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ORICA BOTANY GROUNDWATER PROJECT

DNAPL AND GROUNDWATER REMEDIATION TECHNOLOGY ANNUAL REVIEW NO. 4

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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 – now the Department of Environment, Climate Change and Water (DECCW)) on 28 February 2007 (Orica, 2007). The second annual review was submitted on 29 February 2008 (Orica, 2008). The third annual review was submitted on 27 February 2009 (Orica, 2009). This report constitutes the fourth 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 0), 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/anthracite filtration for suspended solids removal;
- Activated carbon digestion/adsorption for non-volatile organics removal;
- Sand/anthracite 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."

It has been reported previously (Orica, 2008 and 2009) that trials had been conducted and a number of modifications to improve operating conditions and plant configurations had been undertaken during 2007 and 2008. Further investigations and improvements in this reporting period are described in Section 3.2.

In 2007 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 (i.e., the treated water produced by the GTP), 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.

In 2008 five of the activated carbon filters have been converted to Biological Aerated Filters (BAFs) to remove readily biodegradable organics and thereby reduce the potential for biological fouling, reduce monochloramine dosing by removing the organic material which feeds the biota, and improve product water quality. Last year's annual report (Orica, 2008) reported that introduction of the BAFs had allowed a significant reduction in the addition of monochloramine, and in conjunction with selective replacement of worn RO membranes, had allowed the plant to achieve very low Total Organic Carbon (TOC) concentrations in the treated water. Further enhancements are described in Section 3.2.

At the time of writing, an estimated total of 750 tonnes of chlorinated hydrocarbons (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

As reported previously (Orica, 2009), in late 2007 Orica convened a technical workshop to review the remediation strategy of the Orica Botany Groundwater Project and the cleanup technologies that were being employed and investigated.

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.

Dr Kavanaugh's assessment was also presented to DECC and the CLC in September 2008. It 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).

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

Following submissions to and discussions with DECCW and the CLC, on 30 October 2009 Orica submitted a draft Voluntary Management Proposal (VMP) under the amended *Contaminated Land Management Act*. The VMP was reviewed by the DECCW and now comprises the following undertakings for future management of Botany groundwater contamination:

- Maintenance of hydraulic containment;
- Source area management;
- Contingency measures for the GTP;
- Community consultation;
- Chemical monitoring programs for groundwater and surface water;
- Assessment of risk to human health and the environment (using data from the groundwater and surface water chemical monitoring programs and from additional monitoring programs for air and other environmental media); and
- Reporting requirements.

To achieve maintenance of hydraulic containment Orica will:

- Maintain effective hydraulic containment of contaminants of concern at the Primary Containment Area (PCA) Containment Line.
- Maintain effective hydraulic containment of contaminants of concern at the Secondary Containment Area (SCA) Containment Line.

- Maintain effective hydraulic containment of contaminants of concern at the BIP Containment Line commensurate with the available GTP treatment capacity and operational performance. When available GTP treatment capacity does not allow full treatment of groundwater extracted at the BIP Containment Line, priority will be given to areas in the vicinity of Springvale Drain and Second Street, where most benefit to human health and environmental protection from pumping can be achieved.

To achieve source area management Orica will:

- Conduct ongoing review of developments in remediation technologies and techniques for treatment of DNAPL, sorbed mass and dissolved phase CHC contamination, and their practical applicability to the Botany Groundwater Cleanup Project.
- Convene a Strategy Review Workshop every three years to which it will invite a minimum of three overseas experts in the field. EPA will be consulted on the selection of the experts prior to the experts being engaged. 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 developments in technology and its applications) 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) (as agreed with the CLC) and EPA will be invited to attend the workshop. Should the consensus of the participating experts recommend remediation trials, Orica will accept such recommendations.
- Provide an annual report to EPA that would assess the practical application and effectiveness of appropriate technologies in relation to the remediation. Every three years, this would also include a detailed summary of the outcomes of the Strategy Review Workshop.

As a contingency measure for the operation of the GTP Orica has developed the Groundwater Injection and Recovery (GIR) System. The GIR System is not designed to provide backup for hydraulic containment on all containment lines; it is designed to provide a system to enable continued extraction of groundwater from critical locations in the event of a prolonged outage of the GTP. Further description of work on the GIR System is provided in Section 3.2.

