VALIDATION OF DUAL MEMBRANE TREATMENT FOR INDIRECT POTABLE REUSE

K Linge, P Blair, F Busetti, C Rodriguez, M Handyside, J Blythe, M Bromley, O Lord, S Higginson, A Heitz, C Joll, C Newby, S Toze

Abstract

The Western Australia's Premier's Collaborative Research Program (PCRP) project 'Characterising Treated Wastewater for Drinking Purposes Following Reverse Osmosis Treatment' commenced in October 2005, to determine the potential risks of replenishing drinking water aquifers with MF/RO treated secondary wastewater from Perth's wastewater treatment plants.

A brief report on the project won the Michael Flynn Award for the best poster paper at Ozwater'10. The results included those published in Water, February 2010, by Rodriguez *et al*, entitled *Efficiency of RO for Removal of Chemical Contaminants*. Consequently, this version has been drafted to cover the other aspects of the study, principally the identification of suitable indicators which could be used to validate treatment performance.

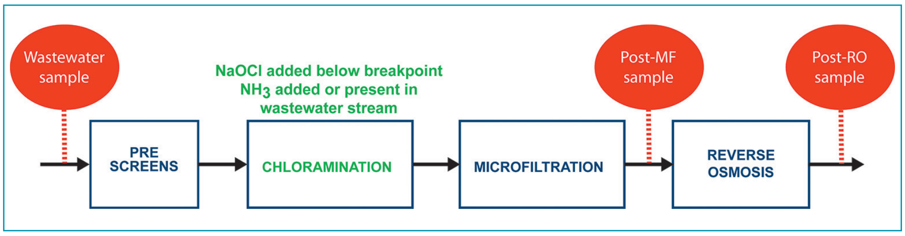

Figure 1. A schematic showing MF/RO treatment process and the sampling locations for wastewater, post-MF and post-RO samples. A pre-chloramination step used to protect the RO membrane is also highlighted and was found to increase concentration of some chemicals, such as disinfection by-products, during MF/RO treatment.

Introduction

In recent years Perth has experienced a significant reduction in water available from dams and groundwater.

Population growth, decreases in traditional drinking water sources and climate variability mean that Perth needs to look increasingly at using water more efficiently and developing new water sources. One of several government strategies is through recycling of treated wastewater. However, a lack of knowledge of health and environmental risks associated with chemicals in wastewater has been a barrier preventing establishment of large reuse schemes.

In 2005 the Western Australian government awarded a grant to the Department of Health, Department of Environment, Water Corporation of Western Australia, Curtin University, ChemCentre, CSIRO and the National Measurement Institute to complete a collaborative project on recycled water quality in the context of potential re-injection to groundwater. The specific objectives of the project were:

- To analyse the final treated wastewaters from the Water Corporation's three large metropolitan wastewater treatment plants (WTTPs) to characterise their microbial and chemical constituents and understand any seasonal and catchment differences in trace contaminants of concern in relation to human health and health of the environment;
- To assess the performance of microfiltration and reverse osmosis (MF/RO) membrane treatment at the Kwinana Water Reclamation Plant (KWRP) and the specially constructed Beenyup Pilot Plant (BPP), to consistently produce water meeting the various health and environmental guidelines for augmentation of drinking water supplies by re-injection into groundwater;
- To use the research output to develop and refine health and environmental guidelines for aquifer recharge of recycled water for indirect potable reuse on the Swan Coastal Plain.

Evidenced-based approach to recycled water safety for groundwater replenishment.

Chemical and Data Analysis

Almost 400 chemicals, in 15 different chemical classes (see Table 1), were tested in the project. Eight laboratories were involved in the analysis and more than 20,000 records produced, not including field and trip blanks. Chemicals were selected for analysis based on their current use in Western Australia, their toxicological concern and evidence of detection in wastewater reported in the literature. Measured contaminant concentrations were compared with established drinking water standards and requirements or other toxicological guidelines to determine human health risks (Rodriguez *et al*., 2007). As guidelines and standards had not been developed for many chemicals, the threshold of toxicological concern was used for the preliminary health risk assessment to determine key contaminants that need to be monitored (Rodriguez *et al*., 2007).

The data collected was used to calculate the percentage detection and median concentrations in wastewater and MF/RO treated water (post-RO water) for each chemical. Analysis by wastewater treatment plant (WWTP) and by season was also conducted. Treatment efficiency was calculated for chemicals detected in wastewater using wastewater and post-

RO samples matched for plant, date, and type of sample (grab or composite). Treatment efficiency was calculated as a percentage of removal from secondary treated wastewater, based on the concentration in the post-RO sample. For those chemicals not detected in post-RO water, the efficiency was calculated assuming a concentration equal to half the limit of detection as a conservative estimate. In these cases removal efficiency calculation was strongly influenced by the concentration measured in secondary wastewater. Where concentrations in secondary wastewater were close to detection limits then the calculated removal was an underestimate.

