Alberta Environment's Interpretation of the Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil Validation of Performance-Based Alternative Methods

September 2003

Pub. No. T/711
ISBN: 0-7785-3024-8 Printed Edition
ISBN: 0-7785-3025-6 On-line Edition
Web Sites: http://www.gov.ab.ca/env/info/infocentre/publist.cfm and under search by topic, choose 'soil'
http://www.gov.ab.ca/env/protenf/soilgrndwater/index.html under "Publications"

Any comments, questions or suggestions regarding the content of this document may be directed to:

Science and Standards Branch
Environmental Assurance Division
Alberta Environment
4th Floor Oxbridge Place
9820 – 106 Street
Edmonton, Alberta T5K 2J6
Fax: (780) 422-4192

Additional copies of this document may be obtained by contacting:

Information Centre
Alberta Environment
Main Floor, Great West Life Building
9920 – 108 Street
Edmonton, Alberta T5K 2M4
Phone: (780) 944-0313
Fax: (780) 427-4407
Email: env.infocent@gov.ab.ca

Alberta Environment Interpretation of the Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil
Validation of Performance-Based Alternative Methods

1. Use of Alternative Methods

This validation procedure is intended to ensure that modifications to the PHC-CWS Reference Method (ISBN 1-896997-01-5) are as accurate and precise or more accurate and precise than the original published method using benchmark procedures.

Laboratories submitting PHC CWS data to Alberta Environment must be accredited for the PHC CWS method by the Standards Council of Canada (SCC). The validation procedures described below were developed to ensure that accredited laboratories may demonstrate equivalency based on analyses of Alberta soils. In addition, laboratories must maintain SCC accreditation through successful participation in the proficiency testing (PT) administered by the Canadian Association of Environmental Analytical Laboratories (CAEAL). Qualifying laboratories must carry out CAEAL PT on both the benchmark method and performance-based alternatives. Finally, documentation for any performance-based alternatives must be developed to a similar level of detail as the benchmark procedures, and such documentation must be maintained on-site and provided to Alberta Environment. Documentation must include the detailed documentation of the protocol being used and the results of the equivalency method. Alberta Environment will not validate alternative procedures but may audit laboratory results.

The PHC-CWS method contains prescriptive elements that may not be modified (Sec. 6, 10.1, 11.1, 12.1, 13.1). These prescribed elements were recommended by the CCME Analytical Methods Technical Advisory Group, which examined the results of round robins conducted prior to the development of the PHC CWS. These round robins showed that much of the dispersion in replicate soil hydrocarbon analyses was caused by systematic error. Many of the prescribed elements address detection and quantification procedures, where instrumentation and operating parameters must be specified.

The PHC-CWS also has general elements that are performance based and allow laboratories to modify the method to achieve improved efficiencies (Sec. 7, 10.2, 11.2, 12.2). Any modification must meet the Quality Control Criteria in Sec. 8, and must include quality control samples that are prepared, processed through the entire analytical method, and reported in accordance with Sec. 9. Any modification must be validated and documented (Sec. 6, Appendix 2).

Method modifications validated under this protocol are suitable for reporting data to Alberta Environment as equivalent to data produced using the PHC-CWS benchmark procedure. This validation procedure is recognized by Alberta Environment, which is the champion jurisdiction for this standard. Data produced under a modified PHC-CWS

analytical procedure and validated by this protocol will be accepted as scientifically valid and legally defensible in Alberta.

2. Protocol for Verification of Alternative Methods

The protocol for verification of alternative methods is based on meeting a minimum data quality objective for the means and the variance. The data quality objective was chosen to simplify the procedure and maintain consistency with the Reference Method. Data quality objectives were based on the mean and variance of the Reference Method, as determined through the results from the Interlaboratory Study of the Canadian Council for Ministers of the Environment (CCME).

Documentation for any performance-based alternatives must be developed to a similar level of detail as the benchmark procedures, and such documentation must be maintained on-site and provided to Alberta Environment upon completion of the validation protocol. Documentation provided to Alberta Environment must include the detailed documentation on the protocol being used and the intralaboratory test results.

Documentation must be provided to

Alberta Environment
Science and Standards Branch
4th Floor, Oxbridge Place
9820 106 Street
Edmonton, Alberta
T5K 2J6

The validation protocol is a preliminary intralaboratory procedure. In order to continue to use an alternative protocol, laboratories must maintain SCC accreditation through successful participation in the proficiency testing administered by the Canadian Association of Environmental Analytical Laboratories. Successful proficiency testing must be verified both on the benchmark test used to verify the alternative procedure and the alternative procedure itself.

