

# **Demonstration of Robust Water Recycling:** Operating Performance and Water Quality Report

A report of a study funded by the Australian Water Recycling Centre of Excellence

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# Demonstration of Robust Water Recycling: Operating Performance and Water Quality Report

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## About the Australian Water Recycling Centre of Excellence

The mission of the Australian Water Recycling Centre of Excellence is to enhance management and use of water recycling through industry partnerships, build capacity and capability within the recycled water industry, and promote water recycling as a socially, environmentally and economically sustainable option for future water security.

The Australian Government has provided \$20 million to the Centre through its National Urban Water and Desalination Plan to support applied research and development projects which meet water recycling challenges for Australia's irrigation, urban development, food processing, heavy industry and water utility sectors. This funding has levered an additional \$40 million investment from more than 80 private and public organisations, in Australia and overseas.

ISBN 978-1-922202-58-1

#### Citation:

J. Zhang, A. Knight, P. Scales, M. Packer, K. Northcott, J-P. Croué, S. Allard, J. Tan and S.Gray (2015). *Demonstration of Robust Water Recycling: Operating performance and water quality report*, Australian Water Recycling Centre of Excellence, Brisbane, Australia.

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Date of publication: August, 2015

#### Publisher:

Australian Water Recycling Centre of Excellence Level 5, 200 Creek St, Brisbane, Queensland 4000 www.australianwaterrecycling.com.au

This report was funded by the Australian Water Recycling Centre of Excellence through the Australian Government's National Urban Water and Desalination Plan.

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# 1. Executive Summary

The Advanced Water Treatment Plant (AWTP) for Australian Antarctic Division's (AAD) Davis Station was located at Selfs Point Wastewater Treatment Plant (SPWWTP), Hobart, to demonstration its performance and reliability. This report outlines the operations and water quality (microbiological, metals, nutrients, DOC) demonstrated during the trial. It does not cover micro-contaminants or robustness of the plant, which are presented in other Australian Water Recycling Centre of Excellence reports.

A major issue for the trials was the inability to have the entire process fully commissioned until late into the trials period, and thus further evaluation of the AWTP is recommended.

The main outcomes from this report are:

- The ozone system suffered several failures during commissioning, but once the power of the ozone generation system was matched to the individual ozone cell it performed reliably.
- High feedwater turbidity led to reduced or no ozone residual from the ozone system. However, LRV 2 for *E. coli* and somatic coliphage was claimed based on ozone dose >11.7 mg/L, even if the ozone residual was zero.
- Backwashing and CEBs effectively managed the fouling of ceramic MF, and the filtrate turbidity was <0.3 NTU.
- BDOC in the BAC filtrate (>1 mg/L) remained significantly above the 0.5 mg/L required for biological stability.
- The RO CIPs were required every 4-5 months, so 3 CIPs are expected each year.
- The cartridge filter required replacement every 2 weeks and AAD were accepting of this.
- Regrowth of coliforms was detect in the RO permeate after 5 months operation. No regrowth was observed 2 months after cleaning.
- Metals, DPBs, *E. coli* and virus in the product water were all below the ADWG. DOC, P and TN were also low in the product water.
- The RO concentrate was high in Zn, P, and DBPs, but bioassay and toxicity results indicated the RO concentrate was significantly improved in terms of toxicity and bioassay activity compared to the feedwater.

#### Recommendations:

A further 10-12 months of operational trails are recommended to demonstrate:

- The reliability of the plant in fully unattended operation mode.
- The readily achievable ceramic MF filtrate turbidity readings now the turbidity meter configuration is finalised, and that these turbidity values be used to update the CCP alert value.
- The reliability of the chlorination system, as it was only fully operational in the last month of current operations.

Once the plant is installed at Davis Station, the following actions are recommended:

• Check the concentrations of Zn and other metals, and P, as well as the bioassay and toxicity values and compare to the values for Selfs Point.

- Undertake a water quality review of the feedwater, product water and other process streams as part of the re-commissioning process.
- Compare the water quality performance achieved by each treatment barrier (ie. similar ceramic MF filtrate turbidity etc) to that achieved at Selfs Point, and review CCP target, alert and critical alarm values.
- Consider chlorinating stored water prior to its distribution at Davis station.

If further AWTPs are built, then the following design alterations be considered:

- Increasing in the EBCT of the BAC to reduce biofouling fouling of the subsequent RO process.
- Consider including automated cleaning of the RO permeate lines to control biofilm growth.
- Increasing the residence time of the calcite contactor.
- Construction of pipework and fittings downstream of the chlorination dosing point in plastic or other material less prone to corrosion.

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# Nomenclature

AAD	Australian Antarctic Division
ADWG	Australia Drinking Water Guidelines
ANDS	Australian National Data Service
AWTP	Advanced water treatment plant
AWRCoE	Australian Water Recycling Centre of Excellence
BAC	Biological activated carbon
BDOC	Biodegradable organic carbon
CIP	Clean in place
CCP	Critical control points
СТ	Concentration x time
DBP	Disinfection by-product
DOC	Dissolved organic carbon
EBCT	Emptied bed contact time
HACCP	Hazard analysis and critical control point
HRT	Hydraulic residence time
HRT <sub>10</sub>	Hydraulic residence time for 10% of the flow to pass
LRV	Log removal value
LSI	Langelier Saturation Index
MBR	Membrane bioreactor
MF	Microfiltration
PDT	Pressure decay test
QRMA	Quantitative microbial risk assessment
RO	Reverse osmosis
RWQMP	Recycled water quality management plan
SCADA	Supervisory control and data acquisition
SEM	Scanning electron microscopy
SPWWTP	Selfs Point wastewater treatment plant
TDS	Total dissolved solids
TMP	Transmembrane pressure
TN	Total nitrogen
TOC	Total organic carbon
TSS	Total suspended solids
UV	Ultra-violet disinfection

# 2. Introduction

The Australian Antarctic Division (AAD) is upgrading their wastewater treatment system at Davis Station to reduce their effect on the pristine environment. As part of the upgrade, AAD also wished to investigate the potential to further upgrade their wastewater treatment system to potentially enable potable water recycling. Water recycling on Antarctic stations has the possibility to significantly reduce energy consumption as the current system at Davis Station utilises water from a hypersaline tarn and requires heating of the water.

A membrane bioreactor (MBR) was chosen for treatment of wastewater and an advanced water treatment plant (AWTP) was designed and constructed to treat MBR effluent to have lower environmental impact and to produce potable water. A quantitative microbial risk assessment (QMRA) was undertaken<sup>1</sup> to identify the required log reduction values (LRV) for potable water production in these small communities. For Davis Station, the required LRVs are: 12.1 for virus, 12.3 bacteria, and 10.4 for protozoa.

The AWTP plant was initially designed assuming that no LRV could be credited to the wastewater MBR, as biological processes were required to be validated on-site and validation of a biological process at Davis Station by intensive water quality sampling was deemed infeasible. The AWTP consisted of ozonation, ceramic microfiltration (ceramic MF), biological activated carbon (BAC), reverse osmosis (RO), ultra-violet disinfection (UV), a calcite contactor and chlorination. The large number of unit processes was required to achieve the high LRVs for pathogens using conservative estimates of achievable LRV across each unit.

The AWTP was constructed by AAD and located at Selfs Point Wastewater Treatment Plant, Hobart, Tasmania (SPWWTP) so that its performance could be verified before installation at Davis Station. The purpose of the trials was to:

- 1. Verify reliable water quality production of the demonstration plant over an extended period of time (approx. 12 months)
- 2. Demonstrate reliable operation of the plant, including maintenance requirements and sensor calibration frequencies, and
- 3. Produce a draft Recycled Water Quality Management Plan (RWQMP) and a Hazard Analysis and Critical Control Point (HACCP) analysis report.

SPWWTP is a biological nutrient removal process that relies on settling for particle removal. As such, turbidity values were likely to be higher at SPWWTP than for Davis Stations MBR, and the water quality was assumed to be of worse quality than will be experienced at Davis Station. Thus, the trials at SPWWTP provide a conservative measure of its operating performance at Davis Station.