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 range of trials and improvements have been undertaken to address these issues.

- **Improving reliability of hydraulic containment**

  Investigations of reduced pump performance in the Secondary Containment Line in mid 2009 revealed that pressure in the Foreshore Road pipeline had increased notably since the system was commissioned. The increase in pressure made it more difficult for the pumps – especially the smaller ones – to move water into the main header pipe, and was the most likely cause of the reduced pump performance. The increased pressure was thought to be the result of a blockage somewhere in the pipeline between Foreshore Road and the GTP, most likely occurring in the Southlands section of the pipeline.

In mid August 2009 the pipelines in Southlands were cleaned by forcing a plug through the pipelines with high pressure water. This plug is referred to as a “pig” and the process is called “pigging”. This has resulted in significant improvements in line pressures, and consequently improved groundwater extraction at the SCA. To achieve further improvements the underbore sections of the pipeline are planned to be pigged in March/April 2010.

- **Reducing air stripper fouling**

  As reported in previous annual reports (Orica, 2008 and 2009), 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. It has been found that operation at pH 4.9 best mitigates biological fouling while maintaining inorganic fouling at tolerable rates. Trials involving the sterilising agent chlorine dioxide had been found to provide benefit in mitigating fungal growth and extending intervals between manual cleaning of air stripping units. During 2009 a detailed design was undertaken for a permanent dosing system for chlorine dioxide, along with bulk storage of the precursor chemicals. Construction and commissioning will be complete in the first half of 2010.

- **Improving Actiflo performance**

  It has been previously described how efficient operation of the reverse osmosis (RO) units (to maximise time between cleaning) requires low iron and aluminium concentrations (Orica, 2008). Trials to improve Actiflo operation by optimising operating pH and feed alkalinity and investigations into the impact of feedwater pH and redox potential (influenced by pH and chlorine dioxide) on Actiflo performance have been described previously (Orica, 2008 and 2009).

  During 2009 additional Actiflo investigations were undertaken. The primary focus was on optimising the use of polyelectrolyte (flocculant), which includes selection, dosing amount and location. A second project focused on optimising the use of sand for floc formation and mitigating the effects of biomass on sand recovery. This has resulted in significantly lower dissolved iron concentrations exiting the Actiflo process, enabling longer run times and less cleaning in the downstream RO units.

- **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 reports (Orica, 2008 and 2009).

During 2009 additional studies were undertaken to improve TOC removal by the BAFs. Mechanical upgrades to the aeration spargers and replacement of the filter medium with a smaller grade of zeolite have been made. The best results, though, have come about through optimising phosphate dosing (to facilitate biomass consumption of readily biodegradable carbon in the feedwater).

- **Cartridge filter cleaning**

  It had been previously reported (Orica, 2009) that cartridge filter life had 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. Results from using cleaning solutions had been inconsistent, achieving only temporary regeneration of cartridges.

  Evaluation of alternatives to the ultipleat cartridge filters occurred in 2009. The results showed that depth filters provided only a 10% improvement, which was regarded as being within the order of experimental error. However, optimisation of the remaining activated carbon filters has increased the operating life for the ultipleat style filters, which means these filters will be retained.

- **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 and 2009) revealed activated carbon provided minimal benefit in reducing ammonia. Most improvement was achieved with TOC reduction in RO feedwater (e.g., in the BAFs), which allowed significantly less monochloramine to be used, and consequently less ammonia generated during dechlorination. Further improved performance in the BAFs has allowed for consistently lower monochloramine dosage in 2009. The net result has been even lower residual ammonia in Treated Water discharge to the environment.

- **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 (Orica, 2009). The experts' view was 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 more frequent cleaning of demisters, replacement of demisters with finer sections and improved installation to restrict demister movement.

  In the 2009 annual shutdown the refractory was in much better condition than previously, suggesting the changes have been beneficial. A decrease in the frequency of plant trips will further benefit the oxidiser.

Orica has also been investigating ways to ensure consistent hydraulic containment even during protracted GTP shutdowns. Studies of the aquifer's response to groundwater extraction indicate that shutdowns of up to around two months could be tolerated without compromising hydraulic containment of the contaminant plumes. Groundwater that had passed the containment lines during the shutdown could be drawn back to the extraction wells by pumping the wells at a higher rate once the GTP was back on line. But beyond two months, sufficient reversal of the hydraulic gradients could not be assured.

