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Evaluation of a Cost Effective Technique to Remove Biogeni Compound Interferences in Soil Samples

CONFIDENTIAL

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Acknowledgments

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ConocoPhillips Canada

OVERVIEW

- What is the potential bias with the CCME hydrocarbon method?
- Review of other research on the issue
- Inside the lab - Extraction and cleanup method
- Key findings of why silica gel cleanup as prescribed is not effective for all soils
- Case Studies
- Recommendations

Not Your Typical Contaminated Site

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Ontario MOE Background Soil Survey

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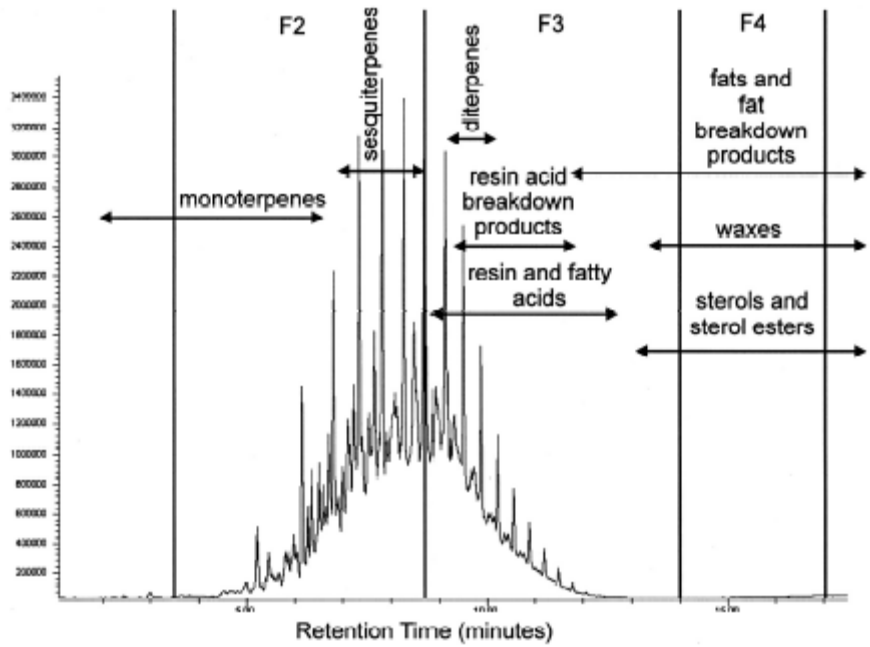
- In the summer of 2009, Ontario MOE revisited 180 rural and old urban parkland sites that were originally sampled in 1991 to update Ontario Typical Range values for chemicals of concern
- 218 surface soil samples were selected for PHC analysis
- Only 36 of 218 were ND for F3
- 8 samples exceeded AT1 or MOE Table 3 criterion
- Average concentration 78 ug/g
- F4 not as prevalent

Why do we have this Problem?

- Biogenic Organic Compounds (BOCs) such as sterols, fatty acids and fatty alcohols although highly polar are partially extracted in the hexane:acetone solvent mix
- If not removed by extract cleanup strategies, these compounds are considered petroleum hydrocarbons by regulators
- Mainly elute in the F3 (C16-34) and some in the F4 (C34-C50) fraction
- This is a well documented old issue, but a clear solution is not available



