DENSE NON-AQUEOUS PHASE LIQUID (DNAPL)

WHAT IS DNAPL?

Orica has been investigating dense non-aqueous phase liquid (DNAPL) source areas on the Botany site since they were first identified in the Stage 2 Environmental Investigations in 1993-1996. These are locations where chlorinated hydrocarbons (CHCs) have entered the aquifer and, as they slowly dissolve, act as a source of contamination in the groundwater. These substances are often collectively referred to as DNAPL because they usually enter the aquifer as a separate-phase organic liquid that is heavier than the groundwater.

How DNAPL Behaves Underground

DNAPLs are generally not very soluble in water, so tend to persist as separate-phase, slowly-dissolving liquids for a long time. Being heavier than water, they also tend to percolate downwards through the aquifer until they reach layers that have low permeability (like peat or clay) or that are impervious (like sandstone). They then tend to spread out across these layers as a thin pool, and may also slowly work their way into the low permeability layers (a process called sorption) or into cracks (fractures) in otherwise impervious layers.

DNAPL movement through an aquifer is driven predominantly by gravity; groundwater flow has relatively little influence. As DNAPL moves through an aquifer it tends to leave a trail, or residue, of tiny droplets sandwiched between soil particles (these discrete, often elongated and contorted droplets are called ganglia) and can be adsorbed onto the surfaces of individual soil particles. Large pools of free-flowing DNAPL are relatively uncommon.

How Does DNAPL Get Underground?

There are many different ways in which DNAPL can enter an aquifer. Some of the more common means include leakage from tanks and drums onto unsealed ground or through cracks or joints in pavement, leakage from effluent pits and drain lines, leakage from pipes, spills from disconnected hoses, unlined drains, soakaway ponds and disposal onto unpaved surfaces. The nature of the release - large or small, over a short or long period of time, above or below ground - and the physical properties of the DNAPL will influence how it moves through the aquifer and how it slowly contaminates the groundwater.

DNAPL at Botany

CHC contaminants at the Botany site (including the Botany Industrial Park [BIP] and Orica Southlands) are present as DNAPL (free-phase), dissolved in groundwater (dissolved phase), adsorbed onto aquifer grains (sorbed phase) and diffused into
low permeability areas. When DNAPL dissolves into the groundwater it forms plumes. Plumes are relatively easier to find/locate compared to DNAPL/source areas. Adjacent is a conceptual image of a cross section of the area depicting the transportation and transformation of DNAPL (adapted from Figure 7.2 of Conceptual Site Model Report). Orica extracts groundwater plumes (dissolved phase DNAPL) for treatment at the Groundwater Treatment Plant and contains residual or free-phase DNAPL (source areas), sorbed phase and diffused phase masses through hydraulic containment using three extraction well fields.

Right: Conceptual cross section of Botany area showing transportation and transformation of DNAPL from its source area (free-phase DNAPL) through to containment via the extraction well systems

Investigating DNAPL Source Areas

The 2003 Notice of Clean Up Action (NCUA) required Orica to identify DNAPL source areas to the maximum extent practicable. Orica conducted a series of investigations in 2004, 2005 and 2006 and identified nine inferred DNAPL source areas. Each source area is different in composition, location and depth distribution, suggesting different origins. It is very difficult to accurately delineate and characterise these source areas. Some have only been inferred from downgradient groundwater concentrations/groundwater plumes (i.e., groundwater contamination implies that there must be a source area) even though extensive investigations in the inferred source area have failed to reveal any traces of DNAPL. There have only been two or three locations where free-phase DNAPL has actually been found. The reports on these investigations can be accessed at DNAPL Investigations. Further investigations are to be undertaken as required to support the implementation of source area remediation/removal if practicable.

The diagram on the left shows the distribution of the nine identified inferred DNAPL source areas beneath the BIP and Southlands. These DNAPL source areas create contaminant groundwater plumes in the south-westerly direction according to the direction of the groundwater flow.

Most of these DNAPL source areas are found beneath or near to areas that were formerly chemical drum storages, chemical storage tanks, or former manufacturing plants. The plants operated during the 1940s to 1990s. Orica has grouped the DNAPL source areas into three geographical groups, namely, the Northern Plumes, Central Plume and Southern Plumes.
Northern Plumes source areas (N1-N5): Investigations have confirmed that the major dissolved phase contamination in the Northern Plumes are 1,2-dichloroethane (EDC) and carbon tetrachloride (CTC). The predominantly EDC plumes (composed of CHC waste mixtures known as EDC Lights and EDC Heavies from the former Vinyls Plant) are inferred to be derived from the storage of drummed EDC wastes in former open storage areas. These plumes could also be associated with the Central Plume (see below) that might have once extended significantly further to the north due to historic groundwater extraction to the north-west of BIP. The N4 source area is mainly comprised of CTC, which is likely to be related to a former bulk storage tank farm.

Central Plume source area (C1): The Central Plume is identified in the centre of the BIP. The source area is believed to have originated from leaks from former EDC Storage Tanks that were operational from 1965 to 2000, and from the Vinyls Plant (operational 1965-1996 [vinyl chloride] and 1965-1998 [EDC]).

Southern Plumes (S1-S3): Chemicals that escaped into the environment during the operation of the former Solvents Plant (operational 1963-1991; demolished in 1999/2000) and former Trichloroethene (TCE) Plant (operational 1948-1976; demolished in 1994) are the likely sources of the contamination in the area of the Southern Plumes. Major components of DNAPL located in the area are tetrachloroethene (PCE), CTC, and TCE.

