# CL:AIRE
# Petroleum Hydrocarbons in Groundwater: Guidance on assessing petroleum hydrocarbons using existing hydrogeological risk assessment methodologies

# Petroleum Hydrocarbons in Groundwater

**History of the guidance**

**What are hydrocarbons?**

**Why new guidance?**

**How does it fit in with existing guidance?**

**What's in the guidance (and why)?**

# History

**2005 EA commission Entec to write guidance**

**2006 Draft guidance**

**2008 Revised draft**

**2009 Project abandoned**

**2016 CL:AIRE**

# What are petroleum hydrocarbons?

## Products

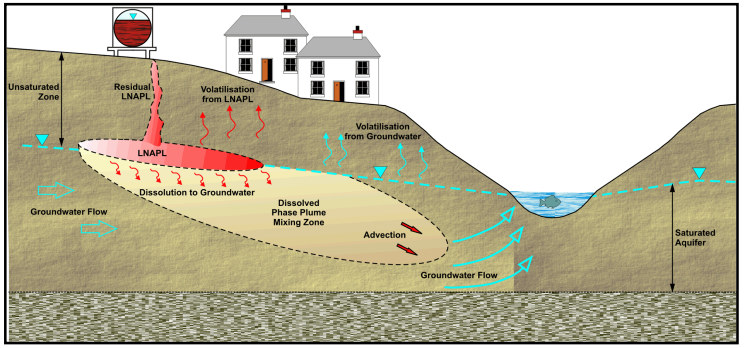
- Petrol
- Diesel
- Kerosene
- Heating oil
- Lubricants
- Bunker fuel
- Crude oil

## Compounds

- Aromatics
  - BTEX compounds
  - PAHS
- Aliphatics
  - Alkanes
    - Hexane
    - Octane
  - ….

# Petroleum Hydrocarbons in Groundwater
# The need for additional guidance

- Commonest group of contaminants
- Need for consistent approaches to:
  - Selection of analysis
  - Contaminants modelled (risk drivers)
  - Degradation
  - NAPL



# Petroleum Hydrocarbons in Groundwater
# The Challenge

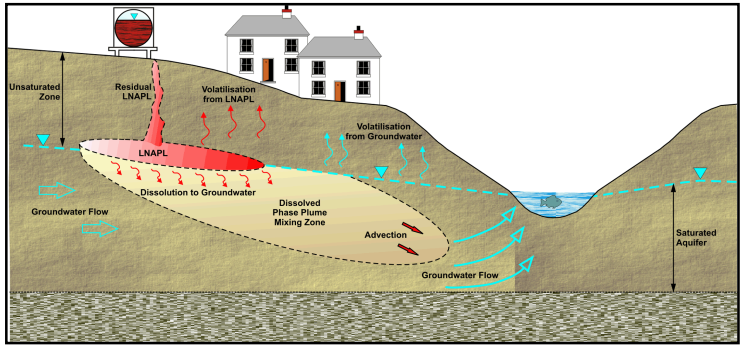
## Complex mixtures
- Not possible to identify every compound
- Not practical to incorporate all in a DQRA

## Choice of analysis - Lots of techniques available
- Not all suitable for risk assessment
- Need to avoid duplication
- Need to avoid gaps

## Multiple phases
- Vapour
- Free phase (mobile and residual)
- Sorbed to solid material
- Aqueous
- Contaminants move between phases
- Existing methodology based on aqueous / solid phases

