydrophobic organics such as PCBs. ***Filtration is not recommended for PAH and other organic tests due to adsorptive losses on filtration.***

Highlights Section 3 Sampling

- Dissolved Metals in Water
  - "Must be Field Preserved[10]"

10. In general, for metals, mercury and hexavalent chromium, groundwaters are field filtered and preserved, surface and potable waters are unfiltered and preserved. If field filtration is not possible, lab filter and preserve asap. This must be noted on the C of A. Total metals samples and field filtered dissolved metals may be preserved at the laboratory in the original container. Samples must be allowed to sit for 16 hours prior to subsampling.

- Room Temp storage permitted for preserved metals / Hg in water

Highlights Section 3 Sampling

- VOC in Soil
  - Field Methanol - 40 day hold time
  - Field Aqueous Bisulphate if necessary to meet LRLs - 14 day HT
  - Hermetic Sampler 48 hr.

    “14 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”.
  - No other alternates

Highlights Section 3 Sampling

- VOC in Water
  - “Samples are also examined for headspace and if, on inversion, there is an air bubble present that covers the bottom of the vial (> approximately 2 mL air volume), the samples may be compromised and should not be analysed. If the client requires analysis, the data reported must be qualified accordingly. Note that an air bubble of up to 5% of the total volume of the sample container has been shown to cause almost no significant loss of most VOCs if samples are stored appropriately”.

Highlights Section 3 Sampling

- Plastic Bags allowed for soil inorganics

"For physical parameters and stable inorganic analytes such as chloride and pH, samples may be collected in plastic bags designed for soil collection"

Highlights Section 4 Methods

- Specific Parameter Lists for each test group
  - Lists cover all CCME and OMOE parameters

Parameters

Aniline	Di(2-ethylhexyl) phthalate	Dinitrotoluene, 2,4-(2,6-)**
Biphenyl, 1,1'-	Dichlorobenzidine, 3,3'-	Di-n-octyl phthalate
Bis(2-chloroethyl)ether	Diethyl phthalate	Phthalic acid esters (each)†††
Bis(2-chloroisopropyl)ether	Dimethyl phthalate	
Chloroaniline, p-	Di-n-butyl phthalate	

* Selected ABN parameters contained within the CEQG and O. Reg. 153/04.

Highlights Section 4 Methods

- Colourimetric Phenol analysis not included
  - Specific target phenols instead:
    - **Non-chlorinated phenolic compounds** include 2,4-dimethylphenol; 2,4-dinitrophenol; 2-methyl 4,6-dinitrophenol; 2-nitrophenol; 4-nitrophenol; *o*-, *m*-, *p*-cresol (methylphenol).
    - ** CCME has not selected a list of **mono- and dihydric-phenols** for monitoring. For this compendium, the list is the phenolic compounds: non-chlorinated plus phenol, 4-hydroxyphenol (hydroquinone), 3-hydroxyphenol (resorcinol), which have British Columbia guidelines.

Highlights Section 4 Methods

- Method Principles as opposed to prescriptive methods
- Alternates allowed as long as DQOs are met with some exceptions:
- Some specific clarifications / requirements
  - Handling non detects in SAR
  - Specifies soil / water ratios for extractions
  - Sand : Silt : Clay ranges
  - F in soil requires fusion
  - Hardness by Calculation based on dissolved metals

Highlights Section 4 Methods

Alternates allowed as long as DQOs are met with some exceptions:

- NP NPEO TEQ calculation
- PAH & Dioxin Toxic Equivalents calculations

Highlights Section 4 Methods

Alternates allowed as long as DQOs are met with some exceptions:

- Soil extraction protocols (to promote consistency between labs):
- E.g. Cyanide in Soil

A minimum **10 g** sample as received is extracted with **100 mL of 0.05 N aqueous sodium hydroxide** at a pH > 12. The sample is shaken for a minimum of **six hours**, followed by centrifuging and decanting. Sodium hydroxide is used to ensure proper pH is maintained. This is verified by a pH check after the extraction. If the pH is < 10 the extraction should be repeated using a stronger base

Highlights Section 5 – Reporting Requirements

Table :

- Lowest CCME OMOECC Guidelines
- Laboratory Reporting Requirements (LRLs)
  - Achievable

“For three analytes, reactive chlorine and deltamethrin in water, and toxaphene in sediment, the lowest CEQG is not achievable”.