Initial operation during commissioning identified that achieving an ozone residual in the first barrier was unreliable for SPWWTP feed. Additionally, the ceramic MF was

<sup>1.</sup> S. Fiona Barker, Michael Packer, Peter J. Scales, Stephen Gray, Ian Snape, Andrew J. Hamilton, Pathogen reduction requirements for direct potable reuse in Antarctica: Evaluating human health risks in small communities. Science of the Total Environment, 461-462 (2013) 723-733

accredited by the California Department of Health for lower LRV than was originally to be claimed by the AWTP. Claiming lower LRV for the ceramic MF negated any requirements for challenge tests for the ceramic MF, but required reassessment of the claimed LRV across each barrier, as did the inability to reliably maintain ozone residual. The final LRV for each unit process and the rationale and operating conditions associated with these LRVs are detailed in the LRV Table<sup>2</sup>. LRV are claimed across the MBR, as during the course of the project, data from the NatVal MBR project identified that conservative LRV of 2 for pathogens could be claimed. The LRV table was reviewed by water industry professionals with significant experience in regulation and compliance. Details of each LRV are discussed for each unit process.

No challenge tests were undertaken, apart from a Rhodamine WT challenge test of the RO system during commissioning and use of native pathogens across the ozone system. The LRV claimed are, therefore, related to pre-accepted performance monitoring of the system (eg. pressure decay test (PDT) across the ceramic MF, conductivity and PDT across RO, UV dose for UV disinfection, use of CT times for chlorination). Details of these are provided in the Log Reduction Value Table report<sup>2</sup>.

This report summarises the operation and water quality results for the trials, excluding the micro-contaminants results. Separate reports detail micro-contaminant removals<sup>3,4</sup>. Likewise, there are separate reports for the Robustness and Energy Consumption of the plant, RWQMP and HACCP reports.

This report considers each unit process in series, outlining the performance required and the critical control points (CCP). Data on the operation of each unit process is presented and discussed, along with the barriers ability to meet CCP and operational requirements. General water quality covering dissolved organic carbon (DOC), metals, nitrogen, *E. coli*, and virus are also provided at the end of the report.

The production of bromide and iodide disinfection by-products was also considered and is reported on. This work was undertaken by Curtin University, and their report is attached in Appendix F while a summary of the outcomes is provided in the main text.

<sup>2.</sup> S. Gray, J. Zhang, A. Knight, P. Scales and K. Northcott (2015). *Demonstration of robust water recycling: Pathogen log reduction value table*, Australian Water Recycling Centre of Excellence, Brisbane, Australia. 3 Allinson G, Allinson M, Kadokami K, Shiraishi S, Nakajima D, Zhang J, Knight A, Gray S, Scales P (2015). *Demonstration of robust water recycling: Monitoring the levels of trace organic chemicals (TrOCs)*, Australian Water Recycling Centre of Excellence, Brisbane, Australia

<sup>4</sup> P.J. Scales, A. Knight, M. Allinson, G. Allinson, S. Gray, J. Zhang, M. Packer, K. Northcott, and D. Sheehan (2015). Demonstration of robust water recycling: Risk assessment of the removal of chemicals of concern in the Davis Station Advanced Water Treatment Plant, Australian Water Recycling Centre of Excellence, Brisbane, Australia.

# 3. Experimental Method

The AWTP constructed by AAD was contained in two shipping containers and was located at SPWWTP during May 2014 (see Figure 1). Feed was sourced from the Selfs Point effluent channel prior to UV disinfection. A 2 mm screen was placed on the entrance to the demonstration plant feed line to remove large particles and flocs within the SPWWTP effluent. This screen was back flushed every 1-2 weeks.



Figure 1: AWTP on site at SPWWTP.

The process design of the AWTP is outlined in the Functional description<sup>5</sup> and a schematic diagram of the process flowsheet is presented in Figure 2.



Figure 2: Schematic diagram of the AWTP Flowsheet.

<sup>5.</sup> J. Zhang, M. Packer and K. Northcott (2015). *Demonstration of robust water recycling, Functional design*, Australian Water Recycling Centre of Excellence, Brisbane, Australia.

The plant was operated at a continuous flowrate of 20 L/min. A virtual tank was filled at a rate lower than 20 L/min and the plant operated until the virtual tank was at 500 L. The plant recommenced operation once the virtual tank was filled to 3500 L. This operation was designed to simulate operation at Davis Station, where the MBR effluent fills a holding tank that activates and shut downs the AWTP once high level and low level set points are reached. This resulted in the plant operating for approximately 6-7 hours before shutting down for approximately 4 hours. Consequently there were many start up and shut down routines implemented. This regime was altered on occasions to allow continuous operation during critical periods associated with sampling, as a shutdown would have resulted in representative samples not being taken. This was particularly important for micro-contaminant samples that were taken monthly and that were required to be sampled at a set time on a particular day to allow sample preparation to be undertaken in a suitable time period.

The sampling protocols are detailed in the Experimental plan report<sup>6</sup>. The experimental runs focused on on-line verification, and sought to confirm water quality of the final product and water quality changes through the plant, the water quality of the RO concentrate, as well as the performance of unit processes (ie. ability of ozone to maintain the set point residual etc).

Ammonia, phosphate, turbidity and pH were measured by TasWater on-line sensors in the effluent channel, and provided an indication of the feedwater quality. On-line water quality sensors within the AWTP were verified weekly by measurements taken from grab samples. Table 1 (taken from the Experimental plan<sup>6</sup>) shows the online water quality parameters that were monitored. Additional samples were also taken for verification of the on-line instruments and for checking the performance at locations elsewhere in the plant. The measurements included turbidity, conductivity and pH with handheld sensors calibrated on the day of sampling, as well as colour, and chlorine concentration using a spectrophotometer and Hach analysis chemicals and procedures.

Water quality analyses were also performed weekly by TasWater's NATA accredited laboratory at Selfs Point. These analyses included Total Coliforms, *E.coli*, total dissolved solids (TDS), ammonia, nitrate, total nitrogen, BOD, total suspended solids (TSS), alkalinity and UV absorption. Virus analysis was performed by a NATA accredited ALS laboratory in Melbourne following overnight delivery of samples, and biodegradable organic carbon (BDOC) was performed by Research Laboratory Services Pty Ltd following overnight delivery of samples.

Weekly samples were also taken for metals analysis and dissolved organic carbon (DOC) analysis at Victoria University. The planned anion analysis was not undertaken as there was little variation of these compounds during characterisation of the feedwater<sup>7</sup>, and none were at concentrations that posed health issues. Similarly some metals were consistently below the Australian Drinking Water Guideline (ADWG) values and these metals were not analysed for.

<sup>6.</sup> N. Milne, M. Allinson, A. Knight, P. Scales (2014). *Demonstration of robust water recycling: Experimental plan*, Australian Water Recycling Centre of Excellence, Brisbane, Australia.

<sup>7.</sup> S. Gray, J. Zhang, A. Knight, P. Scales and K. Northcott (2015). *Demonstration of robust water recycling: Feedwater report*, Australian Water Recycling Centre of Excellence, Brisbane, Australia.

Further details on the sampling and analytical procedures are detailed in the Experimental plan<sup>6</sup> and identification of metals removed from the sampling list are detailed in the feedwater report<sup>7</sup>. Sampling and testing was reduced following several weeks of operation, as some data provided little value to understanding the operational performance of the plant (eg. UV absorbance).

Water quality testing for bromide and iodide disinfection by-products was undertaken by the Curtin Water Quality Research Centre, Curtin University. The demonstration plant feedwater was spiked with potassium bromide and potassium iodide to represent feeds of low, medium and high concentration as might be found in groundwater systems, and samples taken following ozonation, ceramic MF, BAC, RO and in the final product water. Further details are contained in Appendix F, the Curtin University report, and summarised comments appear in the main text.

Water quality data for each water quality parameter across each treatment barrier is presented in Appendix B. The appendix contains dissolved organic carbon (DOC), total nitrogen (TN), phosphorus (P), and metals data (B, Ba, Fe, Mn, P, Zn). Water quality data is discussed for each unit process along with the operational data for each process unit.

