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ORICA BOTANY GROUNDWATER PROJECT

DNAPL AND GROUNDWATER REMEDIATION TECHNOLOGY ANNUAL REVIEW NO. 3

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REVISION 0

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1 INTRODUCTION

Under the subheading of Best Practice Technology, Condition 7E of Notice of Clean Up Action (NCUA) No. 1030326 (issued under Variation of Notice of Clean-Up Action no. 1052882) states

> "Orica must consider best practice technology in the remediation of DNAPL and groundwater containing dissolved phase contaminants, through:
>
> (a) continued review of relevant, emerging technologies; and
>
> (b) ongoing investigation of the practical application and effectiveness of these technologies in relation to the remediation."

Condition 7F of the NCUA additionally states

> "Orica must provide an annual written report to the EPA on the progress of actions required by Condition 7E, with the first report to be provided to the EPA no later than 28-Feb-2006."

In early December 2005 Orica submitted to the then Department of Environment and Conservation (DEC) a copy of its report on DNAPL Source Area Remediation Technical Mission, USA and Canada, May 2005 (Orica, 2005). That report constituted the first report issued under Condition 7F.

The first annual review of Orica's progress against Condition 7E issued under Condition 7F was submitted to the Department of Environment and Climate Change (DECC) on 28 February 2007 (Orica, 2007). The second annual review was submitted on 29 February 2008 (Orica, 2008). This report constitutes the third annual report. Being an update report, it does not provide as much background information as provided in the 2007 report. In addition to this, brief progress summaries have been included in the quarterly Groundwater Cleanup Plan Progress Reports issued under Condition 4BA of the NCUA.

This report discusses cleanup technologies that are currently being employed in full-scale applications (Section 2), technologies that are currently under review by way of desktop evaluations through to pilot-scale or field trials (Section 3), and ongoing investigation Orica is undertaking into innovative applications of existing technologies and emerging technologies (Section 4).

2 TECHNOLOGIES CURRENTLY IN USE

2.1 Groundwater

The Orica Botany Groundwater Cleanup is being achieved by groundwater extraction along three containment lines and ex situ treatment of the water in the Groundwater Treatment Plant (GTP).

Commissioning of the GTP commenced in late 2005, beginning with towns water and groundwater was first introduced into the plant in January 2006. The principal unit processes employed in the plant at the time were:

- Air stripping for removal of volatile organic compounds (VOCs);

- Thermal oxidation of VOCs, waste heat recovery and gas scrubbing;
- Actiflo® based iron and aluminium removal;
- Sand filtration for suspended solids removal;
- Activated carbon digestion/adsorption for non-volatile organics removal;
- Sand filtration for suspended solids removal;
- Cartridge filtration for finer solids removal; and
- Reverse osmosis (RO) for dissolved salts rejection.

The GTP was designed to treat the groundwater extracted in the three hydraulic containment lines in a manner consistent with best practice. The Joint Determining Authority Report for the Botany Groundwater Cleanup Project (DEC et al., 2005), which was prepared to evaluate the Environmental Impact Statement (EIS) Orica had submitted for the GTP and ancillary equipment, stated:

> "This determination concludes that Orica's preferred strategy for the collection and treatment of the contaminated groundwater is consistent with accepted best practice and satisfies best international air emission standards. It also maximises the quantity of extracted water that can be recycled for industrial use significantly reducing the demand on potable supplies."

No technologies have been subsequently found to better achieve 'best practice'. However, some refinements to the GTP processes have been made.

It was reported in last year's annual report (Orica, 2008) several trials had been conducted during 2007 (see Section 3.2) and a number of modifications to improve operating conditions and plant configurations had been undertaken. At the time of preparing that report, five Granulated Activated Carbon (GAC) filters were being converted into five Biological Aerated Filters (BAFs) to remove readily biodegradable organics and thereby reduce the potential for biological fouling and improve product water quality. The BAFs have been commissioned after an extended trial period to evaluate flow orientation and media size.

In the previous reporting period monochloramine (NH_2Cl) dosing into RO feedwater had been included to mitigate biological fouling in cartridge filters and RO membranes. High concentrations of monochloramine proved to be effective at limiting biological fouling. However, as the monochloramine was found to pass into the RO permeate, a dechlorination system was installed to remove the monochloramine from the treated water stream before its discharge to the environment. The ammonia generated by dechlorination is the subject of a Pollution Reduction Program. The principal aim of the program is to reduce monochloramine addition into the RO feed, but still provide sufficient residue to mitigate biofouling.

The BAFs mentioned above were installed as a primary initiative to reduce monochloramine dosing by removing the organic material which feeds the biota.

Phosphoric acid dosing at the inlet to the BAFs was required to produce enough biomass to consume the readily biodegradable carbon in the feedwater. The success has allowed a significant reduction in the addition of monochloramine, and in conjunction with selective replacement of worn RO membranes has allowed the plant to achieve very low Total Organic Carbon (TOC) concentrations in the treated water. Strategies for maintaining biomass viability during plant outages (e.g., annual shutdown) have been developed.