Typical BOC Signature

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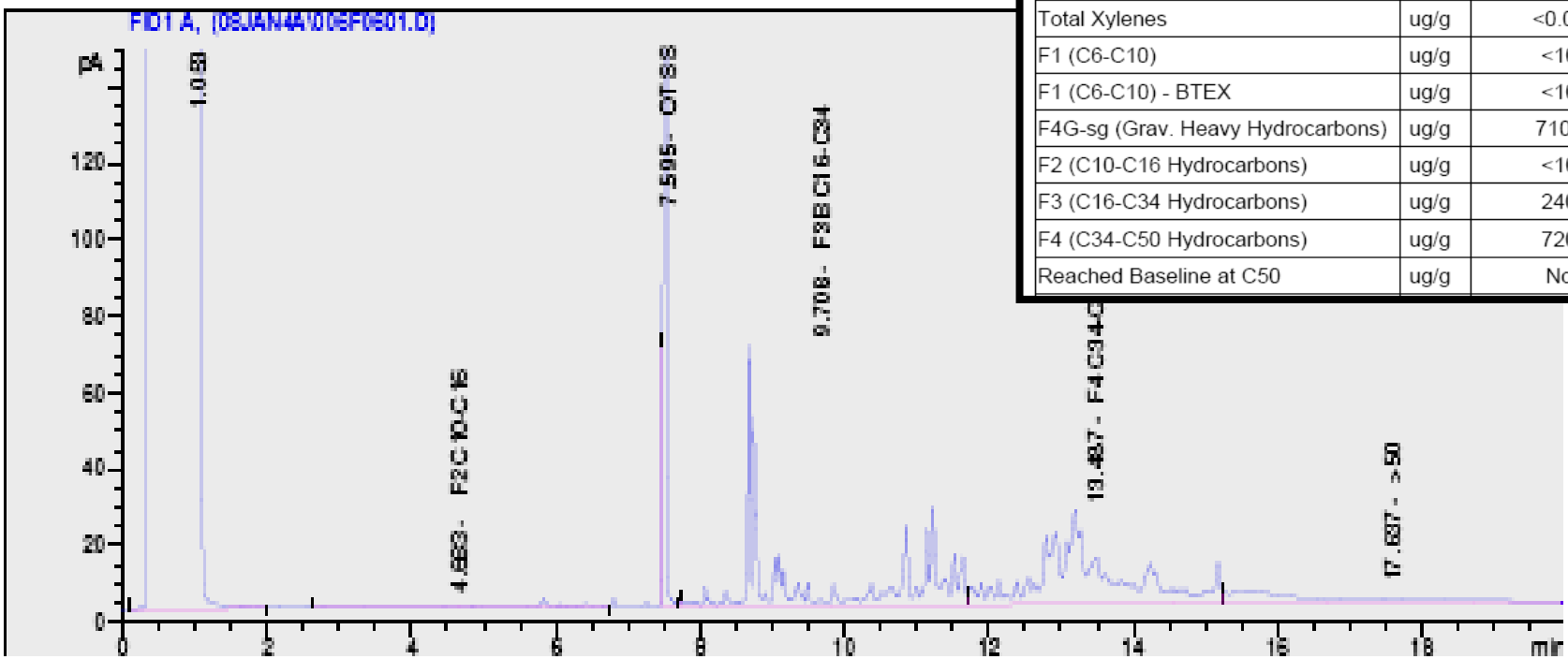
Moisture	%	40

Benzene	ug/g	<0.02
Toluene	ug/g	<0.02
Ethylbenzene	ug/g	<0.02
o-Xylene	ug/g	<0.02
p+m-Xylene	ug/g	<0.04
Total Xylenes	ug/g	<0.04
F1 (C6-C10)	ug/g	<10
F1 (C6-C10) - BTEX	ug/g	<10
F4G-sg (Grav. Heavy Hydrocarbons)	ug/g	7100
F2 (C10-C16 Hydrocarbons)	ug/g	<10
F3 (C16-C34 Hydrocarbons)	ug/g	240
F4 (C34-C50 Hydrocarbons)	ug/g	720
Reached Baseline at C50	ug/g	No



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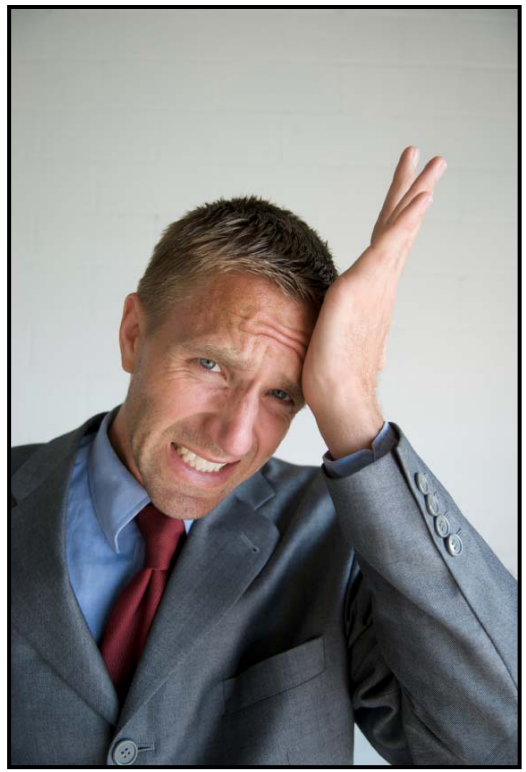
Potential Impacts of False Positives

