The legacy of chlorinated solvents in contaminated land and groundwater

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Outline

• Nature of the legacy
• CFB Borden site, Canada
• Sabre site, UK
• Birmingham aquifer – river Tame, UK
• History matters: a RSC contribution
• Conclusions
Nature of the legacy

Chlorinated solvents

- **TCE**: Trichloroethene ($\text{C}_2\text{Cl}_3\text{H}$)
  - Metal degreasing solvent
- **PCE**: Perchloroethene ($\text{C}_2\text{Cl}_4$)
  - Textile/leather dry cleaning solvent
- **TCA**: 1,1,1-Trichloroethane ($\text{C}_2\text{Cl}_3\text{H}_3$)
  - Circuit board cleaner, metal cleaner
Solvent use and recognition in groundwater

1975 - TCE found in US water supplies, recognised as potential carcinogen

1980-81 - “First” UK publication on TCE in groundwater

Cambridge Water Company v. Eastern Counties Leather

Mackay & Cherry (1989)
DNAPLs: a 1980s paradigm shift

- Not the classical leachable source zone…

Heterogeneity

- Control on NAPL and plume migration
- Heterogeneous source zone architecture
Discrete heterogeneity control

- Compromised clay aquitards
- Sand stringer (<1 cm) transmitting DNAPL

DNAPL conceptual model

- Dissolution of DNAPL source zone parts may vary from years to decades to centuries
Timing and legacy remaining

- Date periods of chemical release relative to dates of remedial action(s)
- Groundwater and remediation fluids will increasingly by-pass DNAPL source
- Increasingly left with more difficult DNAPL

![UK production of chlorinated solvents graph]

The nature of the legacy

- How much mass is in the DNAPL – source zone and how deep in the aquifer is it?
- How much mass is in the dissolved-phase plume and how far has it travelled to potential receptors?
- Is natural attenuation of the dissolved plume due to dispersion, sorption and (bio)degradation significant?
- Do we need to remediate, and if so, how?
- and, for how long?

![Groundwater flow diagram]
CFB Borden site, Canada

Journal Publications

Plume dispersion

Source

TCM 322 Days
Plan Section at 95.4m

Plume sorption

Field data

Modelling of field data

Lab batch isotherm studies
Plume sorption

- Retardation was relatively low in this low $f_{\text{oc}}$ aquifer
  - $R_{\text{TCM}} \approx 1.0$, $R_{\text{TCE}} \approx 1.1$, $R_{\text{PCE}} \approx 1.6$
- Non-ideal sorption was, however, important due to:
  - Concentration non-linearity, multi-solute competition, kinetic
- Significant $R_{\text{PCE}}$ difference to adjacent Borden site

Remediation

- Pump-and-treat containment
- Zero valent iron permeable reactive barrier (PRB)
- In-situ chemical oxidation
  - potassium permanganate
- Confirmatory excavation
Birmingham aquifer – river Tame, UK

VOCs in the Birmingham aquifer
1986 – 2008 data
Triassic Sandstone aquifer

- $K \approx 2 \text{ m/d}$
- $n \approx 0.27$
- $S_y \approx 0.1$
- $V_{gw} \approx 15 \text{ m/yr}$

Groundwater rebound

(30 m x 40 year hydrographs)
TCE (Trichloroethene) 1987
Survey of licensed boreholes (~50 – 120 m screens)

Birmingham groundwater abstractions / network

VOC surveys
• Rivett (1988)
• Taylor, Shepherd (1998)
• Brennan (1999)
• Botha (2006)
• Murcott (2008)
Comparison to 1987 individual sites

1987 v 1998
- 26 of 36 surveyed

1987 v 2008
- 7 of 15 surveyed

- Persistent DNAPL sources probable
- Few sites can now be historically compared
Natural attenuation at the edge: groundwater – surface-water interface

- Birmingham aquifer – river Tame system

Hyporheic zone

- Potential natural attenuation of discharging dissolved-phase groundwater plumes?
- Rather ‘last gasp’ groundwater remediation…

- Infiltration of oxygenated SW
- High organic carbon, nutrients
- High microbiological activity
- Steep redox gradients
- Dynamic flows
7 km river Tame reach over the effluent Birmingham aquifer

