CL:AIRE technical bulletin

TB11
(September 04)

CL:AIRE technical bulletins describe specific techniques, practices and methodologies currently being employed on sites in the UK within the scope of CL:AIRE technology demonstration and research projects. This Bulletin summarises the recently published Environment Agency Report entitled "An illustrated handbook of DNAPL transport and fate in the subsurface".

A Practical Guide to Investigating DNAPL Releases in the Subsurface

1. INTRODUCTION

Dense non-aqueous phase liquids (DNAPLs) are heavier-than-water organic liquids that have been widely used in industry from the early 1900s to the present. DNAPLs are only slightly soluble in water, and therefore exist in the subsurface as a separate fluid phase, immiscible with both water and air. Common types of DNAPLs include wood treating oils such as creosote, transformer and insulating oils containing polychlorinated biphenyls (PCBs), coal tar and a variety of chlorinated solvents such as trichloroethene (TCE) and tetrachloroethene (PCE). Unlike light non-aqueous phase liquids (LNAPLs) such as petrol and heating oil, DNAPLs have the ability to migrate to significant depths below the water table where they slowly dissolve into flowing groundwater, giving rise to aqueous phase plumes. A release of DNAPL at the ground surface can therefore lead to long-term contamination of both the unsaturated and saturated zones at a site.

This bulletin provides a summary of a recently published Environment Agency (EA) report entitled, "An illustrated handbook of DNAPL transport and fate in the subsurface". The purpose of the bulletin is to describe how the report came about and to introduce some of the terms, concepts, problems and solutions relating to DNAPL contamination in the UK which are addressed in more detail in the EA report.

2. BACKGROUND

Although DNAPLs have been produced and utilised widely since the early 1900s, recognition of their importance as soil and groundwater contaminants did not take place until the 1980s. This lack of recognition by the research, regulatory and industrial communities is due in part to the fact that the analytical methods and equipment required to detect low concentrations of organic compounds in groundwater were not widely available or used until relatively recently. In addition, some chemical manufacturer material safety data sheets distributed from the 1940s through to the early 1970s suggested that 'acceptable practice', for the disposal of waste chlorinated solvents and the residues of distillation, was to spread them onto dry ground to allow them to evaporate. These early material safety data sheets recognised the volatile nature of many DNAPL chemicals, but they did not recognise the ability for DNAPLs to rapidly infiltrate into the subsurface, causing soil and groundwater pollution. Additional factors which have contributed to the relatively late awareness of the impact of DNAPLs on soil and groundwater quality include:

(i) society's general lack of understanding of the importance of groundwater as a supply of potable water, and

(ii) the widespread use of shallow soil systems as a location to dispose of unwanted materials.

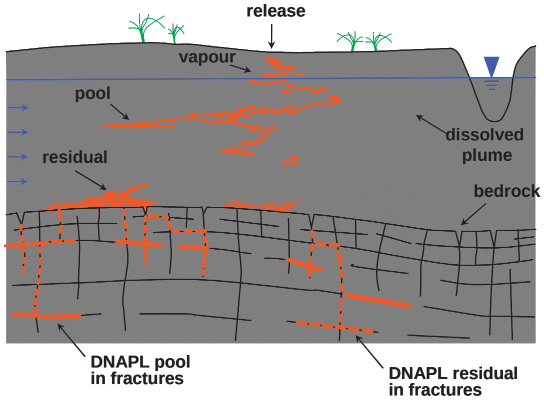

Fig.1: Overview of the major fate processes undergone by DNAPL in the subsurface environment

There are potentially several thousand DNAPL-impacted sites throughout the UK. Many of these sites are affected by releases of DNAPL that took place in the mid-1900s, coincident with the rise in industrial activity after World War II, as well as by more recent discharges. In addition, it is known that there are thousands of DNAPL-impacted sites in North America, continental Europe, and other industrialised areas of the world. Experience from the past 20 years has demonstrated that DNAPL sites are difficult to investigate and challenging to remediate. It is known that DNAPL can penetrate fractured rock and clay, and that many decades are required for natural groundwater dissolution to dissipate DNAPL sources in most hydrogeologic environments. Finally, given that most DNAPL compounds have been found to be toxic to mammals and other fauna; that certain DNAPL compounds are highly mobile in the subsurface; and that groundwater forms an integral part of the hydrologic cycle, it follows that DNAPL impacted soil and groundwater is of major concern in the UK.

