Workshop on Development of a Consistent and Harmonized Approach to the Analysis and Reporting of TPH

Workshop Outline

8.30am	Registration
9:00am	Welcome and Introduction to TPH Workshop
9:10am	Presentation on CRC CARE HSL work
9:30am	Discussion on TPH methodology and reporting
10.30am	Break
11.00 am	Discussion on TPH continued..
12.30pm	Follow up discussion on NEPM Schedule B(3)
1:30pm	End and Lunch

Presentations

1. HSL Presentation - Eric Friebel
2. TPH Presentation - Danny Slee
3. TPH Presentation - David Springer

Environmental Laboratory Industry Group


CRCCARE
CRC for Contamination Assessment
and Remediation of the Environment
Development of HSLs
for Petroleum Hydrocarbons
Workshop on Development of a Consistent and Harmonized Approach to the Analysis and Reporting of TPH
Eric Friebel
1st May 2009
GHD

HSL Project

Project Objectives

- Limited Human Health and Ecological Tier 1 criteria for petroleum hydrocarbons in soil and groundwater in Australia
- Guidance exists in Australia and overseas on developing soil and groundwater criteria using risk assessment principles

- Stage 1: Identify key issues for resolution
- Stage 2: Derivation of Health Screening Levels (HSLs) for petroleum hydrocarbons in soil and groundwater

- Goal is for guidelines to be adopted nationally, possibly through the NEPM review process

Consultation Process

Project Working Group

- Commissioned by CRC CARE
- Working Group
  - Dr Peter Nadebaum (Project Leader) - GHD
  - Eric Friebel - GHD
- Program Advisory Group (PAG)
  - Environmental/Health Regulators
  - Industry Representatives
  - Research Groups (UniSA, UniQld, UTS, CSIRO)
  - Environmental Consultants
- Technical Working Group (TWG)
  - Subcommittee of PAG
    - Dennis Monahan – Chairman
    - Prashant Srivastava – Project Manager, CRC CARE
    - (Albert Juhasz – CRC CARE / Uni SA)
    - Brian Priestly – Monash Med
    - Erwin Benker – NSW DECC
    - Andrew King – BP Australia

Project Methodology

Staged Approach

- Stage 1 (2006-07) Literature Review & Issues and Options.
  - Comment on current practices and methods for developing and applying HSLs and clean-up guidelines (local and international)
  - Indicate information sources that are available and relevant to the development of HSLs
  - Number of workshops with PAG to get consensus on issues or identify requirements for further study

- Additional studies from Stage 1 research (2007-08)
  - TPH fractionation (Coffey / GHD)
  - Vapour Model Selection (CSIRO)
  - Vapour degradation (CSIRO)

- Stage 2 (2008-09) Detailed derivation of HSLs for soil and groundwater for petroleum hydrocarbons

Literature Study

Study Sources

- NEPM and EnHealth Documents
- AIP “Guidelines for the Management of Petroleum Hydrocarbon Impacted Land”, Draft, April 1999
- Documents from International Jurisdictions
    - NZ Ministry for the Environment (MfE)
    - United Kingdom Environment Agency (UK EA)
    - Canadian Council of Ministers of the Environment (CCME)
    - USEPA and regional jurisdictions
    - Dutch
    - Germany
- Papers from the Fifth National Workshop on the Assessment of Site Contamination and previous monographs
- CSIRO documents

Literature Study

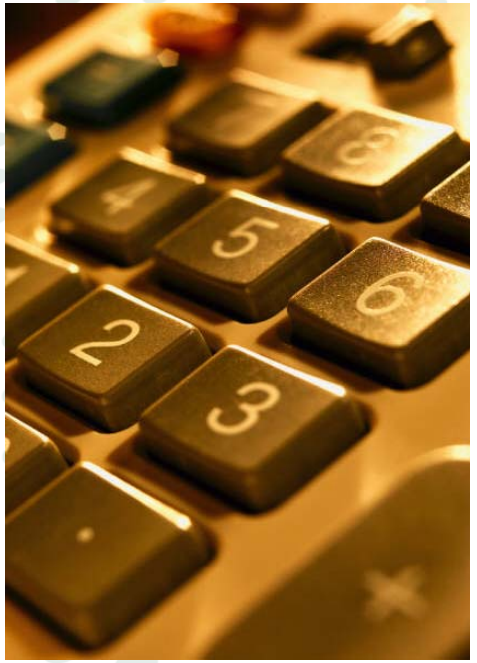
Key Discussion Points

- Sources of toxicity information and toxicity criteria
- Sources of exposure data
- Land use settings
- Multiple chemicals exposure
- Scope for consideration (Health – Aesthetic – Ecological)
- Chemicals to be included
- Background exposure
- Sub-surface maintenance workers (trench)
- Whether the HSLs should extend to include groundwater use
- Consideration of exposure via consumption of home-grown produce
- Whether soil criteria should be developed to protect groundwater quality
- Saturation / solubility limits of chemicals in mixtures
- Vapour Model Selection (CSIRO)
- Vapour degradation (CSIRO)
- TPH fractionation

Literature Study

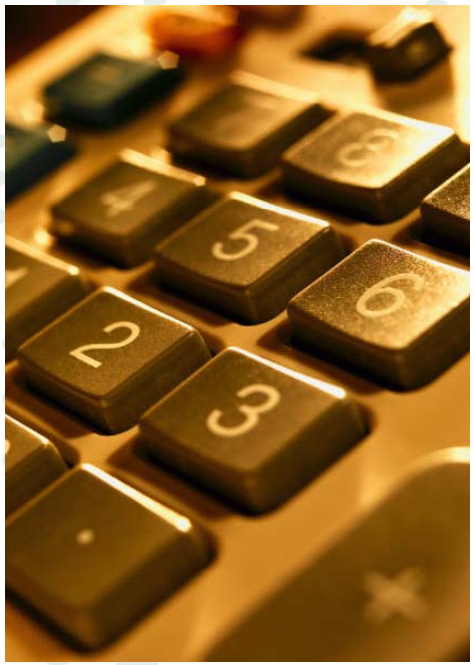
Chemicals to be included

- Benzene, Toluene, Ethylbenzene, Xylenes
- Naphthalene
- Carcinogenic PAHs Toxic equivalent – 16 PAHs
- Total Petroleum Hydrocarbons (TPH)



TPH Studies

Considerations for Selecting TPH Fractions



- What is the best source of toxicity information for TPH?
- What is the best representative physical properties for modelling vapours?
- Aliphatic / aromatic speciation?
- Laboratory analytical technique constraints and consistency?
- Cost impacts on analytical costs?

