PHC CWS Analytical Methods Workshop II 2002: Participants' Report

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PHC CWS Analytical Methods Workshop II 2002: Participants' Report
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Introduction

The Canadian Ministers of the Environment endorsed the Canada-Wide Standard for Petroleum Hydrocarbons in Soil on May 1, 2001, allowing jurisdictions to begin their implementation activities. Alberta Environment has moved on several fronts including assessment of issues and directions for implementation of the PHC CWS analytical method. An initial workshop was held on May 31, 2001 to gain input from Alberta laboratories and consultants on implementation options for Alberta. Outcomes from the workshop included agreement among the participants to implement the PHC CWS method as written for compliance testing and recommendations to implement an interlaboratory evaluation of the PHC CWS method and a validation process for performance-based aspects of the analytical method.

Over the past year, the Canadian Association for Environmental Analytical Laboratories (CAEAL) completed an interlaboratory study of the PHC CWS analytical method. With the CAEAL study results in hand, Alberta Environment convened a second workshop to discuss the study results and to identify appropriate steps for developing a performance based validation process. The Research Council (ARC) was contracted to provide a background on the necessary elements of a validation protocol.

The thirty-nine participants in the workshop (Appendix A). A series of presentations provided background material. During two breakout sessions, workshop participants raised a number of issues. At the close of the workshop these issues were summarized in the form of recommendations. This report is intended to capture the will of the participants and provide input for Alberta Environment's consideration when making implementation decisions related to the method.

Workshop Recommendations

Recommendation 1: Validation Procedures for Performance-Based Alternatives

- CAEAL should play a role in validating performance-based alternative methods.
- Reference materials should be soil, not artificial matrices.
- Explore the possibility of using real world samples where possible, since spiked samples may not adequately test the extraction component of the method.
- Audit and performance test (not in-house) the reference method and performance-based alternatives.

Recommendation 2: Validation Protocol

- Use 3 hydrocarbon concentration levels.
- Use a range of petroleum hydrocarbon types

- Use 3 textures (coarse, clay loam, heavy clay) and peat.
- Use t-tests to compare reference method with performance-based alternatives. Further discussion needed regarding appropriate mean differences.

Recommendation 3: Priority Performance-Based Alternatives

- Accelerated Solvent Extraction (ASE)
- Automated Soxhlet
- Cold shake

Recommendation 4: Follow-up to CAEAL Report

- Isolate the data from the CWS standard method from other methods.
- Gather the missing information from the participating laboratories.
- Use a follow up questionnaire or telephone contact.
- Gather external data for other methods.

Record of Discussions

Ted Nason, Alberta Environment, provided an overview of the PHC CWS method and a recap of the 2001 workshop. Richard Turle, Environment Canada, outlined the development of the method and summarized the findings of the CAEAL interlab study. Henry Bertram, Alberta Research Council, provided background information on options for validating performance-based components of the method.

Following the presentations participants were randomly assigned to four groups for the two breakout sessions. Questions were provided to guide discussion and each group reported on their conclusions. The first breakout session focused on the results of the CAEAL interlaboratory study. Following this, Richard Turle provided a response to the comments received from the breakout groups, based on his involvement in developing the method and implementing the CAEAL study. The second breakout session identified priority performance-based alternatives and made recommendations for a validation protocol for these alternatives.

Presentations

Presentation 1: Overview of PHC CWS, Ted Nason, Alberta Environment

Presentation 2: Development of the PHC CWS Analytical Method, Richard Turle, Environment Canada

Presentation 3: Recap of May 31/01 PHC CWS Analytical Workshop I, Ted Nason, Alberta Environment

Presentation 4: Design, Implementation and Results of CAEAL Interlab Study, Richard Turle, Environment Canada

Presentation 5: Validation of Performance-Based Options, Henry Bertram, Alberta Research Council

Presentation 6: Comments on the Present Status of CWS PHC Method, Mark Hugdahl, ALS Environmental (Canada)

Presentation 7: CCME CWS Norwest Labs Experience, Chris Swyngedouw, Norwest Labs

Presentation 8: Comments and Experiences with CCME-PHC Method, Don Laberge, Enviro-Test Laboratories

Presentation 9: Observations, Phil Heaton, Maxxam Analytics Inc.

