CHEMISTRY FOR LAND CONTAMINATION

Yorkshire Contaminated Land Forum

30 September 2016

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CHEMISTRY FOR LAND CONTAMINATION

- Introduction to DETS
- Total Petroleum Hydrocarbons
- Poly Aromatic Hydrocarbons
- Summary

CHEMISTRY FOR LAND CONTAMINATION

- **Introduction to DETS**
- Chemical testing lab based in NE and Scotland
- Offer accredited chemical testing on soils, waters, waste, fuels
- 115 staff
- Client base: environmental consultants, consulting engineers, site investigation companies, civil engineers, groundworks contractors, local authorities, utility companies, manufacturing companies, waste management companies, landfill operators

CHEMISTRY FOR LAND CONTAMINATION

- **Introduction to DETS**

- **DETS Specialities!**
- Speciated mercury
- Asbestos – respirable fibres in respirable dust
- Target screen test on waters – 950 compounds – 0.1ug/l
- Low level cyanides on waters – 0.1ug/l
- Low level monohydric phenols on waters – 0.5ug/l

CHEMISTRY FOR LAND CONTAMINATION

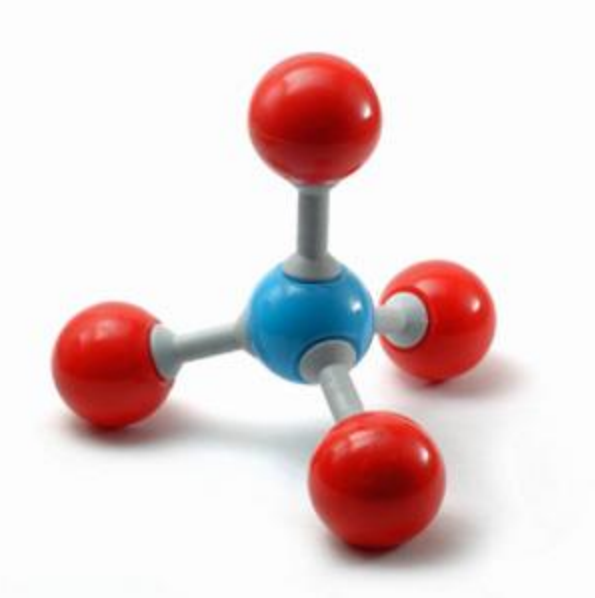
- **Total Petroleum Hydrocarbons**

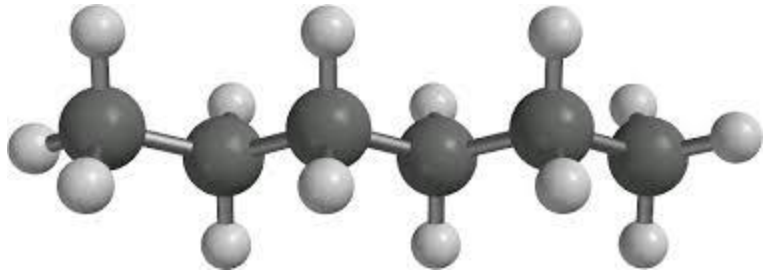
  What are they?

  Organic compounds containing carbon and hydrogen

- **CH4 – methane**
- **C2H6 – ethane H3C-CH3**
- **C3H8 – propane H3C-CH2-CH3**
- **C4H10 - butane – H3C-CH2-CH2-CH3**
- **C5H12 – pentane – H3C-CH2-CH2-CH2-CH3**
- **C6H14 – hexane H3C-CH2-CH2-CH2-CH2-CH3**

❖**Straight chain, SATURATED hydrocarbons - ALKANES**





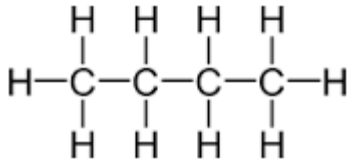
CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**

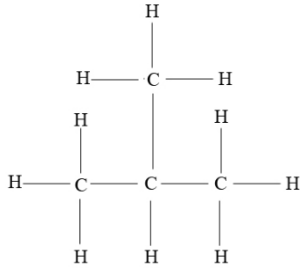
- H3C-CH3 – ethane, straight chain, saturated - ALKANE
- H2C=CH2 – ethene, straight chain, unsaturated – double bond between 2 carbon atoms so fewer hydrogen atoms - ALKENE
- HC≡CH – ethyne, straight chain, unsaturated – triple bond between 2 carbon atoms so fewer hydrogen atoms - ALKYNE