3. THE HANDBOOK

3.1 The Concept

It was with the foregoing in mind that back in 1997 researchers from the Universities of Sheffield and Greenwich together with colleagues from the British Geological Survey undertook an investigation into the depth of penetration of chlorinated solvent DNAPLs into a dual porosity Permo-Triassic sandstone aquifer. This work was funded by the EPSRC and the Environment Agency, and benefited from industrial support and steer from ICI. Emerging from the investigation was the idea to collate their knowledge in the form of a handbook and describe in pictorial terms their understanding of the fate of DNAPLs in important UK aquifers. The purpose of this handbook was to provide a user-friendly overview of the nature of DNAPL contamination in a UK context.

The handbook is intended to assist site investigators, site owners, and regulators in conducting site investigations, conducting risk assessments, and selecting remediation approaches. While the authors feel that this handbook reflects the state-of-the-art at the time of publication (in 2003), it should be noted that the discipline of groundwater and soil contamination by hazardous organic liquids is continuously evolving and is relatively young in comparison to many other areas of science and engineering. Any potential reader is therefore advised to keep abreast of the new advances in understanding and approaches that are expected in the foreseeable future.

3.2 Rationale for the Handbook

There are several reasons why an illustrated handbook is both timely and necessary for site investigators, site owners, and regulators. DNAPLs are widely encountered groundwater pollutants. Their presence is very often detected at coking works, old manufactured gas sites, creosote facilities and solvent recycling plants. Yet the presence of DNAPLs at a site is often inferred rather than observed; and to accurately infer their presence requires a "lines of evidence" approach. Thus a major aim of this handbook is to provide guidance on what evidence is required to sustain such an approach.

Observations from field studies and the use of increasingly complex modelling have improved our understanding of how DNAPL properties and geological features affect DNAPL distribution and fate. Yet no single text exists which provides a specific overview of DNAPL fate given well-defined DNAPL physical properties coupled with specific geological features. Moreover, a pictorial depiction of fate will provide practitioners with a powerful tool for site investigation.

3.3 Aims of the Handbook

The authors of the handbook had two major aims which were:

(i) to collate and synthesise, in a single text, the current understanding of DNAPL behaviour in the subsurface; and

(ii) to be a useful reference manual for practitioners by considering:
  the wide diversity of field DNAPL physical properties and chemical compositions and
  the wide variety of possible geological contexts within which DNAPLs are encountered.

The following sections (4, 5 and 6) go further in describing the nature of DNAPL contamination in the UK by looking at the following: the main problems posed by DNAPL contamination; the physical properties which influence DNAPL transport and fate; and the type of information that is needed if DNAPL is suspected to be present on a site.

4. THE DNAPL PROBLEM

Fig 1 provides an overview of our current understanding of the key fate-processes involving DNAPLs once they have been released into the subsurface environment. DNAPL transport in the subsurface is dominated by gravitational, buoyancy and capillary forces. The risk drivers associated with DNAPL releases are the chemical composition of the DNAPL along with the solubility and volatility of the components of the DNAPL release.

In a nutshell, the key problems faced by site owners, regulators and the general public are:

DNAPL mobility: The mobility of a DNAPL release is a major concern, because both off-site migration and DNAPL penetration into an aquifer formation are possible outcomes.