## Identifying risk drivers can be difficult
- Hundreds of compounds present
- Variable properties / risk profile

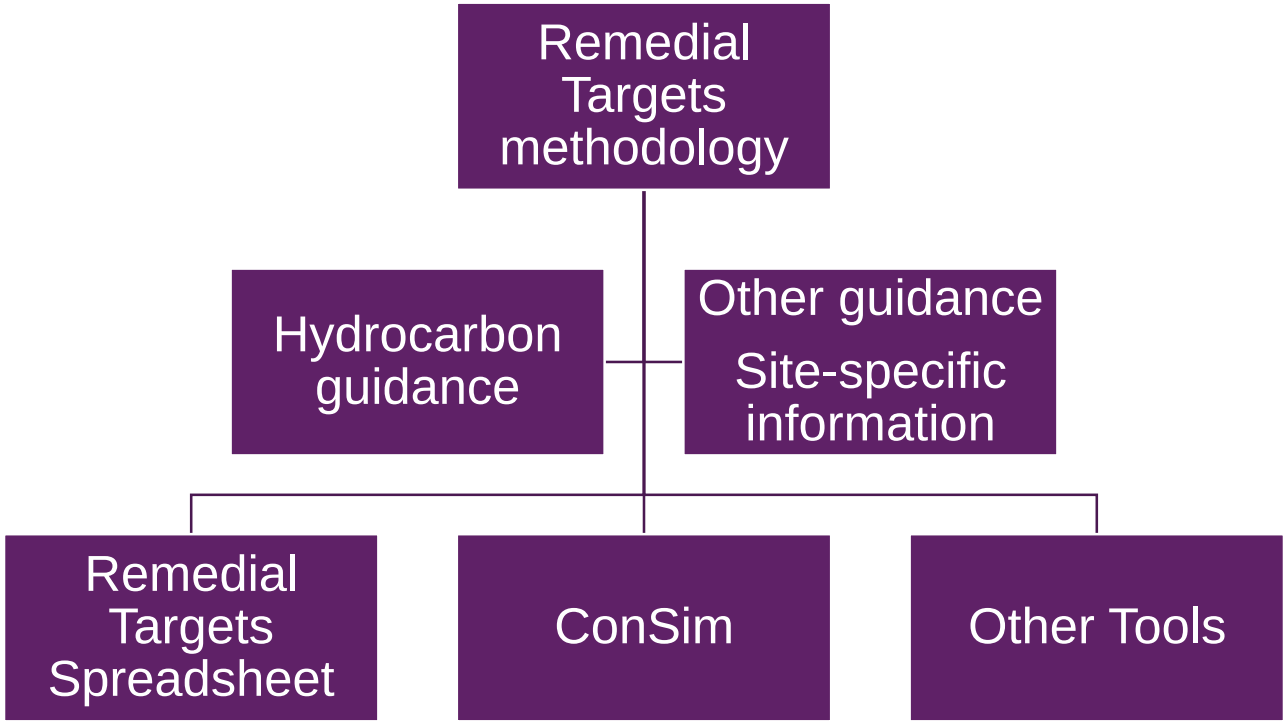
## Degradation
- Important process
- Needs to be understood & quantified
- No published rates for EC bands



# New Guidance – February 2017

- Evaluate the risk from hydrocarbon mixtures
- Consider analytical techniques available
- Estimate the implications of non-aqueous phase liquid (NAPL) for dissolved phase groundwater risk assessments
- Promote a lines-of-evidence approach to evaluate the importance of biodegradation of other natural attenuation processes

# Where does it fit in?



# Complex mixtures – e.g. petrol (44 compounds)

1,3-Butadiene
cis-2-Butene
trans-2-Butene
2-Methyl-1-butene
2-Methyl-2-butene
cis-2-Pentene
trans-2-Pentene
Benzene
Toluene
Ethylbenzene
m-Xylene
o-Xylene
p-Xylene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
1-Methyl-2-ethylbenzene
1-Methyl-3-ethylbenzene
1-Methyl-4-ethylbenzene
Isobutane
Isopentane
2,2-Dimethylbutane
2,3-Dimethylbutane

2-Methylpentane
3-Methylpentane
2,4-Dimethylpentane
2-Methylhexane
7 3-Methylhexane
2,2,4-Trimethylpentane
2,3,3-Trimethylpentane
2,3,4-Trimethylpentane
2,3-Dimethylhexane
2,4-Dimethylhexane
3-Methylheptane
Cyclopentane
Cyclohexane
Methylcyclopentane
Methylcyclohexane
n-Butane
n-Pentane
n-Hexane
n-Heptane
Naphthalene
1-Methylnaphthalene
2-Methylnaphthalene