Coffey Initial Study

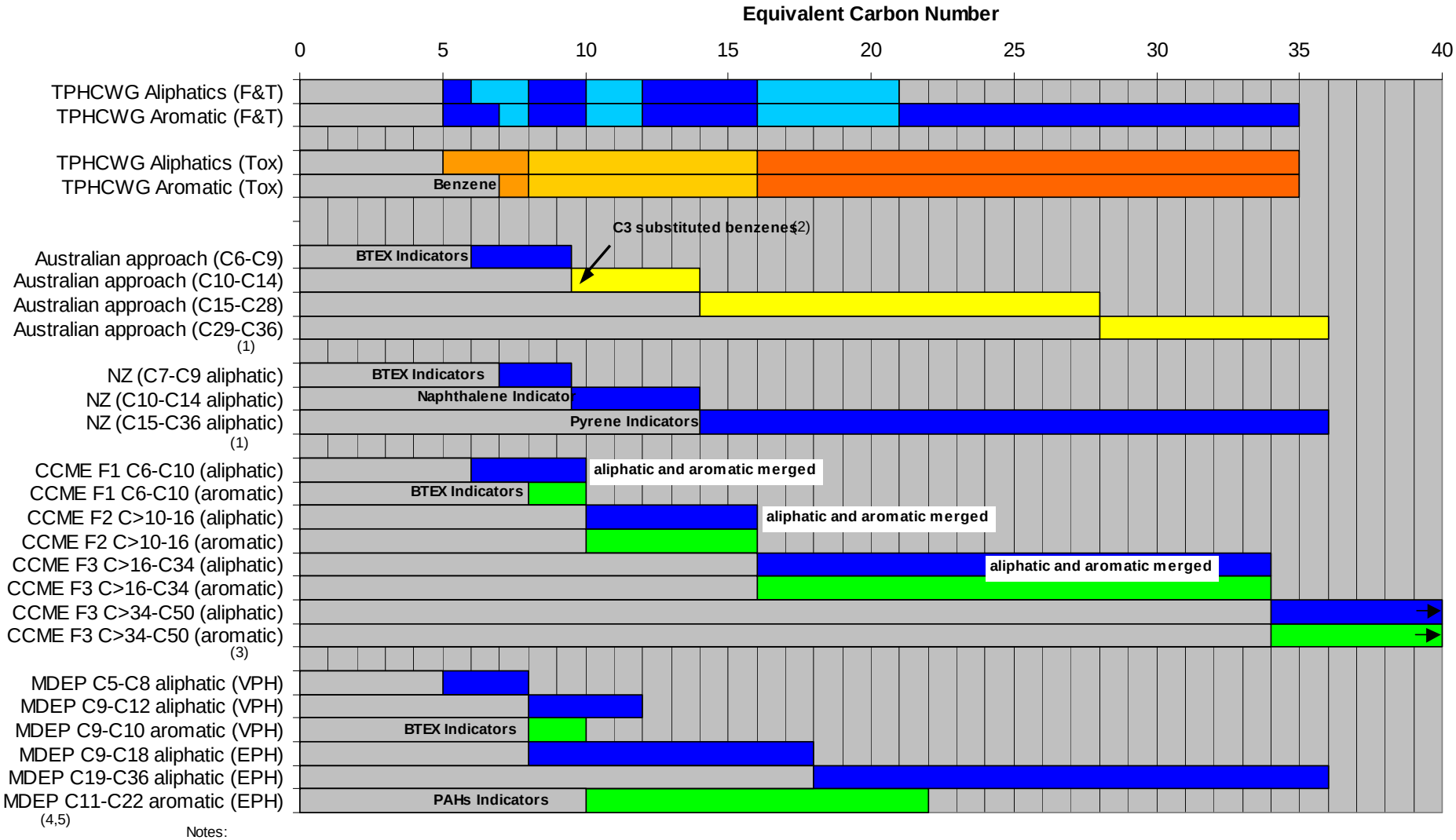
- Review of the different jurisdictions and how TPH is addressed
- Nearly all jurisdiction used the TPHCWG toxicity and fate and transport properties in some way
- The rational for each jurisdiction's approach is not all apparent

Assessment Summary

Methods / Jurisdictions

- Australian Institute of Petroleum (AIP) - current
- TPHCWG
- Canadian Council of Ministers of the Environment (CCME)
- New Zealand Ministry for the Environment (MfE)
- Massachusetts Department of Environment Protection (MDEP)
- Also looked at UK, Dutch

Figure 1 - TPH Carbon Fraction Ranges



Notes:

1) Australian and NZ fractions not based on Equivalent Carbon fraction nomenclature

2) C3 substituted benzenes captured in C10 fraction which effectively is EC9.5

3) CCME merge aliphatic and aromatic components into one measured fraction.

4) MDEP do not specify equivalent carbon, but derivation of fractions indicate these are closely align with original TPHCWG fractions which are based on EC.

5) MDEP separate aromatic and aliphatic components in the analytical testing procedure.

Assessment Summary

Findings

•The TPHCWG provides the soundest theoretical base for toxicity information and fate and transport properties for TPH

•The use of “collapsed fractions” is carried out by a number of countries, and is supported by the MDEP, a group that is highly regarded in the field. The review has determined that the use of collapsed fractions does not necessarily result in a significantly different outcome from using the complete set of TPHCWG fractions, especially when indicator chemicals like BTEX are assess concurrently with TPH.

•The ability to undertake the required analytical methods is an important consideration. Analytical methods available overseas are not currently practised in Australia, and this needs to be considered in the decision making process.