Parameter	Stream Being Tested	Expected Range	Critical Value	Location	Reasoning					
	CRITICAL COMPONENTS									
Ammonia (TasWater)	Plant feed	0.1 to 30 mg.L <sup>-1</sup>	> 5 mg.L <sup>-1*</sup>		Used to establish the ongoing robustness of upstream processing (CCP1)					
pH (on intake device)	Plant feed	6 to 8	< 6 or > 8*	In-line	Used to establish the ongoing robustness of upstream processing (CCP1) and to set limits for operation of ozonation process (CCP2)					
Turbidity (TasWater)	Plant feed	0 to 20 NTU	> 10 NTU*	Side stream	Used to establish robustness of upstream processing and to establish worst case conditions under which ozone validation process is valid. (CCP1)					
Temperature (L3033)	Plant feed	15 to 25 °C	< 12 or > 40 °C*	In-line	Used to determine ozone contact time requirements (CCP4)					
Residual Ozone (L3045)	After O <sub>3</sub> reactor tank	0.01 to 12 mg.L <sup>-1</sup>	< 0.05 mg.L <sup>-1</sup>	In-line	Used in the determination of ozone CT to ensure a minimum ozone residual (CCP2) and estimate the ozone concentration on the ceramic MF membrane.					
Turbidity (L3088)	After ceramic microfiltration system	0 to 10 NTU	> 0.5 NTU	Side stream	Indirect integrity measurement (CCP3)					
Conductivity (L3121)	RO feed	400 to 3000 µS.cm <sup>-1</sup>	R	In line	Indirect integrity measurement (CCP4)					
Conductivity (L3154)	RO permeate	0 to 500 µS.cm <sup>-1</sup>	R	In line	Indirect integrity measurement (CCP4)					
UV Intensity (L3167)	At wall of UV Tank 1	300 – 900 mJ/cm <sup>2</sup>	R	In line	Used to calculate UV dose (CCP5)					
UV Intensity (L3171)	At wall of UV Tank 2	300 – 900 mJ/cm <sup>2</sup>	R	In line	Used to calculate UV dose (CCP5)					
pH (L3188)	After calcite contactor	6 to 9	<6.5 and >8.0	Side stream	Used to determine to ensure the correct pH is used for chlorination (CCP6)					
Temperature (L3181)	After calcite filter	5 to 25 °C	<10 °C	In line	Used to ensure the process is in operational limits for the chlorine CT (CCP7)					
Free Chlorine (L3198)	Chlorine contact tank 1	0.4 to 1 mg.L <sup>-1</sup>	< 0.53 mg.L <sup>-1</sup>	Side stream	Used in the determination of residual free chlorine and the determination of chlorine CT (CCP7)					

## **Table 1**: Online monitoring of the demonstration plant.

Parameter	Stream Being Tested	Expected Range	Critical Value	Location	Reasoning			
Free Chlorine (L3205)	Chlorine contact tank 2	0.4 to 1 mg.L <sup>-1</sup>	< 0.53 mg.L <sup>-1</sup>	Side stream	Used in the determination of residual free chlorine and the determination of chlorine CT (CCP7)			
EXTRA MEASUREMENTS								
Phosphate (TasWater)	Plant feed	0.1 to 10 mg.L <sup>-1</sup> as P			Used for process control of the MBR			
Ozone (L3083)	After ceramic microfiltration system	0 to 1 mg.L <sup>-1</sup>		In line	Used to determine ozone residual after membrane filtration and in feed to BAC			
Turbidity (L3105)	After BAC filter	0 to 10 NTU		Side stream	Used to determine the BAC backwash requirements. Last on-line turbidity measurement prior to UV			
Conductivity (L3126)	Feed to 2 <sup>nd</sup> RO vessel	400 to 12000 µS.cm <sup>-1</sup>		In line	Secondary measurement of membrane integrity (not under HACCP)			
Conductivity (L3131)	Feed to 3 <sup>rd</sup> RO vessel	400 to 12000 µS.cm <sup>-1</sup>		In line	Secondary measurement of membrane integrity (not under HACCP)			
Conductivity (L3136)	Feed to 4 <sup>th</sup> RO vessel	400 to 12000 µS.cm <sup>-1</sup>		In line	Secondary measurement of membrane integrity (not under HACCP)			
Conductivity (L3141)	Feed to 5 <sup>th</sup> RO vessel	400 to 12000 µS.cm <sup>-1</sup>		In line	Secondary measurement of membrane integrity (not under HACCP)			
Conductivity (L3146)	RO concentrate	400 to 12000 µS.cm <sup>-1</sup>		In line	Used in determination of rate of brine recycle			
Conductivity (L3124)	Permeate from 1 <sup>st</sup> RO vessel	0 to 500 µS.cm <sup>-1</sup>		In line	Secondary measurement of membrane integrity (not under HACCP)			
Conductivity (L3124)	Permeate from 2 <sup>nd</sup> RO vessel	0 to 500 µS.cm <sup>-1</sup>		In line	Secondary measurement of membrane integrity (not under HACCP)			
Conductivity (L3124)	Permeate from 3 <sup>rd</sup> RO vessel	0 to 500 µS.cm <sup>-1</sup>		In line	Secondary measurement of membrane integrity (not under HACCP)			
Conductivity (L3124)	Permeate from 4 <sup>th</sup> RO vessel	0 to 500 µS.cm <sup>-1</sup>		In line	Secondary measurement of membrane integrity (not under HACCP)			
Conductivity (L3124)	Permeate from 5 <sup>th</sup> RO vessel	0 to 500 µS.cm <sup>-1</sup>		In line	Secondary measurement of membrane integrity (not under HACCP)			
Chlorine (L3187)	After chlorination static mixer	0 to 5 mg.L <sup>-1</sup>		Side stream	Used to determine chlorine dose			

\* Critical values for the demonstration plant at Selfs Point are different to those for Davis Station as the feedw ater qualities w ere different. <sup>B</sup> Values used to calculate critical LRV or UV dose

# 4. Results

### 4.1 Commissioning

The demonstration plant was located at Selfs Point Wastewater Treatment Plant (SPWWTP) during May 2014. The plant was initially subject to several operational issues with non-reliable performance of the ozone generator and ozone cells failing on several occasions<sup>8</sup>. This was overcome after several visits from Wedeco servicemen and worked reliably since mid-August. Measurement of the hydraulic retention time (HRT) of the ozone unit and UV system were undertaken in July – August, 2014. The HRTs were measured by dosing rhodamine WT into the feed of these units and detecting the concentration at the outlet as a function of time. The data is given in Appendix A and the HRT<sub>10</sub> for the ozone unit was 4.8 minutes and for the UV units it was 67 sec. The LRV for the RO unit was also measured using rhodamine WT and was determined to be 2.2 LRV.

The plant ran under test conditions from mid-September, 2014 with water quality and operational performance data collected. Plant operation simulated operation at Davis Station by filling and discharging from a virtual tank. The plant operated for 6.7 hours and then went into standby for 4 hours because the virtual tank was empty. There were operational reliability problems associated with the feedwater pump, discharge pump, SCADA and other equipment. These issues were addressed and operational reliability improved during the demonstration period. However, there were still some minor faults that prevented automatic start up that were not resolved until the end of April 2015, and discussion of these issues are contained in the Robustness Report<sup>8</sup>. There were occasions when the plant operated for longer than 6.7 hours continuously so that sampling of the process could be achieved, as shut down of the plant when micro-contaminant sampling was due would lead to missed sample delivery times and loss of data.

### 4.2 Feed water quality

The critical control points (CCPs) for the feedwater are given in Table 2. The feedwater CCPs were based on expected operational performance for the Davis station MBR, data for Selfs Point effluent and the expected influence on the AWTP performance. For ammonia, pH and temperature, the values for Davis Station and Selfs Point were the same, as the expected variation of these parameters at Selfs Point and Davis Station are unlikely to affect the performance of the AWTP. The CCP values for turbidity at Davis Station are lower than those for Selfs Point (shown in brackets) as the MBR is capable of consistently lower turbidity values in its effluent, and the turbidity is known to affect the disinfection performance of ozone systems<sup>9</sup>.

<sup>8</sup> P.J. Scales, A. Knight, S. Gray, J. Zhang, N. Milne, M. Packer, K. Northcott, P. Hillis, D Sheehan and D. Dharmabalan (2015). *Demonstration of robust water recycling: Operational robustness of the Davis Station advanced water treatment plant,* Australian Water Recycling Centre of Excellence, Brisbane, Australia.

<sup>9</sup> US EPA, Effect of particulates on ozone disinfection of bacteria and virus in water, EPA-600/2-79-089, August 1979

	Feed Wastewater Quality					
Key Control Measure(s):	Ammonia (mɑ/L)	Turbidity (NTU)*	pH (units)	Temperature (°C)		
Target Criteria:	<1.0 mg/L	<0.5 (<3) NTU	6.5 – 7.5	19°Ć		
Alert Limit:	> 1 mg/L	>0.5 (>4) NTU	pH<6.5 or >7.8	<16 or >28		
Critical Limit:	>2mg/L	>0.5 (>5) NTU	<6 or >8	<15 or >30		

 Table 2: CCPs for feedwater.