- Potential buyers walk away from “clean” sites
- Consultants may recommend or actually remediate clean sites
- Different labs may yield significantly different data
- Financial impacts can be enormous



Background to the Study

- The CCME method recognizes that BOCs will interfere and create a biased high result for F3/F4 hydrocarbons
- Treatment of extracts with silica gel is incorporated into the method to help remove these interferences
- Despite the silica gel cleanup false positives for F3/F4 still are very common for high organic soils

CCME Recommended Approaches

- CCME recommends:
  - Background subtraction
  - GC/MS analysis
  - Dilution of extracts/column cleanup
- Triple silica gel cleanup often used with some controversy
- These approaches have not effectively dealt with the issue

Previous Research

- Kelly-Hooper & Zhendi Wang (2009), Maxxam (2007), Exova (2007), UMA/ALS (2006)
- Papers/presentation decks from this research indicated that silica gel is insufficient to remove all BOCs in high organic soils
- Work from these groups focused on differentiation of petrogenic from biogenic compounds by GC/MS using biomarkers, odd/even alkane patterns and other strategies

Challenges with These Approaches

- application of these techniques in a commercial setting
- Some data users may not recognize they have background BOC so don't know to ask for additional biomarker or GC/MS analysis
- clients are rarely willing to invest in expensive analysis, detailed subtraction and letter reports
- Regulators may not approve these alternate subtraction techniques
- Do not deal well where samples contain both BOCs and petrogenic hydrocarbons

No one seems to have asked why the silica gel is not working?

Research Goal

Determine a ***cost effective, validated*** option for customers that have samples rich with natural organics or a mix of petroleum and Biogenic Organic Compounds (BOCs) which will allow the laboratory to report a result that is representative of the true value of only petroleum hydrocarbons in soil samples.

Summary of the F2-F4 Extraction Method

Silica Gel Treatment

- Petroleum products are complex mixtures of aliphatic, aromatic and other additives
- Aliphatic PHCs are non polar
- PAHs are more polar than aliphatics, but still considered non polar
- PAHs “stick” to silica gel based on their unsaturated ring structure
- Most BOCs are very polar and will bind to the silica gel based on their polarity

Ex-Situ Column Cleanup

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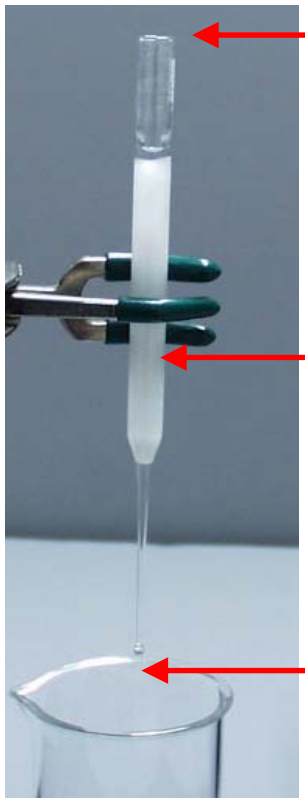
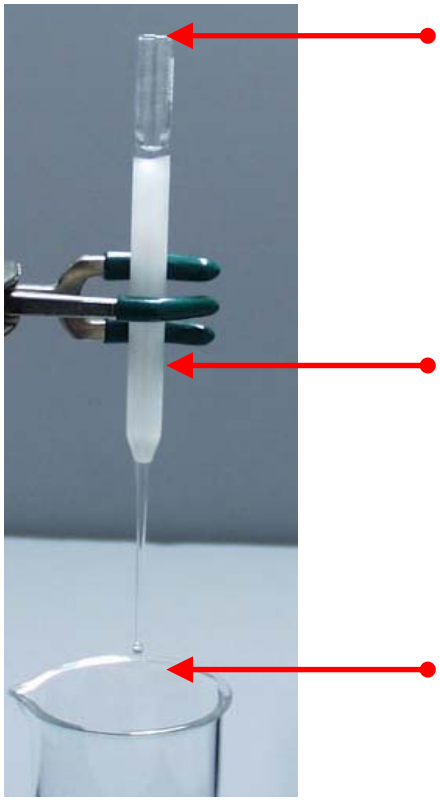


