Risk assessment modelling for petroleum hydrocarbons in groundwater

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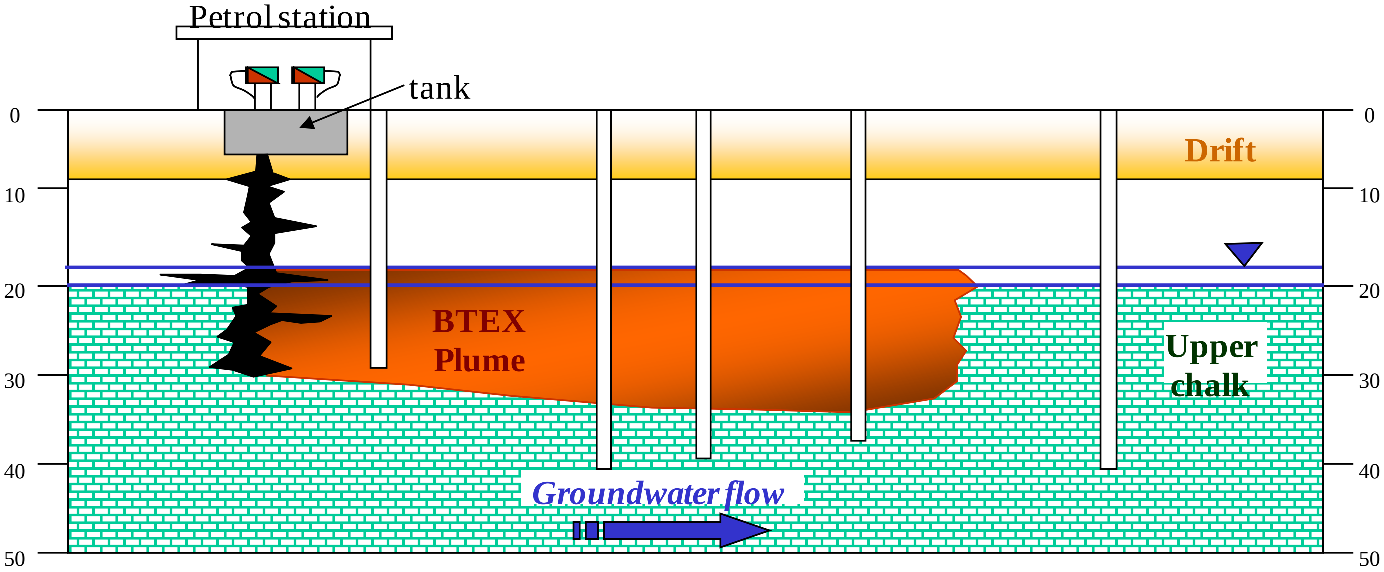
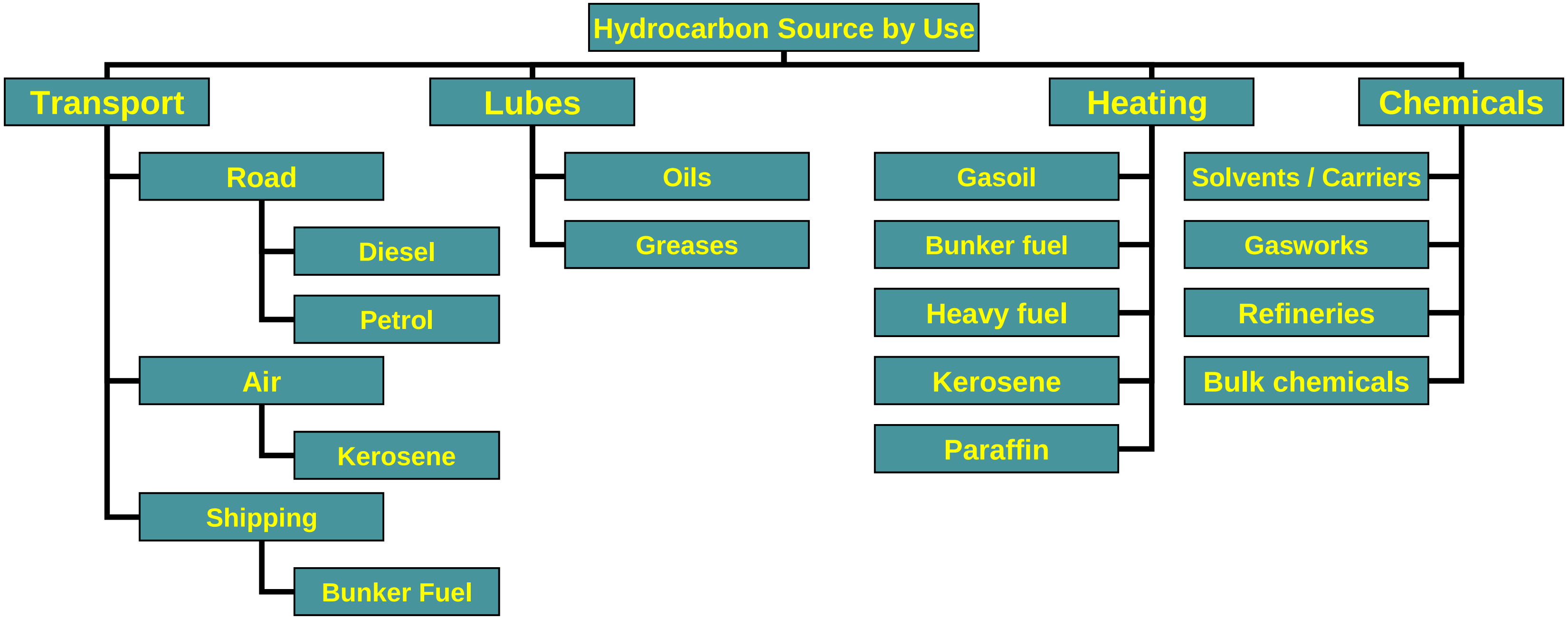