\* Turbidity values are for the Davis Station MBR effluent; Values in brackets are for Selfs Point wastewater effluent

Ammonia data for the feedwater is given in Figure 3, and shows that the ammonia concentration was below the target criteria before 8<sup>th</sup> October and increased above the critical limit of 5 mg/L after the SPWWTP doubled the required settling rate of the settlers (maintenance on one settler). The feedwater ammonia levels returned to <1 mg/L on the 19<sup>th</sup> November. During this time the total nitrogen (TN) also increased (see appendix B) but the DOC (Figure 3), temperature (>15°C) and pH did not vary significantly (pH between 6.5 and 7.5). Turbidity was usually between 1-2 NTU in the feedwater but during wet weather events this increased to 2-3 NTU. The ammonia, DOC and TN data were obtained from grab samples of the feedwater, while the turbidity, temperature and pH were collected from on-line instruments. During the high ammonia and TN period, the turbidity values averaged 2.5 NTU. Peaks in turbidity were recorded at 5 NTU and on occasion at 25-35 NTU. These extreme turbidity events (25-35 NTU) occurred on the week-end, so no grab samples were taken at this time and the plant was not operating. These turbidity results suggest that larger particles were present in the feed. The turbidity values were measured in the effluent channel and this is screened (2 mm) before it enters the demonstration plant. Hence, some of the turbidity may have been removed before entering the AWTP. A second ammonia peak was also observed during the last 3 weeks of operation.



Figure 3: Feedwater ammonia and DOC concentration versus time.

Except for the ammonia concentrations and turbidity peak values during October/November, all the CCPs met the required values for the feedwater. The high ammonia and turbidity levels during this period may have led to a low LRV value for the ozonation barrier. Additional feedwater quality data is given in the Appendix B. There was no change in metals values during the high ammonia event.

### 4.3 Ozonation Barrier

A packaged ozone system (Wedeco OCS-GSO) was purchased and installed as part of the demonstration plant. This system consisted of a pressure swing adsorption system for generating oxygen, an ozone generator, a contact tank, a side stream venturi ozone dosing system through which the feed was recirculated, and an ozone sensor placed in the side stream re-circulation line. An additional ozone sensor (Hach, Orbisphere) was also placed in-line between the ozone system and the ceramic MF.

Initial difficulties with the stability of the ozone system led to the power of the ozone generator being limited to the maximum tolerance of the specific ozone cell. Once this was implemented, operation of the ozone system was reliable. The ozone sensor in the re-circulation line was decommissioned after plant commissioning, as it had a water bleed stream that constituted a significant portion of the plant flow. The Hach Orbisphere sensor placed between the ozone system outlet and the ceramic MF inlet was then used to measure the ozone residual, and this sensor required no bleed stream. Prior to decommissioning of the original ozone sensor, it was confirmed that the ozone residual measured by the Orbisphere ozone sensor was equivalent to the ozone residual measured within re-circulation line of the Wedeco OCS system.

The ozone system commenced operation by recycling water through the ozone contact tank and dosing ozone through a venturi in a side stream. After 16 minutes of operation in recirculation mode, the ozone system was ready for product flow to commence. The ozone residual was often between 0.8 -1.2 mg/L ozone after the initial 16 minutes of recirculation.

Table 3 shows the CCP values for the ozone barrier, and either ozone residual or an ozone dose may be used. Use of ozone residual is preferred but was not always achievable at Selfs Point due to feedwater quality variations. The inability to always achieve ozone residual led to a change in target LRV across the ozone system. Initially, the target LRV was 0.5 for protozoa and 4 for virus and bacteria. However, this was later downgraded to LRV 0 for protozoa and 2 for virus and bacteria. Ozone residual will be used to maintain a LRV>2, and if no ozone residual can be maintained an ozone dose greater than a minimum verified dose (>11.7 mg/L) will be used.

It is expected that better quality feed water will be achieved by the Davis Station MBR and that ozone residual will be maintained at Davis Station. Use of particle free feed to the ozone system (MBR feed) will allow the US EPA Long Term 2 Enhanced surface water treatment rule toolbox guidance manual<sup>10</sup>, April 2010 (http://www.epa.gov/safewater), to define the LRV from CT values. Chapter 11, Table 11.1 of this manual outlines the required CT values for *Cryptosporidium* inactivation

<sup>10.</sup> US EPA Long term 2 Enhanced Surface Water Treatment Rule Toolbox Guidance Manual, April 2010 http://www.epa.gov/safewater/disinfection/lt2/pdfs/guide\_lt2\_toolboxguidancemanual.pdf

from surface waters and these values were determined using reagent grade water. The required CT value = 2.0 mg.min/L at 20°C to achieve a *Cryptosporidium* LRV of 0.5. For virus, the US EPA Guidance Manual Disinfection Profiling and Benchmarking<sup>11</sup>, Appendix C outlines the CT values for inactivation of virus by ozone from surface waters. CT = 0.5 mg.min/L is required for a virus LRV of 4 at 20°C and CT = 0.25 mg.min/L for a virus LRV of 2 at 20°C. The HRT<sub>10</sub> for the ozone system was measured to be 4.8 min, so the target ozone residual for 0.5 LRV *Cryptosporidium* (with >4 LRV virus) is 0.4 mg/L. For a virus LRV of 2 (claimed LRV) the required ozone residual for 2 LRV virus is 0.05 mg/L ozone.

	Ozonation						
Key Control Measure(s):	Ozone residual - initial (mg/L)	Ozone residual - revised (mg/L)	Ozone dose (mg/L)				
Target Criteria:	0.4	0.25	14				
Alert Limit:	<0.4	<0.1	<12				
Critical Limit:	< 0.35	<0.05	<11.7				

Table 3: CCPs	for ozonation	barrier.
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Figure 4 shows on-line ozone residual data on different weeks during September and October 2014. The set point was 0.4 mg/L ozone residual and this was reliably achieved during 17-19 September (Figure 4a) with only minor excursions below this value. However, during 24<sup>th</sup>-26<sup>th</sup> September (Figure 4b) the ozone residual reduced to being consistently <0.3 mg/L, and during 14-16<sup>th</sup> October (Figure 4c) the ozone residual was regularly zero. This data clearly shows that maintaining ozone residual for Selfs Point effluent as feed was problematic, and this led to the revision of claimed LRV across the ozone unit.

The ozone residual behaviour was also complicated by the changing pressure of the ozone outlet (feed to ceramic MF) as shown in Figure 5. As the ceramic MF membrane fouled, the feed pressure to the ceramic MF also increased which allowed a higher concentration of ozone to dissolve in the water. This trend is shown in Figure 5 for a feedwater quality that prevented reliable ozone residual to be obtained (i.e. high turbidity). Such behaviour indicates that placing a control valve on the outlet of the ceramic MF would allow control of the ozone system outlet pressure that would enable more reliable ozone residual to be obtained for high turbidity waters. However, installation of such a valve was not possible during the life of the trials and use of a MBR prior to the ozone unit at Davis Station is likely to negate the need for the valve.

Correlation of the ozone residual with feedwater quality is shown in Figures 6, 7 and 8. Figure 6 shows the ozone residual, feed ammonia and feed DOC from grab samples against time. The ozone residual decreases to zero from early November 2014 to February 2015. During this time the DOC concentration in the feed did not change and the ammonia concentration in the feed was also low. The feed ammonia concentration was also high during periods of high ozone residual. This data indicates that neither feed DOC nor ammonia concentrations were responsible for the low ozone residuals.

<sup>11.</sup> US EPA Guidance Manual Disinfection Profiling and Benchmarking, August 1999, http://www.epa.gov/ogwdw000/mdbp/pdf/profile/benchpt1.pdf



Figure 4: Ozone residual in the treated water on different weeks.



Figure 5: Relationship between the feed pressure and ozone residual.



Figure 6: Ammonia and DOC concentrations in the feed water plotted with ozone residual.

Figure 7 shows on-line feed turbidity measured in the effluent channel prior to the feed screen against the on-line ozone residual. As the feedwater turbidity increased between December 2014 and March 2015, the ozone residual decreased to zero. Figure 8 plots the residual ozone concentration against feed turbidity and there is a drop of ozone residual as the feedwater turbidity increased. The low ozone residuals are associated with high turbidity events.



Figure 7: Turbidity in the feed water plotted with ozone residual.

**Ozone vs Turbidity** 



Figure 8: Turbidity in the feed water plotted against ozone residual.

