REMOVAL OF ENDOCRINE DISRUPTERS IN ADVANCED TREATMENT- THE AUSTRALIAN APPROACH

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1. INTRODUCTION

Water recycling plays an essential role in integrated water management, especially in an arid country like Australia but also worldwide [1]. Water recycling, however, has suffered extensive constraints due to “toilet to tap” media campaigns and "yuck factor" attitudes in the community. The support of the community for water recycling projects generally decreases as the personal contact with the recycled water increases [2]. Some of the very valid concerns of the community stem from uncertainties involved in water recycling, such as the issue of persistent organic pollutants (POPs) or endocrine disrupting chemicals (EDCs) potentially present in recycled waters. The ever growing group of EDCs have been of particular concern to sections of the community in Australia. Those concerns are to be taken seriously as the effects are potentially severe - endocrine disrupters have the potential to interfere with our normal growth, development and reproduction. Modulation of that system could cause severe adverse health effects over many generations. Industrial chemicals, consumer chemicals and chemicals in the environment can be endocrine disrupters that mimic, enhance or inhibit the action of hormones [3, 4]. Sewage disposal to water sources may be a major exposure pathway for pharmaceuticals, synthetic and natural hormones, industrial chemicals to humans and wildlife, directly and via the food chain. This concerns disposal of treated effluents and applications of recycled water. While many Australian authorities and funding bodies take a conservative approach and wait for clear scientific evidence that endocrine disrupters indeed directly affect humans to proceed to action, others are more open and driven by industry to deal with the issue. The project presented here is one such example and emphasises on hybrid membrane processes for removal of endocrine disrupters.
2. PROJECT OVERVIEW

The current “Optimised Use of Membrane Hybrid Processes for Water Recycling” Project is an ARC SPIRT Project (2000-2003) with the Queensland Government as the Industry Partner. Endocrine Disrupter Removal is the core issue of this project. The topic is of high relevance to Australia, as media campaigns and public upheaval have stopped several water recycling projects. While there are many emotions involved, especially in potable recycling, in many places in the world unplanned or even planned indirect potable recycling is common practice. Both potable and non-potable recycling encompass risks, which are currently not well understood.

The aims of this project are to investigate trace contaminant removal by hybrid membrane processes from wastewaters such that these resources may be of beneficial use. Studies will give further information on the water quality that is achievable and possible risks involved. The project involves the use of innovative approaches to water recycling for optimal holistic solutions - accounting for full life cycle, energy usage & source, environmental impact, social consequences, as well as governance, health and economic aspects. The approach being adopted by the project team is highly collaborative and inclusive with a view to contributing to development of solutions to two of the planets largest problems- water shortage and environmental degradation. Figure 1 shows how the project evolves around the water recycling/wastewater treatment cycle.

![Figure 1 Integration of the Project into the Wastewater Cycle.](image-url)

Effluent from the wastewater treatment plant is exposed to a range of membrane technologies. A first step is pretreatment using the more open membranes such as microfiltration (MF) or ultrafiltration (UF). Those membranes may be able to remove pathogens, but will not remove small chemical pollutants. However, with appropriate pretreatment it may be possible that a hybrid process of MF or UF, combined with, for example, powdered activated carbon (PAC), coagulation or magnetic ion exchange (MIEX), removes a considerable amount of small-sized...
contaminants (such as pharmaceuticals, endocrine disrupting chemicals including hormones and certain agrochemicals, viruses). In this stage it is also important to understand the interactions between pollutants and naturally occurring particles as this determines fate and ultimately the efficiency of treatment. Tighter membranes are also to be investigated as it is largely unknown how effective MF and UF membranes will be in removing trace contaminants. Investigations of both fundamental and applied aspects of membrane operation and performance will assist in optimising plant performance and contribute to important practical issues such as membrane integrity and possible treatment failures.