Highlights Section 5 – Reporting Requirements

- The following table is by parameter group
- Also alphabetical List as an Appendix
- Federal Interim Groundwater Quality Guidelines Flagged in Red

Table 5.1 Laboratory Reporting Limits – Water and Soil/Sediment

Chemical Name (Inorganics in Bold)	Chemical Groups	CAS RN	Parameter Group	Lowest Water Criterion (µg/L)	Recommended Maximum LRL – Water (µg/L)	Lowest Soil/Sediment Criterion (mg/kg)	Recommended Maximum LRL - Soil/Sediment (mg/kg)
Section 2.1.1 and 4.1.1 Acid/Base/Neutral Extractable Organic Compounds (ABNs)							
Aniline	Organic Other Organics SVOC	62-53-3	ABN	2.2	0.4	2.2	0.4
Biphenyl, 1,1'-	Organic ABN	92-52-4	ABN	0.5 OMOE	0.1	0.5 OMOE	0.1
Bis(2-chloroethyl)ether	Organic ABN	111-44-4	ABN	5 OMOE	1	5 OMOE	1
Bis(2-chloroisopropyl)ether	Organic ABN	39638-32-9	ABN	4 OMOE	1	4 OMOE	1
Methyl tertiary-butyl ether (MTBE)	Organic Non-halogenated aliphatic compounds Aliphatic ether	1634-04-4	VOC	5000 CCME 340* 15 OMOE	10	0.05 OMOE	0.05

Highlights Section 5 – Reporting Requirements

"To ensure legally defensible data, the Certificate of Analysis provided by the laboratory must contain sufficient detail to ensure traceability to site and define the methods of conducting the analysis and abnormalities, if any."

- Client Information (site, identifiers, etc)

- Time Markers
  - Date & Time Sampled
  - Date extracted / digested
  - Date analyzed
  - Date reported
  - Comment if report is reissued

- Data Reportables
  - Chain of Custody
  - Sample temperature on receipt
  - Presence of custody seals and whether intact
  - Any other issues impacting sample integrity

Highlights Section 5 – Reporting Requirements

- QC Reportables

"In order that the QP can properly assess the quality of the analytical data, unless requested otherwise, all associated QC is reported as follows":

- Laboratory duplicate analyses (including % recovery, relative percent difference (RPD) or absolute difference for each parameter)
- Field/travel blank(s) (where applicable)
- Method blank(s)
- Laboratory control sample analyses
- Matrix spike analyses (where applicable) (including % recovery)
- Reference materials (where applicable) (including % recovery)
- Surrogate recoveries (where applicable) (including % recovery)

QC reportables must include flags of QC exceedances.

Highlights Section 5 – Reporting Requirements

Analysis Reportables:

- Laboratory Reporting Limits
- Data Qualifiers (interference, dry weight, etc.)
- Measurement uncertainty (if requested)
- Method title, reference

Remarks / Comments:

- Any unusual behaviour that might impact data quality (e.g. sample inhomogeneity, headspace in VOC analysis)
- Any regulatory required comments (e.g. adherence to CCME performance requirements)
- Analysis conducted in 3rd party labs, including sister labs, must be identified.

Highlights Section 6 – Required QA / QC

- Accreditation
  - "CCME recommends the use of laboratories that are accredited for the required tests by an internationally recognized accreditation body"
- Method Validation
  - MDL as per current practice
  - Precision and Accuracy
    - Waters 2 x 5 samples 2 MB
    - Soils 2 x 5 x 2 samples (2 soil matrices) 2 MB

Highlights Section 6 – Required QA / QC

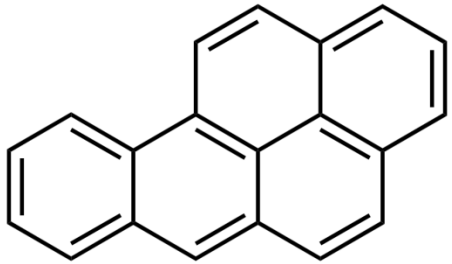
- Ongoing Performance
  - Every 2 years
  - Use existing data