Particles in wastewater have been previously shown to require higher ozone CT values<sup>12</sup> for feedwater turbidity vales between 1-5 NTU. Work by Melbourne Water<sup>13</sup> has shown that ozone CT values required for *Cryptosporidium* inactivation in biological media filtration (BMF) filtrate with turbidity between 0.5-2 NTU was similar to those determined in reagent grade water<sup>13</sup>. The BMF water in the Melbourne Water work was pre-ozonated before the BMF, and the pre-ozonation process showed variable inactivation of pathogens. Removal of feedwater particles (turbidity), as will be the case at Davis Station, should allow the US EPA CT values to be used as a CCP for pathogen inactivation across the ozone system.

The use of ozone dose as an alternative to the US EPA CT values for use as a CCP was considered. The ozone dose was determined by measuring the difference in gas flowrates from the ozone system when no ozone was being produced and when ozone was being produced. The measured ozone doses are given in Table 4. The ozone dose was consistently between 11.7 - 14 mg/L, giving an ozone:DOC dose of approximately 1.3 - 1.7 mg  $O_3/mg$  DOC (DOC varies between 7-9 mg/L).

Date	Ozone Dose (mg/L)
27/11/14	13.5
27/1/15	14.7
10/2/15	11.7
25/2/15	14.9
23/4/15	16.9
6/5/15	12.9

Table 4. Measured Ozone doses
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The removal of *E. coli* and of somatic coliphage across the ozone system was measured over an extended period of time, and during periods of low ozone residual. The *E. coli* and somatic coliphage data was measured from grab samples and the instantaneous ozone residual reading was recorded at the time of sampling. *E.coli* is the surrogate for both bacteria and virus validation of ozone systems in the Draft Australian Guidelines for Ozone Validation (AWRCoE), so this data represents inactivation of bacterial and viruses more generally. The data is shown in Table 5 and Figure 9.

Both Table 5 and Figure 9 show that an LRV of >2 can be achieved across the ozone system even when the ozone residual is close to zero. Indeed, many of the LRV values less than 3 correspond to greater than LRV values (eg. >LRV) as the measured feedwater *E. coli* concentration was reported as being greater than the maximum detection limit or the treated water was reported as being below the minimum detection limit. From this data, a LRV of 2 is claimed across the ozone system provided the dose of ozone is >11.7 mg/L.

<sup>12.</sup> US EPA, Effect of particulates on ozone disinfection of bacteria and virus in water, EPA-600/2-79-089, August 1979.

<sup>13</sup> Mieog and McNeil, Recycled water treatment on a large scale using multiple disinfection barriers at Melbourne Water's Eastern Treatment Plant. AWA Water Recycling conference, Brisbane, 2-3 July, 2013.



Figure 9: LRV and ozone CT over time. Blue circles identify > LRV where the feed concentrations were >2419.6 MPN/100 ml.

There were no significant changes in water quality across the ozone unit identified by the sampling program other than the reductions in microbiological parameters. While organic carbon is oxidised by ozone, the DOC before and after ozonation (Appendix 2: Figure B1a and B1b) showed no consistent trend and the DOC values were the same. The biologically degradable organic carbon (BDOC) did increase across the ozonation system as a result of the oxidation, as shown later in Table 7.

## **Table 5**: *E. coli* and Somatic Coliphage LRV across the ozone system.

Date		E.coli		Somatic Coliphage			Residual
	Feed	Post ozone	LRV	Feed	Post ozone	LRV	Ozone
	(MPN/	(MPN/100		(pfu/100	(pfu/100mL)		(mg/L)
	100mL)	mL)		mL)			
17/9/14	1986.3	3.1	2.81				0.47
24/9/14	1553.1	4.1	2.58				0.21
1/10/14	1732.9	5.2	2.52				0.39
8/10/14	1553.1	4.1	2.58				0.48
15/10/14	>2419.6	2.0	3.08				0.30
22/10/14	>2419.6	4.1	>2.77				0.16
29/10/14	>2419.6	1.0	>3.38				0.87
5/11/14	>2419.6	3.1	>2.89				0.23
12/11/14	>2419.6	4.1	>2.77				0.28
19/11/14	>2419.6	1.0	>3.38				0.04
26/11/14*	13500	1.0	4.13				0.00
2/12/14	24300	2.0	4.08				0.01
10/12/14	290900	4.1	4.85				0.04
17/12/14	285100	39.9	3.85	834	<1	>2.92	0.00
21/1/15	770100	24.3	4.50				0.00
28/1/15	90900	12.2	3.87				0.02
28/1/15	53300	7.5	3.85				0.00
4/2/15	62000	9.7	3.81				0.00
4/2/15	18700	12	3.19				0.01
11/2/15	>2419.6	21.6	>2.05				0.00
11/2/15	>2419.6	12.1	>2.30				0.00
18/2/15	150000	72.3	3.31				0.00
18/2/15	108100	37.9	3.46				0.00
25/2/15	25300	3	3.93	3000	1	3.48	0.00
25/2/15	27500	15.8	3.24				0.03
4/3/15	28200	6.3	3.65				0.00
4/3/15	28100	55.4	2.71				0.00
11/3/15	74300	24.6	3.48				0.00
11/3/15	70600	14.6	3.68				0.00
25/03/15	39300	2	4.29	12000	7	3.23	0.14
25/03/15	48700	10.8	3.65				0.12
1/04/15	8600	4.1	3.32				0.00
1/04/15	9700	18.9	2.71				0.10
15/04/15	14800	2	3.87				0.10
15/04/15	5200	1	3.72				0.05
22/04/15	3100	7.5	2.62	4200	5	2.92	0.16
22/04/15	5200	1	3.72				0.05
29/04/15	9700	7.3	3.12				0.19
29/04/15	7500	8.7	2.94				0.15
6/05/15	16100	3	3.73	2500	<1	>3.40	0.46
6/05/15	14600	3.1	3.67				0.63
20/05/15	128650	27.5	3.67				0.10
20/05/15	133300	23.3	3.76				0.42
27/05/15	178500	7.4	4.38				0.36
27/05/15	222400	5.2	4.63				0.39

### 4.4 Microfiltration

Two Metawater  $\alpha$ -alumina micro-filtration membranes (0.1 µm) formed the ceramic MF system. One ceramic MF was in standby mode while the other was in duty. At 20 L/min feed flowrate, the flux through the membranes was 48 L.m<sup>-2</sup>.h<sup>-1</sup>, which is a low flux for ceramic MF. Each batch of water that was treated through the AWTP had the CCPs check before discharge. For chlorine CT batches, the turbidity was used for the CCP check, while the PDT was performed for each batch of water from the virtual tank. The duty/standby ceramic MF were changed when the duty ceramic MF required backwashing. During the trials there were occasions when the ceramic MF appeared to fail the PDT, but this was later recognised as an issue with a valve not sealing correctly and hence leaking during the PDT. Therefore, a pressure leak test was subsequently instigated following this event to check for leaks.

The ceramic microfiltration process has CCPs related to pressure decay testing and turbidity of the filtrate (see Table 6). The pressure decay CCP has been accredited for 4 log removal of protozoa (*Crytosporidium* and *Giardia*) and 1 log reduction for virus by the Department of Health Services, California (see Appendix C). Turbidity is used to verify the performance of the ceramic MF and the turbidity was measured by a Hach Ultraturb turbidity meter in the ceramic MF permeate line. Air bubbles in this line led the sampling point for the turbidity measurement to be moved to the BAC launder, so that there was additional time for air bubbles to escape the filtrate.

Micro-Filtration							
Key Control	Pressure Decay Test (PDT) – LRV	Turbidity (NTU)					
Measure(s):	(Particle size exclusion ≥3 µm)						
Target Criteria:		< 0.3 NTU					
Alert Limit:		> 0.4 NTU					
Critical Limit:	< 4 from PDT(PDT <1.4 kPa/min)	> 0.5 NTU					

#### Table 6: CCPs for Ceramic MF.

The Pressure Decay Rates of the two ceramic membranes are shown in Figure 10. It can be found that the pressure decay rate was below the 1.4 kPa/min decay rate limit except when there were leaking valves. The trend is for no change in the PDT results with time indicating the membranes reliably achieved this CCP.