Key issues identified as requiring attention are listed below:

- Energy requirements and concentrate disposal may be drawbacks of membrane technology, which must be addressed.
- Ultimately, the extent of contaminant removal and discharge water quality sought must be linked to the likely application of the treated water. Irrigation of foodcrops, usage as industrial cooling water or toilet flushing will demand very different quality standards. The level of treatment required will also depend on the wastewater characteristics, and the economics of treatment on local conditions.
- The likely risk of exposure to any trace contaminants remaining in reuse waters will be compared to the risk of exposure to contaminants from other sources, such as food.
- Trace contaminants are difficult and expensive to measure and monitor. Simple methods are required to measure cumulative effects, but also qualitative and quantitative techniques to identify potential hazards.
- Environmental impacts of various options will be assessed and the integration into the public’s perception of the appropriateness of and need for water reuse will be evaluated and should in the search for better decision making and management tools.

The various research interests can be grouped into five categories as illustrated in Figure 2.

Analytical issues cover parameters such as estrogenic activity of a water, compound identification & quantification, speciation and fate modeling (fate in treatment plants and the environment). Treatment is split into two areas- more open and tighter membranes. Porous membranes cover particle interactions and implications on removal of compounds, the effectiveness of MF and UF as pretreatment processes, submerged membrane systems and their combination with other processes such as coagulation, PAC or MIEX, and membrane bioreactors, which may be essential processes to treat the waste from water recycling.

The more advanced treatment includes nanofiltration (NF) and reverse osmosis (RO), MIEX, crossflow system testing and ultimately (for all treatment systems) verification of results using the Queensland EPA demonstration plant.

The last two categories cover the public and environmental issues of water recycling. Environmental tools such as life cycle assessment (LCA) or indicators will help establish sustainability criteria while considering also economic factors to determine the most attractive application and treatment for a wastewater. Public perception and consultation evaluates perceived and technical risk, policy and legalities, issues such as decentralisation and source separation to establish a new framework for decision making.
3. CURRENT PROGRESS - OVERALL PROJECT

In this workshop a progress report on the first 2 years of the project; just over 70% of the total effort completed. Five academics are formally involved in the project, one senior research associate, three PhD candidates and many shorter term research students. We are satisfied with the progress achieved in the project and we hope to see an increased involvement with industry and, potentially, other State agencies and overseas institutions with an interest in water recycling issues. In the first half of the project we have, of necessity, focussed on fundamental issues of technique development, membrane performance and laboratory-based optimisation. In the second half of the project, as these areas come to fruition, we are in progress of addressing issues at the pilot and full-plant size scale. First experiments are being conducted at the Advanced Water Recycling Demonstration Plant (AWRDP) which is shown in Figure 3 looking at the removal of hormones and pharmaceuticals. To this end, we look forward to additional input from practising engineers, managers and the community as we address the challenge of finding sustainable solutions to water cycle management.

Figure 3 The Advanced Water Recycling Demonstration Plant, Brendale (Pine Rivers Shire, QLD)
3.1 Technical Issues - Treatment Technology

The majority of results in paper are on technical issues and will be discussed in detail later, while a summary is given in this section. The first milestone of the project was the identification of the most relevant compounds based on abundance in waters and wastewaters, persistence in the environment, endocrine disrupting potency and feasibility of analysis at trace (sub nanogram per litre) levels. A thorough literature review very clearly identified natural and synthetic hormones as the most troublesome compounds and in addition those compounds are found in any domestic wastewater worldwide.

While the analytical tools are being developed, a technique using radiotracers was developed for laboratory research, which has led to a large number of cutting edge results due to the high sensitivity of analysis using this method.

A number of processes were investigated regarding their removal potential of endocrine disrupters. Those processes are ferric chloride coagulation, powdered activated carbon, magnetic ion exchange combined with microfiltration (MF) or ultrafiltration (UF), as well as nanofiltration (NF) and reverse osmosis (RO).