Hexane extract transferred to column

BOCs and PAHs are trapped on the column

Cleaned extract collected for GC analysis

Second Rinse of Silica Gel Column



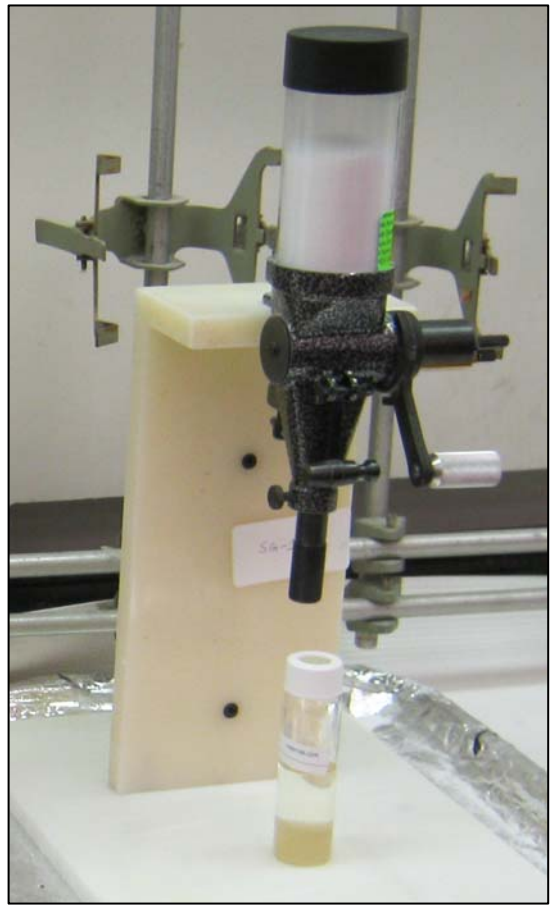
1:1 Hexane:DCM added to recover PAHs

Trapped aromatics and potentially BOCs are pulled off column by DCM

This extract combined with hexane rinse for GC analysis

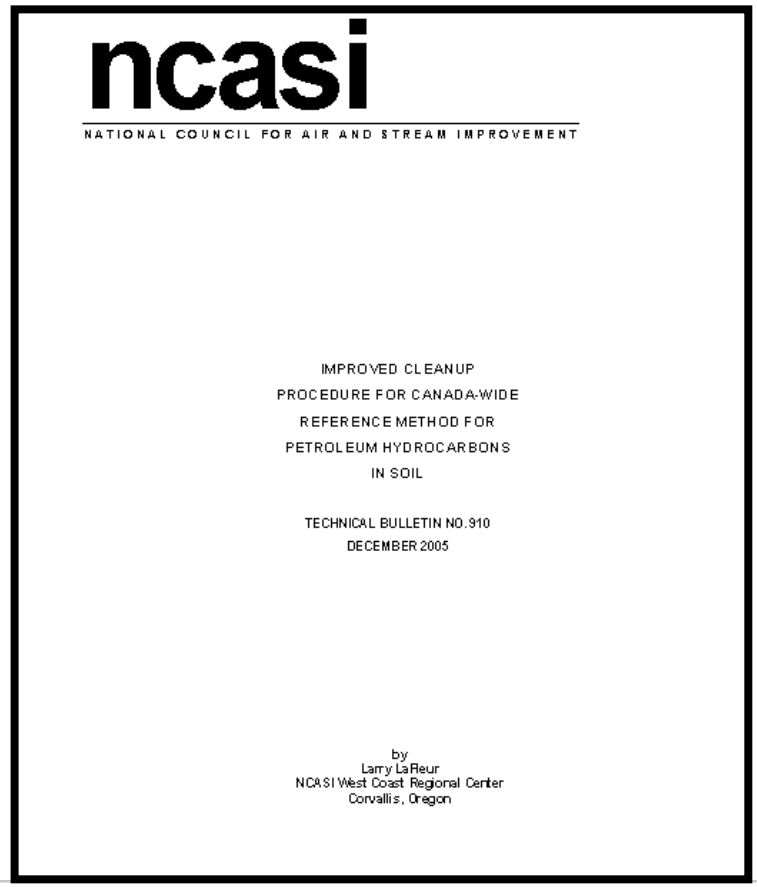
In-situ Silica Gel Cleanup

- The most common approach to silica gel cleanup by commercial labs is the in-situ method
- Activated silica gel is stirred in to the soil/solvent mixture then agitated by mechanical extraction (paint shaker)
- 1:1 Hexane:DCM added to the extract after mixing