Outline

- Nature of petroleum hydrocarbons
- Why hydrocarbons present a problem
- Fate and transport of hydrocarbons
- Risk assessment

Sources of hydrocarbons: by use

- Ranges of activities using hydrocarbons
- Above and below ground storage tanks, pipelines, transport
- Spillages/ leaks/ tank failures



Hydrocarbon Source by Use

- Transport
  - Road
    - Diesel
    - Petrol
  - Air
    - Kerosene
  - Shipping
    - Bunker Fuel
- Lubes
  - Oils
  - Greases
- Heating
  - Gasoil
  - Bunker fuel
  - Heavy fuel
  - Kerosene
  - Paraffin
- Chemicals
  - Solvents / Carriers
  - Gasworks
  - Refineries
  - Bulk chemicals

Analytical Methods

- Screening analysis
  - DRO/EPH, PRO, TPH
  - determine presence and extent of contamination
  - Indicate concentration
  - Indicate source (petrol and diesel)
- Detailed analysis
  - provides information on the concentration of individual compounds or discrete carbon bands.
    - targeted – identifies named compounds
    - VOCs / BTEX
    - SVOCs
    - PAHs (speciated)
    - non-targeted – identifies carbon bands (aliphatic/aromatic split)

- Detailed analysis will always be required to support a HRA.

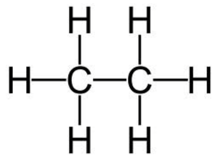
TPHCWG Carbon Banding & Equivalent Carbon No.

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

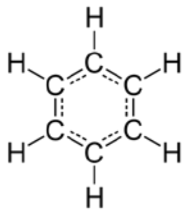
- Aromatics
  - EC6-EC7 (benzene)
  - >EC7-EC8 (toluene)
  - >EC8-EC10 (ethylbenzene, xylenes)
  - >EC10-EC12 (naphthalene)
  - >EC12-EC16 (anthracene)
  - >EC16-EC21 (pyrene)
  - EC21-EC35 (B[a]P)
- Aliphatic
  - EC5-EC6 (pentane+)
  - >EC6-EC8 (heptane+)
  - >EC8-EC10 (nonane+)
  - >EC10-EC12 (ondecane+)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

Characteristics of hydrocarbons

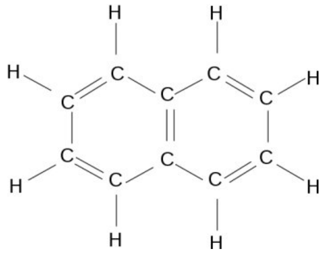
- Liquids (density/viscosity)
    - lighter than water
- Complex mixtures
    - aliphatic (alkanes, alkenes, alkynes etc.)
    - aromatic – including BTEX + PAHs
    - composition variable
- Range of environmental properties
    - mobile => immobile
    - soluble => insoluble (>1000 mg/l to <0.1 ug/l)
    - volatile => non volatile
    - poorly retarded => strongly retarded (Rf (benzene) ~ 4, Rf (benzo(a)pyrene) ~ 40000
    - rapidly degraded => recalcitrant