Presentation 10: Performance Based Methods and In-House Method Validation – CCME PHC's Validation Issues, Barry Loescher, PSC Analytical Services

Presentation 11: Performance Based Method, Henry Bertram, Alberta Research Council

These presentations are available on Alberta Environment's website:
http://www.gov.ab.ca/env/protenf/soilgrndwater/index.html

Breakout Sessions

Breakout Session 1

Question 1: What are the major conclusions from the CAEAL study?

Group 1

- Not enough laboratories used the CCME standard method as written
- Sample cleanup should be reserved for Tier 2. Keep Tier 1 more routine/cost effective.
- Using 50% dichloromethane to elute PHC from the silica gel column makes the silica gel cleanup useless.
- Spike samples don't effectively test the efficiency of extraction.

Group 2

- Study results were inconclusive because of too many questions, data entry errors, partial data, and standard deviation.
- Suffered from lack of appropriate reference materials.

Group 3

- Study suffers because all labs did not use the CCME standard method as written.
- The standard method may need more prescriptive elements to be evaluated in a CAEAL study.

- Labs disagree with the conclusions of the study. Variability is not understood because CCME standard method results were not separated from modified methods.

Group 4

- Cannot determine homogeneity or stability of performance testing materials from the study. 30/160 day stability determined by the Environment Canada lab is not long enough.
- It is possible to produce a large quantity of performance testing samples but it is not known whether they will be stable.
- We need to compare CCME standard method to the rest of the data before we can know if the interlab study was inherently sound.
- The RSD of the study was too high to state with confidence that 75% of the labs produced quality data.

Question 2: What improvements/additional analyses do you recommend?

Group 1

- Re-analyze data to sort labs by extraction method, use of silica gel cleanup, and GC analysis method used.
- Concentration of samples by Rotovap or Kuderna-Danish (KD) makes a big difference (i.e. lose Fraction 2)
- Need to establish one method as the reference method. Use the prescribed method for comparison.
- Make concentration of the sample by KD one of the prescribed steps of the reference method. (Note: As feedback to the draft workshop report, one member of the group clarified that Group 1 was recommending benchmark status for the KD technique as opposed to prescribed element status.)
- There should be only one method to measure F4+, preferably without silica gel.

Group 2

- Re-assess the data based on laboratory experience.
- Group data for comparison by regions.
- Reference materials should include naturally occurring organic matter.
- There may be merit in performing a "sub-validation" with the 5 best-performing labs

Group 3

- Interview labs to get more information on the methods used and use to re-evaluate the study results.
- Silica gel clean up needs further investigation.
- BTEX method not defined, prefer GC-MS.
- Develop protocols for F4 high temperature chromatography and gravimetric procedures.
- Add additional minimum QA/QC for on-going use (i.e., batch testing, real world samples).

- Evaluate applicability to organic soils
- Identify the range of materials, etc. for which the method is applicable.
- Working group recommendations should be adopted as Alberta Environment policy.

Group 4

- Review the original AMTAG data from the 13 lab study.
- Take 9 labs that used the CCME standard method and compare to the rest.
- Complete the 5 prescriptive data points from all labs.
- Try to identify what deviations from the CCME standard method were used and correlate with the study results.
- Get data from labs that did controlled experiments and evaluate their results.
- May be able to evaluate the quality of CAEAL round robin by comparing the results to similar U.S. round robins conducted by the TPH Criteria Working Group.
- There is reason to re-dredge the earlier round robin studies conducted by AMTAG – there are some good data there that may add value to current information.

Question 3: Would a CAEAL proficiency testing program fulfill Alberta's quality assurance needs for the PHC CWS?

Group 1

- There should be a CAEAL proficiency testing program in place at a minimum.

Group 2

- Not yet, no validation criteria.
- Once a procedure is set up, yes.

Group 3

- Not entirely.