Sampling Sites

Figure 2. Composite samples were taken using an automated ISCO 4700 refrigerated sampler over 24h.

Samples were collected from Perth's three main WWTPs: Woodman Point, Subiaco and Beenyup. These plants treat 85% of the wastewater produced in the Perth metropolitan area and receive water from varied sources. The Beenyup WWTP serves the north of the city, which is mainly residential. The plant has a current capacity of 120 megalitres per day (ML/day) that serves a population of about 600,000 and a planned upgrade to treat 200 ML/day. The Subiaco WWTP services the Perth central area and has a capacity of 61 ML/day, serving a population of about 300,000. This plant receives the effluent of several major Perth hospitals, though it is estimated that only 0.34% of wastewater to Subiaco WWTP is sourced from hospitals, of which only 36% is classed as medical waste. The Woodman Point WWTP serves the south metropolitan region with a capacity of 160 ML/day, serving a population of about 800,000. The Woodman Point catchment, the source water to KWRP, is a more industrialised catchment than the Beenyup and Subiaco catchments and industrial waste forms 6% of wastewater. However all WWTPs have low industrial loading by international standards.

Recycled water quality after MF/RO treatment was evaluated at two plants: the operational plant located at KWRP, and the Beenyup Pilot Plant (BPP), which was installed during the project to treat water produced by Beenyup WWTP. KWRP treats up to 24 ML/day of wastewater to produce about 17 ML/day of product water, while BPP treats about 96 kL/day of secondary treated wastewater to produce about 67 kL/day of RO permeate. As part of the MF/RO process, it is standard practice to chloraminate wastewater before MF to minimise RO membrane fouling, and this occurs at both BPP and KWRP. While the MF/RO treatment process is slightly different at each plant, both consist of an

Table 1. Summary of the 15 chemicals classes tested in the project, including the number of analytes in each class, and analytical methods used. More than 20,000 records were produced during the project, not including field and trip blanks.

Laboratory	Chemical Classes	Number of Analytes	Analytical Method
Curtin University	VOCs	57	Purge and trap gas chromatography mass spectrometry (GC-MS)
	Halogenated DBPs	32	Purge and trap GC-MS, liquid-liquid extraction (LLE) and derivatisation GC-MS, LLE-GC-MS
	Inorganic DBPs (Anions)	3	Ion chromatography
	N-nitrosamines	9	Solid-phase extraction (SPE) GC-MS
	PAHs	17	Stirbar sorptive extraction (SBSE) GC-MS
	Phenols	16	Derivatisation and SBSE-GC-MS
	Complexing Agents	4	LLE and derivatisation GC-MS
	Hormones	4	SPE and liquid chromatography tandem mass spectrometry (LC-MS/MS)
	Pharmaceuticals	36	SPE-LC-MS/MS
	Miscellaneous	11	SPME-GC-MS, SBSE-GC-MS, LLE and derivatisation GC-MS, derivatisation and SBSE-GC-MS
National Measurement Institute	Dioxin, furans and dioxin-like PCBs	29	High resolution GC and high resolution MS
	Chromium VI	1	Inductively coupled plasma optical emission spectrometry (ICP-OES) and colorimetric methods
ChemCentre	Pesticides	117	GC with electron capture detection or nitrogen phosphorus detection, or GC-MS
	Metals and Metalloids	28	ICP-OES, inductively coupled plasma mass spectrometry, or chemical vapour generation atomic adsorption spectrometry
	Radionuclides	2	Sample preparation only for gross α and gross β particle activity
Radiation Health WA and ARPANSA	Gross α and gross β particle activity	2	Gas flow proportional counting
SGS	General wastewater parameters	32	Various analytical methods

initial coarse pre-screening, chloramination and pH adjustment, MF, and RO membrane treatment, as depicted in Figure 1. The majority of samples from KWRP and BPP were either wastewater or post-RO water. However, on a number of occasions, a post-MF sample was also taken, which provided an indication of the impact of chloramination on the chemicals tested during the project.

Sampling Events

Sampling during the PCRP project was carried out during seven approximately quarterly sampling events from December 2006 to October 2008 (PCRP, 2009, Rodriguez *et al*., 2010). Six sampling events were undertaken for all chemical classes, with an additional seventh sampling event undertaken for *N*-nitrosamines only. For most chemical classes, composite samples were taken over 24 h using an automated and refrigerated ISCO 4700 sampler (Figure 2). However composite sampling was not appropriate for unstable or volatile analytes and therefore grab samples were collected for those chemicals for which concentrations were time-dependent. Field and trip blanks were collected on each day of sampling.