NCASI Method

- 2005 - National Council for Air and Stream Improvement (NCASI) out of Oregon issued improved cleanup method to members
- NCASI members are companies in the forest products industry
- The research evaluated the BOCs in bark and wood debris of various tree species and different removal techniques



ncasi

NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

IMPROVED CLEANUP
PROCEDURE FOR CANADA-WIDE
REFERENCE METHOD FOR
PETROLEUM HYDROCARBONS
IN SOIL

TECHNICAL BULLETIN NO.910
DECEMBER 2005

by
Larry LaFleur
NCASI West Coast Regional Center
Corvallis, Oregon

NCASI Method

- NCASI method requires an ex-situ column cleanup
- Comparing In-situ versus ex-situ was not within the scope of the study
- NCASI discovered that too much DCM will pull off not only the PAHs, but the very polar BOCs in the second rinse of the silica gel column
- How much DCM is really needed to recover > 95% of a weathered diesel?
- NCASI concluded a 1:4 (DCM:Hexane) recovers PAHs and does not pull off as much BOCs
- The improved method reduced the BOC interference by an average of 68% across bark tree species and an average of 75% in wood debris as compared to the CCME method

NCASI Method vs Benchmark CCME

PHC Fraction	CCME Benchmark Method (ex-situ)	NCASI Method (ex-situ, 4:1 Hexane:DCM)	% Reduction
F2 (C10-C16)	45 ug/g	36 ug/g	20%
F3 (C16-C34)	2680 ug/g	1110 ug/g	62%
F4 (C34-C50)	2580 ug/g	286 ug/g	89%

BC Method 10

- British Columbia does not require silica gel cleanup of hydrocarbon extracts for routine soils unless BOCs are suspected
- For these samples an additional cleanup method is available (Method 10, June 2004)
- Method prescribes ex-situ silica gel column cleanup
- 2 water washes to remove excess acetone
- Reverse surrogate (decanoic acid) to ensure cleanup is working and no break though occurred
- Is there less squawking from BC consultants on the BOC issue?

In-situ or Ex-situ Silica Gel Cleanup?

- CCME method allows either in-situ (add silica gel to soil/solvent mixture and stir) or ex-situ column cleanup approaches
- Unless specifically requested the default method for most private commercial laboratories is in-situ
- less laborious and is suitable for most subsurface soils
- Market price for CCME PHCs has dropped by more than 50% since 2004

Efficiency of In-Situ vs Ex-Situ – F3 Fraction

*all samples treated in 1:1 DCM:Hexane

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Sample	F3 Concentration - No Cleanup (ug/g)	F3- In-Situ (ug/g)	% Removal	F3 Ex-situ (ug/g)	% Removal
Parkland 1	2400	610	75%	220	91%
Parkland 2	3100	870	72%	300	90%
Parkland 3	2600	580	78%	180	93%
Parkland 4	2900	590	80%	220	92%

Ex-situ column cleanup alone on these parkland soils remove enough BOCs to bring the F3 values at or below AT1 and just above MOE Table 1 standards

Efficiency of In-Situ vs Ex-Situ – F4 Fraction

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*all samples treated in 1:1 DCM:Hexane

Sample	F4 Concentration - No Cleanup (ug/g)	F4- In-Situ (ug/g)	% Removal	F4 Ex-situ (ug/g)	% Removal
Parkland 1	1200	350	71%	170	86%
Parkland 2	1600	490	69%	330	79%
Parkland 3	1200	180	85%	100	92%
Parkland 4	1300	210	84%	180	86%

Why is the Silica Gel not 100% effective?

- 1 g of silica gel will remove 10 to 30 mg of interferences – EPA Method 1664
- 0.6g of silica gel per gram of sample is prescribed in the CCME method
- in theory (according to EPA) it should be capable of removing 100% of polar BOCs up to 30,000 ug/g (ppm)
- So why do we have a problem?