Ethane

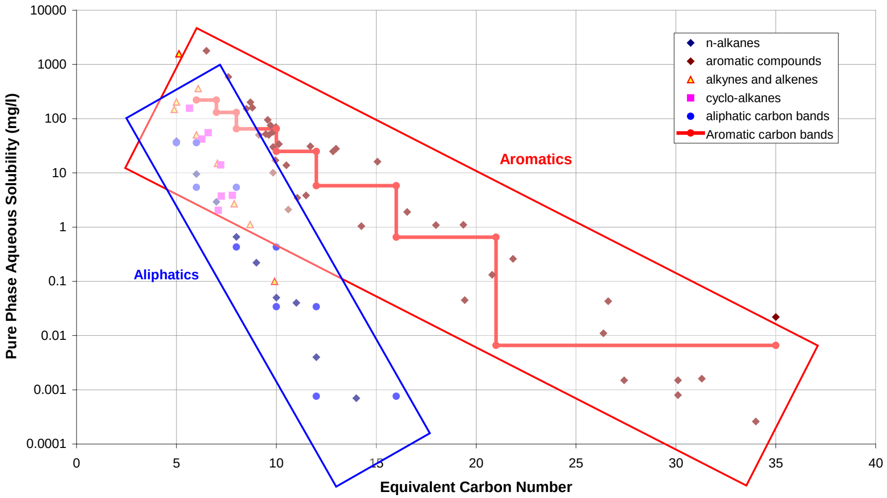


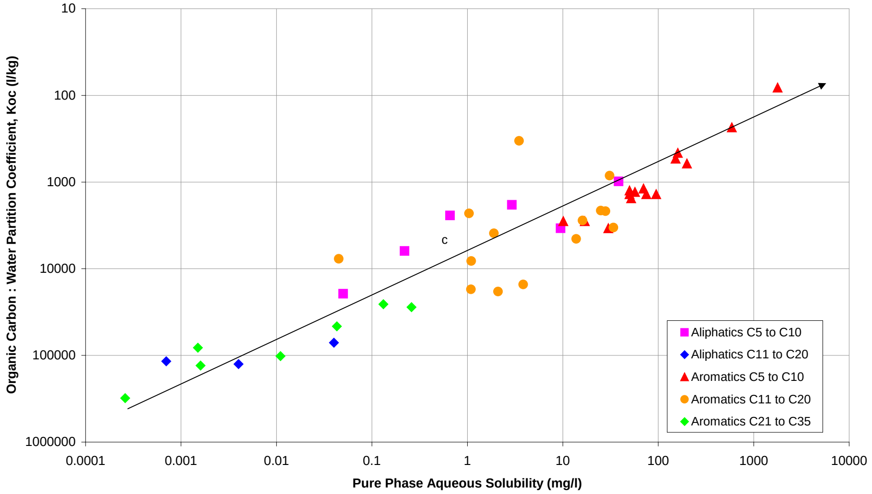
Benzene

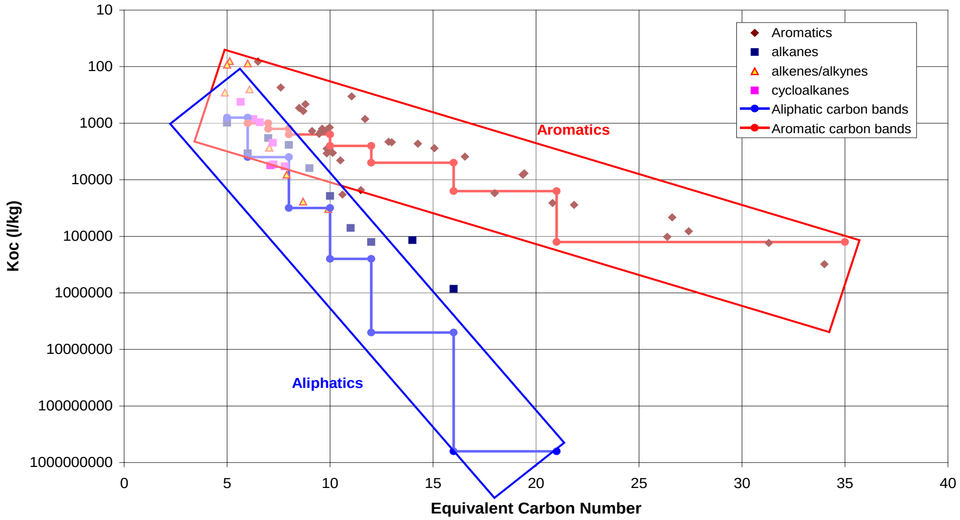


Naphthalene

Hydrocarbon properties


The relationship between Equivalent Carbon Number and Pure Phase Aqueous Solubility


The relationship between Koc and Aqueous Solubility


The relationship between Equivalent Carbon Number and Organic Carbon:water partition coefficient

Soil water partitioning

$$K_d = f_{OC} \times K_{OC}$$

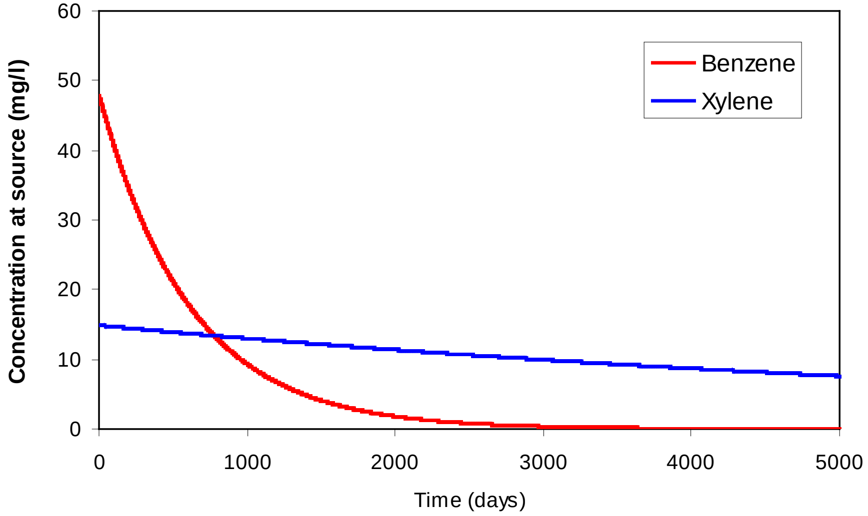
Dissolution

- Effective solubility << pure phase solubility
- Raoults Law

$$C_w = X_o.S$$

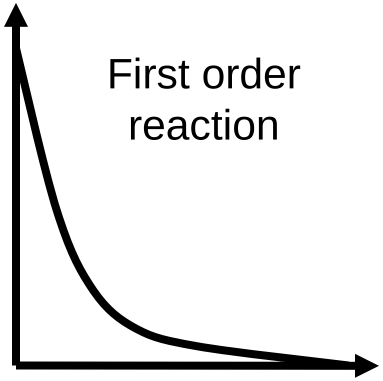
Cw = Effective solubility
Xo = mole fraction (of chemical in free product)
S = solubility

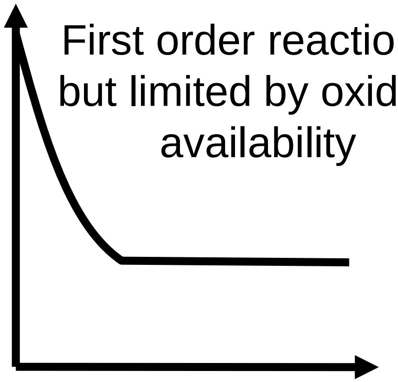
- Dissolved phase concentrations can change over time

