

Update on Changes to BC Hydrocarbon Test Methods

On behalf of ...

BCELTAC

***BC ENVIRONMENTAL LABORATORY TECHNICAL
ADVISORY COMMITTEE***



CSAP Society

Update on Changes to BC Hydrocarbon Test Methods

Presented by

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BC ENVIRONMENTAL LABORATORY TECHNICAL ADVISORY COMMITTEE

Outline

- New EPH Water Method
 - Issues with previous EPH water method
 - Triplicate LEPH Interlab Comparisons
 - Dawn Zemo's work – relevance of polars??
 - Changes to EPH water method
- LEPH/HEPH reporting changes
- VPH reporting changes

Issues with Previous EPHw Method

- Performance Based Method (PBM), in use since 1999
 - Encourages innovation
 - Critical elements are “prescribed”
 - non-critical modifications allowed w/ proof of equivalence
 - “Reference Method” = DCM separatory funnel extraction
- Consistent inter-lab results for unweathered Petroleum Hydrocarbons (PHCs)
 - Including PHC spikes, Proficiency Test samples, etc.
- Inconsistent results for biodegraded (polar) PHCs. Why?
 - Current PBM allows solvent change (DCM vs Hexane)
 - Extraction techniques, solvent ratios can also be changed

Triplicate LEPH_w Interlab Comparison

- **Objective:** Determine if LEPH concentrations and chromatograms were reproducible between labs for groundwater samples containing weathered PHCs.
- Study conducted December 2013 & March 2014
- December - Samples submitted to 3 ISO 17025 accredited labs

Triplicate LEPH_w Interlab Comparison

Extraction Technique Differences:

- **BC Reference Method – 3 step extraction:** 50 mL DCM, shake 2 minutes (x3).
Total = 150 mL DCM
- **LAB 1 (PBM) – 1 step extraction:** 6 mL hexane (12 ml for 500 mL bottle),
shake 30 seconds, tumble for 1.5 hours Total 6 mL hexane
- **LAB 2 (PBM) – 2 step extraction:** 60 mL DCM, stir 20 minutes; 40 mL DCM,
shake 30 seconds. Total = 100 mL DCM
- **LAB 3 (PBM) – 3 step extraction:** 50 mL DCM, shake 1 minute (x3).
Total = 150 mL DCM

Triplicate LEPH_w Interlab Comparison

December 2014 Study

- Poor reproducibility between labs using PBM's
- Could be due to differing extraction solvents
- Could be due to complexity of samples

- Second triplicate study done March 2014...
 - Primarily using Reference Method
 - One lab – reference method and PBM

Interlab Study: March 2014 EPH₁₀₋₁₉ Results

Sample	Lab 1 (DCM-Ref)	Lab 2 (DCM-PBM)	Lab 2 (DCM-Ref)	Lab 3 (DCM-Ref)
1	1300	1990	4050	2100
2	840	800	2500	1400
3	1140	1150	2770	1600
4	2390	1630	2470	1700
5	3150	1620	4330	1900
6	2710	1030	3150	1100
7	2020	1950	3820	3000

LEPH_w Interlab Study - Conclusions

- *Too much variability between labs...*
- Method needs to be more prescriptive, but how?
 - Must prescribe extraction solvent & technique!!
 - Classical DCM extraction or Hexane micro-extraction??
- Needed to consider new science...
 - Dawn Zemo's work on polar PHCs
 - New EPA 3511 Micro-Extraction method
(EPA approved July 2014)

Dawn Zemo - CSAP 2014 Presentation

- Dawn presented research regarding polar compounds in degraded petroleum hydrocarbon mixtures
- Biodegradation of PHCs forms polar metabolites, eg:
 - *Organic acids, alcohols, ketones, aldehydes, phenolics*
- Dawn's research indicates polar PHC metabolites generally exhibit less human toxicity than PHCs
 - *More work needed for aquatic toxicity assessments?*

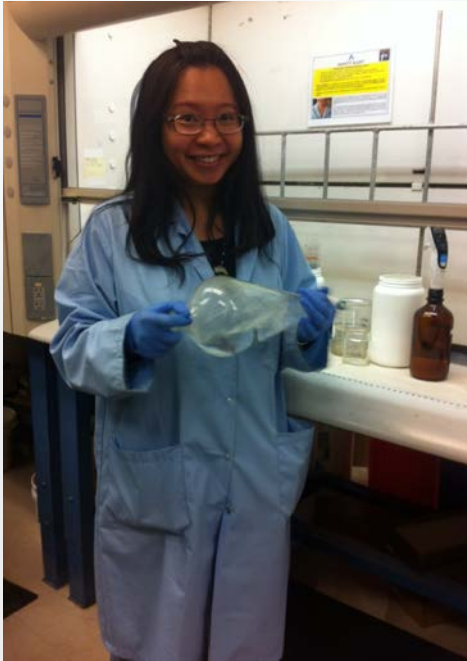
2016 BC MOE EPH Method (Director Approval Pending)

- BCELTAAC recommended Hexane micro-extraction PBM.
 - Based on EPA 3511 reference method
 - Much more prescriptive to ensure consistency
 - Comparable to methods used for CCME F2-F4 waters
- Hexane micro-extraction directly targets non-polar PHCs.
 - Polar metabolites are partially recovered – better representing their reduced toxicity.
- MOE posted Draft Method for comment Mar 26, 2015
 - CS e-Link message delivered April 10, 2015
 - Good support received for new method
 - BCELTAAC endorsed Final draft Oct 15, 2015
 - Jan 1, 2016 Effective Date anticipated

Advantages of New EPHw Method

- More prescriptive – much better inter-lab consistency expected.
 - Solvent (hexane) & hexane:water ratio prescribed
 - Minimum shaking time prescribed
 - Default: 10 mL hexane / 250 mL sample; 30 min. in-bottle extraction
 - Can be used for EPH & PAH
- Test results will be more representative of PHC contaminants, for which CSR standards are derived.
- Sustainability advantages:
 - Reduces solvent use by up to 93%
 - Avoids chlorinated solvents (DCM)
 - Smaller sampling containers – default 250 mL (reduced sampling & shipping costs!)
 - Reduced health and safety risks for laboratory staff!

Advantages of New EPHw Method



The Old: "Sep Funnel"



The New: Mechanical Shaker



Old vs New Bottles...



Reduced Space Req'm'ts

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LEPH / HEPH Reporting Changes

- Lab reporting of LEPH / HEPH with Silica Gel Cleanup will be permitted.
 - No change to applicability of Si-Gel cleanup
 - Si-Gel cleanup still allowed only if natural source organics suspected
- New PAH Co-Reporting Requirement.
 - PAHs are subtracted from EPH to arrive at LEPH/HEPH, only because PAHs have independent CSR standards
 - Therefore PAHs must be co-reported when LEPH/HEPH are reported

VPH Reporting Changes

- Changes to VPH Calculations
 - Styrene subtraction added for VPHw & VPHv

$$VPHs = VHS6-10 - \Sigma [BTEX, styrene]$$

$$VPHw = VHw6-10 - \Sigma [BTEX, styrene]$$

$$VPHv = VHv6-13 - \Sigma [BTEX, styrene, n\text{-hexane}, n\text{-decane}]$$

- New Co-Reporting Requirement
 - All parameters subtracted from VH must be co-reported with VPH results.

Thank You...

Questions?

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