On-line turbidity values in the ceramic MF filtrate were initially high once filtration commenced, but reduced to lower, steady values after 10 minutes filtration. The stabilised turbidity values were used as being indicative of filtration performance, as turbidity readings from handheld instruments during the initial stages of filtration indicated the on-line turbidity values were high because of bubbles in the water. On-line turbidity values of the MF filtrate once filtration had been stabilised were 0.2 to 0.26 NTU (see Figure 11), which is less than the alert value. These values are in-line with the expectation that ceramic MF will produce a high quality filtrate of low turbidity. Additional data obtained from the on-line turbidity meter following relocation of the sampling point to the BAC launder is shown in Figure 12, and demonstrates lower, reliable turbidity values of less than 0.1 NTU data could be obtained. However, the initial difficulties experienced in achieving reliable turbidity readings means further operation of the plant is required to demonstrate robust operation of the turbidity sensor. Another 10-12 months operation is recommended.



Figure 10: Pressure decay rate of the ceramic membranes.



Figure 11: Handheld turbidity of the MF filtrate with sampling prior to the BAC launder.



Figure 12: On-line turbidity values for the ceramic MF filtrate after the turbidity sampling point was moved to the BAC launder.

The feed pressure over time for both ceramic MFs 1 and 2 is shown in Figures 13a and 13b. The recommended chemically enhanced backwash (CEB) was 50 mg/L hypochlorite solution every 15 backwashes, and a sulphuric acid CEB (pH=2) after every 15 hypochlorite CEBs. Initially the CEBs used sulphuric acid, but this was changed to hypochlorite during November, 2014. The sodium hypochlorite CEB was operated at 100 mg/L, two times the recommended dose as no CIP was used. The red arrows in Figures 13a and 13b indicate the time at which CEBs were conducted. While the pressure increased during filtration, the pressure returns to the starting pressure following backwashes and CEBs. No significant long term fouling was observed over the 10 months operation.



Figure 13a: No.1 membrane TMP changed with time.



Water quality data is reported in Appendix B. DOC appears to be reduced by approximately 5% across the ceramic MF (Appendix B: Figures B1a and B1b). TN and most metals have no significant removal across the ceramic MF. The exception is iron (Fe), which appears to decrease by approximately 0.02 mg/L following

ozonation and ceramic MF (see Figure B5, Appendix B). Oxidation of iron by ozone would lead to precipitation and potential removal on the ceramic MF. An acid CEB will be helpful in controlling Fe build up on the ceramic MF. Manganese (Mn) may also be removed by ozonation followed by ceramic MF, although the trend in Figure B6 (Appendix B) is less clear with Mn concentrations in the filtrate being higher than the feed Mn concentrations on occasions. Turbidity was reduced to approximately <0.26 NTU following filtration as shown in Figure 11, and reduced to <0.1 NTU at the end of the trials period (Figure 12).

## 4.5 Biological Activated Carbon (BAC)

The BAC was designed for removal of trace organic contaminants, and no pathogen removal or inactivation was claimed for the BAC. The BAC was designed for a 20-minute empty bed contact time (EBCT) and contained activated carbon as the media. A turbidity meter was placed in the BAC filtrate line to assist in detecting changes within the BAC and to identify if high turbidity filtrate was flowing into the mixing tank and into the RO system. Once the headloss across the BAC increased to 25 mbar or the filtrate turbidity reached 1.5 NTU, the BAC was backwashed using town water. The backwashing flowrate was 3.3 L/s. The feed to the BAC was intermittent due to the batch operation of the treatment plant. During periods of non-flow, air was intermittently fed to the BAC filter to prevent anaerobic growth within the biofilter, with 30 seconds of air every 2 hours. The air dose was not optimised and the addition of air for 30 seconds every 2 hours and is unlikely be sufficient to prevent anaerobic conditions occurring because of the high organic load fed to the BAC.

The biological activity in the BAC was confirmed by undertaking bacterial counts from activated carbon. Activated carbon samples were taken from different depths in the BAC and sent to Research Laboratory Services Pty Ltd for analysis. Bacteria from the activated carbon were sampled via a standard washing procedure, and then growing bacteria in the wash solution on agar plates. The results are shown in Figure 14, and scanning electron microscopy (SEM) images of activated carbon taken from the BAC are shown in Figure 15. The highest microbial concentrations were at the top of the BAC where the water enters, and cell numbers reduced as the water flows through the BAC and the amount of food declines. The concentrations of bacteria are high, indicating significant biological activity.

The BDOC was measured across unit processes from the feed to post BAC, and the results are shown in Table 7. The DOC in the feed was between 8.5-9.0 mg/L. The DOC only reduced to 6.8-8.7 mg/L following ozonation and ceramic MF, but fell to 3.6-4.0 mg/L following the BAC demonstrating that most of the organic carbon was removed biologically. The BDOC, however, increased from 2.4-2.7 mg/L in the feed to 4.4-4.9 mg/L following ozonation. Ceramic MF removed approximately 0.5-0.6 mg/L BDOC and following the BAC the BDOC was 1.1-1.9 mg/L. The data is consistent with organic material being oxidised by ozonation to form more easily biodegradable compounds that were primarily removed by the BAC. The resultant BDOC of >1 mg/L in the BAC filtrate, however, is indicative of water that is still significantly bioactive and biofouling downstream of the BAC was likely. BDOC values of <0.5 mg/L are required for the water to be considered biologically stable. A longer EBCT (>20 minutes) within the BAC filter would assist in further reducing the BDOC to values less likely to support downstream biofouling. Improved DOC

removal from MBR treatment compared to the SPWWTP effluent will reduce the need for a longer EBCT, and this may be achieved at Davis Station.







Figure 15: Scanning electron microscopy (SEM) images of BAC granules.

Sample	9 Oct 2014		28 Jar	n 2015	25 March 2015	
	DOC	BDOC	DOC	BDOC	DOC	BDOC
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Plant Feed	8.5	2.7	8.9	2.6	8.7	2.4
Post Ozone	7.5	4.4	8.7	4.9	8.1	4.5
MF filtrate	6.8	3.8	8.2	4.4	7.6	4.0
Post BAC	3.9	1.9	4.0	1.5	3.6	1.1

 Table 7: DOC and BDOC data across unit processes.

Organic carbon may be removed by biological activity within the BAC and by adsorption on the activated carbon. Over time the adsorption sites fill and less adsorption of compounds occurs on the activated carbon, while the biological activity remains relatively constant with time. Figure 16 shows the DOC removal across the BAC filter over time and a gradual reduction in performance is shown. The initial removals were approximately 50% but reduced to 30-45% after 5 months of operation (the BAC was conditioned with secondary effluent from June, 2014). This reduction in DOC removal is likely to be as a result of the BAC adsorption capacity reducing with time.



Figure 16: DOC removal across the BAC with time.

The turbidity of the post-BAC filtrate was monitored to verify the filtration performance of the BAC and as a means to detect changes in the biological activity of the BAC. The start stop operation of the plant meant that feed to the BAC was also intermittent. When flow through the BAC recommenced (virtual tank was full), elevated turbidity readings were recorded in the filtrate as shown in Figure 17, but after approximately 20 minutes of flow the turbidity values reached steady values of <0.2 NTU. The elevated turbidity values immediately following the recommencement of flow were attributed to air bubbles, as handheld turbidity values were similar to the values obtained 15 minutes after recommencement of flow when left to stand for a short period of time. Oxidation of manganese (Mn) within the BAC might also produce fine manganese dioxide particles that could lead to high turbidity values. However, autopsies for the cartridge filter and RO membranes downstream of the BAC did not detect elevated levels of Mn in the foulants, so manganese dioxide particles were considered not to be responsible for the high turbidity values upon start up. These initial high turbidity readings are ignored by the process control system, and only data after 15 minutes of flow were used.

High turbidity values were also observed following backwash of the ceramic MF as shown in Figure 17. The cause of the increased turbidity is thought to be increased solids in the MF filtrate arising from the backwashing process. The turbidity reduced to <0.2 NTU once backwashing ceased. Therefore, the high turbidity values for the BAC filtrate during ceramic MF backwashing were ignored as there were not indicative of poor BAC performance.



Figure 17: Typical turbidity values in the BAC filtrate.

Nitrification within the filter would lead to a reduction in alkalinity and pH across the BAC, and these parameters were measured over a period of two months. The results are shown in Table 8. The results show reductions in alkalinity and pH indicating that nitrification is taking place.

