CL:AI RE
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2006 Draft guidance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?

- Remedial Targets methodology
  - Hydrocarbon guidance
  - Other guidance
    - Site-specific information
  - Remedial Targets Spreadsheet
  - ConSim
  - Other Tools
### Complex mixtures – e.g. petrol (44 compounds)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Butadiene</td>
<td>2-Methylpentane</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>3-Methylpentane</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>2,4-Dimethylpentane</td>
</tr>
<tr>
<td>2-Methyl-1-butene</td>
<td>2-Methylhexane</td>
</tr>
<tr>
<td>2-Methyl-2-butene</td>
<td>7 3-Methylhexane</td>
</tr>
<tr>
<td>cis-2-Pentene</td>
<td>2,2,4-Trimethylpentane</td>
</tr>
<tr>
<td>trans-2-Pentene</td>
<td>2,3,3-Trimethylpentane</td>
</tr>
<tr>
<td>Benzene</td>
<td>2,3,4-Trimethylpentane</td>
</tr>
<tr>
<td>Toluene</td>
<td>2,3-Dimethylhexane</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>2,4-Dimethylhexane</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>3-Methylheptane</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>Cyclopentane</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>Cyclohexane</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>Methylcyclopentane</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>Methylcyclohexane</td>
</tr>
<tr>
<td>1-Methyl-2-ethylbenzene</td>
<td>n-Butane</td>
</tr>
<tr>
<td>1-Methyl-3-ethylbenzene</td>
<td>n-Pentane</td>
</tr>
<tr>
<td>1-Methyl-4-ethylbenzene</td>
<td>n-Hexane</td>
</tr>
<tr>
<td>Isobutane</td>
<td>n-Heptane</td>
</tr>
<tr>
<td>Isopentane</td>
<td>Naphthalene</td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>1-Methynaphthalene</td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>2-Methynaphthalene</td>
</tr>
</tbody>
</table>
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 (undecane+)
  ► >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

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

Decreasing solubility / mobility
Risk Drivers: Solubility

The relationship between Equivalent Carbon Number and Pure Phase Aqueous Solubility

- n-alkanes
- aromatic compounds
- alkynes and alkenes
- cyclo-alkanes
- aliphatic carbon bands
- Aromatic carbon bands

Aromatics

Aliphatics
Risk Drivers: Koc

The relationship between EC and Organic Carbon:water partition coefficient (Koc)

Aromatics
Aliphatics
Aromatic carbon bands
Aliphatic carbon bands
alkanes
alkenes/alkynes
cycloalkanes

Equivalent Carbon Number
Koc (l/kg)
Risk Drivers: Mobility

![Graph showing the relationship between Pure Phase Aqueous Solubility (mg/l) and Organic Carbon : Water Partition Coefficient, Koc (l/kg)].

Key:
- n-alkanes
- Alkynes and alkenes
- cyclo-alkanes
- aromatics
## Recommended risk drivers

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