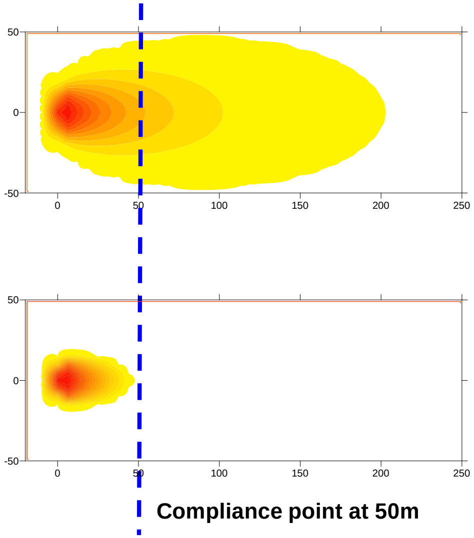


Degradation

- Degradation and plumathon studies
  - Benzene plumes typically < 100m
- Degradation process
  - Type of reaction
  - Aerobic or anaerobic
  - Competition
- Site specific derived degradation rate
  - time needed to obtain sufficient monitoring data to derive degradation rates (can be years)
  - supporting lines of evidence
    - size of plume
    - depletion of oxidants
    - modelling
- Laboratory (e.g. microcosm experiments)
  - time to complete experiments (can be 100s days)
  - scaling up to field
- Literature
  - range of values
  - site conditions may not be appropriate