Alberta Environment will not validate alternative procedures but may audit laboratories from time to time. The audit process will be based on documentation submitted detailing the alternative procedure being performed, results for the validation protocol, and all records pertaining to the CAEAL PT. Laboratories using an alternative protocol must maintain records of this information on site and be prepared to submit the information to Alberta Environment upon request.

3. Procedure for Validation of Alternative Methods

The validation procedure in this document is intralaboratory (within a laboratory). Validation must be in accordance with Appendix 2 of the PHC CWS Analytical Method

("the reference method"). The procedures outlined in this document are supplemental to Appendix 2.

In addition to the procedure outlined here, the Quality control criteria, as outlined in the reference method must be met. Quality control criteria (sections 8, 9), method validation (Appendix 2), minimum detection limits (appendix 3, section 8) and sample performance (sections 10,11) must be consistent with the Reference Protocol for the new method.

The validation procedure, as outlined here is acceptable for mineral soils. See section 15.1 of the PHC CWS method for information on dealing with organic soils.

3.1. Preparation of Reference Material

When available, certified PHC soil reference materials should be used. Due to the lack of availability of certified PHC in soil reference materials (certified by the PHC-CWS method), validation is by comparison of means and variance between the PHC-CWS and the modified PHC-CWS methods for samples prepared by the laboratory. If at a later date, reference materials become readily available, any further validation testing must be conducted using these materials.

Soil samples prepared by the laboratory must be in accordance with Appendix 3 and section 9 of the Reference Method and the procedure as outlined below with the following exceptions:

1. Soils may be contaminated with crude oil materials in addition to, or in combination with gasoline, diesel, or motor oil as outlined in the Reference Method in order to obtain the required fraction concentration.
2. Soils obtained from historically contaminated fields may be used in place of spiked soil samples (section 3.1.2 of this document).
3. Where necessary, different contaminated soils may be prepared or obtained from the field that meet one or more of the required contaminant concentrations outlined in sections 3.1.1 and 3.1.2 of this document. However, all the required contaminant concentrations must be met over the range of samples used. For example, if a given soil sample meets the concentration objective for F2 and F4 but is outside the range for F3, a different soil sample may be prepared or obtained to meet the objective for F3 provided the new sample still meets the soil condition requirements as outlined in table 1.

The comparison requires between 4 and 7 replicates at the same concentration and analyzed by each method for each soil condition. Method validation requires use of natural soils rather than artificial matrices. Analytical protocols may be compared using soil samples received by the lab from contaminated sites in the field or using spiked soil samples.

3.1.1. Procedure for Spiked Soil Samples

Spiked soil samples must be prepared in accordance with Appendix 3 of the Reference Method and Sec. 9 paragraph 5 & 6 except where noted in section 3.1.

Soil conditions are as follows. Three soil textures are recommended for validation; a fine textured soil having a texture of clay loam or clay with a minimum of 30% clay, a loam soil, and a sandy loam or loamy sand soil. A minimum of one high and one low organic matter soil is required for the fine textured soils. The high organic matter soil must contain a minimum of 3.5% organic carbon (6% organic matter) and the low organic matter soil must be equal to or less than 0.6% organic carbon. (1% organic matter). The high and low organic carbon soils may be obtained from different horizons within the same soil pedon. For the fine textured, high organic matter soil, a minimum of 2 soil moisture contents is required, one near the air dried value for the soil and one at approximately 20% moisture content by weight.

Alberta Environment recommends that the modified method be compared at PHC concentrations between approximately 3 times the PHC-CWS MDL and 15% of the Tier 1 criteria for low concentration samples and at concentrations comparable to the Tier 1 guidelines for high concentration samples. The low concentration sample may be run on the high organic matter, high water content, fine-grained material only.

For the purpose of this protocol only, Tier 1 guidelines are based on the eco-contact value for the texture and hydrocarbon fraction being analyzed (table 2). For values near Tier 1, concentrations are considered acceptable if they are calculated to be between 50% and 150% of the appropriate fraction concentration. An exception is made for the F4 fraction, where the acceptable concentration range extends down to 400 mg/kg soil (table 2). This exception is made due to the difficulty in obtaining or preparing homogeneous F4 samples spiked at the higher concentration ranges. The range of concentrations to be tested is in accordance with Sec. 2, 6, and Appendix 2 of the Reference Method.