Date	Alkalinity (mg/L CaCO₃)		Δ alkalinity	р	Η	∆ рН
21/1/15				7.65	7.56	0.09
28/1/15	165	157	8			
4/2/15	172	163	9	7.74	7.62	0.12
11/2/15	163	155	8			
18/2/15	166	140	26	7.57	7.18	0.39
05/03/15	138	128	10	7.57	7.41	0.16
10/03/15	152	126	26	7.04	6.87	0.17
25/03/15	135	128	7	7.06	7.04	0.02

**Table 8**: Alkalinity and pH changes across the BAC.

As shown in Table 7, the DOC reduced by approximately 4 mg/L from ~8 mg/L in the BAC feed to ~4 mg/L in the BAC filtrate. Additional water quality data is shown in Appendix B. There was no detectable change in TN, B, Ba or P across the BAC. However, Fe, Mn and Zn were reduced. Iron and manganese are often removed by biologically oxidising bacteria, and iron was reduced by approximately ~0.05 mg/L (~50%; see Figure B5), Mn by ~0.02 mg/L (~50%; see Figure B6) and Zn by ~0.02 mg/L (~20%; see Figure B8).

### 4.6 Reverse osmosis (RO)

The RO system consisted of 5 x 4" BW30 (Dow Filmtec) membranes in series that were contained in individual housings. The overall system recovery was set for 70%, and this was achieved by a single pass recovery of approximately 50% and recycling of a portion of the RO concentrate back to the feed. The design flowrates for the RO system were: RO feed flowrate = 25 L/min, RO permeate = 14 L/min, RO concentrate return = 5 L/min, and RO concentrate discharge = 6 L/min.

The feed to the RO systems comprised 20 L/min of BAC filtrate and 5 L/min of RO concentrate return that were combined in the "mix tank". The feed was filtered

through an in-line, 1µm cartridge filter before entering the RO membranes. The concentrate from the RO process was split into the RO concentrate return (5 L/min) and the RO concentrate discharge (6 L/min). The RO concentrate discharge is the stream that will be discharged to ocean when installed at Davis Station.

The pressure drop across the RO cartridge was monitored to identify when the cartridge filter required replacing. The TMP across the RO membranes was also calculated from the feed pressure and assuming a pressure of 0 kPa on the permeate side. The conductivity of the feed to the RO system and each RO element was measured on-line, as were the conductivities of the permeate from each RO membrane and the conductivity of the combined permeate. The calculation of the RO conductivity LRV was based on the feed water conductivity and the combined permeate conductivity. A PDT was also implemented as a CCP for protozoa. The PDT was performed for each batch of water from the virtual tank and required a test pressure of 45 kPa transmembrane pressure (TMP) (45 kPa + 40 kPa backpressure = 85 kPa total test pressure). A pressure decay rate of <3.7 kPa/min was required to confirm the CCP was being achieved, and the system recovery needed to be >60% and the specific flowrate above 1.09 L.min<sup>-1</sup>.bar<sup>-1</sup>. The CCPs for the RO system are shown in Table 9. The CCPs are expressed as LRVs based on calculations from the PDT and conductivity rejection measurements<sup>2</sup>. The corresponding pressure decay rates and rejections are shown in brackets.

T	ab	le	<b>9</b> :	<b>CCPs</b>	for RO.
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Reverse Osmosis			
Key Control	Pressure Decay Test (PDT) – LRV	Conductivity (LRV)	
Measure(s):	(Particle size exclusion ≥3 µm)		
Target Criteria:	2.5 LRV(<1.18 kPa/min @ 45 kPa	> 1.7 LRV (>98.0%	
	TMP - 85 kPa with backpressure)	rejection)	
Alert Limit:	2.1 LRV(<2.9 kPa/min @ 45 kPa	< 1.6 (<97.5%	
	TMP - 85 kPa with backpressure)	rejection)	
Critical Limit:	< 2 LRV (<3.7 kPa/min @ 45 kPa	< 1.5 LRV (96.8%	
	TMP - 85 kPa with backpressure)	rejection)	

The RO CCP data based on the PDT is shown in Figure 18 and that based on conductivity rejection is shown in Figure 19. Neither the CCP based on the PDT or conductivity rejection failed during the test period, although the specific flowrate of the RO system fell below 1.09 L.min<sup>-1</sup>.bar<sup>-1</sup>prior to CIP cleaning. It should be noted that the conductivity LRV during the first 10 minutes of initial start-up was ignored, as flushing of the RO membranes with permeate when the plant shuts down means that the initial feed had low conductivity. The most accurate conductivity LRV will occur at the end of a run when the feed conductivity is high.



Figure 19: RO system LRV based on conductivity rejection.

All *E.coli* concentrations in RO permeate were below the level of detection. Regrowth in the permeate lines was detected between 19/11/2014 and 15/04/2015, where total coliforms were measured in the permeate lines on 57% of occasions (1 - 649 cfu/ml). Regrowth in the permeate lines needs to be managed and cleaning via regular chemical flushing of the permeate tubes requires further investigation. Further regrowth in the permeate lines has not been observed in the 2 months since cleaning and the total coliform counts in the permeate have been consistently low (1 or <1 cfu/100 mL).

The pressure drop across the cartridge filter prior to the RO membranes was monitored to determine how frequently the filter required replacement. Once the pressure drop across the cartridge filter reached -28 kPa, the filter was deemed in

need of replacement as the pressure increased quickly after this point. Figure 20 shows the pressure build up with time across the cartridge filter, and that the filter required replacement every 2 weeks. While this frequency of replacement is usually regarded as being very high, AAD are willing to operate under such conditions. Replacement of a cartridge filter requires a low level of operator skill, and the used filter can be disposed of in the site incinerator.



Figure 20: Pressure drop across the cartridge filter.

An autopsy of a cartridge filter was undertaken to identify the foulants. Figure 21a shows the fouled cartridge filter after 2 weeks service, and Figures 21b and 22c show SEM x-ray mapping of the filter surface for Mn and for C respectively.



Figure 21: Fouled cartridge filter: a) after 2 weeks service; b) x-ray map for Mn; c) x-ray map for C.

The cartridge filter is shown to be extensively fouled by black particles in Figure 21a, while Figures 21b and 21c show that there is little Mn present but an extensive presence of carbon. Carbon would be expected to be present because the cartridge filter is made from plastic, however, when combined with Figure 21a it indicates that activated carbon fines were fouling the cartridge filter. Digestion of the foulant in nitric acid identified only minor traces of Mn consistent with activated carbon fouling the cartridge filter.

An aim for the project was to limit the number of membrane chemical cleans to as few as possible, and it was originally hoped that the RO membranes could operate

for 12 months between cleans. A study in the USA<sup>14</sup> identified the potential for oxidation prior to RO membranes to reduce membrane fouling and extend filtration times between cleaning. The decrease in normalised flowrate for the RO membrane with time is shown in Figure 22.



Figure 22: Normalised flowrate versus time.

Figure 22 shows that after approximately 4-5 months operation the RO membranes required a clean-in-place (CIP). This was more frequently than desired, and suggests that 2-3 CIPs will be required each year. The CIP was conducted with hot NaOH (95 ml of 40% NaOH in 90 L water, 40°C) followed by HCI (130 ml of 32.5% HCI in 90 L water, 20°C). Flux recovery following the CIP was very good and the specific flowrate increased above the 1.09 L.min<sup>-1</sup>.bar<sup>-1</sup> required for the PDT test. A RO membrane autopsy (see Appendix D) identified biofouling as the cause, with only minor amounts of inorganic fouling present on the membrane. Additionally, it was noted that the fouling layer was easily removed from the membrane via wiping of the surface. The oxidation of the organic compounds have been identified as the initial organic RO foulants on which further fouling occurs<sup>15</sup>. Therefore, removing these via oxidation may reduce the adhesion between the biofouling layer and the membrane.

Rejection of metals (Ba, Fe, Mn, Zn), P and TN by the RO system were all high (>90%), while B rejection was approximately 50% (see Appendix B). These rejections are typical for RO membranes, and demonstrate the membranes were performing as expected.

<sup>14</sup> B.D. Stanford, A.N. Pisarenko, S.A. Synder, R.D. Holbrook, Pilot scale oxidative technologies for reducing fouling potential in water reuse and drinking water membranes. WateReuse Research Foundation, US Bureau of Reclamation, WRF-08-08-1, 2013.

<sup>15</sup> M.T. Khan, C-L De O Manes, C. Aubry, L Gutierrez, J-P Croué, Kintetic study of seawater reverse osmosis fouling, Environ. Sci Tech., 47(19) (2013) 10884-10894.