Adopted Approach

CCME Collapsed Fraction Approach

- The smaller number of fractions is simpler for comparison to analytical results
- Deriving criteria based on TPHCWG fractions before merging into collapsed fractions removes the uncertainty of combining physical and toxicological properties associated with NZ and MDEP methods.
- The selected fractions of CCME fit within the TPHCWG fractions. There is no need to split a TPHCWG fraction, only merge. Eg. C>10-C16 is the combination of C>10-12 and C>12-16
- Assumption of combining aromatic and aliphatic fractions captures aromatic components not measured as indicator chemicals
- The assumption of combining aromatic and aliphatic fractions means that speciation analysis does not need to be adapted into Australian laboratory analytical methods. This approach does not require significant changes to current analytical methods in Australia

Adopted Approach

CCME Collapsed Fraction Approach (cont)

- The derived criteria are dependent on the assumed proportion of aliphatic/aromatic species in each fraction. CCME have made the assumption of 20% aromatic, 80% aliphatic (after BTEX is removed from the mixture).
- Petrol and Diesel composition breakdown supplied by BP and Shell. C10-C16 aromatic in diesel makes up 19%, for >C16 aromatic makes up 25%
- Consistency is required by Australian analytical laboratories on adapting proposed methods.
    - Currently use a “purge and trap” method to capture the C6-C9 fraction (which includes BTEX), using n-hexane (C6) and n-nonane (C9) as markers
    - purge and trap method can capture up to C12
    - FID is used to detect fractions in GC above C9, and that changing from fraction of C10-C14 to C10-C16 is a reporting issue, not a technique change. Hence changing from C14 to C16 should not cause too many difficulties for laboratories
- Initial enquiries with laboratories indicates that the analysis needed to support the fractions is feasible

Adopted Approach

Other considerations

•Irrespective of the particular splits it is understood that there is currently no consistency in the analysis and reporting of TPH for contaminated soils between laboratories

•There will need to be careful consideration of what chemicals should be used as end markers for the fractional ranges, and what the boundary should be, eg EC10 or EC10.5

•Review of the components in the C10 range indicate that physical properties have a large cross-over of the TPHCWG fractions C>8-C10 and C>10-C12. Hence there is no definitive line which indicated that EC10 must be the exact line to divide the fractions, giving some flexibility to the selection of the boundary

•The toxicity information is generally based on direct toxicity measurements of mixtures of fuel and not individual chemical components. Hence, there is unlikely to be a definitive line that divides the toxicity at C16, giving some flexibility to the selection of the boundary (eg EC16 or EC16.5)

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Total Petroleum Hydrocarbons

Danny Slee,

TPH Workshop

Citigate Central Hotel

Sydney, May 1, 2009

measurement.gov.au

Australian Government
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Outline

- Introduction & Background
- TPH Naming (TRH versus TPH/silica?)
- Reporting TPH & Bands
- Instrumentation
- A TPH method - “Performance based”

Introduction

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TPH Definition

- *Petroleum is a complex mixture of organic liquids called crude oil and natural gas, which occurs naturally in the ground and was formed millions of years ago. Crude oil varies from oilfield to oilfield in colour and composition, from a pale yellow low viscosity liquid to heavy black 'treacle' consistencies.* Extracted from AIP website(1).
- TPH (Total Petroleum Hydrocarbons): *TPH is defined as the measurable amount of petroleum-based hydrocarbon in an environmental media. It is, thus, dependent on analysis of the medium in which it is found. Since it is a measured, gross quantity without identification of its constituents, the TPH "value" still represents a mixture. Thus, TPH itself is not a direct indicator of risk to humans or to the environment.* Extracted from Agency of Toxic Substances and Disease Registry (2).

Petroleum Compounds

Some “Petroleum” compounds & classes –

- Paraffins – alkane hydrocarbons with the general formula C_nH_{2n+2}.
- Unsaturated alkanes - olefins
- Naphthenes – or cyclic alkanes
- Aromatics – monoaromatics & polycyclic aromatics
- Asphaltics - bitumen

Not considered Petroleum compounds?

- Phthalates
- Humic acids
- Fatty acids & esters – stearic
- Sterols

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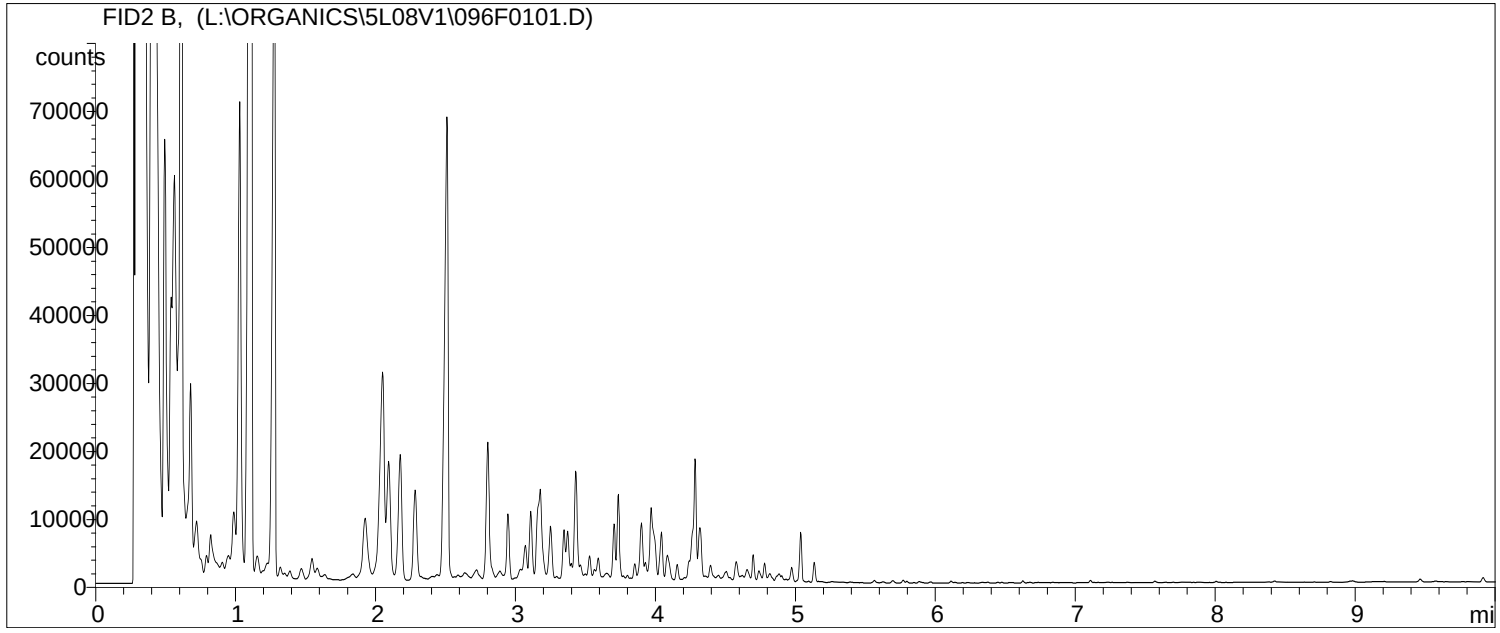
Determine TPH