Riverflow$_{\text{min}}$ ~180 Ml/d
Baseflow ~7% $Q_{\text{tot}}$
Quality Class E/F

Monitoring
Chlorinated VOCs dominant in baseflow

- 7 km reach
- Piezometers are 0.5 m below riverbed

Multilevel sampling of 50 m sub-reach
Ethene was rarely detected (not always analysed though)
Surface water impact: ‘modest’

- River increases from 1 to 3 μg/l TCE over 7 km city reach (EQS = 10 μg/l)
- Volatilization loss half-life ≈ 0.1 days ≈ 7 km travel time

Mass flux estimates

- **7 km city reach** (TCE) [Q•C methods]
  20 – 200 kg/yr (0.8 – 7.5 mg/d per m² riverbed)

- **50 m reach** (individual VOCs)
  0.3 – 7 kg/yr (2– 40 mg/d per m² riverbed)
  → ~0.1 μg/l increase in surface water (700x dil’n)

- **Borehole abstractions from aquifer**

  - 1461 kg/yr 1987
  - 157 kg/yr 1998
  - 254 kg/yr 2008
Frances Lyne (1913-96) & Thomas McLachlan (1894-1991) were “Public Analysts” and members of the RSC until their deaths.

Lyne later worked for Reading Borough (Environmental Health) and operated commercial analytical consultancy “Lyne, Martin & Radford”

**CONTAMINATION OF WATER BY TRICHLOOROETHYLENE**

Cases of contamination of wells by trichloroethylene have come to our notice. In the first, the well was situated beside a factory that used large quantities of trichloroethylene as a solvent. During a fire at the factory a tank of the liquid burst and the ground was saturated with the solvent. After more than four years the water in the well still had an odour of trichloroethylene and the well had to be abandoned. The well was sunk in gravel only about 30 feet from a creek and one might have expected that the movement of water through the gravel would have removed the contamination.

In the other case, the well was situated (186 to 396 yards) from a pit in an open field where waste trichloroethylene had been dumped. It was in valley gravels and in the direct line of flow towards the river. The water in it had a slight odour of trichloroethylene and was said to cause stomach disorders, gallstones, etc. The amount of trichloroethylene in the water was found to be 18 parts per million when entrapped by the following method, a modification of the Fippens pyridine–sodium hydroxide reaction.

From these two cases it is evident that contamination by compounds of this nature is likely to be very persistent and there is some evidence of toxicity at very low concentrations.

**METHOD**

**Standard solution**—A convenient standard can be prepared by first dissolving 1 ml of commercial trichloroethylene in alcohol and making up to 100 ml, and then diluting 1 ml of this solution to 500 ml with water, to give a solution containing 20 parts per million.

**Procedure**—Place 5 ml of the sample in a test tube, add 2 ml of colourless pyridine and 4 ml of a 50 per cent. w/v solution of sodium hydroxide in water, shake thoroughly and stopper with cotton wool. Place the tube, and a similar tube containing the standard solution, in the same way, in a boiling water-bath for 5 minutes. Cool and compare the orange colour obtained in the representative liquid with that of the standard.

For a more accurate estimation prepare a series of tubes containing different amounts of trichloroethylene and match with the sample treated in parallel. It should be possible to estimate 5 parts per million with ease and the method would probably detect 1 part per million.

**REFERENCE**


Rather lost in the literature

- Paper “re-emerged” in 1996 in USA legal cases, but not in the UK until 2004
- The paper has received more citations in the last decade than previously

Highlighted ones are citations to L&M (1949)

Lyne & McLachlan (1949) in context

- I conclude Lyne & McLachlan (1949):
  - was insignificant in contributing to the general recognition of the solvents-in-groundwater problem in scientific, engineering or regulatory communities.
  - is essentially immaterial in the determination of liability for historic solvent pollution events
- Others may disagree...

Conclusions

• The legacy of chlorinated solvents in groundwater remain a significant challenge
  – to delineate
  – to assess risks posed
  – to remediate
  – to manage affected resources


• Rivett, M.O., Clark, L., 2007. A quest to locate sites described in the world’s first publication on trichloroethene contamination of groundwater. Quarterly Journal of Engineering Geology & Hydrogeology, 40(3), 241-249. DOI: 10.1144/1470-9236/06-047