First order reaction


First order reaction – but limited by oxidant availability

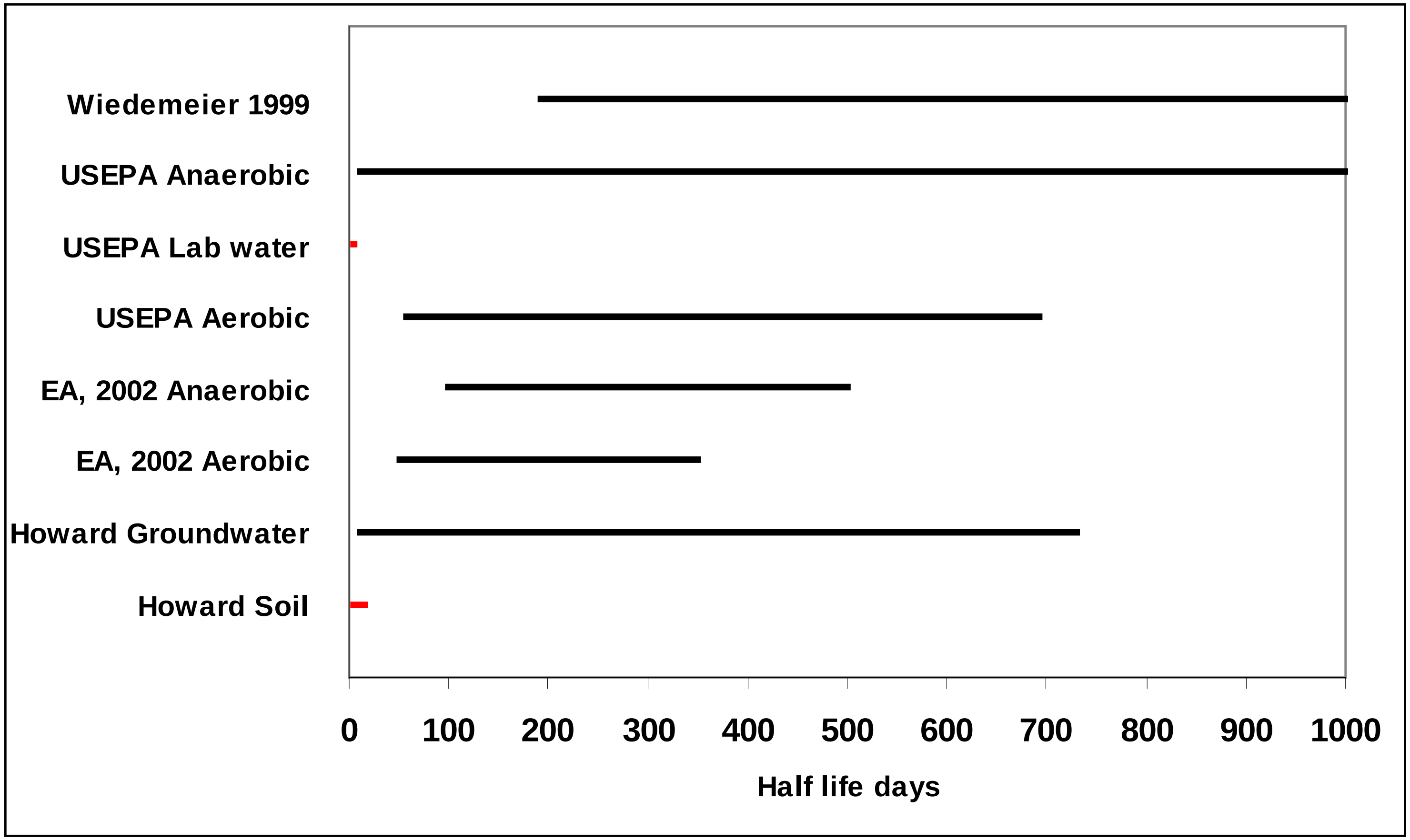


Slow rate of degradation in plume, limited oxidant availability

Slow rate of degradation in plume centre, rapid degradation at plume margins

Compliance point at 50m

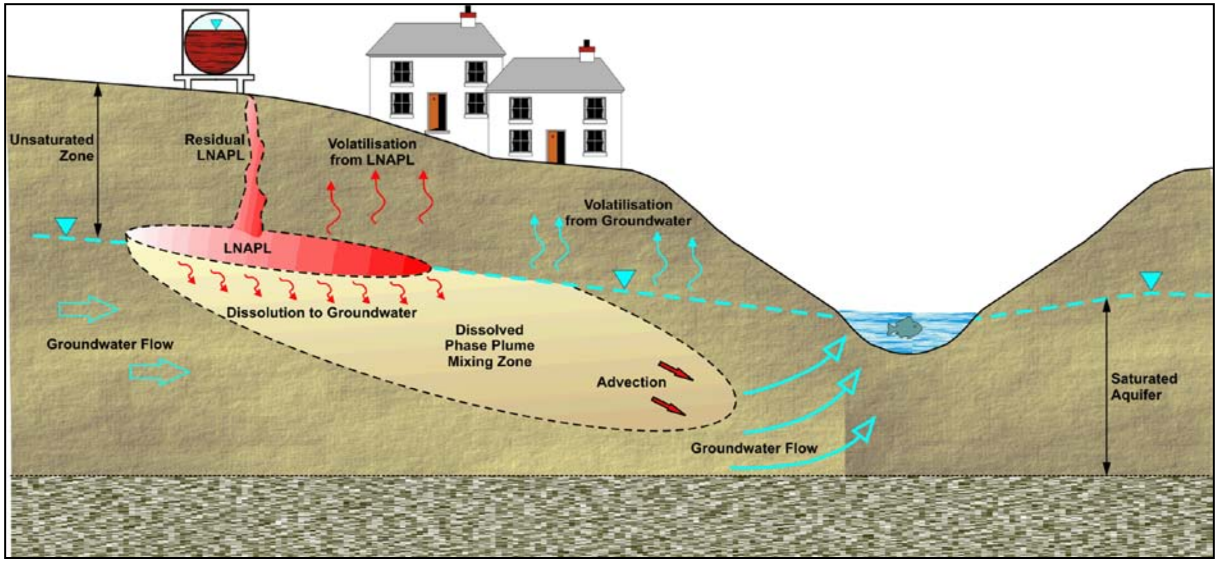
Benzene degradation rates



Conceptual Model

- Initial spill
- Vertical downward movement
- Lateral spreading (at capillary fringe / water table)
- Stabilisation of NAPL extent
- Growth of groundwater plume
- Stabilisation of groundwater plume
- Shrinkage of groundwater plume
- Residual product weathering

- Multiphase (vapours, NAPL, dissolved)
- Weathering (dissolution, volatilisation)
- Dilution (mixing), dispersion
- Sorption
- Degradation