Key findings were a negligible removal (<10%) of estrone with ferric chloride coagulation and very high removal (>90%) with powdered activated carbon. Magnetic ion exchange varied from 40 to 70% removal depending on solution chemistry and dissociation of the hormone. Nanofiltration showed an initial retention of 70-95% but for most membranes this retention dropped significantly after an initial filtration period. For some reverse osmosis membranes retention was similar to nanofiltration, but others showed a very high and stable retention of the compounds. Microfiltration also showed near complete retention initially followed by a drop to 0% as expected. The presence of matrix compounds from water and wastewaters affected retention for some membranes.

These results, while initially surprising, showed a common theme, which is the adsorption of polar contaminants on materials used in treatment. This includes ion exchange resins, membranes and many other materials that come in contact with the trace contaminants.

Implications of those findings are that there may be a significant risk in water recycling where contaminants accumulate to comparably high quantities and may be release during treatment. This requires further investigations to understand how easily those contaminants are released and where they accumulate in the water cycle. Results are currently confirmed on larger scale systems and experiments will also be scaled up for tests at the Advanced Water Recycling Demonstration Plant.

3.2 Fate of Contaminants and Analysis of Pollutants

Water recycling goes hand in hand with water conservation and is part of a larger water cycle. Many people, including engineers, are not aware that this cycle is closed and that all water is constantly being recycled. This was a clear outcome of a study of fate modelling in which the amount of fish that a woman has to consume to get the effect of the pill was estimated. While the result of 100-150 kg per day is certainly not raising major concerns, the implications are severe. Calculations were based on one compound, not accounting for any cumulative effects of thousands of compounds. The model is based on fugacity- partitioning of compounds to different compartment such as water, air, and solids like sediments or activated sludge. Limitations of this model are a lack of availability of data for many pollutants and their behaviour in wastewater treatment plants.

To understand those relationships of interaction adsorption isotherms were measured for particles representing those occurring in natural waters and effluents- activated sludge, cellulose/toilet paper, clays, and natural organics. This indicated that trace contaminants interact strongly with organics and particulates and hence the presence of such particles has a strong impact on fate in treatment plants. The majority of contaminants remain dissolved or partition into the sludge from treatment plants. This requires further work to expand the model to Australian conditions and include biodegradation of compounds.

On the analysis front a collaboration with the two main experts in Europe has been established - Ternes and Heberer. Analytical tools developed with the Biomedical Mass Spectrometry Facility at
UNSW have lead to detection limits of the hormone suite of 50 ng/L without preconcentration. With a preconcentration step detection limits of well below ng/L can be achieved. At present the analysis of effluent samples is evaluated and once successful environmental samples will be analysed.

3.3 Social and Environmental Issues

Public perception is a major concern in water recycling. The need to understand perceived risk and comparison of this with the actual technical risk has led us to questions of dealing with uncertainty and governance. Making people accept water recycling through strategies of overruling to issues of education have not always been very successful. Our approach explores involvement of all stakeholders, the development of best practise and decision making guidelines and recommendations to policy makers.

For environmental assessment life cycle assessment will be modified to include risk and health issues as well as other environmental tools like material flux analysis. This part of the project is also looking at environmental indicators. At present selected case studies from Australian water recycling operations are assessed with the objective to compare different unit processes available.

Further progress can be followed on our project website http://www.cwwt.unsw.edu.au/membrane/homepage.htm

4. ADVANCED TREATMENT PROCESSES FOR ENDOCRINE DISRUPTER REMOVAL

The results reported here represent a component of a multi-faceted investigation into the mechanisms of removal of natural and synthetic estrogens in advanced water and wastewater treatment. This involves adsorption to common particulates and membrane processes. An understanding of those mechanisms is essential to predict the likelihood of removal and the reliability of treatment.