- Petroleum is a complex mixture of over 250 compounds.
- Too complex to determine individual compounds
- Usual approach – determine by bands



Unleaded petrol by Gas Chromatography-FID

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TPH in Australia

Current TPH Bands -

- C6 to C9
- C10 to C14
- C15 to C28
- C29 to C36

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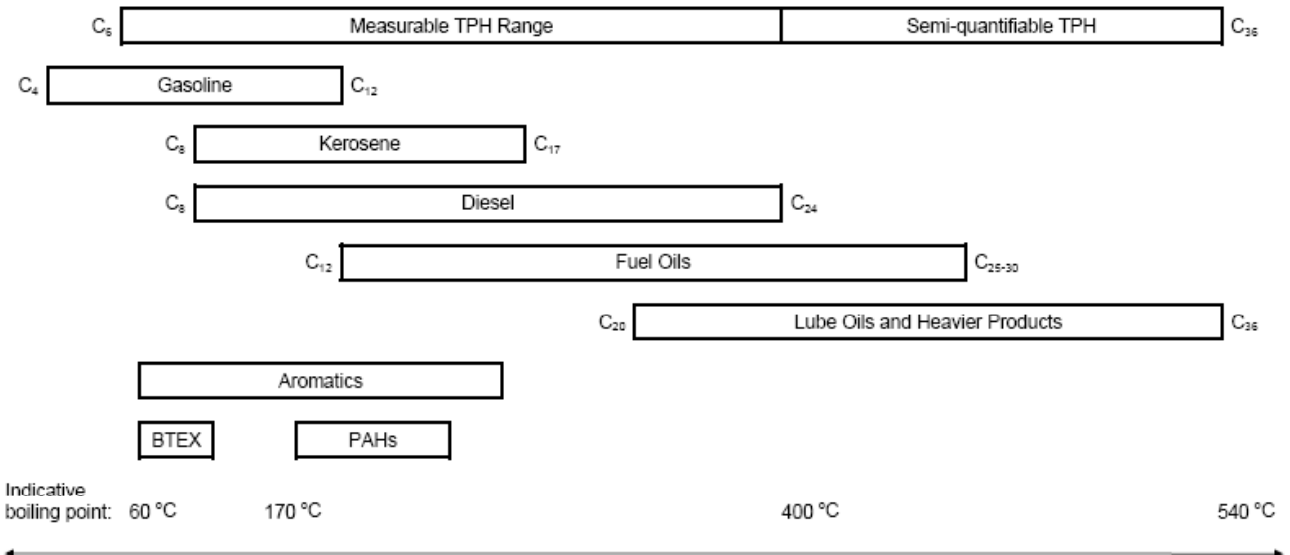
TPH in Australia

What do the results indicate?

- C6 to C9 & BTEX – suggests petrol contamination
- Majority C10 to C14 – suggests kerosene or aviation fuel
- Some C10 to C14 & majority C15 to C28 – suggests diesel
- C29 to C36 & >C36 – suggests mineral oil & lube oil

1.2 Carbon number, total petroleum hydrocarbons (TPH) and indicative boiling point range



This diagram shows the typical carbon number ranges of common products, together with indicative boiling points. This is contrasted against the detectable range of a TPH analysis.

Naming TPH (TRH?)

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Reporting TPH

- Most references and guidelines refer to Total Petroleum Hydrocarbons (TPH), however, is this correct terminology?

- Alternatives include Total Recoverable Hydrocarbons (TRH), Total Recoverable Petroleum Hydrocarbons (TRPH), Solvent Extractable Hydrocarbons (SEH) or Total Extractable Hydrocarbons (TEH).

- A recent survey showed that 7/10 member labs of the Environmental Laboratory Industry Group (ELIG) support the term TRH, unless a silica gel cleanup has been done, in which case the usual TPH term is acceptable.

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Reporting TPH

- **General consensus from ELIG labs is that after a sample has been treated with silica gel the correct terminology is TPH**.

- Silica gel can reduce the presence of non-petroleum interferences – polar organics such as phthalates, fatty acids & humic acids.

Silica gel cleanup

- Go to Envirolab presentation

TPH Bands

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TPH Bands

- All ELIG labs polled used n-alkane markers to define bands

But

- All labs calculated bands slightly differently:

- Example: C10-C14
- Lab A = Calc from C9.5 to C14.5
- Lab B = Calc from start C10 to start C14
- Lab C = Calc from >C9 to end C14

- Also start and end points differ i.e.

  Start of peak, apex of peak or end of peak?

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TPH Bands

- For a standard approach to TPH determination, band definition has to be prescribed.
- Do we adopt the band positions recommended in the CRCCare report?
- What compounds are used to quantify each band?