There have also been a number of improvements made to the groundwater extraction infrastructure to increase the reliability of hydraulic containment:

- As has been reported previously (Orica, 2008), biological fouling and corrosion of extraction pipework – particularly associated with the shallow wells at Foreshore Road (the Secondary Containment Area) – have been observed. The resultant slimes had been causing flow restrictions and pitting corrosion in header pipes beneath the biological build-up. Sections of carbon steel header pipes were replaced with stainless steel. In this reporting period further improvements have been made to the piping in the Foreshore Road pits.
- Adjustments have been made to the control parameters of a number of pumps in the SCA. The outcome has been a more continuous flow of groundwater extraction and improved containment, rather than sporadic flow associated with on/off operation of the pumps.

At the time of writing, a total of 642 tonnes of CHCs had been destroyed in the thermal oxidiser.

2.2 DNAPL

No full-scale DNAPL removal technologies are currently in use at the Botany Industrial Park (BIP).

3 TECHNOLOGIES UNDER EVALUATION

This section describes research and development efforts that have been undertaken within the last twelve months. However the strategic direction for technology evaluation and implementation (described below in Section 3.1) has been closely considered over this reporting period, and has brought about changes to the range of technologies being evaluated.

3.1 Botany Groundwater Strategy Review

In early 2007, the Orica Botany Groundwater Project team considered that a fundamental review of remediation strategy was warranted in the context of:

- the increasing reliability of the hydraulic containment and increasing throughput of the GTP;
- the imminent likelihood of commitment of significant resources to field trials of the most attractive DNAPL technologies;
- the imminent release of the (then draft) Groundwater Guidelines (DECC, 2007);
- the age of the NCUA, the likelihood that at some stage DECC would seek to review the regulatory instrument, and the need to have a remediation strategy

that informed discussion with DECC around the renewal of the regulatory instrument;

- the need for an improved understanding of the scale of the Botany groundwater issues and their potential longevity to better inform decisions about remedial approaches; and
- the ongoing debate in the North American contaminated land industry about the fundamental worth of attempting DNAPL source depletion for large and complex site issues (versus management of risks associated with those source areas). This was the subject of a vigorous panel discussion at the Battelle conference in May 2006.

The following tasks were undertaken in 2007 to more completely inform a discussion of remediation strategy:

- URS Australia Pty Ltd was commissioned to provide an estimate of the CHC contaminant mass in all phases (free phase [DNAPL], sorbed and dissolved phases) within the Botany Sands Aquifer (URS 2007a). In summary, the mass estimates are:
    - Dissolved phase: 1,500 t
    - Sorbed phase: 3,000 t
    - DNAPL phase: 10,000 t (9,000 t of selected CHCs; 1,000 t of other CHCs)
- In order to have a meaningful appreciation of the potential longevity of the groundwater issues, it was decided that a solute transport model should be constructed for selected representative CHCs as solutes. A solute transport model is a combined hydraulic/geochemical model of the dynamic response of an individual solute (component of interest, in this case representative CHCs) within the specific groundwater environment modelled. Al Laase of A.D. Laase Hydrologic Consulting was engaged to undertake the solute transport modelling (AD Laase Hydrologic Consulting, November 2007).

  EDC and CTC were selected as representative solutes, EDC as a ubiquitous solute of relatively high DNAPL solubility and high mobility (slightly retarded plumes), and CTC as a representative volatile CHC solute with low DNAPL solubility and low mobility (high retardation).

  In summary, the solute transport modelling showed that:
    - The EDC cleanup is modelled, with some caveats regarding bleeding from peat layers and dilute solute behaviour, to be complete to a concentration of 0.1 mg/L by 2055 using the existing extraction well field design. This is irrespective of source zone treatment. Given DNAPL source mass is estimated to be exhausted by 2016, this implies about 40 years are required for desorption-controlled aquifer cleanup for EDC; and
    - Even though CTC source dissolution is modelled to be complete by around 2060 (and earlier with different levels of source treatment),

the CTC desorption controlled cleanup is significantly longer than for EDC using the existing extraction well field design, requiring (with the same caveats as above regarding bleeding from peat layers and dilute solute behaviour) at least 300 years after DNAPL dissolution to achieve a concentration of 0.1 mg/L throughout the aquifer.

- URS Australia was commissioned to compile a Conceptual Site Model (CSM) report (URS 2007b). This report has manifold purposes, including:
    - synthesis of the enormous quantity of data, reports and other interpretive information that has been progressively developed for the Botany Groundwater Project. Effectively there has been no “single” document that provides a current summary understanding of all issues since the Stage 2 Survey in 1996 (Woodward-Clyde, 2006);
    - providing a single document which could be used to brief workshop participants, some of whom had no prior association with the Botany groundwater issue;
    - providing a document which would also potentially be of benefit to DECC, other regulators and the community; and
    - providing a document that could be reasonably readily revised periodically to incorporate new findings and developments, and maintain a current, relevant CSM.