4.1 Selection of High Priority Trace Contaminants

The list of trace contaminants or endocrine disrupters stemming from human activity found in wastewaters is long [5-15] and the problem has been apparent since the 1970s [16]. It was chosen to select the most relevant compounds for research activities based on four criteria- abundance in waters and wastewaters, high persistence in the environment, high potency as endocrine disrupters and analysis to below ng/L levels is feasible. Compounds that suit those criteria best are natural and synthetic estrogens excreted by men and women in urine and faeces and with increased levels during pregnancy and hormone replacement therapy. Those compounds have an average persistence, synthetic hormones and chemicals have a much higher persistence, but lower potency. Natural hormones can be expected to be present in all municipal wastewaters and hence have a global relevance. Problems of analysis were overcome by using radiolabelled compounds which can be analysed to about 0.1 ng/L concentrations very accurately.

4.2 Removal of Trace Contaminants in Treatment

Conventional wastewater treatment is not an effective barrier to trace contaminants. While removal rates published in the literature vary greatly, this appears to depend on local conditions and the nature of the contaminant [19-22]. The main characteristics which determine the fate of such contaminants in the water cycle is their ability to interact with particulates. These particulates can be naturally occurring (clays, sediments, colloids coated with natural organics, microorganisms) or added during treatment (activated sludge, powdered activated carbon, ion exchange resin, coagulants). The transition of trace contaminants to the solid phase will greatly enhance chances of removal. In contrast, the interaction of trace contaminants with dissolved
organics can increase their mobility in the environment and through treatment [23]. The fate of natural and synthetic estrogens in wastewater treatment plants is uncertain. It is estimated that less than 10% of the compounds are removed via biodegradation, the majority of the compounds remain in the water phase while a considerable amount is adsorbed to the sludge [24].

### 4.3 Trace Contaminants - Natural Particle Interactions

The interactions of estrogens with natural particles was studied at particle concentrations to be expected in the environment, or in the case of activated sludge, during treatment. A summary of results is presented in Table 1. The adsorbed amount of contaminants depends on particle size and roughness and hence the available particle surface besides material characteristics. While results here are shown as a function of particle mass, one should bear in mind that at identical particle concentration and smooth surfaces, the available area decreases with the square of particle diameter. This is reflected in the results with activated sludge, where the largest particle size of about 100 µm shows the lowest adsorption despite a very high octanol water distribution coefficient of estrone. Corrected for particle surface area the adsorption on activated sludge is the highest of all the compounds studied. These adsorptive interactions are important for treatment: high partitioning of contaminants onto organics can be expected which affects the use of sludge for land application or the selection of adsorbents. It appears as if organic adsorbents may be far more effective in removal of such contaminants if applied in forms with high specific surface areas (e.g. polymers).

#### Table 1 Interactions of Estrone with naturally occurring particulates (pH 7-8, 100 ng/L estrone, 1mM NaHCO3, 24h of adsorption)

<table>
<thead>
<tr>
<th>Particle</th>
<th>Average Particle Diameter [µm]</th>
<th>Particle Concentration [g/L]</th>
<th>Estrone Adsorption [%]</th>
<th>Estrone Adsorption [ng/g*]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>0.075</td>
<td>6.3 (\times) 10^{-3}</td>
<td>0.74</td>
<td>150.64</td>
</tr>
<tr>
<td>Kaolin</td>
<td>0.1-4</td>
<td>0.1</td>
<td>8.87</td>
<td>140.46</td>
</tr>
<tr>
<td>Bentonite</td>
<td>0.1-10</td>
<td>0.1</td>
<td>13.53</td>
<td>175.64</td>
</tr>
<tr>
<td>Cellulose</td>
<td>20</td>
<td>0.1</td>
<td>8.35</td>
<td>113.96</td>
</tr>
<tr>
<td>Activated Sludge</td>
<td>100</td>
<td>5.4</td>
<td>22.38</td>
<td>6.15</td>
</tr>
</tbody>
</table>

* dry weight

When organic matter is added to the particle system, the adsorption of estrone increases considerably (see Figure 4) for all organics used (HA, FA and NOM) and over the pH 3-12 range. The largest increase of adsorption was provoked by HA at pH 3, hence the most aromatic, least soluble compound at conditions where the organics have the lowest charge. The increase due to the presence of natural organics can be explained with a modification of the colloid surface the interaction of estrone with the natural organics which adsorb on the hematite. Due to the high octanol-water partitioning coefficient the contaminants interact strongly with the natural organics.