Fouling of Silica Gel

- CCME method prescribes samples to be extracted with a 1:1 hexane:acetone solvent mixture
- Acetone helps break up soils and ensures complete extraction, particularly in clay soils
- Acetone is a polar solvent and if not removed prior to silica gel cleanup can occupy most of the binding sites
- Water washing or blow down used to remove acetone
- BC Method 10 requires the acetone concentration to be < 3% and have 2 water washes

Acetone Removal Step	Acetone Concentration after water wash
First Water Wash	8.1%
Second Water Wash	0.8%

Method Comparison Data – F3 Concentrations

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Silica Gel	No Treatment	In-Situ	In-Situ	In-Situ
Silica Gel solvent Mix	n/a	1:1 Hexane:DCM	4:1 Hexane:DCM	1:1 Hexane:DCM
Acetone Removal	1 water wash	1 water wash	1 water wash	2 water washes
Compost	255 ug/g	212 ug/g (186)	124 ug/g (121)	107 ug/g (137)

( ) values in brackets are duplicates

Method Comparison Data – F3 Concentrations

Success Through Science®

Silica Gel	No Treatment	Ex-Situ (Column)	Ex-Situ (Column)
Silica Gel solvent Mix	n/a	1:1 Hexane:DCM	4:1 Hexane:DCM
Acetone Removal	1 water wash	2 water washes	2 water washes
Compost	255 ug/g	62 ug/g (91)	70 ug/g (73)
Spiked Compost Recovery	95%	88%	101%

( ) values in brackets are duplicates

F2-F4 Extraction Method Comparison

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Element	CCME Method	BC Method 10	NCASI	Maxxam's OCBO* Method
Insitu/Ex-situ	Lab can pick	Ex-situ	Ex-situ	Ex-situ
Elution Solvent	1:1 (Hexane:DCM)	1:1 (Hexane:DCM)	4:1 (Hexane:DCM)	1:1 (Hexane:DCM) until regulator approval
Acetone Removal	1 water wash	2 water washes	1 water wash	2 water washes
Reverse Surrogates	None	Decanoic acid	none	Decanoic Acid

