ALS Environmental

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Extractable Petroleum Hydrocarbons: an Innovative Method to Reduce False Positives and Improve Data Quality

BACKGROUND

The 2013 NEPM amendment included a change in terminology from Total Petroleum Hydrocarbons (TPH) to Total Recoverable Hydrocarbons (TRH). This was an important terminology correction as the chlorinated solvents that laboratories traditionally used to extract hydrocarbons from soil and water matrices (commonly dichloromethane - DCM) extract both biogenic (biological) and petrogenic (petroleum) hydrocarbons.

In the Environmental Industry, one of the major uses of the TRH analysis is to assess petroleum source contamination. Where significant levels of non-petroleum hydrocarbons are suspected, NEPM recommends a silica gel clean-up be performed (referred to as TRH silica), the purpose of which is to remove non-petroleum hydrocarbon interferences and provide a "TPH' estimate.

EnviroMail-81-TRH-Silica-and-Reducing-Potential-False-Positives-on-TPH

Unfortunately silica gel clean-up is not precisely selective in removing non-petroleum hydrocarbons. CCME methods comment that the use of silica gel to remove polar compounds must be performed carefully with well-defined procedures otherwise hydrocarbons will be lost and by the same token some non-hydrocarbons can pass through silica gel in some samples.

So the question becomes 'is there an alternative way to accurately measure Petroleum Hydrocarbons in environmental matrices?'

A possible solution is to use extracting solvents that are more selective for petroleum hydrocarbons, thus eliminating or reducing the need to perform silica gel clean-up. This method is commonly referred to as Extractable Petroleum Hydrocarbons (EPH)

ALS METHOD INFORMATION

EP071-EPH: EPH in water (LOR: 100µg/L)

EXTRACTABLE PETROLEUM HYDROCARBONS (EPH) - SOLVENT SELECTION

The *Canadian Council of Ministers of the Environment* (CCME) method for Petroleum Hydrocarbons in soil utilises hexane/acetone (also optional in NEPM). Australian methods however typically use DCM/acetone. The difference between analysis in Australia and Canada is the mandated treatment with silica gel to remove polar material in Canadian methods.

Note: The inclusion of acetone is specifically for soil matrices (as beneficial for solvation/wetting of the more complex matrices) and so is not required for water matrices.

Interestingly the CCME method rejected the use of DCM as it can also extract organic compounds other than petroleum hydrocarbons. CCME supported the fact that there is no perfect solvent however Hexane was chosen to be the best compromise. The rejection of DCM was also supported by a move to reduce or eliminate chlorinated emissions and for improving occupational hygiene.

So, if DCM can extract organics other than petroleum hydrocarbons, leading to potential false positives in assessment of petroleum hydrocarbon contamination, what other options are available?

ISO - 9377-2 Water quality - hydrocarbon oil index

This method measures the sum of concentrations of compounds extractable with alkane solvents, boiling point between 36 °C and 69 °C, not adsorbed on Florisil and which may be chromatographed with retention times between those of *n*-decane (C10) and *n*-tetracontane (C40). This method is designed to measure long-chain or branched aliphatic, alicyclic, aromatic or alkyl substituted aromatic hydrocarbons. This method also mentions the interferences of polar compounds and uses a single non chlorinated solvent or technical mixture of hydrocarbons, boiling range 36°C to 69°C.

ALS EPH METHOD

Consistent with the ISO and draft Canadian methods, ALS has investigated the use of hexane as an alternative solvent (from DCM) for more selective extraction of petroleum hydrocarbons. This method has been validated and ALS is now NATA accredited for the analysis of Extractable Petroleum Hydrocarbons in water.

This method has some very appealing benefits to industry and has been developed specifically looking to future needs of the petroleum sector. A summary of the accuracy and precision comparison using laboratory Control samples (LCS) for the current TPH and TRH method follows;

Precision and Accuracy comparison - TPH/TRH vs EPH analysis in water - ALS Australia 2015				
	Accuracy: Average Recovery		Precision: Relative Standard Deviation	
ANALYTE	LCS Recoveries for current TPH/TRH methods (10 LCS)	Average Recovery for EPH (10 LCS samples across three matrices)	LCS Standard deviations for current TPH/TRH methods (10 LCS)	Average Standard Deviations for EPH (10 LCS samples across three matrices)
TPH C10 - C14 Fraction	95.7	100.4	7.1	3.6
TPH C15 - C28 Fraction	96.7	102.9	3.8	2.8
TPH C29 - C36 Fraction	93.5	103.0	7.1	2.9
TRH >C10 - C16 Fraction	95.5	101.6	7.2	3.2
TRH >C16 - C34 Fraction	97.0	103.1	7.7	2.8
TRH >C34 - C40 Fraction	102.0	102.5	5.4	2.9
Mean Stats - all analytes	96.7	102.3	6.4	3.0

The other key technical consideration is the recovery of fresh diesel, i.e. does this method actually provide a good measure of diesel in groundwater excluding breakdown products? To assess this, fresh diesel was spiked into water and a control. The average recovery across all fractions was 90% when calibrated against Alkanes, showing that this method is not only precise and accurate but also an effective tool in accurately quantifying diesel (and by definition heavy components of petrol) in water.