#### Figure 4 Impact of organic matter on adsorption of estrone by hematite

The implication of this is that trace pollutants in water and wastewater treatment systems are likely to be found associated with colloids as in natural systems most colloids have an organic coating.
Further this effect can be taken advantage of to promote the removal of trace contaminants in water and wastewater treatment with the addition of adsorbents.

### 4.4 Removal of Trace Contaminants by Particle Addition

The addition of adsorbents is of advantage for the removal of trace contaminants, especially when membrane processes are used which do not retain trace contaminants. The objective of this study was a comparative investigation of common adsorbents used in the water and wastewater treatment industry, hence powdered activated carbon (PAC), ferric chloride coagulant (FeCl₃) and Magnetic Ion Exchange Resin (MIEX) were used.

Figure 5 shows the impact of pH and ferric chloride dosage on estrone removal in jar test experiments. The removal of such compounds is minimal during coagulation. This was expected as coagulation tends to favour the removal of large and hydrophobic compounds. Adsorption to the iron hydroxide precipitates is very low. This interaction and removal may change in the presence of natural organics and such experiments are yet to be conducted.

With powdered activated carbon this is different. At relatively low concentrations of 5-10 mg/L PAC a substantial removal of estrone can be achieved as shown in Figure 6. Effects of competition are visible where adsorption in a 'clean' buffer solution is much higher than in surface water or secondary effluent. In surface water and effluent other organics compete for adsorption. This competition could be due to the blockage of pores and restriction of diffusion of trace contaminants to the adsorbent surface or due to the competition for adsorption sites. At higher dosages there is a large excess of adsorbent and hence the difference in matrix diminishes.

![Figure 5 Removal of estrone with ferric chloride](image1)

![Figure 6 Removal of estrone with powdered activated carbon](image2)
Magnetic ion exchange resin (MIEX®) has been developed for water treatment applications for enhanced natural organics removal [26, 27]. The resin preferentially adsorbs small and charged compounds from natural organics mixtures [28]. In Figure 7 a light micrograph shows particles in the order of 10-100 µm and an electron micrograph a MIEX® particle with several small fractions broken off from particles. In higher resolution electronmicrographs the particles show a composition of the particles of very dense fibres, presumably magnetic iron compounds which give the resin its magnetic characteristics which lead to rapid aggregation if magnetised.

While the compounds studied are uncharged at neutral conditions, polar or hydrogen bonding interactions are responsible for a removal of up to 45% of the estrone which corresponds to an adsorption of 80-100 ng/g (Figure 8). This increases with pH when the molecules are dissociated at a pH above 10.4, the removal increases drastically to about 70%. This strong pH dependence can be explained with an additional ion exchange mechanism when the molecules are dissociated and carry a negative charge. Given the nature of those contaminants, the removal of small polar compounds is somewhat surprising. The interactions are attributed to hydrogen bonding or hydrophobic interactions.

There are a number of consequences from the above results. Both FeCl₃ and MIEX® are not very suited to remove the majority of the trace contaminant. PAC is better suited and appears to be the preferential choice PAC is added in a sufficiently high dosage. However, both MIEX® and PAC are both commonly used in water treatment. It is very likely that those particles will accumulate contaminants and to date very little is understood about the behaviour of such contaminants during regeneration and changes in feed water characteristics.