Group 4

- Performance testing should be conducted 3 to 4 times per year.
- CAEAL could be the auditor – conduct blind audit of the CCME standard method as well as the performance based alternative methods and validation data.

Question 4: If not, what may be lacking?

Group 1

- Should not use spiked samples to evaluate performance of extraction methods.
- Standard NRC reference materials would be useful.

Group 2

- Validation techniques.
- Reference material with naturally occurring organic matter.

- The study should be conducted a second time using only laboratories that have been accredited by the Standards Council of Canada.
- Decide on appropriate matrix.
- The five best labs should validate candidate reference materials.

Group 3

- Standard reference materials appropriate for Canadian soils and PHCs. Should be commercially available. This is critical for legal defensibility.

Group 4

- Validation protocol.
- Reference materials.
- Blind audit samples. Assurance program could be delivered by CAEAL.

Environment Canada Response to Breakout Session 1

Following the first breakout session, Richard Turle responded to a number of issues raised by the Breakout Groups. His remarks and the ensuing discussion follow:

The CWS PHC analytical method was developed through consensus in response to the need for standardization of PHC analytical techniques. Funds were not available for in-house development nor was method development the primary focus of any participants. Our knowledge of PHC analysis has grown through the process of developing and applying the CWS method. Performance typically improves as analysts gain experience with new methods.

Laboratories must make the case to CAEAL for the development of reference materials for performance testing. CAEAL must recover their costs, so there will be a charge for the samples.

It may be possible to re-analyze the performance testing samples that are still on hand to evaluate their stability. The time limits presented in the CAEAL report are the length of time the samples were in storage for the study. They do not necessarily represent the actual lifespan of the samples.

The previous round robin study results can be re-examined fairly easily.

Environment Canada (River Road Laboratory, Environmental Technology Centre) has done some recent work on silica gel clean up. Mass spec analysis shows that silica gel does remove non-petroleum hydrocarbons. Most of the analysis was done on marine sediments.

It would be difficult to re-form AMTAG. The group met at two workshops and via many teleconferences. The need for consensus slows progress.

Rather than revising the CWS method at this time, it would be preferable to issue an addendum. Ted Nason noted that the method would be reviewed in 2005. This means

that the process of identifying and reviewing candidate changes will have to begin in late 2003.

Despite CAEAL study limitation raised by the group, the CWS method is as valid as possible with current techniques and knowledge. Issues such as application of the method to high organic matter soils may require a Tier 2 approach. This is likely more of a question for soil quality specialists than analytical chemists.

We need to decide on the nature of PT samples. PT samples should include fine textured soils (5-10 g). Although contaminated soils from the field may be preferred to spiked soils, homogenization will be difficult.

A consultant noted that while there is a desire for some improvements, most consultants believe that the CWS method is a step forward because it standardizes the methodology.

Breakout Session 2

Question 1: What are the essential elements of a validation protocol for performance-based procedures in the PHC CWS?

Group 1

- Do not use spiked samples (except for Fraction 1). Find real world samples or existing certified reference material.
  (Discussion followed on the availability and suitability of NIST and NRC certified reference materials. Samples are available that contain hydrocarbons in additions to other contaminants. They have not been certified for hydrocarbons.)
- In-house testing.
- 4 matrix types at a minimum: clay, clay loam, sandy loam, peat. 2 contaminant levels for each. At least 2 of 3 ranges must be covered and all must be tested.
- Apply statistical analysis. (t-test for difference of means, 20% suggested as acceptable.)
- Include Fraction 4 by gravimetric analysis

Group 2

- Identify the type of samples to be validated, i.e., real world or spiked.
- Precision should be equal to or better than the reference material.
- First accredit according to the CWS standard method and then validate performance-based alternatives.
- Use comparisons by paired t-test.
- Require a valid reference material.
- Need to specify matrix types: fine, coarse, organic.
- Define spike levels (3 minimum) and spike compound.

Group 3

- Defensible reference materials
- Ability to perform benchmark method in the absence of standard reference method.
- Assess a wide range of PHCs (C_6 to C_{100}), soils and PHC concentration ranges.