Previous submissions to the EPA have detailed the results of overseas fact-finding missions used to identify remedial technologies and techniques that might be practicably applied for the Botany Groundwater Project. The majority of the expertise in application of these remedial technologies is located in North America.

This culminated in a technical workshop held at Botany in late 2007 in which several North American and local experts were invited to discuss the benefits and practicalities of implementing various remedial technologies to Orica’s groundwater plumes and plume source areas.

Workshop participants comprised:

- Overseas participants – selected from Orica’s knowledge of the North American remediation field (obtained directly from Battelle conferences, and inferentially from industry knowledge and networking). Generally Orica wanted well-respected industry experts, who were familiar with large contaminated site challenges, but people not aligned with a single remedial technology (and certainly with no significant commercial interests in a single remediation technology). Orica also wanted a blend of people who had some “Botany background” and those with no previous experience (i.e., to provide “fresh eyes” on the Botany groundwater issues).
- Local participants – generally those with a significant consulting association with the project and a sound, detailed understanding of the project and all its facets.

- Orica participants – from Orica's senior management and project management with responsibility for the Botany Groundwater Project.
- Dr Garry Clews, facilitator – a former Orica employee who left Orica in late 2002.

Orica's objectives for the workshop are summarised below:

1) A comprehensive independent review of the current remedial strategy;
2) An improved understanding of the DNAPL source area remediation issues, considering:
    i. What extent of DNAPL source area depletion is really possible in the Botany geological and site setting with current likely technologies;
    ii. Whether it is likely there are significant new and more cost-effective technologies that will evolve;
    iii. Other than reduced cleanup duration and costs, what the other drivers for DNAPL depletion (health and environmental risks, regulatory, financial assurance) are; and
    iv. Whether DNAPL source area depletion makes sense if risks are well managed, whilst appraising development of more cost-effective technologies;
3) Other remedial technologies or strategies that might address DNAPL, sorbed mass and dissolved mass more cost effectively than the current remediation strategy; and
4) Depending on the outcome of 3), synthesis of a short-list of alternative integrated remediation strategies for further evaluation.

The remediation strategy workshop was conducted at Botany on 11 to 13 December 2007. The principal outcomes, which were presented to DECC and the Community Liaison Committee (CLC) in September 2008, were:

- With some suggestions for improvements, the key workshop input documents were endorsed.
- The workshop participants were impressed at the scale of the Botany groundwater issue and just as impressed with the scale of the response to the problem, i.e., the scale of the extraction and treatment plant. It was felt that this investment (and its ongoing operating costs) needed to be acknowledged in the debate about the merits of DNAPL source depletion, as well. The monitoring of, and improvements to inputs that affect human health and environmental receptor risk were also noted.
- The workshop endorsed Orica's short-listed DNAPL depletion technologies, noting that complete DNAPL source area depletion would not be practicably achievable due to access issues, scale and costs, and limited quantifiable benefits to overall cleanup duration, which based on modelling and participants judgement, will be a process limited by sorbed mass back-diffusion.
- A key outcome was that the potential costs and limitations of full-scale application of Direct Thermal Treatment (DTT, see Section 3.3) and In Situ

Chemical Oxidation (ISCO) with sodium persulfate (see Section 3.3) should be understood to better inform the "practicability" discussion.

Accordingly Orica engaged Dr Mike Kavanaugh of Malcolm Pirnie, Inc to review relevant case studies of application of DTT and ISCO with base catalysed sodium persulfate, develop conceptual designs and cost estimates for full-scale application, including consideration of the limitations (and advantages as applicable) of application of these remedies at Botany.

The assessment which has also been presented to DECC and the CLC in September 2008, indicated that:

a) DTT is a feasible technology, however would not be able to completely treat all source zones due to significant access constraints. Treatment cost would be of the order of USD 89m (-5/+30%) for gradual treatment of source zones over approximately eleven years for accessible areas. It is noted that this cost estimate is for steam based thermal treatment and would not remediate semi-volatile CHCs in the Southern Plumes source areas; and

b) ISCO with base catalysed persulfate is not a practicable alternative for full-scale DNAPL source zone treatment, with regard to cost (more than USD 300m), efficacy of the remedy (due to difficulties in delivering the oxidant in proximity to DNAPL accumulations) and impacts on the aquifer (e.g., loss of hydraulic conductivity due to mineral precipitation).

Orica has proposed to DECC that this assessment suggests that there are no immediate reasons for DNAPL source depletion, and that the benefits of attempting DNAPL source depletion at Botany using DTT are unquantifiable and likely to be marginal in terms of the long-term clean up of the aquifer, which will be controlled by desorption effects for the low solubility and more highly sorbed volatile CHCs.