4.5 Removal of Trace Contaminants by Membranes

While MF and UF are not expected to remove such small and polar compounds, a similar removal was observed initially for all processes. Removal was high at low and neutral pH, while it decreased substantially at a pH larger than 10.5. This could be attributed to adsorption effects, assumedly hydrogen bonding and hydrophobic sorption. This is shown for submerged MF (Memcor) and UF (Zenon) membranes in Figure 9. Those experiments were performed by adsorption tests of estrone on the membrane material without filtration. The adsorption of contaminants on hydrophobic membranes is higher than on hydrophilic materials.
Adsorption also dominates removal for some NF membranes. Some membranes remove estrone by size exclusion, others by adsorption. Figure 10 shows typical relationships between retention or permeate concentration and pH. As indicated previously the estrone molecule dissociates at pH 10.4 which leads to a drastic drop in retention. This behaviour shows that the retention occurs due to polymer-contaminant interactions as opposed to size exclusion. When the molecules take a negative charge at high pH, a repulsion between the negatively charged membrane and the organic anions causes reduced adsorption and facilitated transport through the membranes. For some very tight membranes (Figure 11) there is no effect of pH on retention which indicates that the 'pores' are smaller than the contaminants and the membrane is an effective barrier independent on solution chemistry.
The adsorption as a function of pH for the tighter membranes is illustrated in Figure 12. Results reflect the shape of the retention curves in Figure 10 and Figure 11. While the materials are different (polyamide on polysulfon support (TFC-S) and polyamide-urea composite (X-20) it appears that much of the adsorption of the TFC-S membrane is due to adsorption on the polysulfon support layer which offers a vast surface area. With the retention on the membrane surface of the X-20 membrane, the support is not available for adsorption and hence observed values are significantly smaller. Those adsorption effects will only be operative during initial stages of filtration, but can cause the accumulation of a significant amount of trace contaminants and retention depends on the solution chemistry.

![Figure 12 Adsorption for the TFC-S membrane and X-20 membrane as a function of pH](image)

It is important to understand such retention and adsorption effects prior to membrane selection if the membrane is expected to act as a reliable barrier to contaminants. Such adsorption effects are also very important for the understanding of fate of pollutants in treatment systems and the possible desorption of contaminants during feed quality changes or cleaning operations.

5. CONCLUSIONS

In water recycling, where a multiple barrier approach may be required to ascertain low risk for water users, treatment is likely to beyond economic feasibility and the product water achieved using such technology would approach ultrapure water. It is hence essential to plan water recycling with an integrated water cycle approach and determine the most sustainable water usage.

In the light of such results and a heated public debate it appears unreasonable to assume that direct reuse of water for personal consumption is a sensible solution. However, if the discharge of moderately treated wastewater persists, one needs to realise that the global water cycle is closed and contaminants will reach our drinking water sources. It is essential that further developments optimise the reduced use of synthetic chemicals, effective removal as well as destruction of the removed contaminants.

6. ACKNOWLEDGEMENTS

The authors wish to thank Dr Sheng Chang, Long Duc Nghiem, Maibritt Mastrup, Rikke Lund Jensen and Peter Ong for provision of experimental data and their contribution to the "Optimised Use of Membrane Hybrid Processes in Water Recycling" Project as well as Prof Tony Fane (UNSW) and Thomas Wintgens (RWTH Aachen, Germany) for useful discussions. The Australian Research Council and the Queensland Government are thanked for research funding through the SPIRT scheme. Most results presented in this paper are reprinted from the Gothenburg Symposium 2002.
7. REFERENCES


8. OTHER CURRENT PROJECTS ON ENDOCRINE DISRUPTERS IN AUSTRALIA

8.1 University of Technology Sydney & Vivendi Water (provided by Keith Craig)

Dr Richard Lim from the Department of Environmental Sciences and Dr Jennifer Batty from the School of Biological Science at Napier University, UK, were the first to report the effects of EDCs in sewage contaminated river water on male mosquitofish in Australia. The mosquitofish has many attributes that make it an appropriate test model to examine the effects of these compounds in the field and in the laboratory. Mature male mosquitofish have a pair of anal fins with hooks that are used to hold on to the female during copulation and the transfer of sperm. The growth of the anal fins is triggered by the male hormone testosterone circulating in the blood system during development.