# Assessment of Complex Mixtures – Use of carbon numbers – TPHCWG

**Equivalent Carbon (EC) No. relates the boiling point of a compound to the boiling point of an equivalent n-alkane**

- Aromatics
  - EC6-EC7 (benzene)
  - >EC7-EC8 (toluene)
  - >EC8-EC10 (ethylbenzene, xylenes)
  - >EC10-EC12 (naphthalene)
  - >EC12-EC16 (anthracene)
  - >EC16-EC21 (pyrene)
  - EC21-EC35 (B[a]P)
- Aliphatic
  - EC5-EC6 (pentane+)
  - >EC6-EC8 (heptane+)
  - >EC8-EC10 (nonane+)
  - >EC10-EC12 (ondecane+)
  - >EC12-EC16
  - >EC16-EC21

# Analysis for Hydrocarbons

## Screening analysis

- TPH / EPH / DRO / PRO
- Provide a single value or
- Limited carbon banding
- Useful in delineation / validation / remediation monitoring

## Detailed analysis

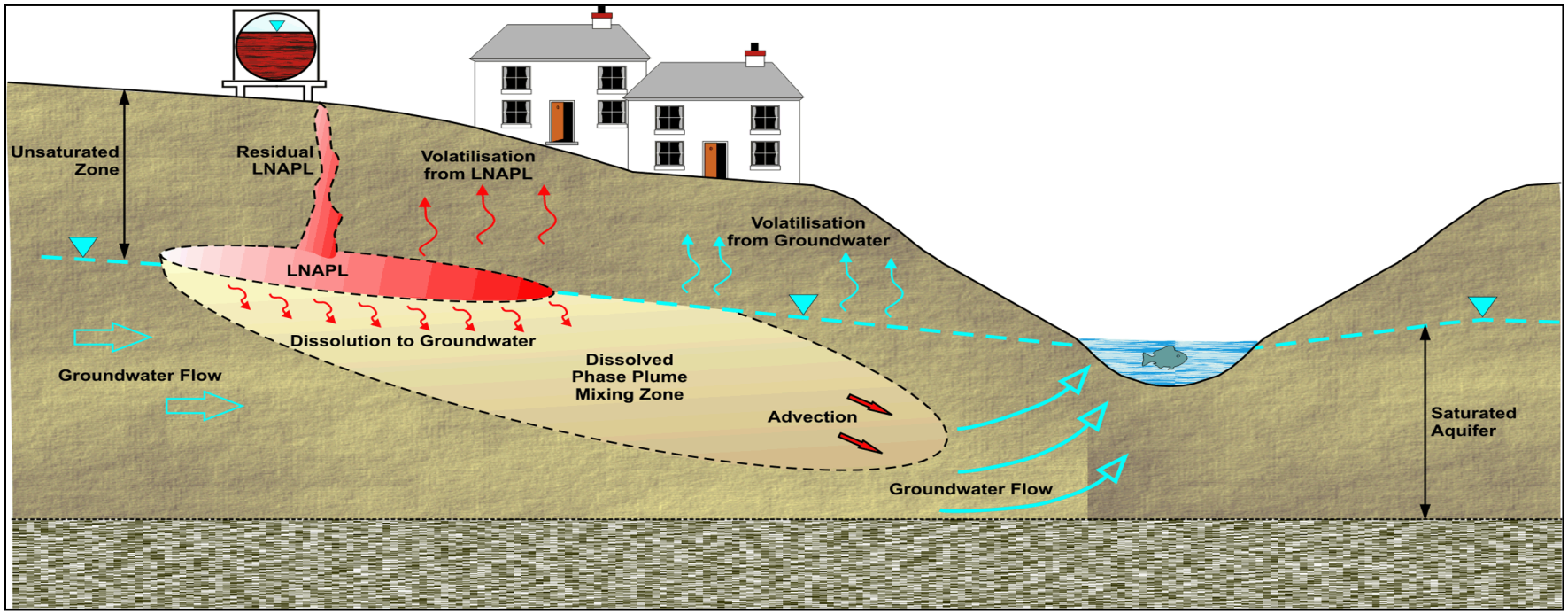
- Concentration of individual compounds or discrete carbon bands.
  - Targeted –named compounds
    - VOCs
    - SVOCs
    - PAHs
  - Non-targeted –carbon bands with aromatic / aliphatic split
    - TPHCWG