Volatility of DNAPL components: DNAPLs are often multi-component liquid mixtures. The more volatile components are normally of major concern since they are capable of creating a contaminant plume in the vapour phase of the unsaturated zone. Since vapour phase transport is up to an order of magnitude faster than advective transport in groundwater, vapour phase plumes may often provide unlooked for contamination of domestic environments.

Solubility of DNAPL components: The solubility of DNAPL components in groundwater is of major concern since in many ways the level of contamination in groundwater represents the primary risk driver for remedial action and the yardstick for regulatory compliance.

Source zone longevity: An important consideration from the point of view of environmental sustainability. Contaminated groundwater, judged unacceptable for domestic use, represents a loss of a resource. Remedial strategies, designed to restore the aquifer to an acceptable state, need an insight into the lifetime of the source zone in order to appreciate the time-scales remedial works may require in order to comply with some agreed end-point. Long time-scales may not represent an effective use of resources and as such may be unsustainable.

5. PHYSICAL PROPERTIES OF DNAPLS

The physical properties of DNAPLs exert an immense influence upon their behaviour in soils, rocks and unconsolidated media. These physical properties, typically, change from site to site.

The defining DNAPL properties, which exert a major influence upon DNAPL transport and fate, are given below:

5.1 Density and Viscosity

Both density and viscosity have a pivotal influence upon the DNAPL transport. Those organic liquids with high densities and low viscosities, such as the chlorinated

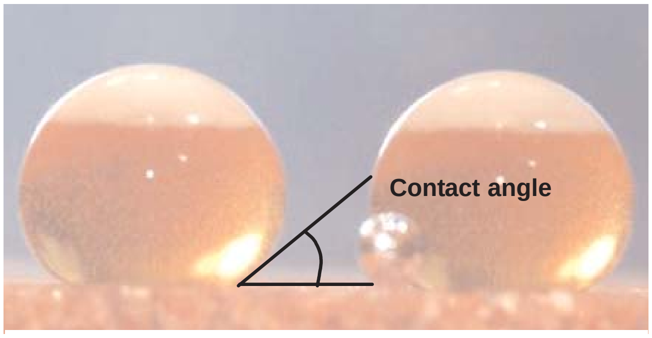

Fig.2: The photograph shows two drops of trichloroethene (TCE) placed upon a sandstone section. The surrounding fluid is water. The shape of the drops clearly indicates that TCE is non-wetting. In other words the water freely spreads over the sandstone surface whilst the TCE minimises its contact with the surface by balling up. The contact angle is defined as shown in the diagram and its value indicates whether the fluid is strongly or weakly water wetting or strongly or weakly NAPL wetting. Contact angles of about 30° (which are quite common) indicate that the NAPL will tend to be strongly trapped in the pore spaces by capillary forces.

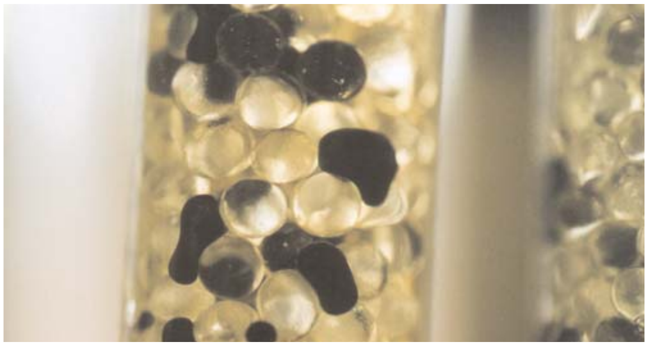

Fig.3: Photograph of coal tar residuals trapped by capillary forces in a water saturated synthetic porous medium.

hydrocarbon solvents, travel relatively fast when released into the subsurface and will tend to become immobile relatively quickly. Whereas coal tars and creosotes which have high viscosities and densities which are only slightly greater than 1.0 kg L^{-1} (the density of water) are relatively slow moving and are potentially mobile for a considerable time after release.