Male mosquitofish collected at sites downstream from two sewerage treatment plants in western Sydney had significantly shorter anal fins than those collected from uncontaminated sites upstream. These effects are caused by oestrogenic compounds that include female hormones which are commonly present in sewage effluent at levels that feminise male fish. This has been confirmed in the laboratory experiments by exposing fish to treated sewage, and testing for changes in their sexual behaviour as well as for specific EDCs like oestrogen.

A reduction in sex drive in male fish collected from waterways contaminated by sewage effluent could also be observed. Female hormone mimics also enhance the production of vitellogenin in male fish, a precursor to the production of yolk that is not normally present in males. Female fish also develop abnormalities when affected by EDCs. Male hormone mimics, like those found in pulp mill effluent, can induce the elongation of the anal fins of female fish.

Dr Lim, Sharyn Gale and Christopher Doyle more recently investigated the potential impacts of EDCs in sewage effluent reused in agriculture. This study was commissioned by Vivendi Water Australia. The impact of treated sewage effluent contaminated with EDCs used in agriculture on crop plants and animals, and indirectly on livestock through the food chain was investigated. The researchers concluded that some of these compounds could potentially be of concern, and are planning to follow up with a larger research project.

Water resource managers and researchers in State agencies and industry are also interested in monitoring endocrine disrupters in sewage effluent and in research conducted by Dr Lim and his colleagues. This has led to the development of collaborative research proposals between the researchers and the NSW Environment Protection Authority, Sydney Water, and Vivendi Water Australia.

Dr Lim is also on the staff of the UTS Institute for Water and Environmental Resources Management, which has drawn together a unique blend of research strengths. Ecotoxicology underpins the Institute’s significant research strengths in groundwater and vegetation interaction, and the urban and rural water cycles. All researchers in this group have been involved in major environmental projects both in Australia and overseas.

8.2 Water Quality Improvements During Aquifer Storage and Recovery (provided by Rai Kookana)

AWWARF Project 2618, (PI) Peter Dillon & (Co PI) Simon Toze and a very large and dispersed group of scientists and engineers in USA, Netherlands, France and Australia

This project originated from a request for proposals by AWWARF, who recognized the importance of aquifer storage and recovery as an emerging technology, accepted in USA as having a significant role for inter-season storage of drinking water, and in Europe and Australia for its potential for water treatment. However a better understanding of water quality changes occurring at aquifer storage and recovery sites, and sustainable treatment processes in aquifers is necessary in order to enable water utilities to take advantage of these. In this project the term
aquifer storage and recovery is taken to include sites where the same well is used for injection and recovery (the strict definition of ASR, as in Pyne 1995) as well as systems having different wells for injection and recovery.

The objectives of this project are therefore:
1. To deliver a comprehensive, quantitative, scientifically robust evaluation of sustainable attenuation rates for selected pathogens and organics (natural and synthetic) in saturated groundwater at artificial recharge sites, based on field and laboratory data.
2. To encapsulate this knowledge into simple models to predict changes in water quality, and to test and report on the predictive performance of these models at field-test sites.
3. To communicate outcomes of the study so as to be of value to water utilities and regulators in re-evaluating pretreatment requirements for aquifer storage and recovery, and improve accuracy of information on protection of the health of consumers and the environment.