- **Groundwater Injection and Recovery (GIR) System**

  In 2008 Orica developed a concept of Temporary Aquifer Storage and Recovery (TASR), which was renamed Groundwater Injection and Recovery (GIR) in early 2009. Using the GIR System Orica proposes to reinject extracted groundwater into the aquifer upgradient of the containment lines on BIP if the GTP is unable to treat groundwater for an extended period of time (i.e., several months). Through 2009 Orica developed the concept with DECCW and the Office of Water and obtained a variation to the BIP Environment Protection Licence (EPL no. 2148) and test bore licences to install injection and monitoring wells and conduct a trial of the GIR System.

  The initial stages of the trial injection were completed in September 2009. A brief summary of key findings is provided below:

  - The trial injection well was highly efficient and injection rates averaging approximately 150 m^3/day were maintained throughout the trial;
  - Based on the observed monitoring well water levels, the trial has demonstrated that the proposed full-scale GIR system is worth pursuing; however
  - The rates and duration of injection were limited due to clogging of the pre-injection filter and reducing capacity within the well over time. The clogging is believed to be biological in nature.

  In order to maximise effectiveness of the GIR System Orica will need to minimise the clogging so as to extend the rates and duration of the injection. Orica proposes an extension of the trial prior to the implementation of the full-scale system. The trial will focus on the use of anti-fouling agents and injection well maintenance techniques. Orica has been discussing the next stage of work with DECCW.

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, 2008 and 2009) described developmental work performed by the Centre for Marine BioInnovation (CMB – formerly the Centre for Marine Biofouling and BioInnovation (CMBB)) 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 were 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, 2009) it was reported that the CMB had successfully isolated cultures tolerant of elevated EDC concentrations, and that their attention had turned to scaling up the quantities of EDC degrading culture. Additional groundwater from the BIP was being used to develop nine 10 L cultures. Through 2009 the culture was scaled up to a total of 130 L, which will be used for the bioaugmentation field trials being undertaken in Southlands (see below).

It was previously reported (Orica, 2008 and 2009) that the original enrichment cultures for EDC degrading activity established at the beginning of the project had 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. Occasional monitoring for ethene production had indicated that the culture had not been active for over 200 days, but by November 2008 this culture had begun showing a modest activity at low pH (1.4 mg/L/day). By the end of February 2009 the activity had further increased to 10 mg/L/day. This is significant because this culture is likely to be effective in the native groundwater without any pH adjustment. This culture has since been scaled up and mixed in with the culture to be employed for the bioaugmentation field trials.

Diffusion rates of the enrichment culture through soil have been evaluated in the CMB laboratory using soil columns in readiness for the field trials.

URS Australia Pty Ltd sampled and analysed groundwater from the proposed field trial area to assess groundwater contaminant concentrations and flow direction, and to provide advice on the use of the proposed trial area. The reported concentrations were mostly similar to those reported for the original bioremediation field trials conducted in the area. Although groundwater levels were lower due to the operation of the hydraulic containment system, flow gradients and directions were similar to those previously observed.

It was previously reported (Orica, 2008 and 2009) that enrichment cultures at neutral pH containing up to 0.5 mg/L of chloroform had shown increasing chloroform degrading activity. However, chloroform degradation rates observed throughout 2008 began to decrease towards the end of the year and chloroform accumulation from regular feeding was reported in early 2009. The culture was diluted with groundwater from the Botany Sands Aquifer to relieve inhibition from high chloroform concentrations, but after dilution the observed degradation rate was only 2 µg/L/day (1000 fold lower than previously observed). Yeast extract and vitamin K2 were added to the culture to assess the possibility that nutrient limitation was the cause of the low rate, however this had no impact. Hydrogen was supplied to the culture to assess the possibility that hydrogenic bacteria had been lost from the consortia, but this also had no impact on degradation rates. An attempt was made to scale up the culture to 10 L, but after 30 days of incubation the amount of chloroform lost from the culture was equivalent to the amount of chloroform lost from an uninoculated control. This suggested that the culture was not suitable for use in field studies and work on these cultures was discontinued in July 2009.