- Poll conducted by ELIG (sample of three labs) –

Fractions	**Lab A**	**Lab B**	**Lab C**
C6-C9	Calculate from C5.5 to C9.5	calculate from start C6 to start C10	Calculate from >C5 to end C9
C10-C14	Calculate from C9.5 to C14.5	calculate from start C10 to start C14	Calculate from >C9 to end C14
C15-C28	Calculate from C14.5 to C28.5	calculate from start C14 to start C28	Calculate from >C14 to end C28
C29-C36	Calculate from C28.5 to C36.5	calculate from start C28 to end C36	Calculate from >C28 to end C36

Instrumentation

Instrumentation

- Gas Chromatography is preferred technique
- Flame Ionisation Detector has almost unanimous support for semi-volatile TPH determination.
- Preferred column is relatively non-polar column
- Stationery phase of column will have to be specified

- A TPH Method – “performance based”

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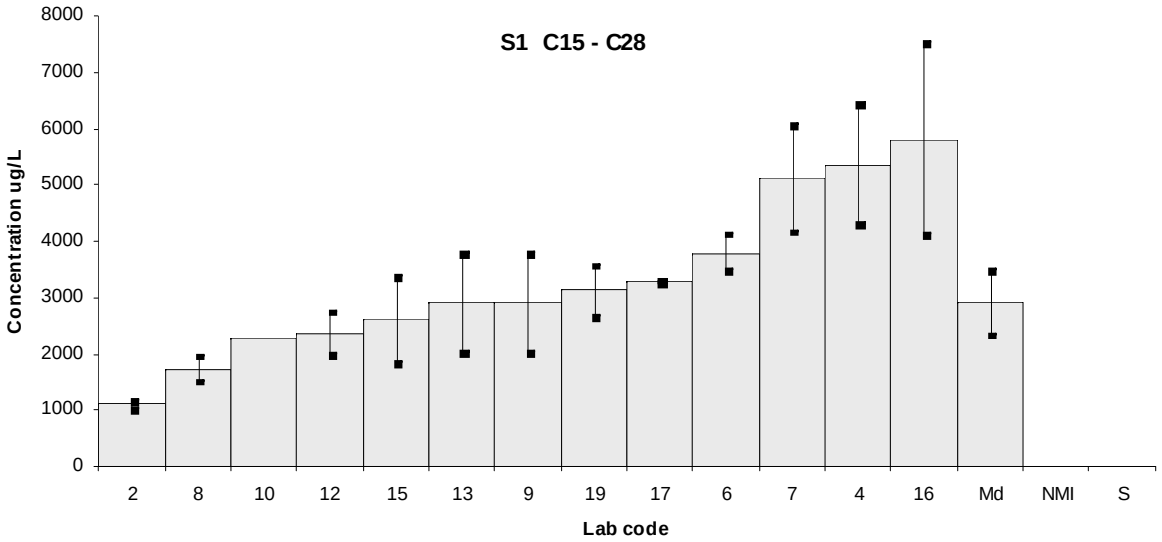
Proficiency Results – NMI Studies



Study AQA 08-12 Hydrocarbons in water

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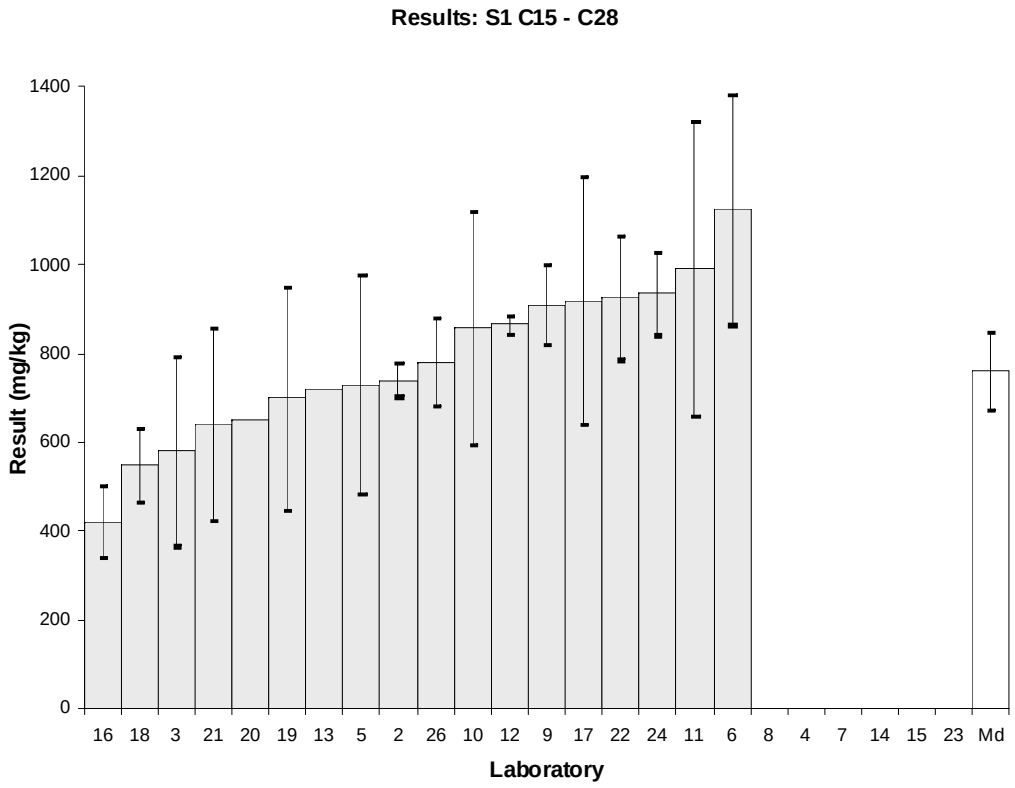
Proficiency Results – NMI Studies



Study AQA 06-07 Hydrocarbons in soil

Advantages of a Performance Based Method

Prescribing methods of analysis means:

- The analyst is denied freedom of choice and thus may be required to use an inappropriate method in some situations;
- The procedure inhibits the use of automation; and
- It is administratively difficult to change a method found to be unsatisfactory or inferior to another currently available.

Performance based alternatives to standard methods

- Allow laboratories to select method options suitable to their situation
- increase efficiency
- allow for technical improvements.