Orica has proposed the following remediation strategy for future management of Botany groundwater contamination:

1) Ongoing management of groundwater contamination to ensure human health and environmental receptor risks are acceptable. This would be achieved through extensive ongoing monitoring of the relevant segments of the environment potentially impacted by contaminated groundwater;

2) Continue to optimise the operation of the hydraulic containment lines and GTP for protection of critical human health and environmental exposures and for gradual clean up of contamination, where containment lines are downgradient of source areas;

3) Installation of a spear point system along Springvale Drain in Southlands that will be implemented should the proposed development of the property proceed;

4) Ongoing review of developments in remedial technology and techniques for DNAPL, sorbed mass and dissolved phase treatment and their practical applicability to the Botany Groundwater Project.

Orica believes this approach is consistent with the relevant sections of the Groundwater Guidelines (DECC, 2007).

Orica also believes that the hydraulic containment system and GTP are having significant beneficial effects, not just in substantial dissolved phase mass removal from the aquifer, but more importantly in sustainable major improvements to surface water quality in Springvale Drain, Floodvale Drain and in Penrhyn Estuary.

Orica will continue to investigate and monitor inputs that drive assessment of human health and ecological risk, and will continue to review available technologies for application to DNAPL, sorbed and dissolved phase treatment. Orica shall convene a strategy review process every three years to which it will invite a minimum of three overseas experts in the field who are familiar with the Botany site. The review process will involve consideration by the experts of the annual reports prepared by Orica and worldwide developments in technology, in order to assess whether any current or emerging technologies (including development in application techniques of a technology) are likely (individually or in combination) to provide a practicable solution and justify the conduct of field trials of those technologies. Appropriate representatives of the Independent Monitoring Committee (IMC) and DECC would be invited to attend any workshop with the overseas experts. Should the consensus of the participating experts recommend a practicable solution be trialled, Orica will accept such recommendation.

3.2 Groundwater

Since start-up of the GTP a number of operational and maintenance issues have adversely affected the reliable operation of the groundwater extraction and treatment processes. A number of trials have been undertaken to address these issues.

- **Improving reliability of hydraulic containment**

  In addition to the completed program to replace carbon steel header pipes with stainless steel sections (described in Section 2.1) to address the biological fouling and corrosion of extraction pipework at the SCA, other work has been done to mitigate the fouling in the header pipe conveying the SCA groundwater to the GTP. Mixing water from different extraction zones in the above ground pipework on Southlands – reported in the previous annual report (Orica, 2008) – is still being trialled.

  It was also reported previously (Orica, 2008) that some of the multistage centrifugal bore pumps at the SCA were fouling with biological material. A positive displacement pump (brand name Mono) and well-screen sleeves are being trialled to address this. Two additional Mono pumps were installed in 2008. The three pumps are showing promising performance and further evaluation is needed. Well sleeving to exclude air ingress into the upper sections of the extraction well screens and subsequent oxygenation of the extracted groundwater was trialled, but found to be ineffective in reducing fouling and improving extraction reliability.

  Furthermore, as the capacity of the GTP increases, Orica proposes to maximise the volume of water that can be sustainably extracted from the aquifer. This will provide maximal remedial effects on Penrhyn Estuary by further decreasing the influx of groundwater into Springvale and Floodvale Drains. This is the subject of discussions with the Department of Water and Energy (DWE)

- **Reducing air stripper fouling**

  As reported in the previous annual report (Orica, 2008), two modes of fouling have been observed within the GTP air stripping units – inorganic (metal precipitation) and biological, which are best controlled with low and higher groundwater pH, respectively. Operation at pH 4.9 best mitigates biological fouling and inorganic fouling is tolerable. Trials involving the sterilising agent chlorine dioxide were found to provide benefit in mitigating fungal growth and extending intervals between manual cleaning of air stripping units. A permanent dosing system is being designed.

- **Improving Actiflo performance**

  Efficient operation of the reverse osmosis (RO) units (to maximise time between cleaning) requires low iron and aluminium concentrations. Trials had been undertaken to improve the Actiflo operation by optimising operating pH and feed alkalinity (Orica, 2008) and have increased understanding of the Actiflo process considerably. Investigation into the impact of feedwater pH and redox potential (influenced by pH and chlorine dioxide) on Actiflo performance – commenced in the previous reporting period (Orica, 2008). Due to operation issues with the hired chlorine dioxide system, the evaluation is continuing. The learnings to date indicate that chlorine dioxide and pH 4.2-4.6 improve Actiflo performance.

- **Removal of readily biodegradable Total Organic Carbon**

  The BAFs and monochloramine dosing (and subsequent dechlorination system to remove monochloramine from Treated Water discharge to the environment) are described in Section 2.1 and in the previous annual report (Orica, 2008).

- **Cartridge filter cleaning**

  Cartridge filter life has been unacceptably short – one to two weeks, rather than three months – due to residual iron and the susceptibility of the filter structure to flow restrictions by even small amounts of biofilms. An Orica proprietary cleaning solution containing nitric and phosphoric acids has been inconsistent with its ability to ‘clean’ cartridges for reuse. Generally the regeneration is temporary and is used in the event that there are delays in deliveries of new cartridge filters. Evaluation of alternative cartridge filters (including a depth filter) is about to commence.