Recently, chloroform degradation was observed in groundwater cultures inoculated with material taken from a reactive iron barrier located in Southlands. After a 90 day lag period chloroform degradation was observed at a rate of approximately 3.5 mg/L/day in the presence of 50 mg/L chloroform at pH 7. This high rate in the presence of unprecedented high concentrations of chloroform was preserved after subculturing into a basal salts medium supplied with acetate and hydrogen suggesting rapid scale-up is possible. The activity of the culture at low pH is not currently known.

<u>Bioaugmentation Trials at Southlands</u>

In conjunction with the CMB and URS Australia, Orica developed plans to conduct field trials at Orica Southlands to evaluate whether the enrichment culture developed by the CMB could be employed in the field to augment the biological degradation of contaminants in the groundwater. The shallow aquifer trials will be taking place in Area A, at the northern end of Block 2 of Southlands, which was used for the bioremediation field trials in 2004-2005. The aims of the pilot test are:

1) To assess the impact of a biostimulation treatment on EDC concentrations in the Botany Sands Aquifer.
2) To assess the impact of a combined biostimulation and bioaugmentation treatment on EDC concentrations in the Botany Sands Aquifer.
3) To investigate the impact of the treatment on the indigenous microbial communities.

The trial will exploit existing infrastructure (with some additional groundwater wells installed in December 2009 to facilitate biostimulant and culture injection and to address the slight change in groundwater flow direction brought about by operation of the hydraulic containment system) that had been employed in pilot tests for biostimulation, carried out by GeoSyntec between 2004 and 2005 to assess the relative merits of emulsified vegetable oil and calcium oleate as slow release electron donors in side-by-side passive injection tests. Pilot test Area A is suitable for simultaneously conducting two pilot tests to meet the objectives described above. It is located along the centre-line of a shallow EDC plume with average concentrations less than 500 mg/L. The infrastructure will be used to compare the impact of a regime of injection with a soluble electron donor (ethanol, which had been used in the deep aquifer - Area B - trials in 2004) with a regime of ethanol injection coupled with bioaugmentation. The impact of the two different treatment regimes will be assessed over a period of six months by collection and analysis of groundwater samples for evaluation of environmental parameters, parent and daughter product concentrations and changes in microbial community composition.

The injection plan schedules one tracer injection (sodium bromide – to confirm groundwater flow paths and rates) and two ethanol injections before the trial, one injection of the enrichment culture for the second network at the beginning of the trial, followed by 16 weekly injections of ethanol scattered over the first four months for both networks. The tracer injection occurred in February 2010. If the tracer tests indicate appropriate groundwater flow rate and direction the culture in March will be injected.

- **Nano-Scale Zero Valent Iron**
  It was previously reported (Orica, 2007, 2008 and 2009) 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.

  It had also been reported (Orica, 2009) that the UNSW researchers had demonstrated continuous production on nZVI at rates of up to one kilogram per hour. This milestone had 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 – "Synthesis of Activated Carbon Supported Zero Valent Iron Nanoparticles and Application to Contaminant Degradation in Benthic Sediments" – was made in mid-2009 with Partner Organisations DECCW, NSW Maritime, Sydney Metropolitan Catchment Management Authority, Sydney Ports

Corporation. This bid was successful. At present Research Agreements are being finalised. It is planned to begin the project in July 2010.

- **Site Investigation Technology Demonstration**
  Although not strictly research relating to the Botany Groundwater Project, Orica also hosted a field demonstration day at Southlands on 7 July 2009. The event was organised by Wendy Morrison, Director of Environmental Services at Consulting Earth Scientists (CES), for the International Association of Hydrogeologists (IAH). A range of site investigation tools and techniques were demonstrated, including:
  - Sonic rig demonstration by BoartLongyear – coring and well installation;
  - Geoprobe rig – using Waterloo Profiler (for real time depth-discrete groundwater sampling);
  - Continuous multichannel tubing (CMT) demonstration by Hydroterra – well information, construction and installation; and
  - Construction and installation of multi-level wells.

  The event was attended by contaminated site consultants, drilling contractors, investigation equipment suppliers and regulators.

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 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 Australia 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 were planned to commence early in the second half of 2009 (following a large maintenance project being undertaken by Qenos in the area). The Qenos maintenance work was completed later than originally anticipated and implementation of the trials was deferred to the first half of 2010.