BENEFITS OF ALS EPH METHODOLOGY

What does EPH offer industry when benchmarked against current TPH/TRH Methodology?

- The EPH analysis is slightly more accurate and consistent across all equivalent Australian carbon band fractions albeit with a 2.3% high bias versus a 3.3% low bias on current methods.
- EPH testing shows a > 100% improvement in precision. The net benefit of this dramatic improvement is that three standard deviations equates to ±9.0% (versus the TRH method at ± 19%). This improvement in analysis precision should assist in identifying trends in ground water concentrations through reduction in 'noise'.
- EPH can exclude the polar degradates of weathered fuel in groundwater thereby giving a better estimation of remaining petroleum hydrocarbon. This method is not subject to as many interferences due to naturally occurring humic materials and may provide an estimation of degradation percentage..
- For some matrices such as landfill leachate – the EPH analysis removes the vast majority of false positives due to organics from decaying material without even the need for silica gel.
- EPH gives superior recovery of heavy end hydrocarbons e.g. lube oils due to solubility
- DCM is removed from laboratory – an important occupational hygiene and environmental (climate change) consideration and also a benefit given this is often a target analyte.
- The method improves turnaround and is cost competitive.

Limitations of EPH are that it does not include (recover) full phenols in the result (nor does TRH) so this needs to be considered if TRH or EPH is used to screen for Phenols.

The following page shows the actual impacts to results on a few different samples.

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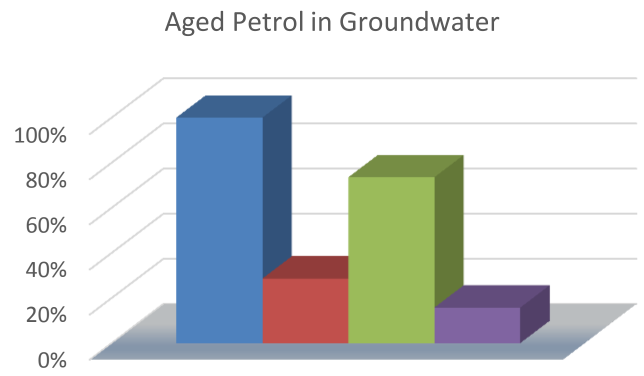
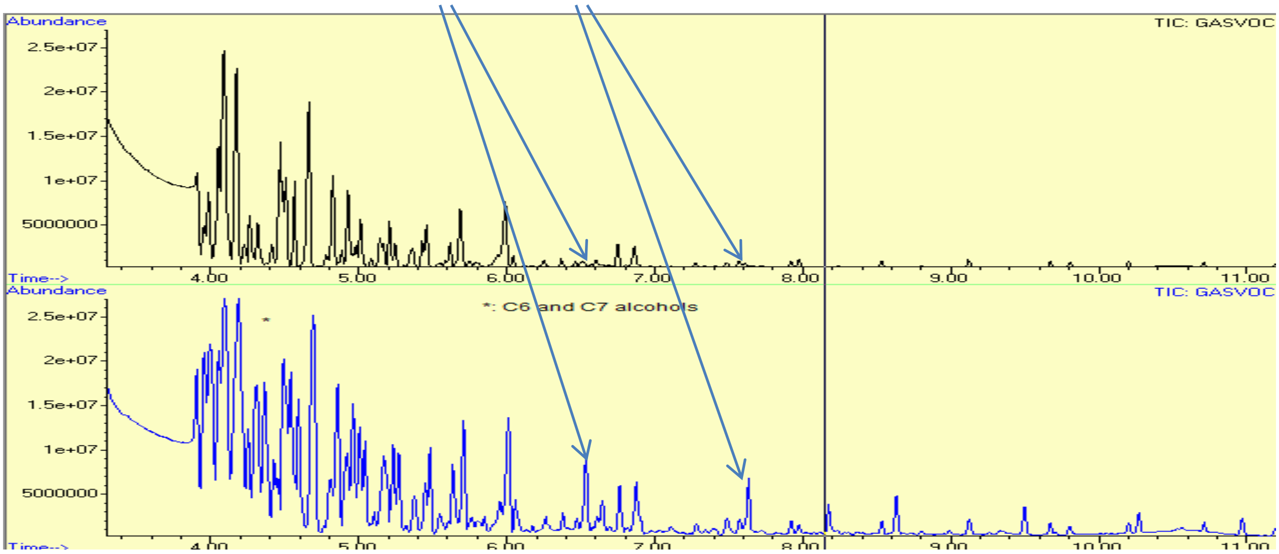
TRH VS. EPH FOR DEGRADED PETROL