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**



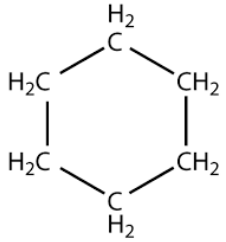
- N-Butane
- **Straight chain**
- 4 carbon atoms
- 10 hydrogen atoms
- BP -1^{o}C



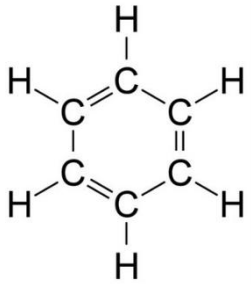
- Iso-Butane/Methyl propane
- **Branched chain**
- 4 carbon atoms
- 10 hydrogen atoms
- BP -11.7^{o}C

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**



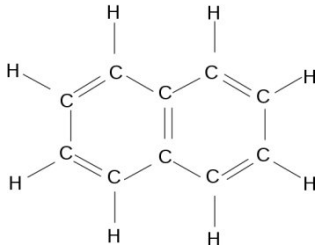
- Cyclohexane
- 6 carbon atoms
- 12 hydrogen atoms
- **Saturated cycloalkane**



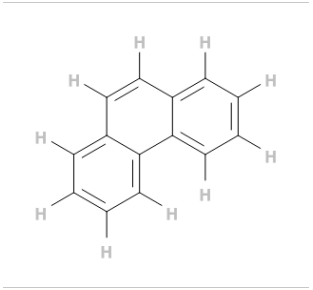
- Benzene
- 6carbon atoms
- 10 hydrogen atoms
- **Unsaturated aromatic hydrocarbon**

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**



- Naphthalene
- 10 hydrogen atoms
- 8 hydrogen atoms
- 2 fused benzene rings
- **Poly Aromatic hydrocarbon**

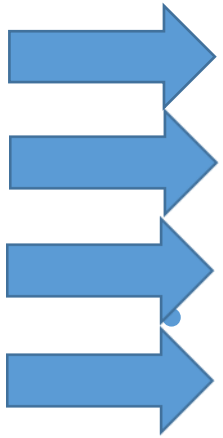


- Phenanthrene
- 14 carbon atoms
- 10 hydrogen atoms
- 3 fused benzene rings
- **Poly Aromatic hydrocarbon**

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**

- Straight chain hydrocarbons
- Branched chain hydrocarbons
- Alkanes, alkenes, alkynes
- Cycloalkanes

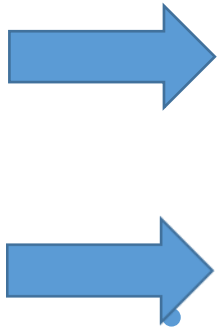


ALIPHATICS

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**

- Mono ring aromatics
  Benzene, toluene, xylenes
- Poly aromatics -
  Naphthalene
  Phenanthrene



AROMATICS

CHEMISTRY FOR LAND CONTAMINATION

- **Total petroleum hydrocarbons**
- Thousands of compounds
- Mostly derived from crude oil
- Varying appearance, specific gravity, toxicity
- Some compounds also contain N, S and O
- Varying polarity

  Non polar – aliphatics

  Slightly polar – polyaromatics

  Polar – NSO containing compounds
- Used for fuel, chemical feedstock

  - Properties - generally with increasing number of carbon atoms:
  - Increase in boiling and melting points
  - Lower vapour pressure
  - Increase in density
  - Decrease in water solubility
  - Stronger adhesion to soils leading to less mobility in subsurface conditions and increased environmental persistence

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**

  Routine methods of analysis:

- Infra red – **IR** – limited availability – good for identifying functional groups, double/triple bonds
- Gas chromatography – flame ionisation detector – **GC FID** – EPH,GRO/PRO
- Gas chromatography – mass spectrometry – **GC MS** – GRO, VOCs PAHs and other organics

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**
- Gasoline Range Organics/Petroleum Range Organics/Volatile Petroleum Hydrocarbons – GRO/PRO/VPH
- GC FID/GC MS
- C5/6-C10
- With/without BTEX and/or MTBE
- No solvent extraction – volatile
- Includes n-alkanes, iso-alkanes, cycloalkanes and aromatics
- Samples taken from 60g glass jars for soils or 40ml glass vials for waters