**Detailed analysis always required to support DQRA**

# Analysis for Hydrocarbons
# Detailed Analysis

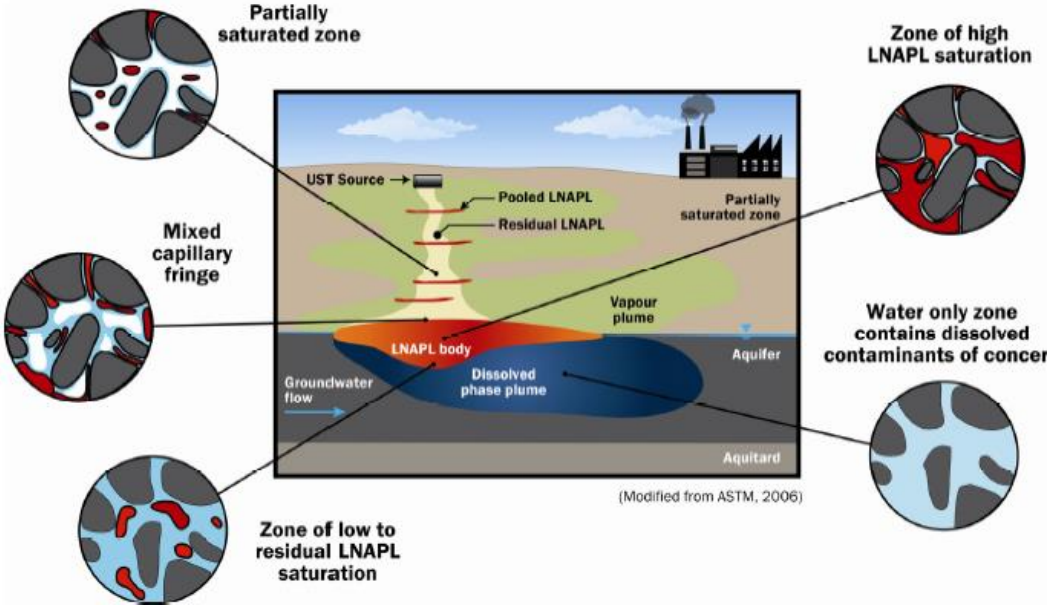
| Name | Variants | Main advantages | Main disadvantages |
|---|---|---|---|
| VOCs/BTEX | • BTEX only<br>• EPA method 8260 (BTEX, naphthalene, trimethylbenzenes) | • Provides quantitative analysis of key determinands often quantified to low detection levels. | • Only identifies compounds on target list (unless TICs are specified). |
| SVOCs (speciated) | • PAHs only | • Provides quantitative analysis of key determinands often quantified to low detection levels. | • Only identifies compounds on target list (unless TICs are specified). |
| Carbon banding with aromatic/ aliphatic fractionation | • Different carbon band ranges can be specified.<br>• Calibration may be against a particular hydrocarbon product. | • Provides values for carbon band ranges rather than individual compounds.<br>• Provides detail of hydrocarbon composition based on the specific carbon range defined. | • Does not detect heavy hydrocarbons >$C_{40}$ |

# Multiple Phases



# Multiple Phases: Considerations where NAPL present

- Spatial extent
  - Is NAPL is expanding, steady or declining?
  - Effect on pathway length
- Vertical extent
  - Driving head
  - Past groundwater levels
- Mobility
  - Risk of NAPL migration
  - Residual?
- Source of dissolved phase
  - Solubility of constituents
  - Proportion (fraction)
  - Effective solubility
  - Accessibility to groundwater
- Potential for depletion of source term (declining source term)
- Potential for complex pathways
  - Vapour migration
- Obtaining representative samples in presence of NAPL
- Determining whether NAPL is present
  - Observation
  - Direct measurement
  - Inferred from sampling results



# Dissolved Phase Risk from NAPL

## Most models do not represent NAPLs

## Standard approach

- Source is dissolved concentration in groundwater in contact with NAPLs using Raoults Law:

$$C = x S$$

where $C$ = effective solubility

$x$ = mole fraction

$S$ = free phase solubility

## Example (petrol):

| | |
|---|---|
| Mole fraction of benzene in mixture | 0.0093 (0.93%) |
| Pure phase solubility | 1780 mg/l |
| Effective solubility | 17 mg/l |