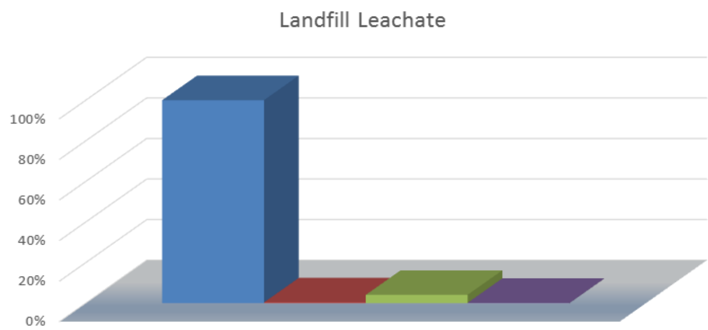
The results for aged degraded groundwater from a service station are shown adjacent via bar chart. Results are presented relative to TRH (set at 100% in blue), with EPH (in green) being 36% lower than TRH due to exclusion of many polar degradates. TRH Silica (red) shows the removal of further polar compounds while EPH Silica (purple) is lower still, showing the importance of silica gel clean-up. The chromatograms follow with EPH profile (black trace) and TRH (blue trace). Arrow pairs show the removal of hydrocarbon peaks from TRH to EPH.

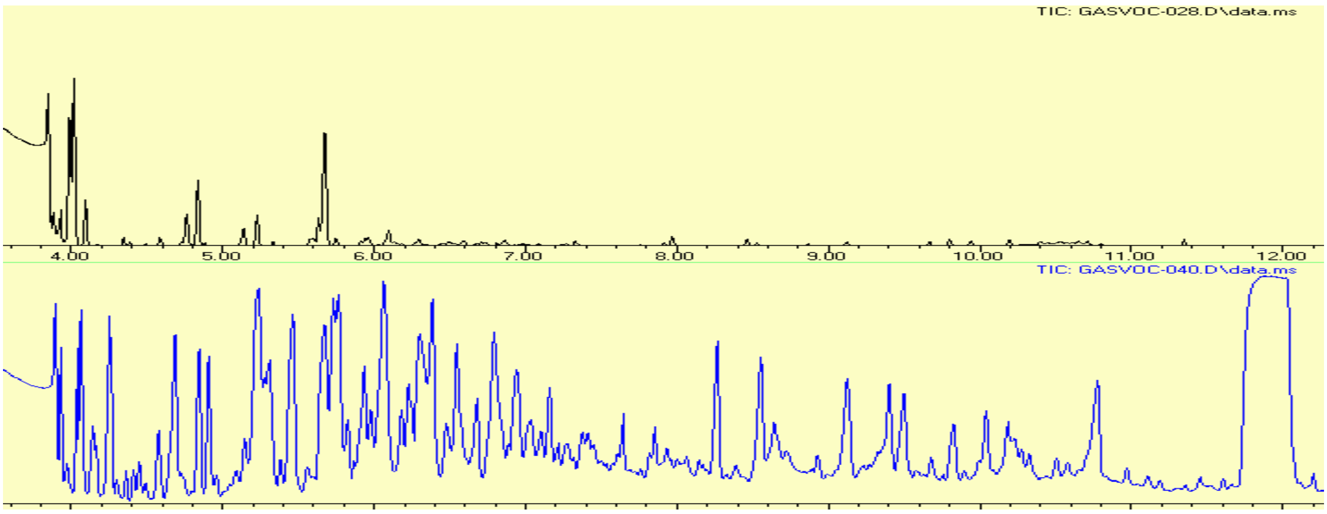




TRH VS. EPH FOR LANDFILL LEACHATE

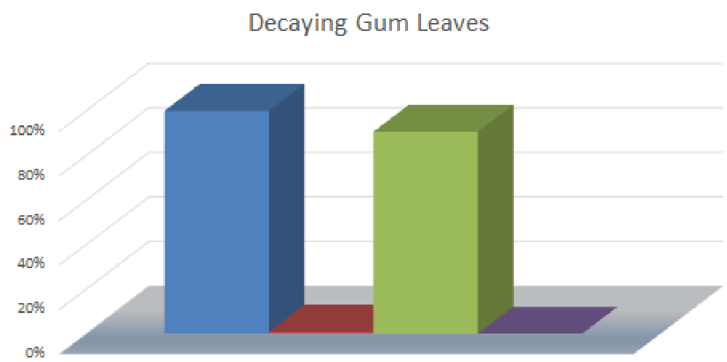
The adjacent bar chart again shows landfill leachate analysis relative to TRH (100% in Blue). The EPH analysis (in green) results were only 4% of the TRH due to the exclusion of many compounds including terpenoids. The Red bar is TRH Silica, and green is EPH Silica – both only about 1% of the TRH result clearly showing minimal petroleum hydrocarbon present. The chromatogram traces below show EPH in black and TRH in blue below with removal of non-petroleum hydrocarbons.

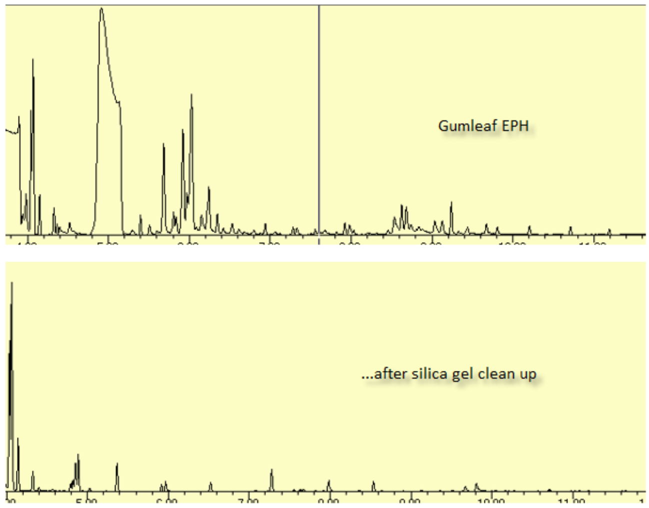




GUM LEAVES – will they impact results?

The gumleaf sample consists primarily of the terpene alcohol eucalyptol. The results indicate that some naturally occurring, medium polar organic matter can be extracted into hexane and give a positive result for EPH. The top trace shows EPH and the lower trace is the same extract after silica gel clean up.





CONCLUSIONS

- EPH can exclude the polar degradates of weathered fuel in groundwater thereby giving a better estimation of remaining petroleum hydrocarbon. This method is not subject to as many interferences due to naturally occurring humic materials and may provide an estimation of degradation percentage.