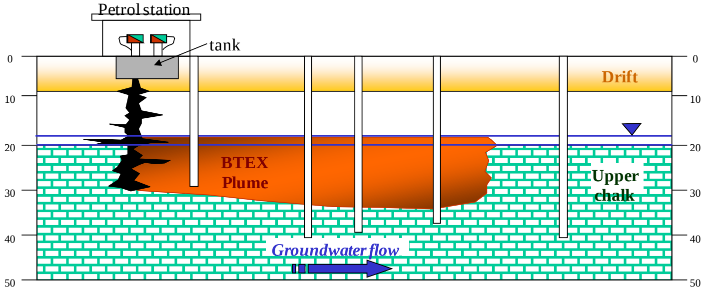


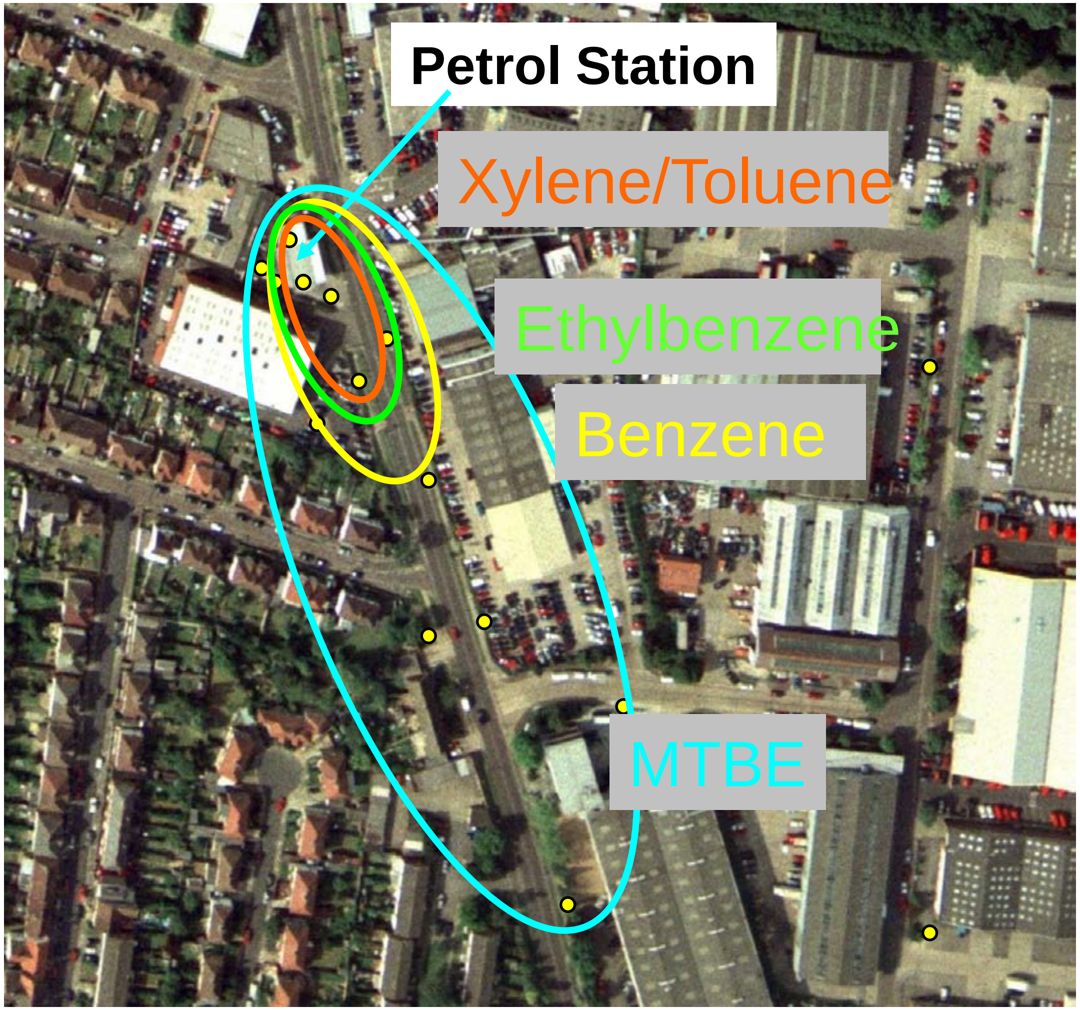
Case study – petroleum plume

- Accidental petrol spill resulted in pollution of chalk aquifer
- Initial rapid expansion of plume (benzene detected in borehole some 100m from source)
- Plume extents: benzene > toulene > ethylbenzene > xylene
    - (also trimethylbenzene, propylbenzene, naphthalene, Isopropylbenzene)
- Depletion of source over time (declining source term)
- Competitive dissolution
- Degradation of BTEX compounds over time and depletion of electron donors (DO, nitrate, sulphate) – variable rates of degradation
- Seasonal changes in plume direction
- Range of mechanisms (declining source, degradation linked to availability of oxygen donors, fissure/pore water diffusion)
- Monitoring 10 years to confirm plume processes (but large spill, in complex hydrogeology)