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**

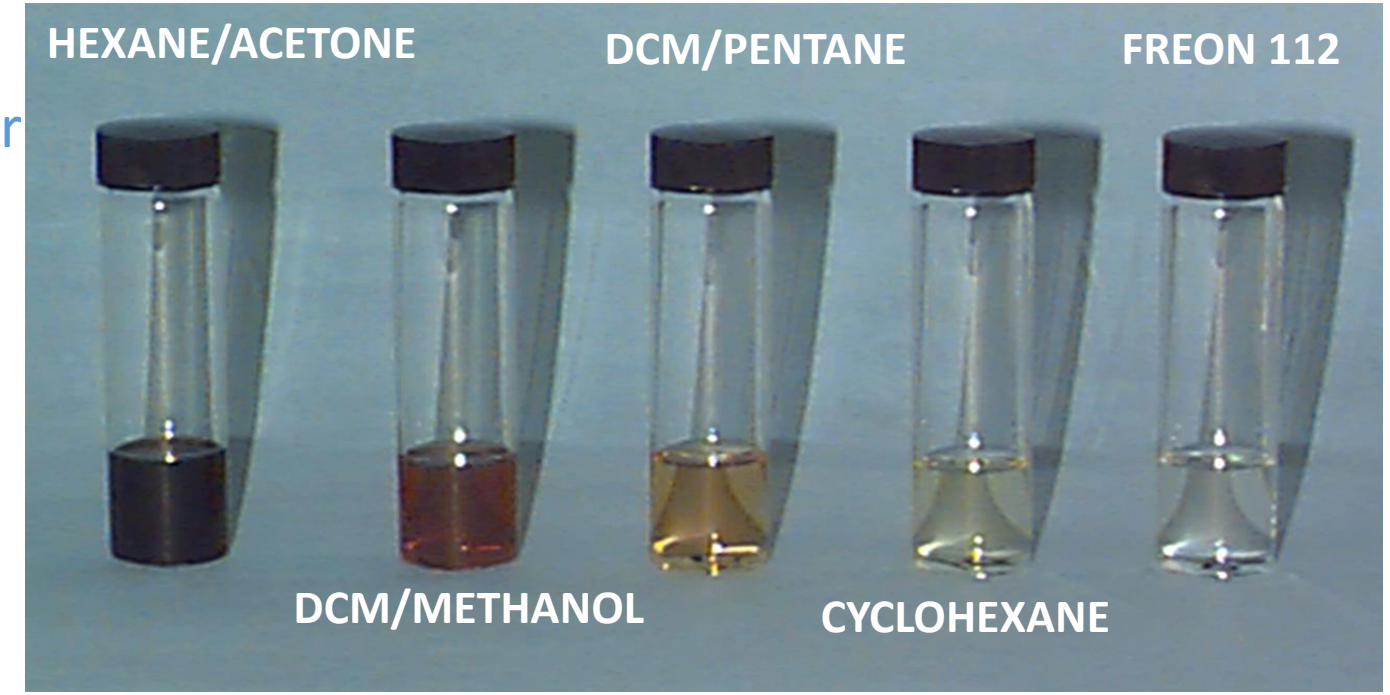
Solvents:

- Inorganic – water – used for Inorganic testing
- Organic solvents

Generally used for organics analysis inc TPH and PAHs

❖Polar

❖Non-polar



CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**

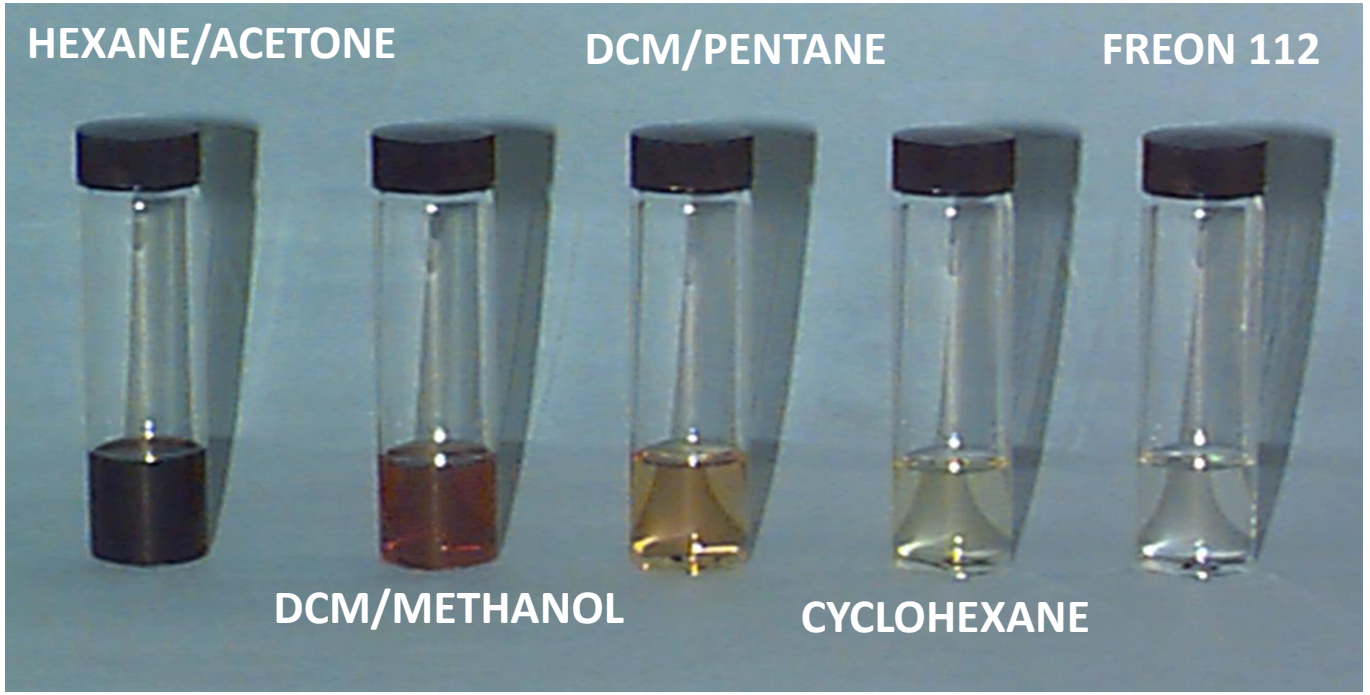
Solvents:

Non polar:

- Freon 112
- Cyclohexane

Polar:

- DCM
- DCM/pentane
- DCM Methanol
- DCM/Acetone



CHEMISTRY FOR LAND CONTAMINATION

- Total Petroleum Hydrocarbons

Polarity of compounds:

- Non-polar – alkanes
- Moderately polar – poly aromatics
- Very polar – nitrogen, sulphur and oxygen containing organics – NSO resins

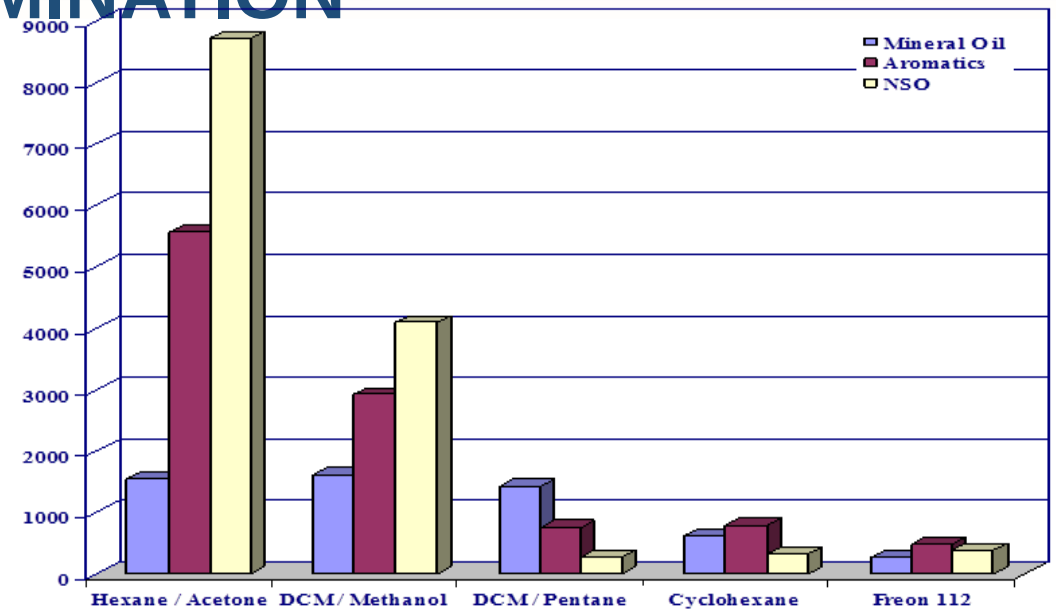
Ideally, the solvent should dissolve the target analytes but not affec the sample matrix