For verification of protocols related to the F1 fraction, the target for the coarse soil, high concentration sample is based on the eco-contact value and is between 70 and 200 mg/kg. For fine soil, the target for the high concentration sample is 130 to 390 mg/kg. For the low concentration sample, the sample must be run at approximately 3 to 6 times the MDL, or from 30 to 70 mg/kg.

For the F1 through F4 fractions, the test for precision (Section 3.2.2 of this document) does not apply to the low concentration sample.

3.1.1.1. Storage Requirements

If spiked soil samples are to be used the following considerations apply.

After preparation, soil samples shall be sealed in an airtight container and stored a minimum of 48 hours at approximately 4^{o}C prior to use. Sample storage time may vary

between individual fraction runs but must not vary between the two methods for a given fraction run.

For the high moisture content, fine-grained material, spiked samples must first be prepared in the dry soil. Sample must be stored for a minimum of 24 hours in the dry state, wetted, and then stored for a minimum of 24 hours, for a total of 48 hours minimum storage time.

3.1.2. Procedure for Contaminated Samples Received by the Laboratory

For contaminated soil samples from the field received by the laboratory and used in the validation protocol, soil conditions must meet the criteria as outlined in the preceding section except where noted in this section. Storage requirements must meet those as outlined in section 5 of the PHC CWS reference method except for procedures involving the F2 through F4 fraction only and for samples where soil heterogeneity is expected to interfere with the attainment of precision requirements for the benchmark method. For these soils, samples may be air-dried and ground using a mild hand procedure (e.g. mortar and pestle) to reduce sample heterogeneity.

For the F1 fraction, sample storage must meet the conditions as outlined in section 5 for samples being received by the lab and used in the validation protocol. No pretreatment is permitted.

Table 1. Summary of the Alberta PHC-CWS Analytical Procedure Validation Protocol.

Soil Texture	Organic Matter	Moisture Content	Hydrocarbon Concentration	Replicate Requirements	Statistic Requirements
Clay Loam (>30% clay) or Clay	≥6%	Air Dried	50 to 150% Tier 1	4 to 7	m, c
		≅ 20% Moisture	50 to 150% Tier 1	4 to 7	m, c
			3X MDL to 15% Tier 1	4 to 7	m
	≤ 1%	NA	50 to 150% Tier 1	4 to 7	m, c
Loam	NA	NA	50 to 150% Tier 1	4 to 7	m, c
Sandy Loam or Loamy Sand	NA	NA	50 to 150% Tier 1	4 to 7	m, c

m=test for means
c=test for precision on the 95% confidences interval
NA=not applicable

Table 2. Summary of Concentration Ranges for Spiked Samples used in the verification Protocol*

Low Concentration Sample, Ranges (mg./kg.)								
	CCME F1 MDL	F1 Range	CCME F2 MDL	F2 Range	CCME F3 MDL	F3 Range	CCME F4 MDL	F4 Range
Clay Loam/ Clay	10.7	30-70	3.9	10 - 140	9	30 -120	8	25 - 850

High Concentration Sample, Ranges (mg./kg.)								
	F1 Tier 1 Guide	F1 Range	F2 Tier 1 Guide	F2 Range	F3 Tier 1 Guide	F3 Range	F4 Tier 1 Guide	F4 Range
Clay Loam/ Clay	260	130-390	900	450-1350	800	400-1200	5600	400-7900
Sandy Loam	130	70-200	450	200-700	400	200-600	2800	1400-4200

*For the purposes of this document only, the tier 1 guideline refers to the tier 1, eco-contact value.

3.2. Validation Protocol

A method is considered valid if it can meet both a standard for means and a standard for precision. Methods that are verified through this protocol must continue to meet the CAEAL proficiency test in order to be considered valid. Minimum criteria to be met are based on the Interlaboratory Study of the Canadian Council for Ministers of the Environment (CCME) Method for the Analysis of Petroleum Hydrocarbons in Soil (September 2002). For F2 through F4 fractions, criteria are based on a series of 4 randomly selected points from laboratories using the standard protocol only. This data set was used to develop a 95% confidence interval for means.

Due to the lack of available data for the standard protocol for the F1 fraction, laboratories with one or more data points that fell outside the 95% Z test for the individual F1 analysis were eliminated from the data set. For the remaining data points, a series of 4 randomly selected data sets were chosen and a 95% confidence limit for the means was developed.

The minimum criteria were based on the highest confidence limit from all data sets.

For the test for precision, the percent deviation from the mean was determined for each trial from the individual laboratories that had been accepted for determination of the mean. This value was used to determine a mean and 95% confidence interval for the standard deviation for laboratories. The minimum requirement was based on the largest value obtained from the 95% confidence interval of laboratories from all fractions.