* Maxxam's New Optimized Cleanup of Biogenic Organics (OCBO) Method

Chromatograms

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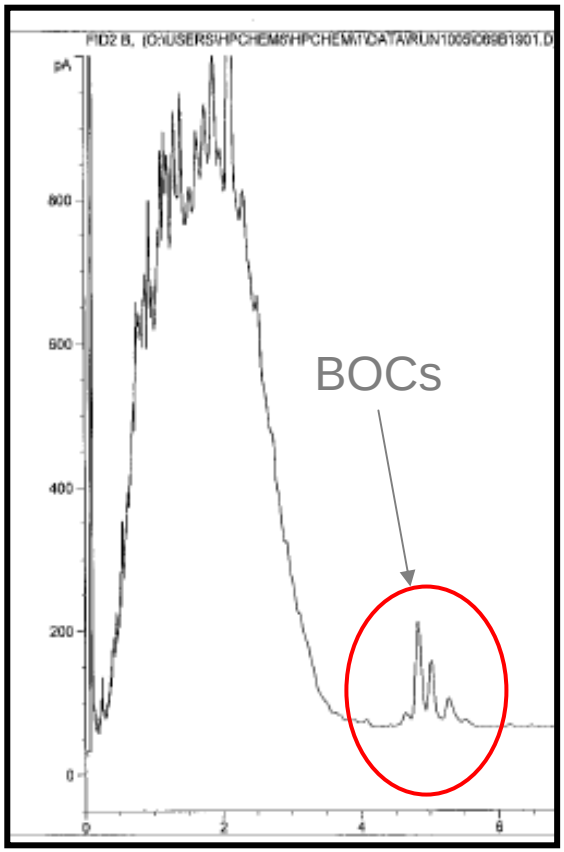
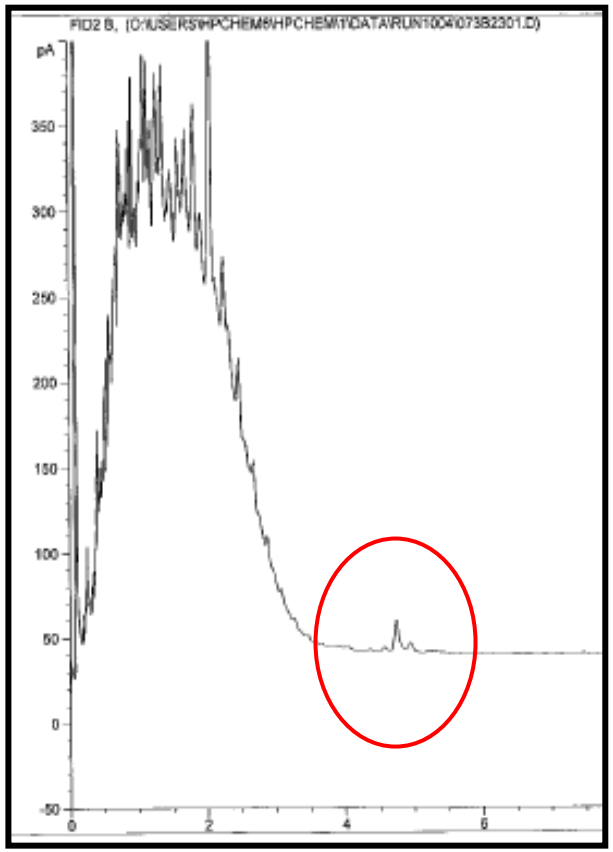
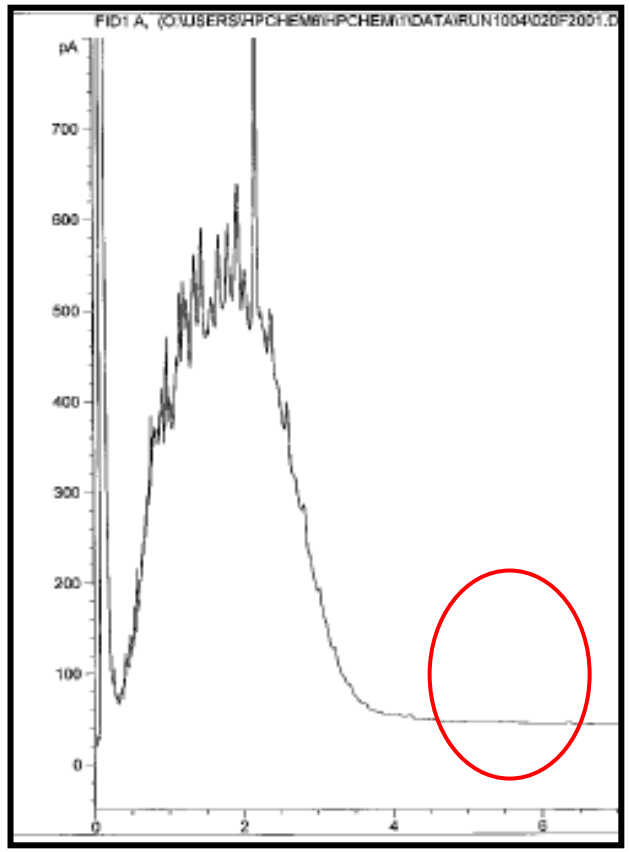