- Solvent polarity should match the target analytes (i.e. like dissolves like)
- Sample matrix may affect efficiency
- **Overall, due to the range of possible contaminants, matrix effects etc choosing the ideal solvent complex decision**

CHEMISTRY FOR LAND CONTAMINATION

- Total Petroleum Hydrocarbons
- **Solvent effectiveness**

Solvent	Ratio	Polarity	Total Extract	Mineral Oil	Aromatics	NSO
Hexane / Acetone	1/1	0.5	15823	1549	5553	8721
DCM / Methanol	10/1	0.48	8625	1613	2923	4089
DCM / Pentane	3/1	0.3	2440	1420	749	271
Cyclohexane	-	0.26	1739	617	796	328
Freon 112	-	0.24	1137	261	485	391



- **Therefore – it can be seen that DCM/acetone and DCM/methanol are most effective in extracting NSOs and less effective in extracting alkanes – they are the most polar solvents**
- **DCM/pentane is most effective in extracting alkanes but less effective in extracting NSOs**
- **Overall DCM/acetone and DCM/methanol are the best solvents overall. Cyclohexane and Freon 112 are the least effective solvents - cyclohexane is fairly effective in extracting aromatics**

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**

- Extractable Petroleum Hydrocarbons - EPH
- C10-C40
- GC FID
- Solvent extracted – semi-volatile range – BP >175^{o}C
  Blue book method – DCM as solvent
- Includes alkanes, iso-alkanes, cycloalkanes, aromatics
- Samples taken from 150g glass jars for soils or 1l glass bottles for waters

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**
- Options:
- EPH C10-C40
- Banded – Diesel Range Organics C10-C24, Lube Oil Range C24-C40 DRO/LRO
- Banded - C10-C20, C20-C30, C30-C40
- Banded - C10-C12, C12-C16, C16-C21, C21-C35, C35-C40

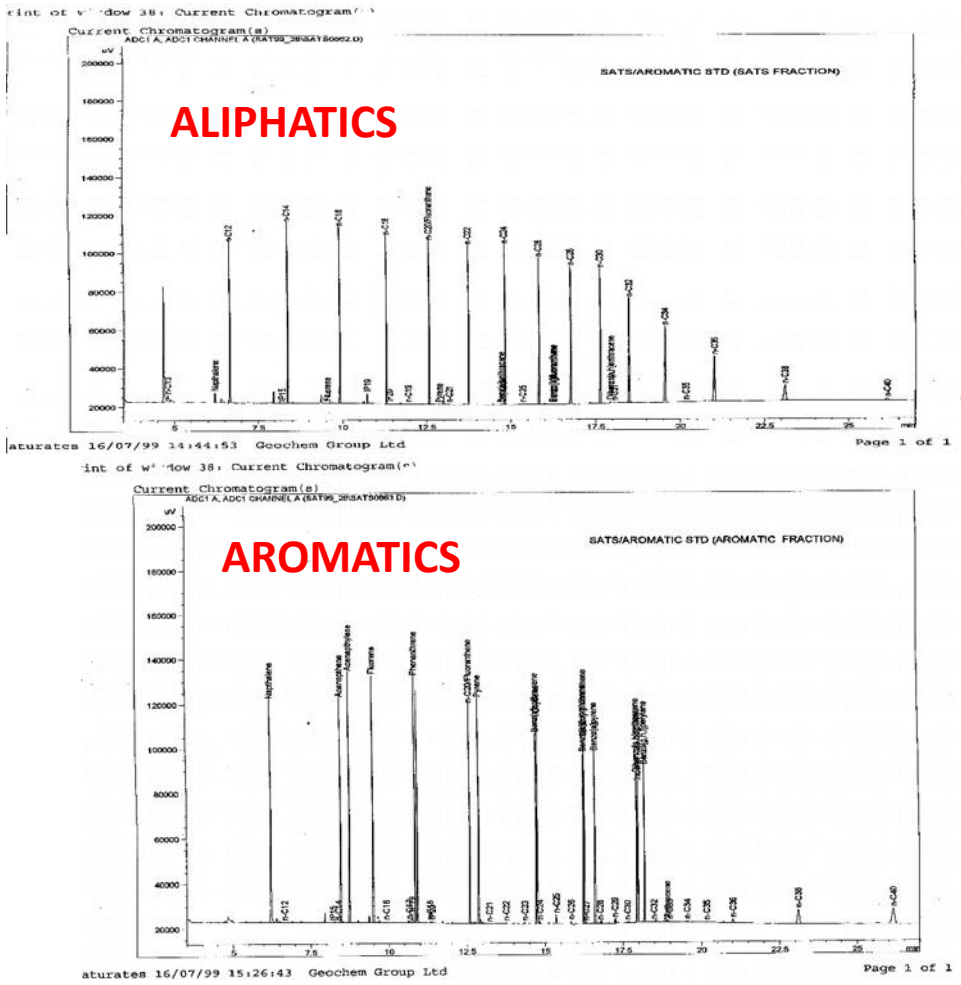
CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**