- For some matrices such as landfill leachate – the EPH analysis removes the vast majority of false positives due to organics from decaying material without even the need for silica gel.
- EPH gives superior recovery of heavy end hydrocarbons e.g. lube oils due to poorer solubility in DCM.
- When EPH or TRH is detected where you might not expect it, the chromatograms become important. The EPH in the landfill leachate is still picking up some compounds (peaks). Data and Chromatograms may be needed to assess whether the profile is really that of petroleum or other compounds that appear as false positives.

ANALYSIS SUITES

- ALS Sydney has a number of analysis suites that may assist in the assessment of hydrocarbons using EPH methodology for waters only. These method codes and suites.

Test	Traditional ALS **TRH** Method or Suite code	Test	New ALS **EPH** Method or Suite code
TRH (C10-C40)	EP071	EPH(C10-C40)	EP071-EPH
TRH-Silica (C10-C40)	EP071 SG	EPH-Silica (C10-C40)	EP071-EPH-SG
TRH/BTEXN	W-4	EPH/BTEXN	W-4A
TRH Silica/BTEXN	W-4 SG	EPH Silica/BTEXN	W-4A-SG
TRH/BTEXN/PAH	W-7	EPH/BTEXN/PAH	W-7A
TRH Silica/BTEXN/PAH	W-7 SG	EPH Silica/BTEXN/PAH	W-7A SG

- Pricing and detection limits are identical to the current equivalent TRH and TRH silica suites except EP071-EPH (only) which is slightly more expensive as a stand along method when not included in suites. EPH bottle requirements are as per TRH, i.e. the Standard ALS 100ml Amber bottles.

REFERENCES

NEPM B3 – Laboratory analysis of potentially contaminated soils – 1999 (Amended 2013)
Canadian Council of Ministers of the Environment Inc., 2001Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method
ISO - 9377-2 Water quality – Determination of hydrocarbon oil index
Canadian DRAFT Extractable Petroleum Hydrocarbons (EPH) in Water by GC/FID – March 6th 2015