For many chemical classes, preservation agents were required to preserve the analyte prior to analysis (PCRP, 2009) and these were added to the bottle prior to sample collection (or in the case of composite samples, prior to sub-sample collection). For bottles containing preservation agent, special care was taken not to overfill the bottle and thereby lose preservative.

Replicate sampling of all samples was impractical because of the total number of samples and analytes collected, as well as limitations on the total volume of sample collected by the composite autosamplers. Replicate samples were, however, taken in Events 4, 5 and 6 of both secondary wastewater (12% of samples) and post-RO water (8% of samples), and at both BPP and KWRP. Duplicate samples were taken for all sample points in Event 7.

Analytical QA/QC and Inter-laboratory Testing

A Quality Assurance (QA) program was implemented as part of the project to ensure data was reliable and of good quality. The National Measurement Institute (NMI) provided the QA/QC coordination to the project and a number of publications and guidelines were taken into consideration, including Australian Standards for test methods (Standards Australia, 1990) and laboratory operation (Standards Australia, 2005), and standard methods for the analysis of water and wastewater (Eaton *et al*., 2005).

During the project Curtin and CCWA developed in-house QA programs for their analytical methods, which were all developed specifically for the project. NMI is NATA accredited laboratory, while SGS uses NATA-accredited methods and therefore QA programs were already in place for the analyses they undertook. In addition to concentration data, each laboratory calculated method uncertainty, limits of reporting, precision, and bias or accuracy. Curtin also ensured that developed methods were scrutinised through appropriate peer review processes including consultation with leading international experts and publication of methods in peer reviewed journals (Busetti *et al*., 2009, Busetti *et al*., 2008, Busetti and Heitz, in press). Inter-laboratory testing was used to aid method validation where possible. Inter-laboratory tests were organised by Curtin during Event 2 (May-June 2007) for selected antibiotics and pharmaceuticals. Other participants were National Measurement Institute (Sydney NSW), and DVGW-Technologiezentrum Wasser (Karlsruhe, Germany). A NATA-accredited proficiency test for 3 *N*-nitrosamines, a group identified to be of particular interest during the project, was undertaken through Proficiency Testing Australia in March 2008. This test was limited, however, because the sample supplied had a deionised water matrix and analyte concentrations about 3 orders of magnitude greater than those measured in the PCRP project. An additional *N*-nitrosamine inter-laboratory test was therefore organised by Curtin and undertaken during PCRP Sampling Event 6 (June 2008) for measurement of realistic concentrations in wastewater and RO water, with participation of 2 external laboratories, Queensland Health Scientific Services, and the Australian Water Quality Research Centre (SA). While there was insufficient data to perform a full statistical analysis, generally there was very good agreement between results from different laboratories.

Results

An overview of the chemical results from the project have already been published in Water (Rodriguez *et al*., 2010) and therefore are not repeated in this article. Of the 396 compounds analysed, 195 were detected at least once in secondary wastewater, while 140 were detected at least once in post-RO water, albeit at very low concentration levels below health significance. Despite variations in wastewater catchment, there were only minor variations in concentrations of chemicals between WWTPs, although seasonal differences were seen for some compound classes.

Health-based risk quotients were calculated for each analyte in secondary wastewater and post-RO water. N-nitrosodimethylamine (NDMA), a disinfection-by-product, was occasionally detected above the *Australian Guidelines for Water Recycling (Phase 2): Augmentation of Drinking Water Supplies* guideline value of 10 ng/L (AGWR, 2008). However, this guideline value is very stringent, being a tenth of the 100 ng/L limit in the *WHO Guidelines for Drinking-Water Quality* (WHO, 2008) and recently proposed for the *Draft Australian Drinking Water Guidelines* (ADWG, 2010). NDMA concentrations never exceeded 100 ng/L. Furthermore the average concentration of NDMA did not exceed 10 ng/L, and this is relevant as post-treatment maximum concentrations will be smoothed by retention in groundwater for months to years. For all other chemicals, the water quality achieved after the MF/RO treatment complied with ADWG and AGWR guidelines. Thus the MF/RO treatment process resulted in recycled water that meets the required health and environmental guidelines for augmentation of drinking water supplies.