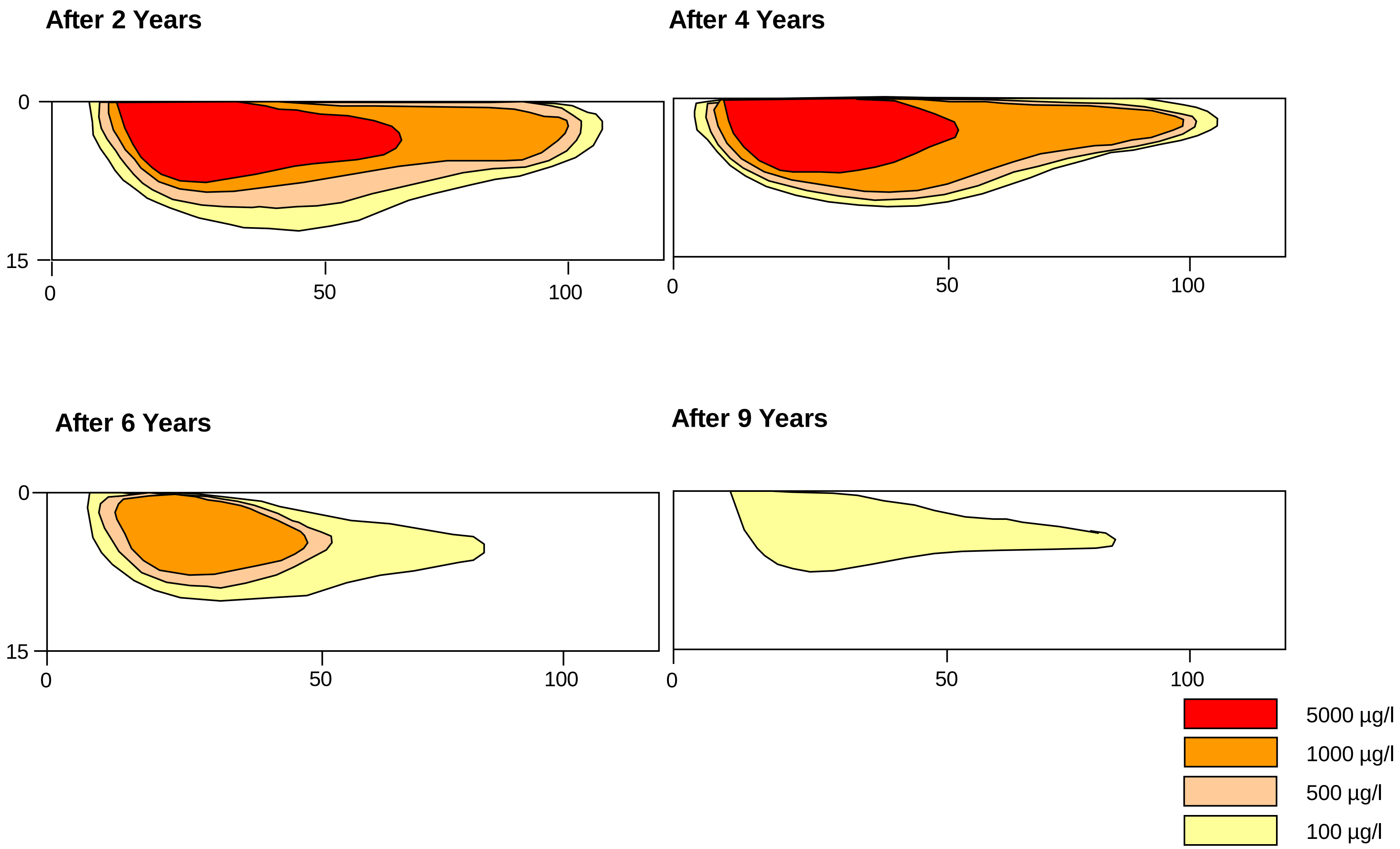
Case Study

- Accidental petrol loss from underground tank
- Groundwater pollution of underlying chalk

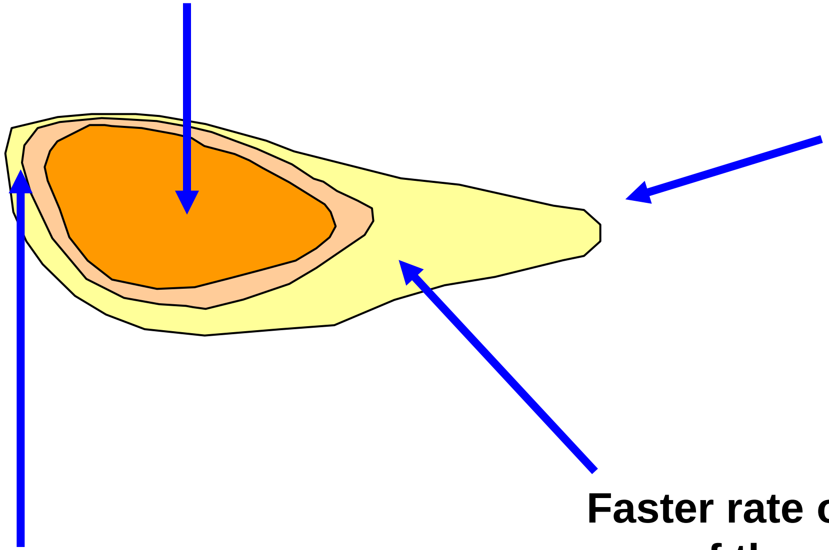




Benzene plume behaviour



Benzene plume behaviour



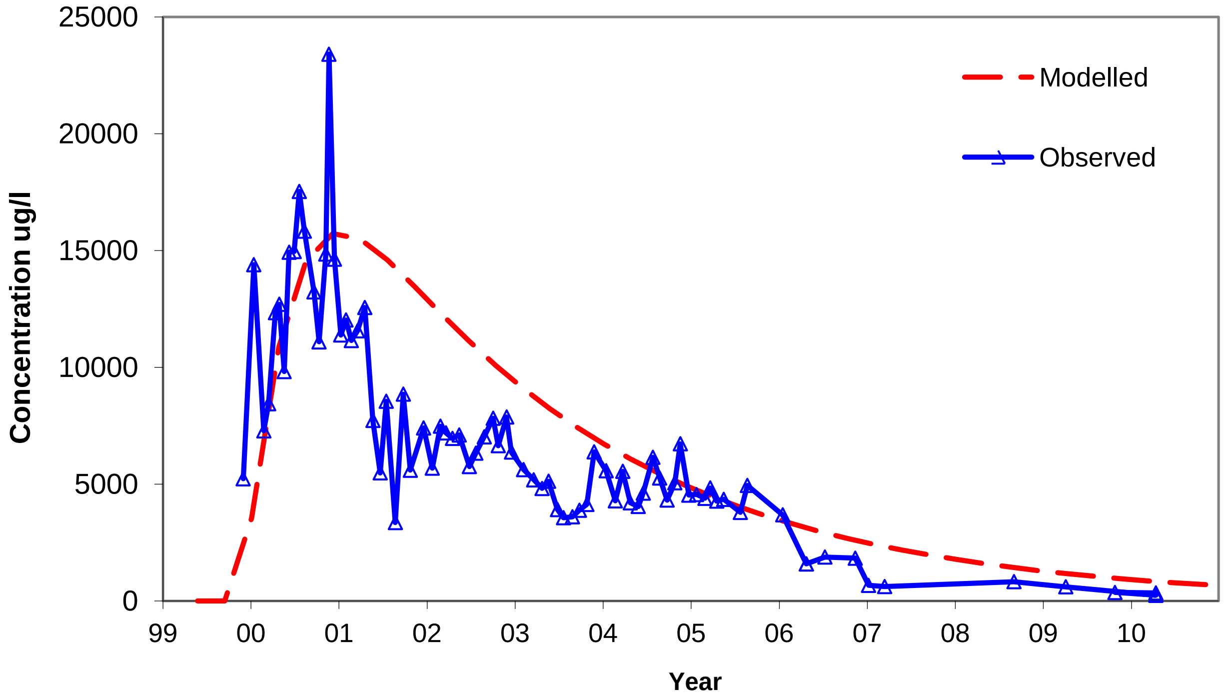
Slower rate of degradation at centre of plume (DO, nitrate and sulphate depleted) – half life ~ 300 days