- **Ammonia pollution reduction program**

  As noted above and in Section 2.1, dechlorination of the discharge water is required to degrade the monochloramine needed for biofouling control in the ROs. Sodium bisulfite addition degrades monochloramine, producing ammonia. Consistent with the Pollution Reduction Program (PRP), Orica has investigated technologies to reduce the ammonia in discharge water. Previously reported trials (Orica, 2008) involving Centaur Catalytic Adsorptive Carbon and other carbons revealed activated carbon provided minimal benefit in reducing ammonia. Most of the benefit has come from TOC reduction (e.g., in the BAFs), which has allowed significantly less monochloramine to be used, and consequently less ammonia generated during dechlorination. There is ammonia in the groundwater feed to the GTP, so the requirements of the PRP have not quite been achieved yet.

- **Refractory investigations**

  During each annual shutdown, repairs have to be made to the refractory in the combustion chamber of the thermal oxidiser. Investigations into the reason for refractory damage have been done using experts from UNSW. It is possible that minute quantities of salts (e.g., sodium) carried over from the air strippers are impacting on the brickwork. These salts act as a flux, to weaken the refractory. A suitable refractory material that is resistant to this attack is not available according to refractory providers. Actions to reduce droplet carryover from the air stripping units have included cleaning of demisters, replacements of demisters with finer sections and improved installation to restrict demister movement.

Outside of the GTP further work has continued to investigate and develop techniques and technologies to remediate groundwater.

- **Enrichment culture for bioaugmentation in groundwater**
  The previous annual reports (Orica, 2007 and 2008) described developmental work performed by the Centre for Marine BioInnovation (CMB – formerly the Centre for Marine Biofouling and BioInnovation) at the University of NSW (UNSW) that is intended to assist with groundwater treatment in the future. This ongoing work is focused on developing enrichment cultures derived from microbial consortia recovered from the bioremediation field trials conducted in Orica Southlands in 2004-2005. The enrichment cultures are intended to enable augmentation of full-scale bioremediation should it be employed as part of the Orica Botany Groundwater Cleanup Project. The enrichment work commenced in January 2006. It consists of seven phases:

  1. Biomass accumulation using confirmed enrichment cultures;
  2. Compositional community characterisation using DNA extracts;
  3. Activity characterisation of active cultures, including evaluation of their metabolic versatility with a range of persistent organic pollutants (POPs);
  4. Scale up active cultures;
  5. Novel stable isotope probing development (research and development work being done by the CMBB funded by an ARC Linkage Grant);
  6. Functional community characterisation using ^{13}C labelled CO_2 and ^{13}C labelled methane; and
  7. Field application using the existing Area A (shallow aquifer) bioremediation field trial infrastructure.

Two different cultures are being developed – one that is capable of degrading high concentrations (around 1,000 mg/L) of ethylene dichloride (EDC or 1,2-dichloroethane), the other for degrading chloroform, which is a biocide, at concentrations that are typically inhibitory to biodegradation (i.e., >5 mg/L).

In the previous annual report (Orica, 2008) it was reported that EDC-degrading cultures had been isolated and been used to inoculate microcosms with varying EDC concentrations and pH levels. A microbial community fingerprinting technique had been employed to demonstrate that pH influences the composition of the cultures. In this reporting period an additional fingerprinting technique – using filtration – was used to size fractionate an active EDC degrading culture. One fraction of free-living bacteria (i.e., 0.8 µm filtrate) was found to harbour 45% of the activity of EDC degradation and ethene production. Although this was unexpected, the relative mobility of microorganisms has a great influence on processes related to subsurface contaminant fate and transport and therefore is crucial for bioremediation strategies. The CMB expect to combine the reliability of attached biomass and mobility of free-living biomass to increase the chances of successful bioremediation.

A clone library has been constructed to characterise the composition of the active biomass. The clone library detected hydrogenic bacteria such as *Desulfovibrio spp.* or *Clostridium spp.* at high relative abundance and bacteria that can potentially use the hydrogen to dechlorinate EDC such as *Desulfitobacterium* at low abundance. *Desulfitobacterium* was found in attached biomass in cultures from pH 4 to pH 7, and was also found in the free-living biomass at pH 5 and pH 6, which is consistent with the results of the size fractionation.

The CMB has also explored the activity of the EDC degrading culture in the presence of different chloroform concentrations. Besides the low pH of the Botany Sands Aquifer, chloroform in excess of 10 mg/L represents the next biggest challenge in the successful deployment of the cultures. It was found that chloroform partially inhibited the activity of both the aggregated and free-living biomass from the EDC degrading culture at 5 mg/L.

Having successfully isolated cultures tolerant of elevated EDC concentrations, attention has turned to scaling up the quantities of EDC degrading culture. Additional groundwater from the BIP is being used to develop nine 10 L cultures.