# Risk Drivers (contaminants of potential concern)

## More soluble / mobile contaminants present the greatest risk

- BTEX
- Naphthalene
- …

Decreasing solubility / mobility

- Benzo[a]pyrene

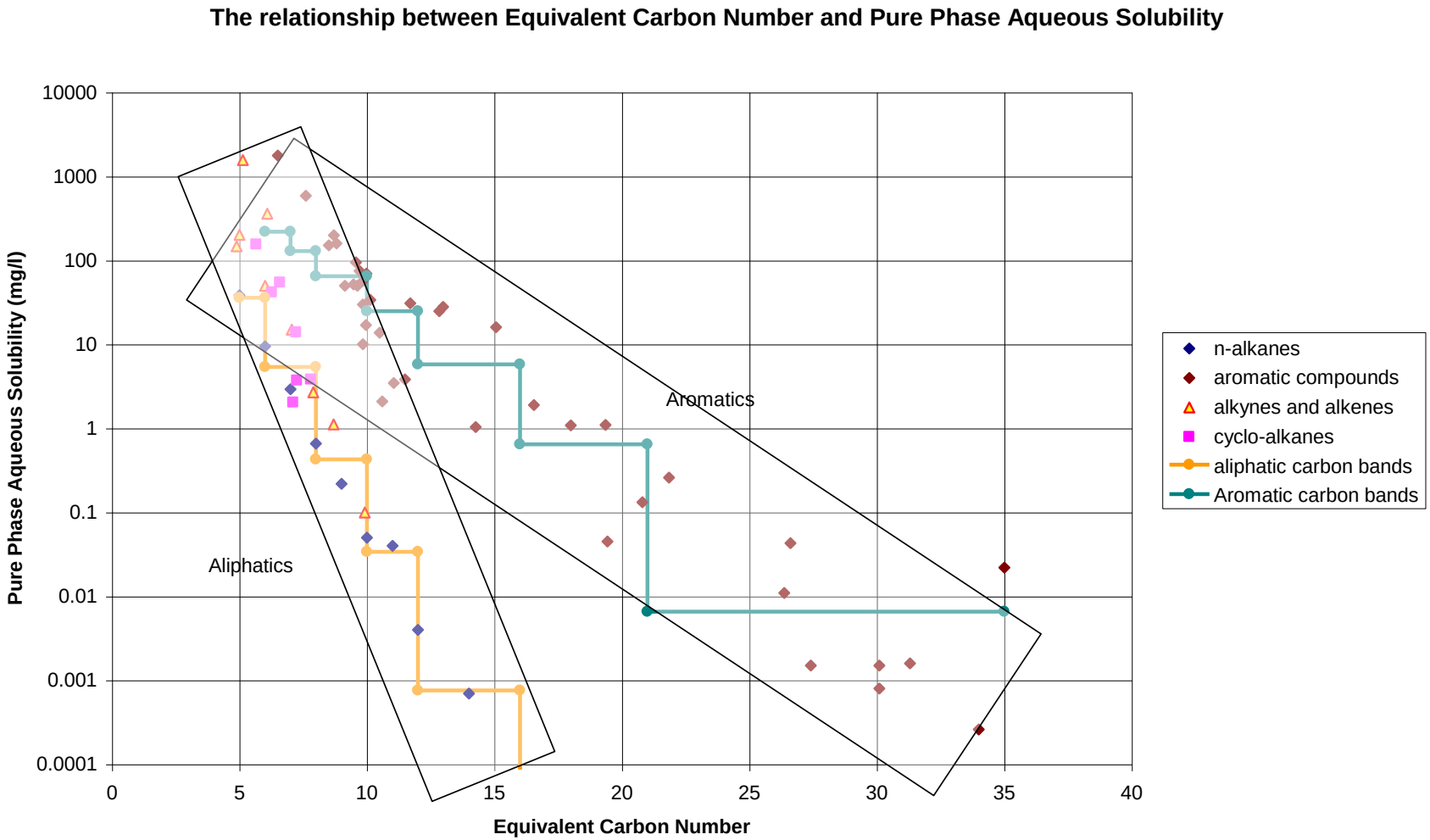
## Risk Drivers are

- Soluble
- Mobile
- Persistent
- Relatively abundant
- Hazardous - compounds with EQS / DWS (toxic)