Features of Proposed Performance Based Method

- The method criteria will be linked to the *Canadian Council of Ministers of Environment (CCME). 2001. Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil – Tier 1 Method. ISBN 1-896997-01-5. Publication No. 1310 (including 'Addendum 1')*

- If the results are to specify total 'petroleum' hydrocarbons (TPH) not total 'recoverable' hydrocarbons(TRH), a cleanup of the extract will be required eg. Silica gel

- The bands will be defined by n-alkane standard markers clearly stating that these are Boiling point reference points and not structural reference points (which has been a common mis-conception). As the apex retention times of these standard marker are well defined, these will be the 'cut-offs' between the bands. This will also require that a column stationary phase is defined.

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Features of Proposed Performance Based Method

- Instrumentation - instrument must be a gas chromatograph. GC detector should provide a consistent response across compound classes but detector will not be specified. Column stationary phase will have to be prescribed to elution order of compounds.

- Validation & ongoing QC should be based on petroleum product rather than individual hydrocarbons. Method will specify an ongoing QC including petrol, diesel and a heavier oil to cover the last band. An acceptance criteria for these products will be established. The bands are to be calculated against appropriate n-alkane standards.

- Ratio of sample to extraction solvent will be defined. 5 gram sample minimum (based on 2 mm particle size).

- Reference Material – NMI hopes to define a reference material for three petroleum products in soil (i.e. petrol, diesel & heavier oil).

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Features of Proposed Performance Based Method

- Proficiency study support - NMI is considering initiating further inter-laboratory proficiency studies to monitor laboratory performance and band positioning will be defined in this study.
- Benchmark method – a benchmark method will be recommended to guide laboratories.

Note

Method performance criteria should provide a more reliable result and lead to a consistent measurement uncertainty determination.

References

(1) AIP Website - http://www.aip.com.au/industry/fact_refine.htm

(2) Agency of Toxic Substances and Diseases - http://www.atsdr.cdc.gov

(3) Diagram of carbon number range - *Sampling Protocols and Analytical Methods for Determining Petroleum Products in Soil and Water Prepared by the Oil Industry Environmental Working Group, May 1999, New Zealand*.

(4) NMI Proficiency Study AQA 08-12 *Hydrocarbon in Water*, March 2009

(5) Canadian Council of Ministers of Environment (CCME). 2001. Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil – Tier 1 Method. ISBN 1-896997-01-5. Publication No. 1310 (including 'Addendum 1')

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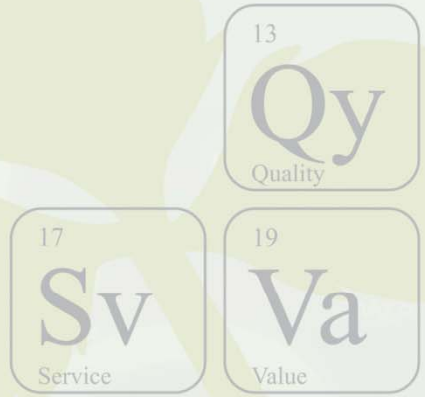
Thanks for your Attention!

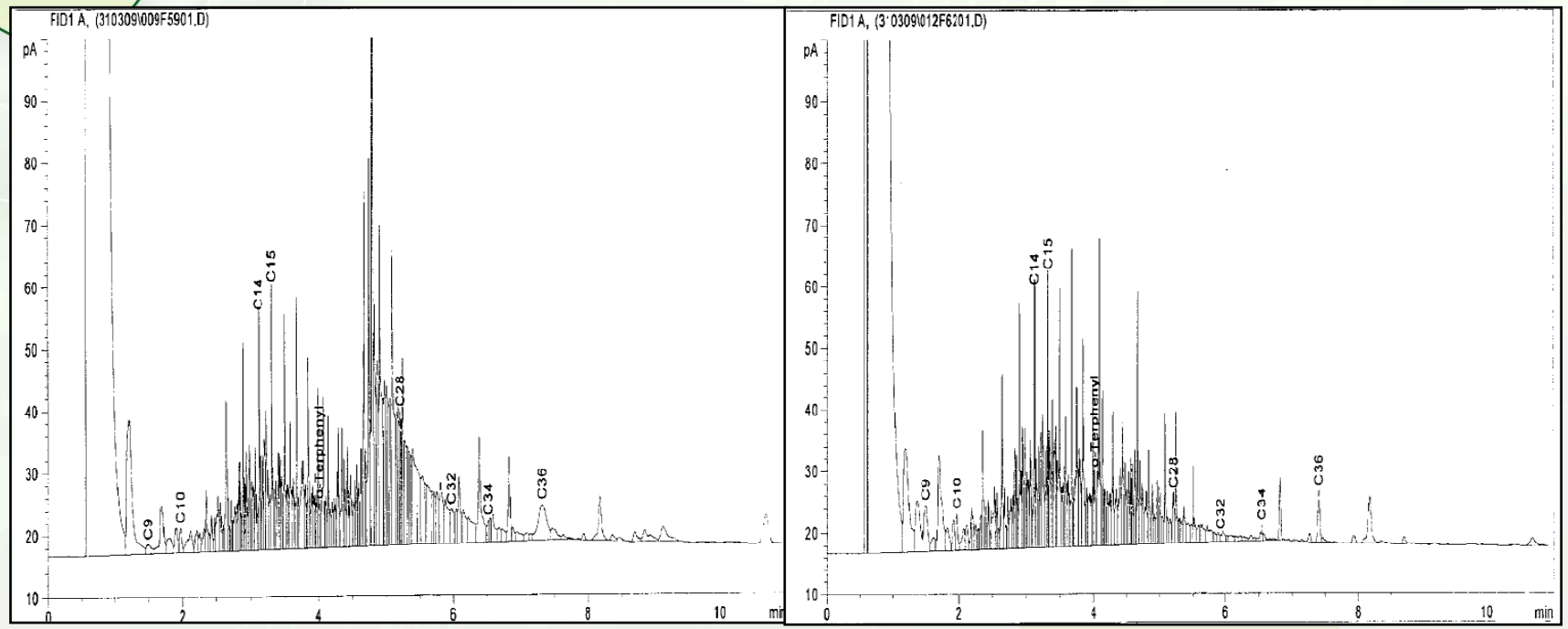
measurement.gov.au

What is a Silica Gel Cleanup?