  Options:
- TPH Criteria Working Group – TPH CWG – Speciated TPH
- Covers VPH/EPH ranges
- With/without BTEX and/or MTBE
- Split hydrocarbons into aliphatics and aromatics
- Aliphatics C5-6, C6-8, C8-10, C10-12, C12-16, C16-21, C21-C35, >C35
- Aromatics C5-7, C7-8, C8-10, C10-12, C12-16, C16-21, C21-35, >35
- Used in risk assessment packages such as RBCA

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**
- **TPH CWG**
- Initial extraction into hexane – non-polar. Elutes aliphatics into the hexane
- Sample is then run through highly polar column which removes and retains polar compounds
- Aromatic fraction is eluted out using DCM which is a polar



CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**

Other uses of TPH analysis

Ageing – combination of weathering and biodegradation

WEATHERING

Most Affected

- C_{10}-C_{20} n-alkanes
- Alkylated aromatics
- 2 and 3 ring aromatics

Least Affected

- C_{20+} alkanes
- Cyclo naphthenes
- 4 and 6 ring aromatics

BIODEGRADATION

Most affected

- C_{35}-C_{10} alkanes

Least affected

- Iso-prenoids
- Pristane
- Phytane
- 6 and 12 ring aromatics

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**

Other uses of TPH analysis

Ageing – combination of weathering and biodegradation

- By looking at ratios of concentrations of these markers the degree of weathering and biodegradation can be calculated
- This can then be used to ‘age’ fuel spills
- Not always conclusive or precise!

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**
- **Issues with choice of 'TPH' test**

- **Incorrect test scheduled due to confusion over terminology**

  TPH? - EPH? C10-C40 - VPH/EPH? – C5-C10, C10-C40

  Speciated TPH? - TPH CWG? - Banded EPH?

  DRO? C10-C24? EPH C10-C40?

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**
- **Issues with choice of 'TPH' test**

- **Incorrect test scheduled due to confusion over terminology**
- Heating oil?
- Heavy fuel oil?
- Road diesel fuel?
- White spirit?
- Lube oils?

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**
- **Issues with interference in 'TPH' analysis**

- Presence of polar hydrocarbons – NSO compounds
- Presence of non-petroleum compounds:
  Biogenic material
  Plant oils and waxes – humic acids
  Coal material
  Fats

All can lead to higher values than expected

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**
- **Issues with not getting results expected with 'TPH' analysis**

- Problem - elevated hydrocarbons on greenfield site

- Possible cause – presence of humic acids from non-petroleum hydrocarbon sources – rotting vegetation etc
- Solution – request 'clean-up' on samples and repeat analysis for EPH. The clean up stage uses a different column in the GC FID which removes polar NSO compounds – humic acids – and leaves aliphatics and aromatics to report

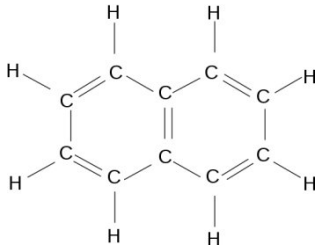
CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**
- **Issues with not getting results expected with 'TPH' analysis**