5.2 Wettability and Interfacial Tension

Wettability describes the ability of one fluid to spread over a solid surface in competition with a second fluid. Wetting properties are normally characterised by the contact angle. The contact angle can be measured as shown in Figure 2. An interfacial tension arises at the interface between two immiscible fluids - as a result of the imbalance in molecular forces and is a measure of the contractile force, which seeks to minimise the area of interfacial contact between the two fluids.

Wettability and interfacial tension define the magnitude of the capillary forces which trap the non-wetting DNAPL as residual blobs and ganglia (see Figure 3) in the pore spaces of a water saturated porous medium.

5.3 Solubility, Vapour Pressure and Chemical Composition.

DNAPLs are often encountered at field sites as multi-component liquid mixtures whose compositions will reflect the predominant industrial processes that occurred on-site and the way in which hazardous liquid wastes were collected, stored and disposed of. The solubility/volatility of the components of a DNAPL mixture will determine the initial composition of the contaminant plume, which will, of course, change over time. The handbook takes particular care to outline these features of DNAPL behaviour in groundwater.

There are a number of commonly encountered DNAPLs namely chlorinated hydrocarbon solvents, coal tar, creosote, PCBs and halogenated aromatic compounds. The very different physical properties of these liquids coupled with their different chemical compositions often means that on site risk assessments need to be site-specific, entailing the need for detailed site-specific characterisation.

6. WHAT DETAILED SITE-SPECIFIC INFORMATION IS REQUIRED?

The important question for all site investigators is essentially what do they need to know if they suspect that they have DNAPL on-site. The following is a comprehensive but not necessarily exhaustive list of key site investigation questions.