Eight compounds were found to have higher percentage detections (albeit lower median concentrations) in post-RO water compared to secondary wastewater, and this was attributed to contamination (e.g. toluene), formation during chloramination (e.g. halomethanes) and unintentional addition during the MF/RO process (e.g. acrylonitrile, chlorate). The ability to sample post-MF (see Figure 3) during the project was essential to understanding the overall impact of MF/RO on the chemicals tested, which demonstrated that the chloramination procedure, membrane materials and anti-scalant chemical usage all need to be considered as potential sources of chemicals in post-RO water. For chemicals that form or are added during treatment, calculations across the whole treatment train do not reflect RO removal efficiency and RO treatment performance requires monitoring immediately prior to RO rather than using secondary wastewater, particularly for disinfection by-products.

Table 2. Treatment Performance Indicators were chosen based on the key properties for chemical rejection by MF/RO (size, hydrophobicity, polarity, acidic/basic character, and solubility in water) from chemicals detected in wastewater at sufficiently high concentrations with sufficient frequency (typically >80% detection).

	Secondary Wastewater % Detection	Median Removal Efficiency	Chemicals represented
NDMA (N-nitrosamines)	96%	Intermediate 79%	Small size, uncharged, highly polar organic molecules
Chloroform (DBP)	85%	Intermediate 82%	Small size, uncharged, non-polar, non-ionic organic molecules
Bromochloromethane (DBP)	94%	Intermediate 63%	Small size, uncharged organic, non-polar organic molecules
1,4-dichlorobenzene (VOCs)	95%	Intermediate 84%	Intermediate size, non-polar volatile organic molecules
EDTA (Complexing Agents)	100%	Good 99.5%	Large size, polar charged, acidic organic molecules
Diclofenac (Acidic Pharmaceutical)	100%	Good 99.6%	Large size, polar, slightly hydrophobic, acidic organic molecules
Boron (Metals and metalloids)	100%	Intermediate 62%	Small size, charged inorganic molecules
Nitrate (Inorganic Anions)	100%	Intermediate 88%	Small size, negatively charged (anions), weak acid inorganic molecules
Carbamazepine (Non-polar pharmaceutical)	97%	Good 99.8%	Moderately large size, non-polar uncharged organic molecules

Microbiological and Toxicity Analysis

The microbiological quality of the secondary wastewater was characterised at Beenyup WWTP and Subiaco WWTP. In secondary wastewater thermotolerant coliforms and enterococci were always detectable. Coliphages, often used as indicators of viral contamination, were detected in 95% of the Subiaco and 100% of the Beenyup samples. Adenovirus were detected in 68% of the Subiaco and in all of the Beenyup wastewater samples. No microbial parameters were detected after MF/RO treatment. Two challenge tests were undertaken at BPP using the coliphage MS2 as an indicator of enteric viruses to assess the capacity of the RO membranes to exclude such viruses. The results showed that the RO membranes alone were able to achieve at least a 4 log removal (i.e. 99.99% removal) of virus.

Health effects of chemical mixtures were not specifically addressed in the screening health risk assessment conducted in this study. However, no cytoxicity and genotoxicity were observed when human cells were exposed for three hours to secondary treated wastewater or post-RO water samples using the cytokinesis-block micronucleus assay, which measures DNA damage, the arrest of cellular growth and multiplication, and cell toxicity (Fenech, 2007).

Indicators for Future Monitoring

A key outcome of this research was the identification of chemical indicators of RO treatment performance and recycled water quality indicators relevant for Western Australia. Following Drewes *et al*. (2008), in this study an indicator was defined as an individual chemical occurring at quantifiable level, which represents certain physicochemical and biodegradable characteristics of trace constituents relevant to fate and transport during treatment. Indicators can be used to regularly validate treatment performance without the need to monitor all chemicals of concern. Indicator chemicals in this project were selected considering percentage detection and concentration in secondary wastewater, and percentage removal by MF/RO treatment. Indicators were selected either to indicate specific performance of a treatment process or safety of the treated water:

Treatment Performance Indicators have chemical or physical characteristics that can be linked to the removal mechanism and are present in wastewater at sufficiently high concentrations with sufficient frequency (typically >80% detection) to determine the degree of reduction through a process. The key properties for chemical rejection by MF/RO are size, hydrophobicity, polarity, acidic/basic character, and solubility in water.

Recycled Water Quality Indicators demonstrate safety of the MF/RO treated water with respect to a group of compounds that share similar physical and chemical properties and provide additional confidence beyond treatment performance monitoring. They are particularly useful for chemical classes where no chemical was detected in wastewater with sufficient concentration or frequency to be used as a treatment performance indicator.