3.2.1. Test for means

In order to pass the equivalency protocol, recovery of PHC must be greater than or equal to the standard method. However, the CAEAL proficiency will be based on an equivalent recovery to the standard method. Therefore, it is recommended that the hydrocarbon recovery be equivalent to the Reference Method for each of the fractions tested. A protocol is considered valid if the means of the alternative method fall within 20% of the standard method for all six soil conditions.

3.2.2. Test for Precision

Test for precision must be carried out on the 95% confidence interval for each of the soil conditions. The 95% confidence limit for both the Reference Method and alternative method must be equal to or less than 25% of the mean for each fraction tested.

3.2.3. Removal of Outliers

Due to the small sample size for each soil condition, removal of outliers from the data set is not recommended. If an outlier is suspected due to technician or machine error, it is permissible to examine the individual replicate as meeting the criteria for outliers using Dixon's test at the 95% confidence interval. If it can be shown that this sample may be classified as an outlier at the 95% confidence interval, the procedure must be re-run for the given soil condition where the outlier was present. In the event that the second run does meet the test for means and precision, Dixon's test for outliers may be applied to the first sample run at the 95% confidence interval. If all of the following conditions can be met, the protocol is still considered valid:

1. The test for means and precision is met with the second sample run.
2. Dixon's test for outliers has positively identified the replicate in question as an outlier.
3. The test for means, in the absence of the outlier, can be met.

A maximum of one outlier can be identified for all soil conditions within a given hydrocarbon fraction. If more than one outlier is suspected for any given hydrocarbon fraction and all 6 soil conditions, the alternative laboratory protocol and/or general laboratory procedures should be re-evaluated before proceeding.

3.3. Use of different methods for different hydrocarbon fractions

In comparing modified methods with the PHC-CWS it may be shown that the modified method produces data comparable for only one or more of the F1 to F4 fractions. Where standard methods differ significantly, Alberta Environment will recognize the modified method as equivalent to the PHC-CWS for those fractions that pass the validation protocol. For example, a unique modified method may be developed for the F1 fraction only. Any modified method must be effective with *all* soil conditions.

3.4 Consistently Low Recovery

The above procedure is based on parametric statistical methods and the assumption that random errors may place a particular outcome above or below a mean value. The ±20% allowance around the mean for the benchmark method assumes that a future re-evaluation of the alternative method is equally as likely to fall on either side of the mean. If repeated testing (e.g. through the CAEAL PT program) shows that method recovery is consistently lower than the mean recovery of the standard method, the alternative method must be re-evaluated. Alberta Environment may withdraw their approval where method recovery is consistently below the mean regardless of whether the method continues to pass the CAEAL PT.

4. Data quality objectives

Data quality objectives are defined under the sampling protocol (Sec. 4, 5). Data produced under modified methods validated under this protocol can be assigned an individual sample uncertainty similar to the PHC-CWS Reference Method (Sec. 8), and are sufficiently accurate and precise to assess soils for Canadian Tier 1 Remedial Standards for soils.

5. Dixon's Test

Dixon's test for outliers can be applied to small sample sizes and where both the mean and standard deviation are unknown. Dixon type tests are only applicable where data is normally distributed. The test should not be applied for data sets with multiple outliers. The test becomes increasingly imprecise for multiple repetitions on the same data set.

As outliers will be identified only in one direction, a one-sided discordancy test is used. For more detail, please see Barnett and Lewis (1984).

The test statistic is determined as,

$$t = \frac{x_n - x_{n-1}}{x_n - x_1}$$

in the case that the highest value is suspect or;

$$t = \frac{x_2 - x_1}{x_n - x_1}$$

in the case where the lowest value is suspect.

The test statistic is compared against the critical value, as noted in table 3. Where the test statistic is greater than the critical value, the null hypothesis that there are no outliers in the data set is rejected and the replicate may be labeled an outlier.

Table 3. Critical value for *t* for Dixon type tests of discordance for one outlier in a normal sample distribution (taken from Barnett and Lewis, 1984 and abridged from Dixon, 1951).

N	3	4	5	6	7
Critical value for *t*	0.941	0.765	0.642	0.560	0.507

5.1 References

Barnett, Vic and Toby Lewis. 1984. Outliers in Statistical Data. 2nd edition. John Wiley & Sons. 463 pp.

Dixon, W.J. 1951. Ratios involving extreme values. Ann. Math. Statist. 22:68-78.