What are the site characteristics?
Site history

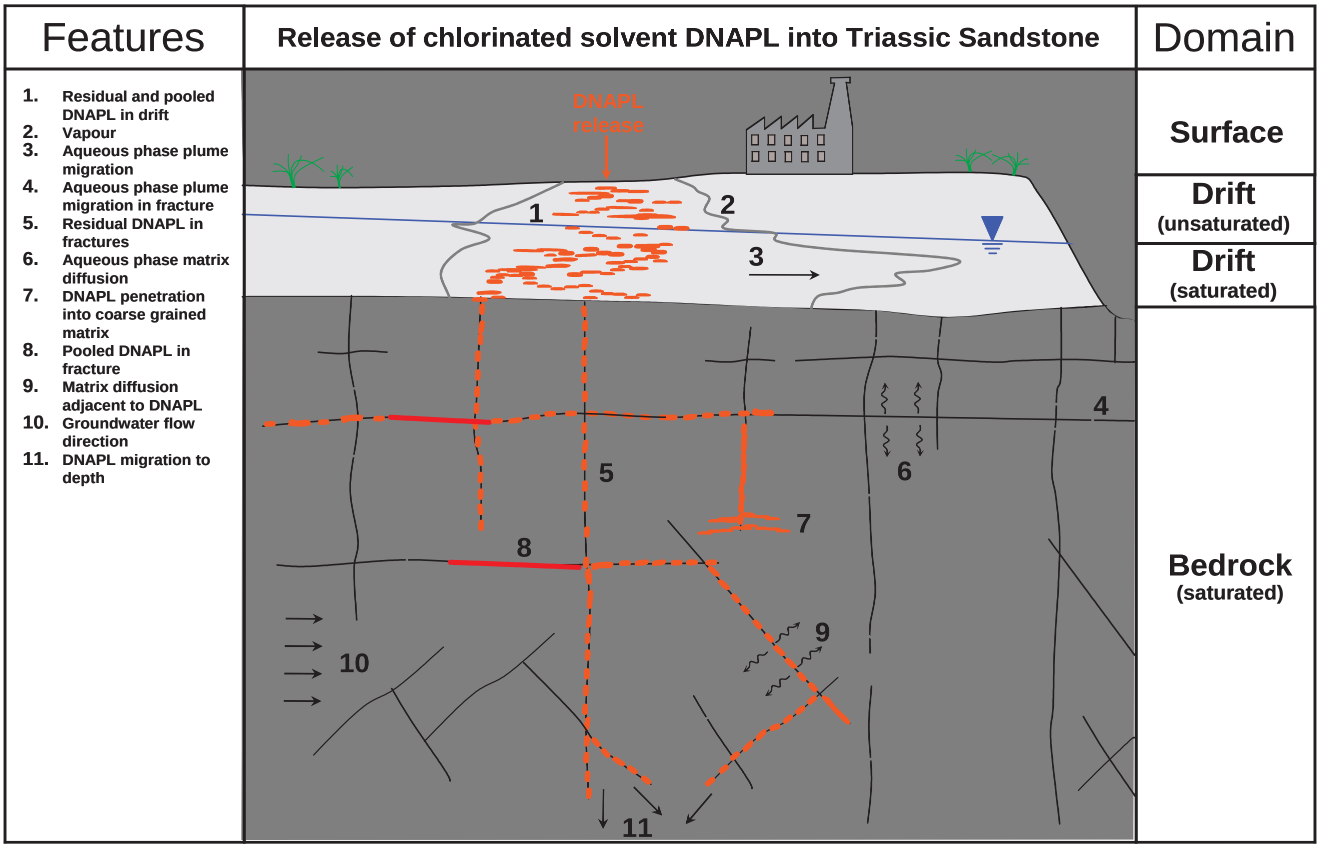

Fig.4: Release of chlorinated solvent DNAPL into Triassic Sandstone

  - Geology
  - Hydrogeology
- Is DNAPL present?
  - Is it mobile?
  - If so, what are the migration time scales?
  - Can I obtain a sample?
  - What is its composition?
  - What are its physical properties?
- Plume evolution
  - Will a plume evolve?
  - What will be its composition?
- What is at risk?
  - Identify sources, pathways and receptors
  - Make exposure assessment
- What is the geometry of the DNAPL source zone?
  - Location
  - Bulk retention capacity
- How should the site be monitored?
  - Well location and problems of interpretation.

The fact that DNAPLs are denser than water results in their ability to migrate to substantial depths below the water table in both unconsolidated deposits and in fractured bedrock. Delineating the spatial extent of the DNAPL source zone at a site can be a substantial undertaking, requiring at times several years of investigation and significant financial resources. The handbook aims to make delineation easier and more effectively directed by providing an overview of DNAPL behaviour in specific geological scenarios. Two examples of DNAPL behaviour in fractured sandstone for two contrasting DNAPLs (chlorinated hydrocarbon solvent and coal tar) are presented in Figures 4 and 5.

Remediation strategies will, of necessity, be site-specific, with separate approaches often warranted for both the DNAPL source zone and the associated aqueous phase plume. At the present time, there has been limited success in removing all DNAPL from below the water table at sites, particularly in a fractured rock environment. Remediation strategies are therefore often directed towards source zone containment, source zone stabilisation, partial mass removal, plume management, or plume interception.

7. WHERE CAN I GET A COPY?

The handbook is published by the EA and has the following reference:
Keuper, B.H., Wealthall, G.P., Smith, J.W.N., Leharne, S.A. & Lerner, D.N., 2003. An illustrated handbook of DNAPL transport and fate in the subsurface. Environment Agency R&D Publication 133. EA, Bristol.

It is available as a free download from the EA website as a PDF file, or in full-colour hard copy from the EA National Customer Contact Centre by emailing enquiries@environment-agency.gov.uk or by telephoning 08708 506506.

Acknowledgements

This bulletin was compiled by CL:AIRE staff from text prepared by Professor Steve Leharne at University of Greenwich, Dr Gary Wealthall at the British Geological Survey, Professor David Lerner at the University of Sheffield and Jonathan Smith of the Environment Agency.