The project is progressing via six tasks as follows;
1. review of saturated zone treatment processes
2. compile information from existing ASR sites
3. develop hypotheses for water quality improvements
4. develop methods for estimating water quality improvements at a given site, and generate predictions at primary sites
5. implement a monitoring plan for testing estimation methods (at several field sites and bench scale testing as appropriate) and filling in any gaps in data
6. write final report and papers

A poster paper on this project will be on display on 19 June 2002 at the AWWA Annual Conference in New Orleans. A number of papers on various interesting and innovative parts of the project will be presented at the 4th International Symposium on Artificial Recharge of Groundwater (ISAR4) in Adelaide Australia 22-26 Sept 2002. The mid-conference tour includes a site visit to the Bolivar ASR site (one of the AWWARF project primary sites). For more details of ISAR4, including provisional scientific program see: http://www.groundwater.com.au/conf/ISAR4.htm

8.3 Use Of Constructed Wetlands To Remove Toxicants From Tertiary Treated Effluent (provided by Heather Chapman)

Investigators: Dr Heather Chapman and Dr Margaret Greenway, School of Environmental Engineering, Griffith University

The principal aim of this research is to investigate the removal of trace organic toxicants and selected heavy metals that are known or suspected environmental endocrine disruptors (EEDs) from tertiary treated water. This involves tracking of the contaminants from the source (raw effluent), through the various tertiary treatments and in a constructed wetland, which is the receiving environment.

**Stage 1. Landsborough Water Reclamation Plant and Ornamental Wetland**

The first stage of this project is to characterise compounds present in the effluent by chemical analysis. Samples of effluent have been taken from the Landsborough Water Reclamation Plant and the Landsborough Ornamental Wetlands and screened for toxicants. This forms a set of baseline data for subsequent comparison. Baseline monitoring of the ornamental wetlands has not detected heavy metals or pesticides above the limit of reporting for the analytical methods. The Landsborough Water Reclamation Plant (WRP) owned and operated by CalAqua, Caloundra City Council is an advanced tertiary treatment facility which includes inlet screening and grit removal, an alternating bioreactor, post denitrification, clarification, tertiary sand filtration, ozonation, biologically activated carbon filtration and UV disinfection.
Compounds detected in the raw sewage into the Landsborough Water Reclamation Plant include chlorpyrifos, diazinon, malathion, piperonyl butoxide, diethyltoluamide (DEET) and simazine. Of these, the only compound that persisted through all of the treatment stages of the plant, was the herbicide simazine, but only at trace concentrations. There is a safety margin of several orders of magnitude based the risk assessment process used by the USEPA and would not be expected to present a hazard to aquatic ecosystems.

Most chemical compounds/elements are removed from the effluent by the secondary and tertiary treatments at the Landsborough Water Reclamation Plant. While this is a demonstration of the effectiveness of the advanced treatments at the plant, it does not however facilitate assessment of the removal of the chemicals by the wetland if they are not present in the final effluent prior to discharge.

The ornamental wetland is a set of seven fully reticulated ponds separated by streams and riffle zones. Water in the wetland was introduced gradually from adjacent Ewen Maddock Dam, to enable the growth of plants. Fauna was not intentionally introduced but the wetlands now support a variety of fauna groups including insects, crustaceans, frogs, fish and a number of vertebrates. The wetlands have been set up with a series of board walks and picnic areas, and it is intended to use the wetlands for educational and research purposes.

**Stage 2. Oxley Sub-surface wetland and Cooroy Free Water Surface Wetland**

It was also shown in the first stage of this project that the advanced tertiary treatments at the Landsborough Water Reclamation Plant were very efficient at removing most chemicals. Because of this even if a discharge of tertiary treated effluent to the Landsborough Ornamental Wetland had occurred, the chance of detecting chemicals in the wetland were minimal. Stage 2 of this project will be a comparison of the toxicant removal efficiency between a sub-surface wetland (Oxley) and a free water surface wetland (Cooroy) both receiving secondary treated effluent. The researchers would like to acknowledge the Queensland Water Recycling Strategy for funding this work and CalAqua (Caloundra City Council), Brisbane City Council and Noosa Shire Council, for inkind support.