The original enrichment cultures for EDC degrading activity established at the beginning of the project have been maintained at low pH (4.5 to 5) and room temperature under anaerobic conditions in the presence of 250 mg/L EDC and 400 mg/L of ethanol. Until now, occasional monitoring for ethene production indicated that the culture was not active. Despite this lack of activity for over 200 days, by November 2008 this culture had begun showing a modest activity at low pH (1.4 mg/L/day). This is significant because this culture is likely to be effective in the native groundwater without any pH adjustment. This culture will be monitored more frequently with the aim of confirming the activity and generating additional culture volume. A mixture of this culture and the cultures currently being scaled up is likely to efficiently degrade EDC over a large range of pH values.

It was previously reported (Orica, 2008) that enrichment cultures at neutral pH containing 0.1 mg/L of chloroform have shown convincing chloroform degrading activity after 120 days of incubation. In this reporting period chloroform enrichment showed even more encouraging chloroform degrading activity at up to 1988 µg/L/day with the chloroform appearing to degrade all the way to methane. Although concentrations of up to 0.5 mg/L chloroform have been fed to the microcosms, work to investigate the maximum chloroform concentration at which these cultures will remain active is yet to be completed.

A concurrent enrichment project was also initiated in April 2007 to develop a culture that could be capable of degrading DNAPL (see Section 3.3 below). This project was discontinued in September 2008 as it was found that the culture was not significantly different from the EDC-degrading culture and it was metabolically inactive in the presence of tetrachloroethene (PCE) and carbon tetrachloride (CTC) at saturating concentrations.

- **Nano-Scale Zero Valent Iron**
  It was previously reported (Orica, 2007 and 2008) that Orica was working with UNSW to develop a method to produce commercially viable grades and quantities of nano-scale zero valent iron (nZVI), which can be used for dechlorination of most dissolved phase aliphatic CHCs (EDC and dichloromethane – DCM or methylene chloride – being, however, notable exceptions). This work follows on from a project conducted by the former Cooperative Research Centre (CRC) for Waste Management and Pollution Control, in which Orica was a partner, that developed a low-cost method to produce high-quality nZVI. Orica has acquired the exclusive rights to the intellectual property.

  In this reporting period the UNSW researchers demonstrated continuous production on nZVI at rates of up to one kilogram per hour. They resultant nZVI has similar reactivity to that of more-expensively produced commercially available nZVI. This milestone marked the culmination of the Australian Research Council (ARC) Linkage-funded project.

  A bid made in mid 2008 for further ARC Linkage funding was unsuccessful. A revised bid is expected to be made in the first half of 2009. In the meantime, though, no further work has been undertaken.

3.3 DNAPL

The primary focus of cleanup technologies evaluation in the last twelve months has continued to be on those for removing DNAPL.

- **Direct Recovery**
  This technique of DNAPL source area removal is not commonly applicable as DNAPL is more typically found in the form of ganglia – mass entrapped in the aquifer matrix due to capillary forces – rather than pooled mass.

Investigations at Botany since 1989 have rarely detected free phase DNAPL, and not in recoverable quantities. However, in October 2005 free phase DNAPL was found in one of the newly-installed monitoring wells on the BIP to monitor hydraulic containment at the southern end of the BIP containment line, about 100 m to the north-west of the former Solvents Plant. An eight-week trial conducted by URS Australia Pty Ltd (URS) to manually gauge and bail out DNAPL from MWD16S, MWD16I and MWD16D in July and August 2006 found that up to 3 litres of DNAPL could be recovered on a weekly basis.

Based on the results of the manual recovery trial URS recommended installation and trialling of an automated low flow DNAPL recovery system. These works were originally planned to be installed in 2007. However the trial area is located on land owned and occupied by Qenos, and obtaining approvals for the trial has taken longer than expected. Furthermore, refinement of the trial design has been required to accommodate Qenos's safety and operational requirements.

A Letter of Notification for Category 2 remediation works under State Environmental Planning Policy No 55 - Remediation of Land (SEPP 55) was sent to the City of Botany Bay (CoBB) Council in late February 2009 informing the Council that the low flow DNAPL recovery trials are planned to commence early in the second half of 2009 (following a large maintenance project being undertaken by Qenos in the area). The trials could be implemented sooner if the Qenos maintenance work is delayed for a sufficient period of time.

It is recognised that this technique of DNAPL removal has limited application and, even at MWD16, is not expected to have a long-term impact. Nevertheless, it is a significantly cheaper method of removing a relatively small quantity of DNAPL compared with other approaches.

- **Hydraulic Displacement**
  Also known as water flooding, this approach consists of the injection of water into a source zone to gradually dissolve the DNAPL, with the resultant dissolved phase contaminants being intercepted and extracted at a downgradient hydraulic containment line. The presence of the hydraulic containment lines and GTP on the BIP makes this treatment option more feasible than it might otherwise have been.