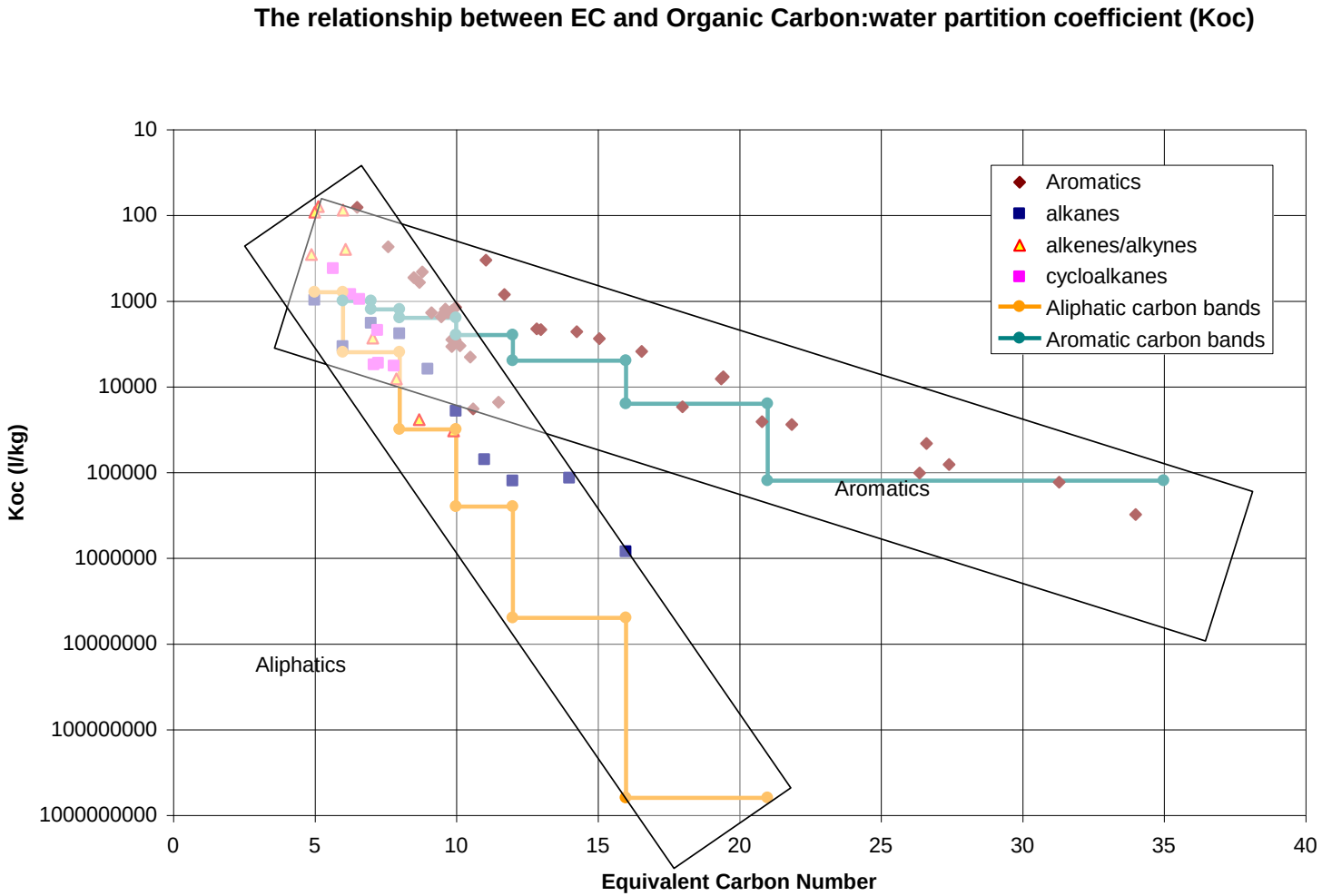
## Identified by

- Analysis of porewater in soils at the source area
- Analysis of groundwater close to, but downgradient of, the source area
- Product analysis and theoretical calculation (Raoult's Law)
- Knowledge of hydrocarbon product type