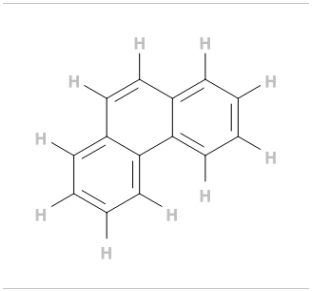
- Problem – 'hydrocarbon' odour on site not reflected in results
- Possible cause – TPH CWG analysis scheduled.
- Solution – request EPH C10-C40 with chromatogram instead.
- TPH CWG includes a clean up stage which removes polar compounds. These can include carboxylic acids, ketones etc. These are odorous compounds which may have been detected on site. They are products of weathering etc.
- Standard EPH analysis will include carboxylic acids, ketones etc and they will show on the chromatogram

CHEMISTRY FOR LAND CONTAMINATION

- **Total Petroleum Hydrocarbons**



- Naphthalene
- 10 hydrogen atoms
- 8 hydrogen atoms
- **Polyaromatic hydrocarbon**



- Phenanthrene
- 14 carbon atoms
- 10 hydrogen atoms
- **Polyaromatic hydrocarbon**

CHEMISTRY FOR LAND CONTAMINATION

- **Poly Aromatic Hydrocarbons - PAHs**

Aromatic compounds – 2 or more fused benzene rings

Included in TPH results and aromatic fraction of TPH CWG

Normally test for US EPA 16 PAHs – in US studies 80% of PAHs attributed to 16 priority pollutants

Other PAHs – coronene inc in WAC testing

National Grid list

Carcinogenic

CHEMISTRY FOR LAND CONTAMINATION

- **Poly Aromatic Hydrocarbons – PAHs**
- **US EPA 16**

Naphthalene	Benz[a]anthracene
Acenaphthylene	Chrysene
Acenaphthene	Benz[b]fluoranthene
Phenanthrene	Benz[k]fluoranthene
Fluorene	Benz[a]pyrene
Anthracene	Dibenz[a,h]anthracene
Fluoranthene	Benzo[ghi]perylene
Pyrene	Indeno[1,2,3-cd]pyrene

- **Others**
- Benzo(e) pyrene
- Benzo (j)fluoranthene
- Coronene

CHEMISTRY FOR LAND CONTAMINATION

- **Poly Aromatic Hydrocarbons - PAHs**

Sources:

- Manufactured gas plants and coking operations
- Wood preserving sites - creosote
- Coal
- Bitumen
- Cigarette smoke
- Bonfires and BBQs
- Products of incomplete combustion of fossil fuels

CHEMISTRY FOR LAND CONTAMINATION

- **Poly Aromatic Hydrocarbons - PAHs**

  Options for analysis:

- Thin layer chromatography – total PAHs – limited availability
- Gas chromatography - GC FID – Co-elution of a couple of peaks. Used in WAC test – US EPA 16 plus coronene. Total of US EPA 16
- Analysis by HPLC – fluorescence detector – required initially for NG work. Good reporting limits but not all PAHs fluoresce
- Analysis by GC MS – best reporting limit, no co-elution of PAHs, pick up and identifies all of the 16 US EPA PAHs. More expensive

CHEMISTRY FOR LAND CONTAMINATION

- **Poly Aromatic Hydrocarbons - PAHs**

PAHs can be used for forensic type analyses:

Double plot ratios

Typically fluoranthene:pyrene is plotted against benzo(a)anthracene:chrysene

This can provide a guide to the source of the original oil contamination in soil – petroleum/coal/product of combustion

When used for several samples from the same site it can be possible to identify if a site has more than a single contamination source

CHEMISTRY FOR LAND CONTAMINATION

- **Poly Aromatic Hydrocarbons - PAHs**

Interferences affecting PAH analysis

- Presence of coal fragments
- Presence of tarmac fragments
- Peaty soils

The presence of any of the above will lead to elevated PAH results over and above what might be expected

CHEMISTRY FOR LAND CONTAMINATION

- Summary

- DETS overview
- Total Petroleum Hydrocarbons
- Poly Aromatic Hydrocarbons

CHEMISTRY FOR LAND CONTAMINATION

Thank you!

Any questions?

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