- After a sample is extracted in solvent the extract is poured through a column containing silica gel. The solvent extract runs down through the column slowly, over the surface of the silica gel particles. The silica gel adsorbs any polar compounds that were extracted from the sample, allowing the non polar petroleum based compounds to flow through.

- Extraction solvent is treated with silica in-situ. The silica gel adsorbs any polar compounds that were extracted from the sample.





Diesel spiked Woodchips - TRH

C10-C14 : **410ppm**

C15-C28: **1500ppm**

C29-C36 : **600ppm**

Diesel spiked Woodchips - TPH – Silica Gel cleaned

C10-C14 : **380ppm**

C15-C28 : **910ppm**

C29-C36: **140ppm**

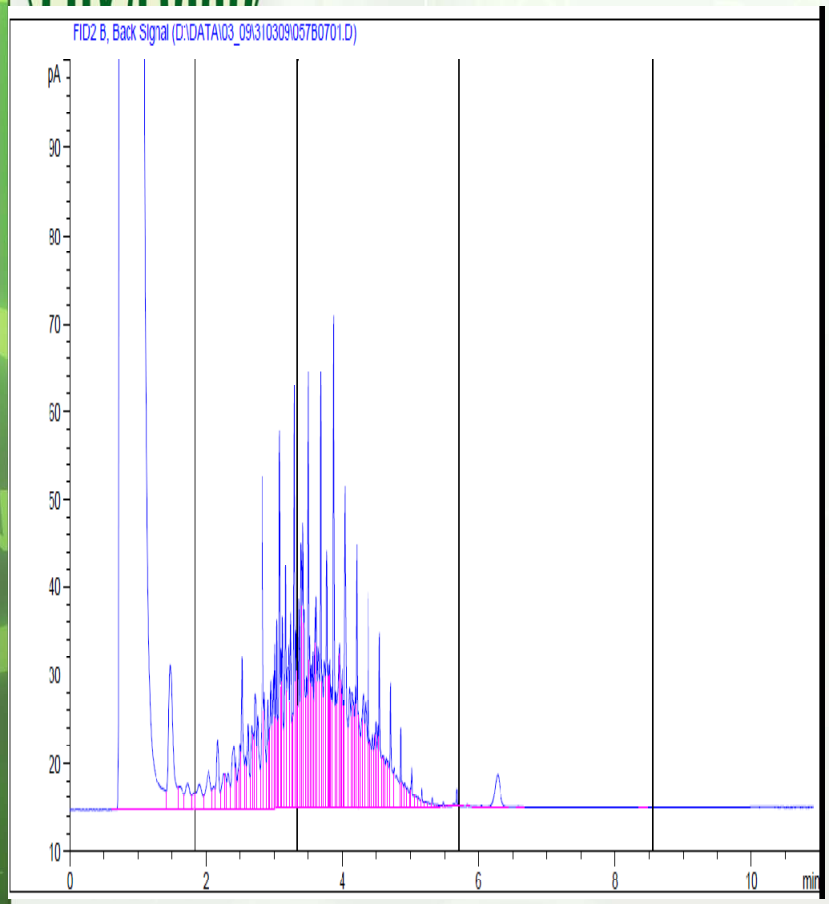
The last 2 fractions have shown the greatest difference after the silica gel cleanup, emphasizing the importance of reporting as TRH unless the sample has undergone silica gel clean up.

Calculating

- All labs calculate slightly differently:

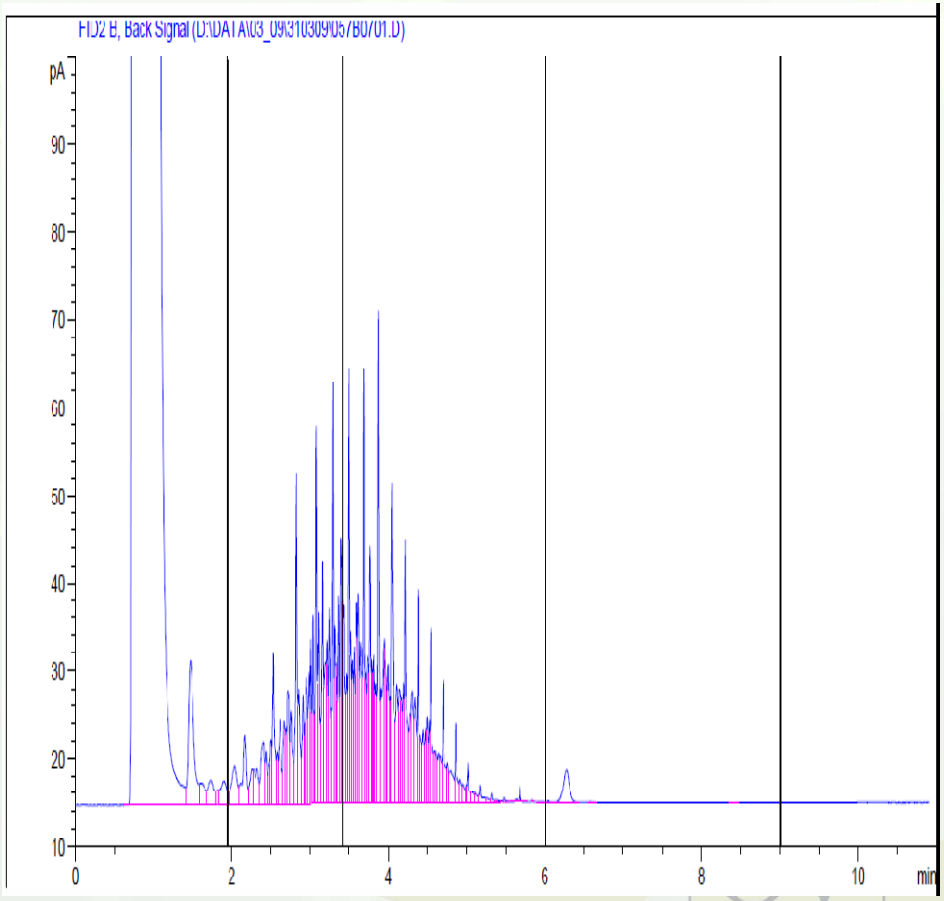
- Example: C10-C14
- Lab A = Calc from C9.5 to C14.5
- Lab B = Calc from start C10 to start C14
- Lab C = Calc from >C9 to end C14