No Silica Gel Treatment



Standard CCME In-Situ

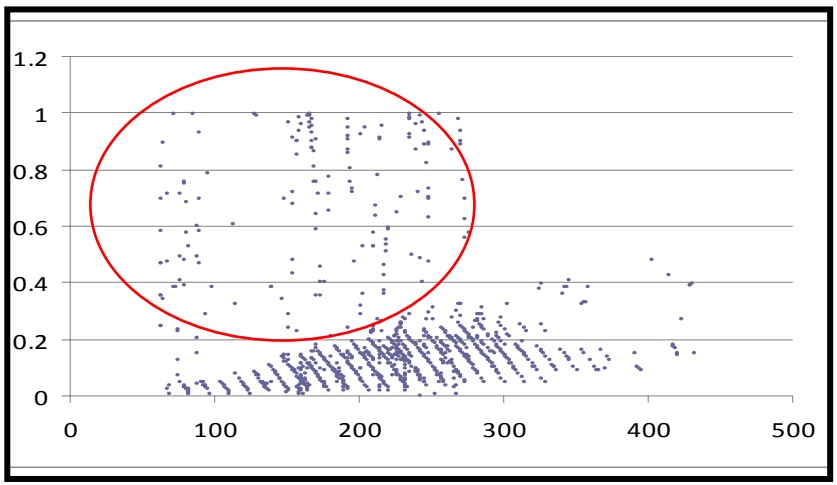


Optimized Method

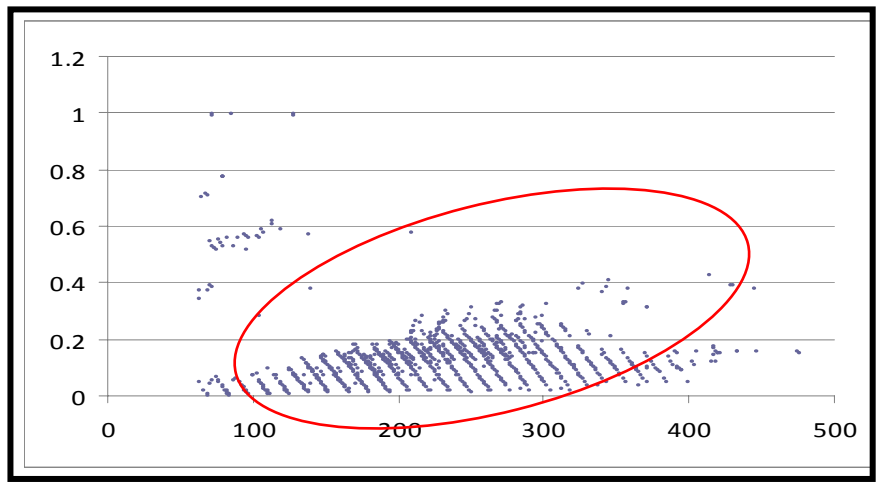
Case Study: BOC and Crude Mix

- Surface soil sample collected in Alberta suspected to be impacted with crude
- Soil is highly organic
- F2-F4 concentration 3950 ug/g, with F3 = 2400 ug/g (no cleanup)
- 3 Techniques used to help estimate BOC content:
  - GC/MS biomarker analysis (told us petroleum is present)
  - Fourier Transform (Ion Cyclotron Resonance) Mass Spectrometer (courtesy of Ontario MOE)
  - Maxxam's Enhanced cleanup procedure

Kendrick Plots of Mass Spectra

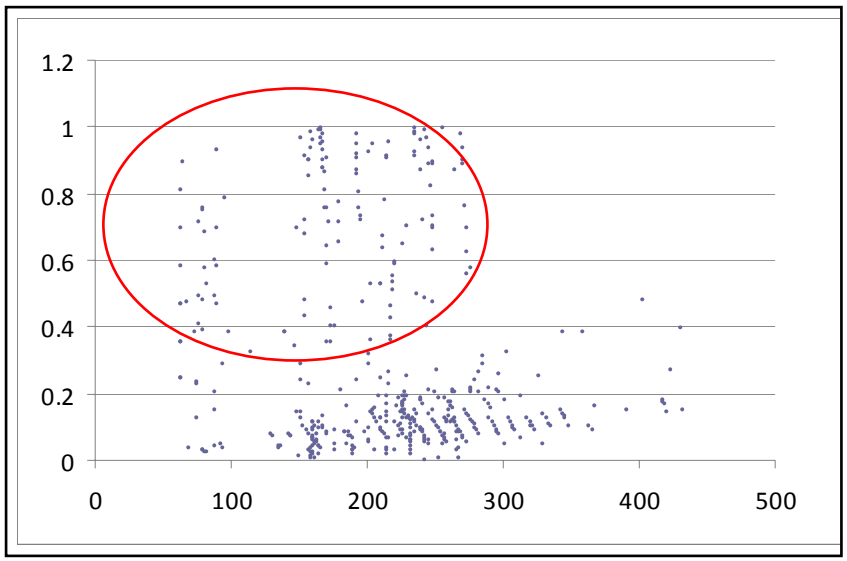


Unknown Sample Mix of BOCs and PHCs



Alberta Pure Crude Standard

Estimating Biogenic Contribution



Unknown sample scrubbed of all crude oil peaks

- Although still a work in progress, FTMS data suggests that ~ 35% of the hydrocarbons present in this sample are biogenic
- FTMS price tag $1.5M
- Enhanced cleanup indicated 33% of sample is biogenic

Conclusions and Recommendations

- In-situ silica gel treatment is efficient at removing typical levels of BOCs but has limitations and is not appropriate for high organic soils
- Request Maxxam's enhanced cleanup method in these situations
- Ex-situ cleanup is more effective than in-situ
- If you don't remove the acetone silica gel treatment is pointless
- NCASI may be on to something
- The environmental professional needs to understand the BOC interference issue, what can be done about it and when to be suspicious of false positives

Future Work

- Evaluation of other high BOC samples that contain different types of BOCs and concentration ranges
- Further evaluation of NCASI approach
- Seek regulator approval if NCASI method is as effective as documented

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