DO, nitrate and sulphate in groundwater at plume margins

Faster rate of degradation at edge of the plume (DO, nitrate depleted) – half life < 100 days

Source depleted, evidence of recovery of oxidants

Modelling of benzene plume



Declining source

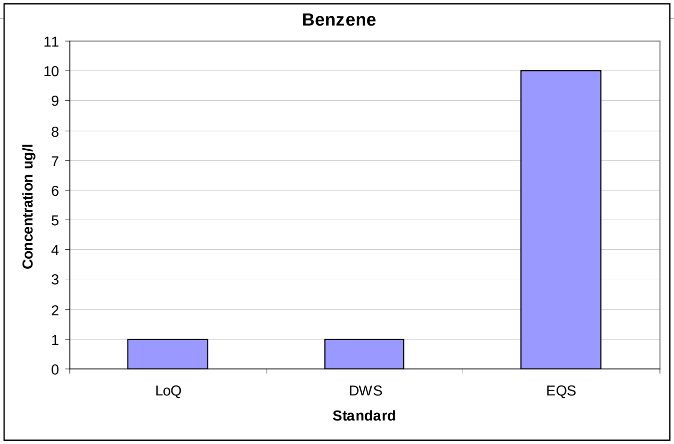
Variable rates of degradation

Why do hydrocarbons present a risk to Controlled Waters

- Large volumes stored (often underground)
- Hazardous substances
- Free and dissolved phases present
- Compounds can be highly soluble and >> water quality standards
    - (benzene solubility ~1800 mg/l compared to DWS 0.001 ug/l)
- Compounds can be highly mobile
- Cases of public water supplies and water courses impacted

- Mitigating factors
    - More mobile compounds – can be readily degraded
    - More complex compounds – low solubility and highly sorbed

Water Quality Targets



- Some standards
  - Limits of quantification/MRVs
    - VOCs – 1 ug/l
    - PAHs – 1 ng/l
  - Drinking water standards (at consumers tap)
    - Benzene 1.0 ug/l
    - PAHs 0.1 ug/l
    - Benzo(a)pyrene 0.01 ug/l
    - *TPH 10ug/l (withdrawn)*
  - Environmental quality standards
    - Naphthalene 2.4 ug/l Anthracene 0.1 ug/l
    - Benzo(a)pyrene 0.05 ug/l
    - Benzene 10 ug/l Toluene 50 ug/l Xylene 30 ug/l

Common risk drivers

- Soluble, mobile, present as significant fraction, slowly degraded

Suspected hydrocarbon source	Carbon banding	Mobile components (main risk drivers)	Other risk drivers
Petrol (gasoline)	**C4-C12**	**BTEX**	**Other VOCs (Fuel additives MTBE, TAME, ETBE)**
Kerosene (paraffin)	**C6-C16**	**BTEX, naphthalene**	**Other VOCs** **Hydrocarbon band**
Diesel + gas oil	**C8-C21**	**BTEX, naphthalene**	**Other PAHs** **Hydrocarbon band**
Heavy fuel oils	**C12+**	**None**	**Other PAHs** **Hydrocarbon band**
Lubricating oils and greases	**C18->C34**	**Not typically a groundwater contaminant source**	

Small percentage fraction

Why is risk assessment needed?

- Risk to groundwater receptors
- Define remedial targets
- Can we leave residual hydrocarbons

Issues with hydrocarbons

- Mixtures: common hydrocarbons are mixtures.
  - not possible to identify every compound
  - not practical to incorporate all of them within an HRA
- Choice of analysis. Lots of techniques available
  - not all suitable for risk assessment
  - need to avoid duplication and gaps
- Phases: Hydrocarbons present in different phases:
  - Vapour, dissolved, sorbed, free phase (mobile and residual)
  - hydrocarbons move readily between phases
- Identification of risk drivers
  - Relatively straight forward for petrol (e.g. BTEX)
  - For heavier fuels (wide range of hydrocarbons and individual species may represent small fraction of total)
- Contaminant properties and especially degradation (carbon bands)

Approach

- Use existing good practice/guidance (Groundwater risk assessment for land contamination)
- Characterisation of problem including conceptual understanding
- Is there pollutant linkage
- Identification of risk drivers (contaminants of concern) and target concs
  - For lighter fuels (e.g. petrol) assessment based on individual compounds (e.g. BTEX)
  - For heavier fuels where range of compounds, then assessment based on band properties (TPHCWG)
- Choose compliance point: Principal (50m) - or Secondary aquifers (250 m)
- Qualitative or quantitative assessment
- Selection and application of appropriate model/tool (e.g. P20 spreadsheet, ConSim, RBCA, RAM, Corona etc)
- Is remediation needed – is it beneficial

Assessing Risk from Free-phase (NAPL)

- Is NAPL mobile
- Is NAPL (immobile or mobile) source of dissolved phase hydrocarbons
  - Likely to be long-term source
  - 100% removal often not possible
  - Dictates maximum aqueous concentration (Raoults Law)
  - Low solubility NAPLs = limited risk to controlled waters
  - Nature of source changes with time – competitive dissolution

Summary

- Petroleum hydrocarbons challenges
    - multi-phase
    - multi-component
    - variable properties and behaviour
- Preferred Approach
    - appropriate detailed analysis
    - identification of risk drivers
    - qualitative vs quantitative assessment
    - appropriate choice of model

- Key is good data + conceptual understanding

The End

Thank you for Listening