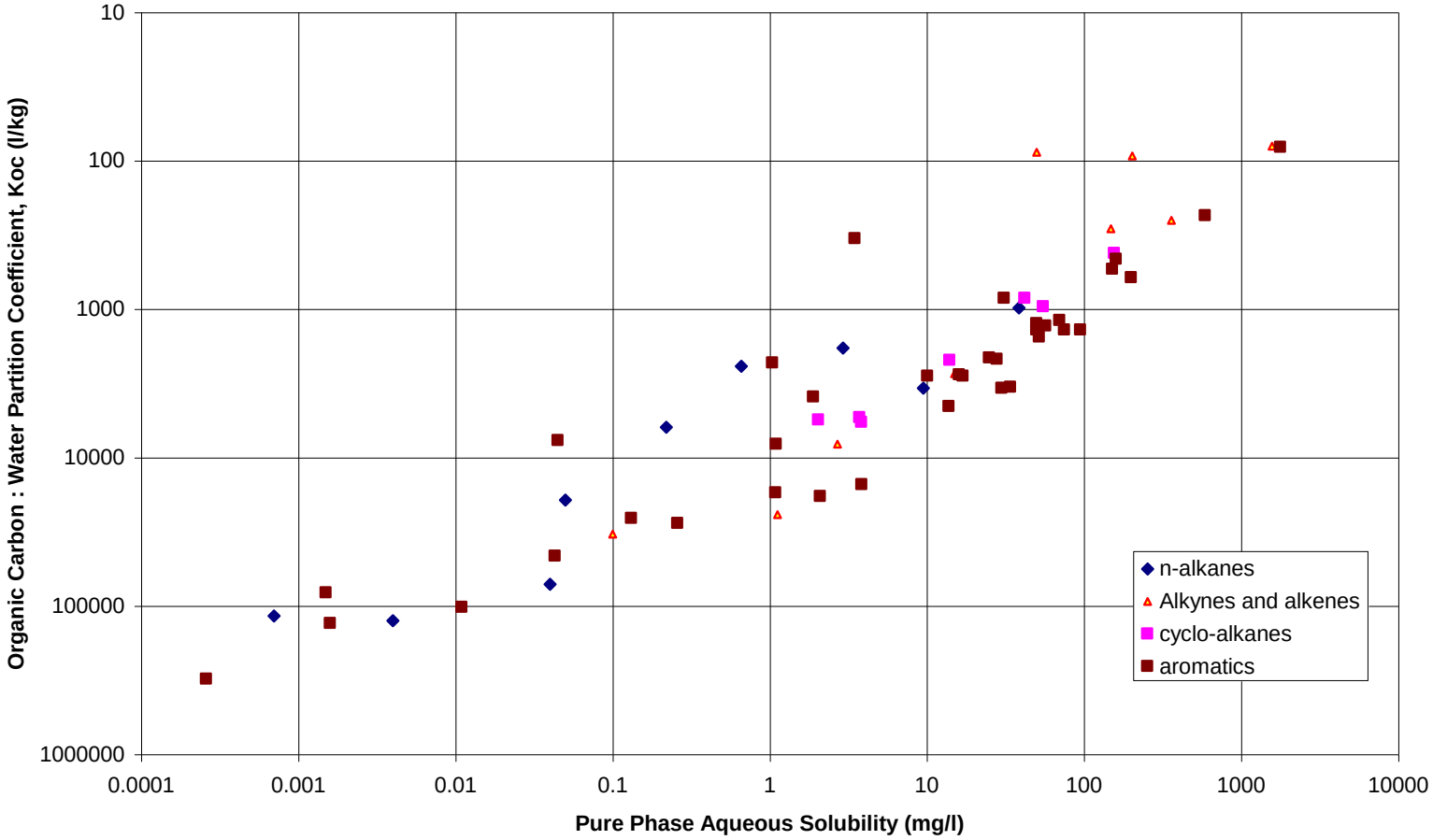
# Risk Drivers: Solubility



# Risk Drivers: Koc



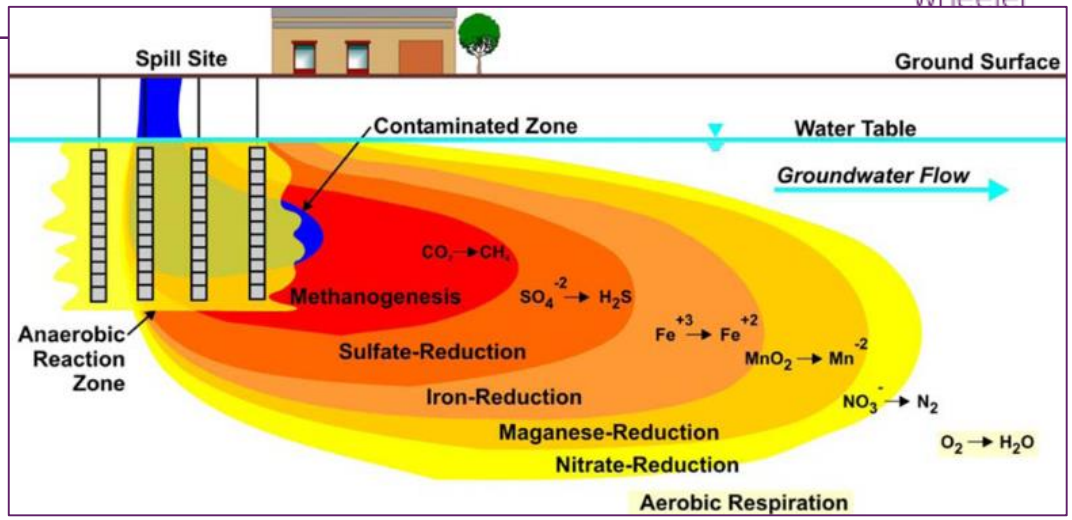
# Risk Drivers: Mobility



# Recommended risk drivers

| Suspected hydrocarbon source | Carbon banding | Recommended petroleum hydrocarbon CoPC | Other substances of potential concern (not crude oil derived) |
|---|---|---|---|
| Petrol (gasoline)[1] | $C_4$–$C_{12}$ | BTEX<br>naphthalene<br>n-hexane | Ether oxygenates (MTBE, TAME, ETBE, DIPE) [3]<br>Lead scavengers [4] |
| Kerosene (jet fuel)[1] | $C_6$–$C_{16}$ | BTEX<br>TPHCWG[5] | 2-methylnaphthalene[1] |
| Light lubricating oils | $C_6$–$C_{10}$ | TPHCWG[5] | |
| Diesel/ domestic heating oil[1,2] | $C_8$–$C_{21}$ | BTEX<br>TPHCWG[5] | 2-methylnaphthalene[1] |
| Heavy fuel oils | $C_{12+}$ | TPHCWG[5] | |
| Lubricating oils and greases | $C_{18}$->$C_{34}$ | TPHCWG[5] | |

# Biodegradation




## Hydrocarbons degrade

- Carbon dioxide and water

## Rates vary

- Fast (days) to slow (years)
- Depend on
  - Compound
    - Simple vs complex
    - Structure (e.g. aromatic vs aliphatic)
  - Hydrochemistry e.g.
    - Electron acceptors
    - Competition
  - Aquifer type

## Variable information availability

- BTEX - lots
- PAHs - limited
- TPH-CWG – none

# Degradation – Assessing the Evidence

**Lines-of-evidence (MNA guidance)**

- Primary: loss of contaminant mass or decrease in concentration
- Secondary: geochemical and biochemical indicators
- Tertiary: microbiological data

**Evaluation of geochemical environment.**

- Aerobic or anaerobic?

**Electron balance**

- Are there sufficient oxidants (oxygen, nitrate, sulphate, iron and manganese) to degrade the mass of hydrocarbon in the aquifer?

**Using analytical or numerical models**

- Calculate the extent of the plume for comparison with field results

Ignoring degradation

- Conservative assessment

# Conclusion

## New Guidance Issued in February 2017

- Sets out existing good practice
- Supplementary to existing risk assessment methodologies
  - Remedial Targets Methodology
- Sets out approaches to:
  - Analysis
  - NAPL
  - Risk Drivers
  - Degradation

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