For more information please contact the Environment Agency at
Website: www.environment-agency.gov.uk/
Tel: 08708 506 506

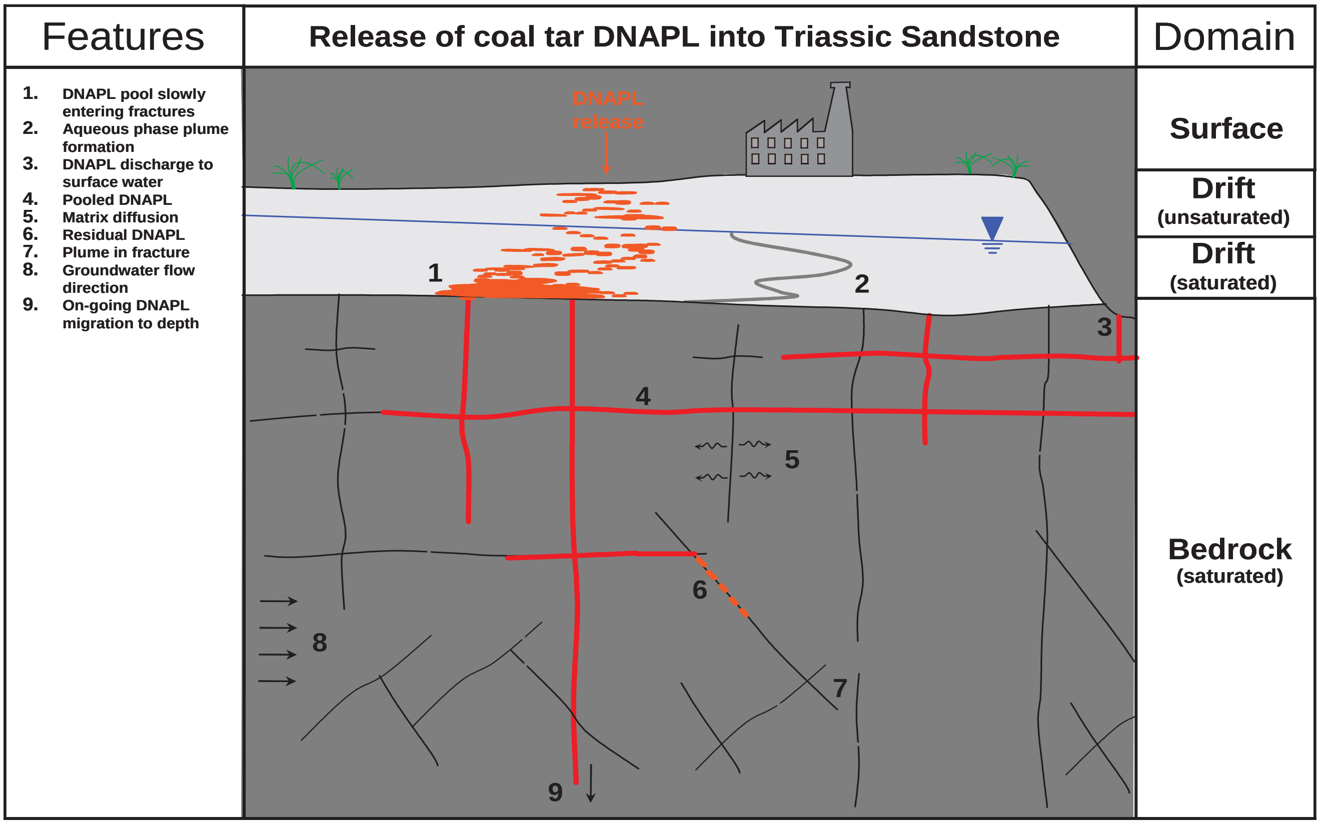

Fig.5: Release of coal tar DNAPL into Triassic Sandstone