- Qualified external audit systems and auditor specific to PHC testing.
- More frequent performance testing.

Group 4
- Method detection limit.
- Repeatability.
- 2 soil types and 3 analytical ranges
- Reference lab for verification

Question 2: What performance-based procedures and options should receive priority for validation?

Group 1
- Accelerated Solvent Extraction (ASE)
- Possibly Fraction 4 by gas chromatography and silica gel cleanup, Fraction 4 by gravimetric analysis, and Fraction 4 by gravimetric analysis and silica gel clean up.
- Laboratories should maintain facility with the reference method alongside any performance-based alternatives to enable in-house comparisons and validation against the reference method.

Group 2
- ASE, automated Soxhlet. Use Soxhlet as reference. Headspace for Fraction 1.
- Iso-octane as keeper solvent.
- Three different contamination levels.
- Na_2SO_4 to remove moisture.
- Solvent reduction by KD, Rotovap, Turbovaps.

Group 3
- Ask Richard Turle to provide recommendations following a re-evaluation of the methods used in the CAEAL round robin.
- Soxhlet extraction, purge and trap (Fraction 1), injection method (Fractions 2 to 4). Change to iso-octane as keeper.
- Fraction 4 gravimetric and Fraction 4 high temperature gas chromatography validation protocols.

Group 4
- Extraction method.
- Extraction time within 48 hours for Fraction 1.
- Validate solvent and RF for high temperature gas chromatography.

Question 3: What validation approach do you recommend?

Group 1
- Evaluate B.C. approach to validation of their PHC method. Establish the reference method (use fewer variables to make it more specific). Compare

performance based alternatives to the reference method using in-house tests. When in-house testing requirements are satisfied, follow with multi-lab round robin.

Group 2

- Validate reference method before starting on performance-based alternatives.

Group 3

- Round robin to establish standard reference method through performance testing.
- Use standard reference method internally to validate performance-based alternatives.
- Participate in a performance testing program using new validated method.
- External audit.

Group 4

- Validate the reference method.
- Use paired t-test. One method is the reference method. Variables are soil type (coarse/fine), hydrocarbon type (gas/crude) and analytical range (3 levels). 10x MDL, 95% confidence.
- Referee laboratory to verify.

Appendix A - Meeting Attendees

Breakout Group	Name	Organization
1	Bob Corbett	Access Labs
1	Mark Hugdahl	ALS Environmental
1	James LeBlanc	AMEC
1	Aaron Rognvaldson	ARC Inc.
1	Julie Roy	Imperial Oil Resources
1	Joanne Baillie	Maxxam
1	Sue McGregor	PSC Analytical Services
2	Derek Fraser	AGAT
2	Scott Hannam	ALS Environmental
2	Corey Higham	ARC Inc.
2	Kathryn Randon	Energy and Utilities Board
2	Lucia McIntyre	Maxxam
2	Chris Swyngedouw	Norwest Labs
2	Barry Loescher	PSC Analytical Services
3	Jennifer Foley	AGAT
3	Brenda Chomin	AMEC
3	Kathryn Bessie	EBA Engineering
3	Ron Minks	Envirotest Labs
3	Jennifer Fisher	Energy and Utilities Board
3	Mary Mayes	Matrix-Solutions
3	Phil Heaton	Maxxam
3	Francisco Fernandez	Unotec
4	Rhodora Tan	AGAT
4	Narine Gurprasad	Environment Canada
4	Don Laberge	Envirotest Labs
4	Iboja Tot	Maxxam
4	Randy Neumann	Norwest Labs
4	Brent Loshney	PSC Analytical Services
	Richard Turle	Environment Canada
	Henry Bertram	Alberta Research Council
	Dan Wispinski	Alberta Research Council
	Ted Nason	Alberta Environment
	Darlene Howat	Alberta Environment
	Gordon Dinwoodie	Alberta Environment
	Mike Zemenek	Alberta Environment
	Gerry Lutwick	Alberta Environment
	Steve Clare	Alberta Environment
	Norman Sawatsky	Alberta Environment
	Jock Forster	Alberta Environment