The results from this project were analysed considering the characteristics of a good treatment performance indicator chemical to derive a group of indicators appropriate for monitoring chemical removal by MF/RO treatment. Selected treatment performance indicators (Table 2) were normally detected in secondary wastewater more than 90% of the time. They were usually detected at higher concentrations than other chemicals of the same group. If more than one compound was commonly detected in secondary wastewater at similar concentrations, the one with the lower percentage of rejection was selected as it is considered more sensitive to assess the performance of the treatment. For each of the chemical classes studied, suitable recycled water quality indicator chemicals were also identified. In many cases, the best chemical indicator for recycled water quality was also a suitable treatment performance indicator. The chemicals chosen as recycled water quality indicators but were not included as treatment performance indicators are listed in Table 3. Both treatment performance and recycled water quality indicators have been recommended for use in the Water Corporation's Groundwater Replenishment Trial.

Conclusions

The Water Corporation's Groundwater Replenishment Trial will treat wastewater with microfiltration (MF), reverse osmosis (RO) and ultraviolet light (UV) before injecting it into the Leederville aquifer, with re-extraction for drinking water planned for the future. The research carried out in the PCRP project has resulted in the development of reliable methods to characterise recycled water quality following secondary and MF/RO treatment and has confirmed that MF/RO treatment reliably produces recycled water suitable for augmenting public drinking water supplies. Chemical

Table 3. Additional Recycled Water Quality Indicators chosen for chemical classes where no chemical was detected in wastewater with sufficient concentration or frequency to be used as a Treatment Performance Indicator.

	Secondary Wastewater % Detection	Median Removal Efficiency	Chemicals represented
Trifluralin (Pesticides)	91%	Good 97%	Large size, polar organic molecules
2,4,6-trichlorophenol (Phenols)	64%	Intermediate 82%	Moderately large size, hydrophobic, moderately acidic organic molecules that are uncharged or charged depending on pH
Fluorene (PAHs)	64%	Intermediate 75%	Moderately large size, non-polar uncharged, hydrophobic, purely aromatic organic molecules
Octadioxin (Dioxins, furans & dioxin-like PCBs)	67%	Intermediate 72%	Large size, uncharged hydrophobic organic molecules
Estrone (Hormones)	48%	Good, 96%	Large size, uncharged, aromatic organic molecules that are capable of hydrogen bonding
Chlorate (Inorganic DBPs)	37%	Intermediate 75%	Small size, weak acid inorganic molecules
1,4 Dioxane (Misc)	100%	Intermediate 89%	Small size, uncharged, slightly polar and water soluble organic molecules

contaminants were removed to levels below health significance and the water quality achieved after the MF/RO treatment complied with the *Australian Drinking Water Guidelines* (ADWG, 2004) and with the *Australian Guidelines for Water Recycling: Augmentation of Drinking Water Supplies* (AGWR, 2008), except occasionally for *N*-nitrosamines. While not considered a significant health risk, *N*-nitrosamines including NDMA require further study, and this is on-going through regular monitoring during the Groundwater Replenishment Trial and through research studying *N*-nitrosamine pre-treatment and formation currently being undertaken by the Curtin Water Quality Research Centre, funded by the Australian Research Council, the Water Corporation and Water Quality Research Australia.

The final PCRP project report provides the information necessary for WA government to develop regulation for conducting indirect potable reuse using MF/RO treatment, and includes health and environmental recommendations for the Groundwater Replenishment Trial. This research has indicated that there will be a high degree of safety associated with further investigation of indirect potable reuse in Western Australia when MF/RO treatment is used in the treatment train. Identification of key chemicals (indicators of treatment performance and recycled water quality) for monitoring, along with the implementation of a risk management framework, provides confidence to proceed with the Groundwater Replenishment Trial. Further information is available in the full technical report: *Premier's Collaborative Research Program* (2005-2008): *"Characterising Treated Wastewater For Drinking Purposes Following Reverse Osmosis Treatment". Technical Report*, Published by Department of Health, Western Australia ISBN 978-0-9807477-0-6. The report is available to download from: http://www.public.health.wa.gov.au/3/1117/2/groundwater_replenishment_trial.pm

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The Authors

Kathryn L Linge (email: k.linge@curtin.edu.au), **Francesco Busetti, Cynthia Joll, Anna Heitz** are at the Curtin Water Quality Research Centre.

Palenque Blair, Mark Handyside and **Simon Higginson** are with the Water Corporation of Western Australia.

Clemencia Rodriguez is with the WA Department of Health, **Justin Blythe** is with KBR Pty Ltd, **Melissa Bromley** with the Department of Water, **Oana Lord** with the National Measurement Institute, **Clare Newby** with ChemCentre and **Simon Toze** with CSIRO, Land and Water.

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