  This is not a remedial treatment that is considered to have significant application for the BGP. No further work has been done in relation to hydraulic displacement in this reporting period.

- **In Situ Chemical Oxidation (ISCO)**
  This technique involves the injection of solubilised chemical oxidant into the source zone to chemically destroy the DNAPL in situ. Based on site conditions and oxidant properties, Orica has selected activated sodium persulphate as its preferred oxidant.

  It was previously reported (Orica, 2008) that VeruTEK Technologies, Inc. (based in Connecticut, USA) had been conducting laboratory bench-scale tests to:

- Evaluate the ability of activated persulfate to treat dissolved-phase chemicals of potential concern (COPCs);
- Evaluate the ability of activated persulfate to treat sorbed-phase and DNAPL COPCs;
- Assess and characterise the formation of by-products and the results of native soil interactions with persulfate;
- Quantify the persulfate soil oxidant demand (SOD) for two soil types, 1) sand and 2) peaty material, collected from one location within the S1 source area containing dissolved-phase and DNAPL COPCs; and
- Assess which method of persulfate activation is superior for treatment of COPCs, and identify any other oxidant, activator, and/or co-solvent/surfactants that could be used to enhance treatment. The required methods of persulfate activation to be tested include iron/EDTA-catalysation, heat, and elevated pH.

The laboratory trials had included parallel evaluation of VeruTEK's surfactant/co-solvent product called VeruSOL™, which can be used to enhance the solubilisation and hence oxidation of DNAPL.

The bench-scale testing had incorporated aqueous and soil slurry tests, and column tests using soil, groundwater and DNAPL collected from Southlands within the S1 source area.

It had also been previously reported (Orica, 2008) that Orica had received a draft report from VeruTEK for the completed laboratory bench tests, and that the report had required considerable rework to extract from it overstatement of the performance and merits of VeruSOL™. Unfortunately this redrafting process has been extremely protracted due to personal and commercial reasons, and is only now reaching resolution.

An additional reporting step was included whereby Aquifer Solutions Inc. was engaged to provide an objective interpretative report of the bench trials based on a pared-down factual report from VeruTEK.

Both the draft Aquifer Solutions report and redrafted VeruTEK report have been received by Orica for review. Although some differences in views need to be resolved between the reports, it is expected that they will be able to be issued to DECC soon.

Orica no longer proposes to evaluate ISCO with field trials. The strategy review process (see Section 3.1) concluded that ISCO with base catalysed persulfate is not a practicable option for full-scale DNAPL source zone treatment, with regard to cost, efficacy of the remedy and impacts on the aquifer.

- **Direct Thermal Treatment (DTT)**
  As discussed in the previous annual reports (Orica, 2007 and 2008), Orica had been evaluating the use of direct thermal treatment in DNAPL source zones, particularly with regard to the S2 source area. Thermal techniques are generally predictable, reliable and robust in low flow aquifers, however are generally the most costly option. Based on the outcomes of the DNAPL Technical Mission in 2005 (Orica, 2005), a combination of steam enhanced extraction (SEE, possibly coupled with air co-injection to mitigate against condensation and mobilisation of NAPL at the edges of the heated zone) and thermal conductive heating (TCH, employing electrically heated wells) was identified as the most promising means of applying the technology in the targeted area. TerraTherm Inc. was engaged to lead the feasibility assessment of TCH and steam/air co-injection. Kellogg, Brown and Root Pty Ltd (KBR) was also engaged to provide engineering design support.

  At the time of issuing of the previous annual report (Orica, 2008) preliminary design work for a field trial plant had been almost completed. Further source area characterisation and bench-scale heating tests (to evaluated vapour rates, compositions and fluxes) were required to finalise the design details.

  However, as discussed in Section 3.1, the strategy review process concluded that although DTT is a feasible technology, it would not be able to completely treat all source zones due to significant access constraints. The benefits of attempting DNAPL source depletion at Botany using DTT are unquantifiable and likely to be marginal in terms of the long-term clean up of the aquifer.

In addition to these evaluations, Orica is also developing other alternative technologies:

- **Enrichment culture for bioaugmentation in source areas**
  1. As mentioned in Section 3.2, the CMB had also been developing a biological enrichment culture for biologically degrading free phase DNAPL. As reported in the previous annual reports (Orica, 2007 and 2008), this work had been instigated after biomass was found to be growing near the interface between the organic and aqueous phases (i.e., on top of the DNAPL) in a small vial containing DNAPL (approximately 57% CTC and 43% PCE) recovered from a monitoring well in the railway corridor (in the S2 source area) in about 1995.

  Work on the three-year project commenced in April 2007. Last year's annual report (Orica, 2008) reported that epifluorescence microscopy of the biomass found in the vial confirmed that there were indeed cells in the biomass and that they were able to maintain their structural integrity in the aqueous phase in the presence of DNAPL. Although the cells had been shown to be viable and could be grown under anaerobic and aerobic conditions (suggesting that they are able to survive under conditions of high solvent stress), there had been no signs of halorespiration.