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)**
  It was previously reported (Orica, 2009) that the injection of solubilised chemical oxidant – in this case activated sodium persulphate – into the source zone to chemically destroy the DNAPL in situ had been evaluated in laboratory bench-scale tests, and also that the Groundwater Cleanup Project strategy review in late 2007 (see Section 3.1) had 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. As a result, no further work has been done to evaluate ISCO for full-scale DNAPL source zone treatment.

- **Direct Thermal Treatment (DTT)**
  As for ISCO, the 2007 Groundwater Cleanup Project strategy review process (Section 3.1), 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 cleanup of the aquifer (Orica, 2009).

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

- **Nano-Scale Zero Valent Iron**
  Development of a process for manufacturing nZVI has been previously reported (Orica, 2007, 2008 and 2009), and follow-on work 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 and 2009), in early 2007 Orica had been 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 included:

  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 and continued through most of 2009. Golder Associates issued a Project Completion report in November 2009 for the Orica-related work. The principal conclusions included:

  - A series of bench trials coupling EK with ISCO (EK-ISCO – primarily using sodium persulfate) were conducted to quantify net persulfate mass flux due to electromigration through low permeability media (clay) and in high organic matter content media (peat). Although the transport rates were lower than theoretically achievable, it was concluded that further process optimisation could enable EK to deliver unactivated persulfate into challenging subsurface media (for subsequent in situ activation).
  - For the low permeability trials the mass balance was accurate, but for the high organic content media no persulfate breakthrough was observed and there were indications of persulfate decomposition. This could not be explained by reaction due to the natural oxidant demand (NOD) of the peat. It was concluded that the enhanced decomposition rates in EK-

ISCO relative to batch tests might be attributable to increased sweep efficiency during EK-ISCO, scaling effects, catalytic effects related to the substrate itself, or potentially due to alkalinity generated by electrolysis at the cathode. This would need to be researched further.

- Experiments were conducted with EDC destruction. While these indicated faster decomposition under EK-ISCO relative to the diffusive case in peat, additional work is required to confirm statistical significance and quantify the underlying reaction mechanisms.
- Activation of persulfate with EK was beyond the scope of this study, but several activation approaches could be considered, such as the use of EK to promote joule heating and subsequent heat activation of the persulfate, or, given the relatively high ionic mobility of the hydroxyl anion, EK could be used to deliver these anions for base activation of persulfate. The alkaline solution could be directly augmented to the system via injection, or generated in situ using the EK process itself, via electrolysis at the cathode.

The researchers are hoping to apply for another ARC Industry Partnership Grant. Discussions are continuing amongst the research partners.

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).

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, in the last twelve months representatives from Orica have attended a number of conferences and seminars:

- EcoForum Conference & Exhibition 2009 was held at the Australian Technology Park, Sydney from 28 to 30 April 2009. The event is one of Australia's leading ecoforums for industry. It incorporated the 2nd Annual Conference of the Australian Land and Groundwater Association (ALGA).
- Cleanup 2009, comprising the 3rd International Contaminated Site Remediation Conference, occurred on 27-30 September 2009 in Adelaide. The program included a range of speakers from Australia and abroad, as well as a small number of trade exhibitors.

- EcoForum Conference & Exhibition 2010 was also held at the Australian Technology Park, Sydney on 23 and 24 February 2010. The program featured presentations on sustainable remediation, site management plans, investigation levels and risk assessment, vapour intrusion, site assessment and remediation, groundwater, and analytical methods and assessment.

Orica representatives will also be attending the Battelle-run Seventh International Conference on Remediation of Chlorinated and Recalcitrant Compounds in Monterey, California in May 2010. This is a biennial conference, widely regarded as the pre-eminent international remediation conference. Orica will present a platform presentation on “Dissolution of Multicomponent DNAPL”.

As discussed in Section 3.1, Orica has submitted to DECCW a draft VMP, which includes the undertaking to convene a Strategy Review Workshop every three years to which it will invite a minimum of three overseas experts in the field. As the first Strategy Review Workshop was held in December 2007, Orica plans to conduct the next Workshop in the latter half of 2010. Preparation of relevant documentation, scoping the Workshop and consultation with DECCW on the selection of the experts will commence shortly.

5 REFERENCES

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