Distribution of Dissolved DNAPL in Groundwater

Because the identified source areas are different in composition, location and depth distribution, the groundwater plumes that are formed by these source areas are also different in composition, location and depth distribution. The movement of these plumes has been stabilised by effective hydraulic containment. Diagrams on the inferred distribution of dissolved DNAPL plumes in the deep aquifer for each of the major CHCs are published annually as an attachment to the November Progress Reports. When viewing these contour maps it is important to note that they only indicate the spatial distribution of DNAPL plumes, showing the highest concentration across all depths at any single location.

REMEDIATION AND REMOVAL OF DNAPL

Investigating Best Available Remediation Technology and Its Application

The 2003 NCUA required Orica to remove identified DNAPL, and one of the conditions stated that ‘Orica must consider best practice technology in the remediation of DNAPL and groundwater containing dissolved phase contaminants, through:

1. continued review of relevant, emerging technologies; and
2. ongoing investigation of the practical application and effectiveness of these technologies in relation to the remediation.’

In May 2005, further information was gathered from the USA and Canada to assess available and emerging DNAPL remedial technologies. Outcomes from the information gathering and assessment exercise was compiled into a report and submitted to the former NSW Department of Environment and Conservation (DEC, now the NSW EPA). A key document considered in the preparation of this report was the USEPA Report The DNAPL Remediation Challenge: Is There A Case For Source Depletion? (2003).

Following the submission of the report to the DEC, Orica narrowed down the expansive list of DNAPL removal technologies that were contained within the report to a shortlist that appeared to have potential application to the BIP DNAPL source areas. Ongoing research, evaluations and development efforts were then undertaken to assess best available remediation technology.

By early 2007 Orica was conducting laboratory trials and starting to plan for field trials on DNAPL treatment using some of the most attractive technologies. Following the first Botany Groundwater Strategy Review, which was completed in 2008, development of these trials was discontinued.

The second Botany Groundwater Strategy Review was conducted in February 2011. With respect to DNAPL source area removal, the 2011 Groundwater Strategy Review did not identify any technologies that warranted further assessment.
The same conclusion with regard to DNAPL was reached at the third Botany Groundwater Strategy Review conducted in February 2014.

Ongoing Review of Relevant and Emerging Technologies

Orica continues to review developments in remedial technology and techniques for DNAPL, sorbed mass and dissolved phase treatment and their practical application to the project. An annual report on the review is published at the end of February as Attachment B to the Groundwater Cleanup Plan Progress Reports.

Previously shortlisted commercially available technologies/techniques:

- **Direct Recovery** – pumping small volumes of separate-phase DNAPL out of wells. Field trials have been conducted with very limited success.
- **Hydraulic Displacement** – injecting water into the aquifer to flush DNAPL from the soil formation and increase solubilisation. A desktop evaluation by environmental consultants in Canada concluded that this technology was not worth pursuing at BIP.
- **In Situ Chemical Oxidation (ISCO)** – injecting chemicals into the aquifer to oxidise (react with) and destroy the DNAPL. Extensive laboratory trials in the US using BIP soil and groundwater was undertaken to evaluate surfactant-enhanced ISCO (S-ISCO®), using sodium persulphate as the chemical oxidant. pH activation was identified as the preferred method for initiating oxidation, however the effectiveness of the oxidant was adversely affected by the range of contaminants and the surfactant addition. A detailed technology review and cost estimate (as part of the Groundwater Strategy Review in 2008) concluded that ISCO was not appropriate technology for cleaning up DNAPL at BIP.
- **Direct Thermal Treatment (DTT)** – heating the aquifer with injected steam and/or electrically heated wells to vaporise the DNAPL and then collect the vapours for destruction in the GTP. A detailed design for a large field trial was developed for one DNAPL source area, but the Groundwater Strategy Review in 2008 concluded that the deployment of in situ thermal treatment was limited by extensive above and below ground infrastructure, the cost was prohibitive, and no net environmental benefit would be achieved by thermally removing DNAPL.

Additional emerging technologies/techniques that have been assessed to date:

- **Enrichment Culture for Bioaugmentation** – injecting special bacteria (grown from biomass collected from Orica Southlands following the previous bioremediation field trials there) to speed up the rate of naturally occurring biological destruction of contaminants dissolved in the groundwater. Three very effective cultures for accelerating the biological degradation of high concentrations of specific chlorinated hydrocarbons were isolated from the Botany aquifer and developed. Field trials have indicated that the cultures can be effectively deployed and have a lasting impact on the microbial population in the aquifer.
- **Nano-scale Zero Valent Iron** – this material is very fine particles of iron, which can be injected into the aquifer (to form a flow-through reactive barrier to destroy contaminants dissolved in the groundwater) or directly into the DNAPL source area to react with and destroy the DNAPL compounds. A unique process for producing nano-scale particles of iron was developed in a collaborative research project, and was patented. Ownership of the patent was transferred to Orica in 2012. Orica continues to be involved in research projects employing nano-scale iron technology.
- **Electrokinetics** – the use of electrical current to manipulate the movement of chemical reactants (e.g., oxidising agents or nano-scale zero valent iron) into targeted areas of the aquifer (e.g., where contaminants might have accumulated) to increase the effectiveness of these reactants. Orica co-funded research into this technology, which clearly demonstrated its effectiveness at laboratory scale.
NEXT STEPS
Following the 2007/2008 Botany Groundwater Strategy Reviews, Orica decided not to test and trial DNAPL remediation technologies until a technology is identified that can be effectively and practically applied at Botany. This position was re-affirmed following the 2011 and 2014 Groundwater Strategy Review Workshops.
Orica will continue to review developments in remediation technologies and techniques for DNAPL treatment. Orica is continuing to operate the hydraulic containment system to prevent further migration of groundwater plumes reaching Botany Bay and to maintain any risks to human health or the environment at acceptable levels.