TPH Banding: 2 examples of current reporting



Envirolab reporting:
C10-C14 = Calculate from >C9 to end C14
C15-C28 = Calculate from >C14 to end C28
C29-C36 = Calculate from >C28 to end C36

In this example:
C10-C14: 180ppm
C15-C28: 280ppm
C29-C36: <PQL

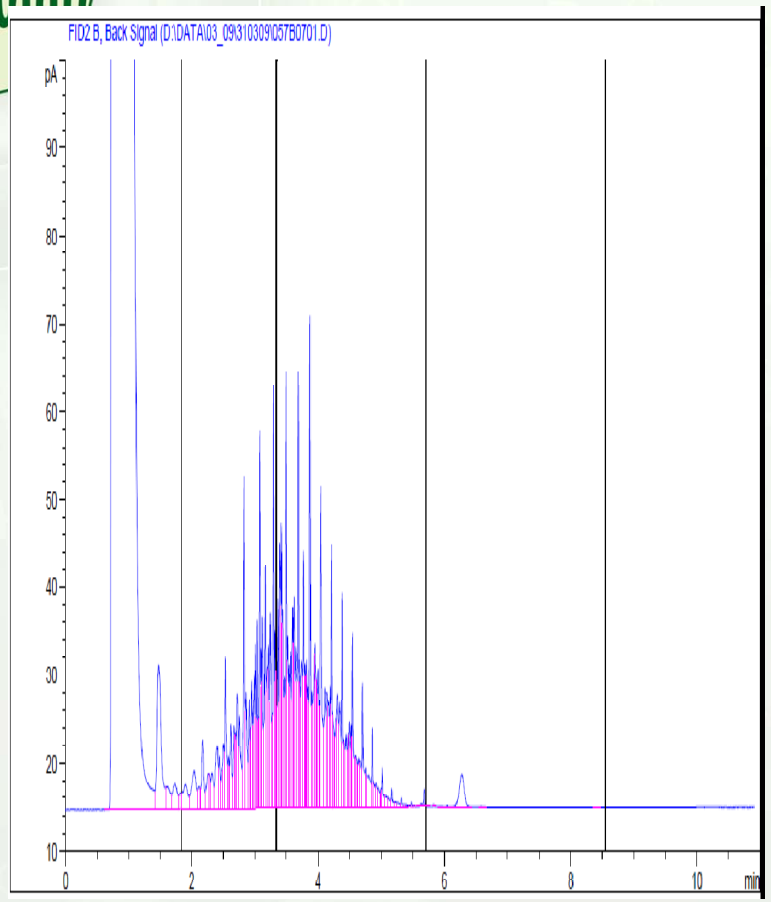


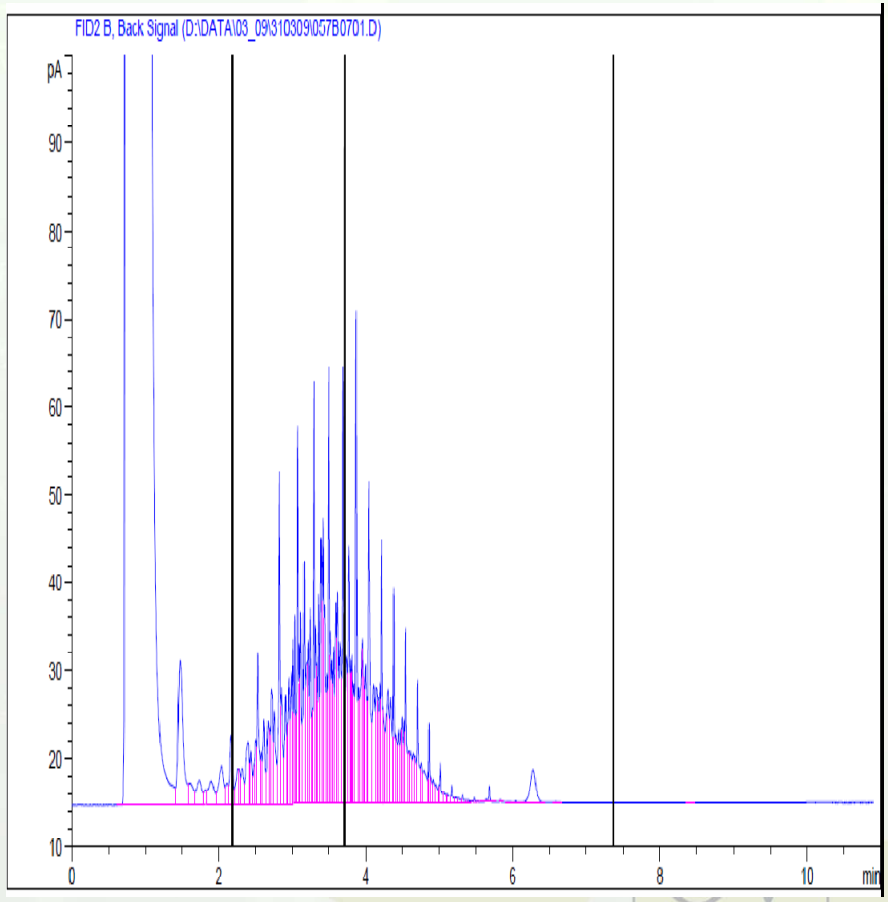
Other lab reporting:
C10-C14 = Calculate from C9.5 to C14.5
C15-C28 = Calculate from C14.5 to C28.5
C29-C36 = Calculate from C28.5 to C36.5

In this example:
C10-C14: 200ppm
C15-C28: 260ppm
C29-C36: <PQL

TPH Banding

Current vs Proposed





Current Envirolab TPH Band Reporting

C10-C14: C>9-C14 : 180ppm

C15-C28: C>14-C28 : 280ppm

C29-C36: C>28-C36 : <PQL

Proposed TPH Band Reporting

C>10-C16: 270ppm

C>16-C34: 190ppm

C>34 : <PQL

The 14 ELIG MEMBERS

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