  Further work in 2008 found that the culture was not significantly different from the EDC-degrading culture already significantly developed, and it was metabolically inactive in the presence of tetrachloroethene (PCE) and carbon tetrachloride (CTC) at saturating concentrations. This project was consequently discontinued in September 2008, and no culture will be developed.

- **Nano-Scale Zero Valent Iron**
  Development of a process for manufacturing nZVI is discussed above in Section 3.2. The DNAPL Technical Mission Report (Orica, 2005) identified nZVI as being potentially applicable to DNAPL source area removal in the context of admixture with clay (bentonite or kaolinite) and augering into DNAPL source areas, and emulsified zero valent iron (EZVI, created by mixing together food grade surfactant, vegetable oil and nano-scale or micro-scale iron). Neither of these technologies is currently being considered for application in the BIP source areas.

- **Electrokinetics**

  As previously reported (Orica, 2008), in early 2007 Orica was approached by Golder Associates Pty Ltd to join them in co-funding research at the University of Western Australia in the field of innovative use of electrokinetics (EK) for the remediation of NAPL source zones in heterogeneous and low permeability soil. EK relates to the application of an electrical current between electrodes installed in the aquifer profile to create an electrical gradient that can be used to facilitate rapid and uniform migration of reductants or oxidants (e.g., nZVI, potassium permanganate, sodium persulphate, etc.) through targeted zones – particularly in low permeability geological formations – totally independently of hydraulic conductivity.

  The research program includes:

  1. Evaluating the influence of the natural charged state of the soil matrix on the technology;
  2. Evaluating the effects of and control measures for the pH gradient and associated geochemistry changes that are associated with the use of a DC current in an aqueous environment;
  3. Evaluating the use of laboratory screening tests (e.g., conductivity) as a surrogate for analytical chemical testing;
  4. Obtaining additional chemical data to allow a mass balance determination; and
  5. Developing a predictive numerical model for the technology.

  Work commenced in May 2007. Progress has been slower than anticipated, largely due to changes in working arrangements for key personnel involved in this research project. The apparatus has been redesigned to get better current density across the system. In terms of our work for Orica, the following has been achieved:

  - Migration of persulfate through cores in a manner similar to that for permanganate; and
  - Migration of chloride and persulfate through artificial peat soils.

However, migration rates have been very slow, due to current density losses (hence the redesign). It has also been found that persulfate activation cannot be performed effectively.

Work targeted at Botany issues is almost complete. It focussed on:

a) Producing repeatable, quantifiable one-dimensional results for persulfate migration in clays, silts, and peaty soils;

b) Two-dimensional demonstration of targeted EK-Ox (persulfate) in peaty beds;

c) Proof of concept with EDC in peaty soils; and

d) Initial trials with heat and iron activation of persulfate.

Orica expects to receive a report of the research results soon. Although Orica has no immediate plans for ISCO at Botany, this work will provide useful input into any such plans if ISCO is revisited in the future (or at other Orica sites). Potential for migration of non-ionic biological amendments could possibly be explored with future EK research.

4 ONGOING INVESTIGATION

Orica continues to evaluate other groundwater and source area remediation technologies. The principal means of doing this include

- Review of technical journals and articles;
- Subscription to email-based technical discussion groups (e.g., regarding bioremediation and environmental health);
- Networking and consultation with local and international specialists; and
- Attendance at industry seminars and conferences.

With regard to the latter point, representatives from Orica attended the Battelle-run Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds in Monterey, California in May 2008. This is a biennial conference, widely regarded as the pre-eminent international remediation conference. Orica representatives presented platform presentations on “Reductive Dechlorination of 1,2-Dichloroethane in a Reactive Iron Barrier” and “Multifaceted Large-Scale Site Cleanup, Botany Bay, Australia”, and posters on “Chemical Oxidation of Chlorinated DNAPL Using Activated Persulfate, Botany Bay, Australia”. Presentations and short courses attended by the Orica representatives covered topics such as

- Monitored and enhanced natural attenuation;
- Source and solvent plume characterisation;
- Vapour intrusion into buildings;
- Visualisation and modelling;
- Enhanced bioremediation of dissolved phase contamination and DNAPL source areas;

- Bioaugmentation;
- In situ chemical oxidation;
- Thermal treatments;
- Characterisation and treatment of DNAPL in fractured media;
- Nano-scale zero valent iron;
- Air sparging and soil vapour extraction;
- Innovative delivery (injection) technologies;
- Advances in permeable barrier construction and materials;
- Mercury remediation;
- Sustainable remediation (panel discussion);
- Community involvement and risk communication;
- Risk assessment and site assessment methods; and
- Long-term monitoring strategies.

No new technologies (i.e., those that had not already been considered previously for application to the BIP contamination issues) were identified at the Monterey conference, although understanding of the technologies discussed in this report was further enhanced.

5 REFERENCES

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