Highlights Section 6 – Required QA / QC

- QC Samples
- Four Required Elements; (Batch QC)
  - All 1 / batch of 20 samples maximum
  - Method Blank: Clean Matrix carried through the entire analytical process
  - Laboratory Control Sample (LCS): Clean matrix spiked with the analyte(s) of interest, carried through the entire analytical process
  - Matrix Spike: 2nd sample aliquot spiked with the analyte(s) of interest, carried through the entire analytical process
  - Laboratory Duplicate: 2nd sample aliquot carried through the entire analytical process.

Highlights Section 6 – Required QA / QC

- Surrogates:
  - All organic tests
  - GCMS tests – deuterated analogs of target analytes: eg. Benzo(a)pyrene, MW 252, d12 BaP MW 264



  - GC tests – similar compounds not normally found e.g. o-terphenyl for F2 – F4

Highlights Section 6 – Required QA / QC

- QC Samples
- Duplicates
  - For organic analyses, soils are analysed as received. As such, duplicates are primarily a measure of sample homogeneity. If samples are visibly non-homogeneous, and acceptance criteria are exceeded, repeat analysis is not necessarily required. Data are reported flagged as “exceedance due to sample heterogeneity”.
  - For water samples requiring organics analysis, the criteria in the following tables are routinely achievable for homogeneous samples. Since water analyses for water-insoluble extractable organics are “whole bottle” tests, laboratory duplicate samples are essentially field duplicates, subject to sampling as well as analytical variability. No action is required if criteria in the following tables are not met. Data may be reported flagged as “field duplicate”.
  - For most inorganic tests, both soil and water samples are homogenised and duplicate subsamples taken from the original container and processed, so the above stipulations do not apply.

Highlights Section 6 – Required QA / QC

- QC Samples
- Acceptance Limits
  - Method Blanks < LRL
  - LCS MS Organics generally 50% - 140% soil & water, PHC 60% - 140% soil & water
  - wider for “difficult compounds”. E.g 2,4-dinitrotoluene 30% - 130% LCS inorganics, metals generally 80% - 120% soil and water
  - MS inorganics, metals generally 70% - 130% soil and water
    - Hexchrome & cyanide qualifier
  - Duplicates Organics generally 30% RPD waters, 50% soils
  - Duplicates inorganics, metals 20% RPD waters, 35% soils

Highlights Section 6 – Required QA / QC

- Hexavalent chromium, cyanide in soil qualifers
  - “Matrix spikes for hexavalent chromium and cyanide are spiked post-extraction. Hexavalent chromium can react with the soil matrix and free cyanide will complex with soil iron, both producing anomalously low recoveries”.

Highlights Section 6 – Required QA / QC

- QC Sample Qualifiers
- Duplicates
  - For duplicates, as the measured result approaches the LRL, the uncertainty associated with the 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 would be acceptable (difference of 15, acceptance 2 x LRL = 20). Note the duplicate RPD in this example is 67%.
- Matrix Spikes
  - Recovery calculated only if Spike conc. > native

Highlights Section 6 – Required QA / QC

- QC Sample Qualifiers
- Multielement Scan Qualifier
  - Applies to the LCS and Matrix Spike
  - As the number of elements in a scan increases, so does the chance of an exceedance by chance alone (as opposed to a method problem)
  - 10% (rounded down) of the elements are allowed to exceed the limits by up to 10% absolute, without corrective action

Highlights Section 6 – Required QA / QC

- QC Sample Qualifiers
- Multielement Scan Qualifier Example
  - PAH scan 17 analytes
  - LCS acceptance limits 50% to 140%
  - 1 analyte may be in the range 40% to 150%
  - Recurring non-random issues with specific parameters must be addressed,

Highlights Section 6 – Required QA / QC

Field QC

"Laboratory QC may be supplemented by various field QC samples such as blind field duplicates, field blanks, equipment rinsate blanks and field or trip spikes. In general, acceptance limits for field QC are broader than laboratory QC, typically, 1.5 to 2 times the laboratory QC limits"

Highlights Section 6 – Required QA / QC

Questions