The DOC in permeate was initially measured at 0.3–0.6 mg/L. However, this was because the DOC was measured using a calibration for a high DOC range so that all the samples from the AWTP could be measured in one batch. Once the instrument was re-calibrated for a more sensitive DOC range (25/2/15), all permeate samples were determined to have a DOC of  $\leq$ 0.2 mg/L. This is consistent with expectations for commercial recycling plants.

Fluorescence measurements of organic compounds in permeate was undertaken and typical results are shown in Figure 23. The fluorescence intensity was low compared to common wastewaters. No humic peaks were observed and only minor protein peaks were present. This is because of the oxidation or organic compounds achieved by the ozonation process.



Figure 23: Fluorescence Excitation Emission Matrix for RO permeate (4/2/15).

Samples of permeate were also taken to Aqua-diagnostic (http://www.aquadiagnostic.com/) for COD testing using their photo-electrochemical oxidation demand (PeCOD) instrument. A specialised low-range instrument was developed by Aqua-diagnostic for determination of COD in RO permeates. However, the oxidised nature of the organic compounds reduced the required detection level beyond that of non-oxidised RO permeate and there was insufficient time in the project to optimise the PeCOD system to obtain reliable results.

### 4.7 Ultraviolet (UV) disinfection

The UV system consisted of two Wedeco Specktron 6 UV disinfection systems in series. Each unit was capable of exceeding 4 LRV virus that requires a dose of 186 mJ/cm<sup>2</sup>. Therefore, should 1 lamp fail there is sufficient redundancy for the system to still achieve 4 LRV. The dose of UV radiation was calculated from the flowrate and the corresponding residence time for 10% of the flow to pass (HRT<sub>10</sub>: see section 4.1 and Appendix A) and UV intensity. This allowed on-line calculation of the UV dose for confirmation of the CCP. The UV intensity was measured by a UV intensity sensor at the wall of each unit. UV transmittance (UVT) was measured with a separate on-line UVT instrument for a short period of time before it was removed from service. This recorded values were >98% transmittance, and weekly UVT measurements will be done manually for confirmation of the required UVT. The CCPs for the UV system are shown in Table 10.

Key control measure	UV dose (mJ/cm <sup>2</sup> )
Target Criteria	>300 mJ/cm <sup>2</sup>
Alert Criteria	<300 mJ/cm <sup>2</sup>
Critical Limit	<186 mJ/cm <sup>2</sup>

Table 10: UV	disinfection	CCPs.
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The calculated UV dose over the course of the trials for both Specktron 6 units is shown in Figure 24. The required dose is 186 mJ/cm<sup>2</sup>, but the dose from each unit consistently exceeded 300 mJ/cm<sup>2</sup>. No *E.coli* or coliforms were detected post UV. Therefore, the UV disinfection system was deemed to be performing adequately. No operational issues were identified for the UV system during the trials.



Figure 24: UV dose for the two Specktron 6 UV disinfection units.

There may have been minor DOC removal across the UV system (see Figure B1b), with lower DOC values for the post-UV stream compared to the combined RO permeate commonly appearing. However, this trend is less common when data after 25/2/15 is compared, which corresponds to the period when more accurate DOC data was obtained, suggesting there was no DOC removal across the UV system.

### 4.8 Calcite contactor

Following the UV unit, water flows through the calcite contactor. The calcite contactor was designed to restabilise the water by putting calcium carbonate into the water. The contactor had a volume greater than 85 L and a minimum empty bed contact time of >4.1 minutes. The contactor was filled with calcite (calcium carbonate), through which the water flows.

The calcite contactor required calcite to be topped up every 3-4 months. An estimation of the calcite consumption was made between topping up the filter on 21/10/14 and 9/3/15, using the volume of calcite required for top up and the total water processed between these dates. The estimated average calcium concentration dosed (calcium consumption) was 80 mg/L.

However, the calcium concentration varied over time and the stability of the water is a function of the calcium concentration, pH, temperature and alkalinity. The calcium
carbonate precipitation potential (CCPP) and the Langelier Saturation Index (LSI), are used as measures of water stability. A CCPP of >0 mg/L CaCO<sub>3</sub> indicates the water is scaling (protective) with respect to calcium carbonate, a value of -5 to 0 mg/L indicates that the water is passive, -5 to -10 mg/L that is it mildly corrosive and <-10 mg/L that it is corrosive (aggressive). Similarly, an LSI >0 indicates that the water might precipitate CaCO<sub>3</sub>, =0 that is saturated with CaCO<sub>3</sub> and <0 that it is corrosive.

CCPP, LSI, pH, alkalinity and TDS of the product water are shown in Figure 25. The alkalinity was measured from weekly grab samples of the product water. The pH and TDS were measured from a grab sample taken after the calcite filter and before chlorination. The pH probe was calibrated just prior to taking the reading and the TDS was estimated from conductivity values obtained from a calibrated conductivity meter. The alkalinity, pH and TDS were used to determine the CCPP and LSI. The pH varied between 6.42 and 8. Figure 25 shows that the CCPP was consistently below 0. There are 3 points that are significantly lower than the rest of the data (-88, -64, -52 mg/L). These three outliers do not make part of a consistent trend and are assumed to arise from errors in the pH measurements, as this did prove difficult to measure on occasions. Removing these values from the data results in an average CCPP of -8.55 mg/L CaCO<sub>3</sub>, which is mildly aggressive. Generally the calculated CCPP varied between -2 to -12 mg/L CaCO<sub>3</sub>, although there were still a few results <-18 mg/L CaCO<sub>3</sub>. Similarly, the LSI was between -0.5 and -1.3 when the outliers were removed, again indicating mildly aggressive water.



Figure 25: CCPP, LSI, pH, TDS and alkalinity of the product water.

There were no operational issues for the calcite contactor, and the only management/control concern was when to re-fill the contactor with calcite. From the operational data this appears to be required after every 3-4 months of operation when run during the trials. However, the mode of operation will vary at Davis Station with near continuous operation during summer and operation every 2 days during winter. Hence, the volume of water treated is a better indicator to use for when to top up the contactor. From the trials, it appears that the contactor should be refilled after 600,000 L of water has been processed. This compares well to the estimate in the Function Description of 630,000 L.

Refilling of the contactor involved removing the contactor cap and filling the housing with calcite. The cap was then re-fitted to the housing. This was not a difficult task as the items are easily accessible. Following re-filling of the contactor, calcite fines were flushed from the contactor upon further water treatment. Diversion of this water to the head of works is recommended so that the pH <8 can be maintained during chlorination.

### 4.9 Chlorination

The chlorination system received water from the calcite contactor and dosed sodium hypochlorite into the water prior to entering the chlorination contact tanks. The water was then recycled around the contact tank via a pump and the chlorine concentration monitored. The recorded concentration used to trim the chlorine dose. Once the chlorine contact tank was filled, the contact time for holding at the required chlorine dose (CT) commenced. The CCPs for chlorine dosing and contact are listed in Table 11.

Key control measure	CT (mg.min/L)
Target criteria	>24
Alert limit	<24
Critical limit	<22

**Table 11**: Chlorination CCP.

It should be noted that for much of the trials, the critical CCP was <16 mg.min/L rather than <22 mg.min/L. This value was revised after there the reliability of the pH probe prior to the chlorination system was downgraded to  $\pm 0.5$  pH units. The reliability of the pH unit was downgraded as calibration in low ionic strength water requires long equilibrium times, and this was estimated based on experience during the trials and the expectation that Davis Station operators may also have difficulties with calibration of this pH meter. This meant that a higher CT value was required as the feed pH when reading pH 8±0.5 may actually be at pH 8.5. The required CT value for pH 8.5 is 22 mg.min/L and at pH 8 it is 16 mg.min/L<sup>16</sup>. Also, the chlorine dose set point was set 0.2 mg/L higher than the minimum dose required to achieve the CT value in 30 minutes so as to provide a safety margin.

The chlorine was dosed from a drum of sodium hypochlorite (12.5%). Sodium hypochlorite is known to decay with time and the concentration of free chlorine in the drum was measured weekly. Data for the concentration of free chlorine in the stock sodium hypochlorite drum is shown in Figure 26. Measurement of the chlorine concentration required a 1:62,000 dilution. This affected the accuracy of the measurements and hence there is a spread of results. The technique improved with time, and it demonstrates the need for good training of operators or an alternative approach to setting the dose rate. For instance, dosing hypochlorite could use the dosing rate of previous runs to set the initial flowrate, and then trim the dose to the required set point. The concentration of the stock hypochlorite could also be calculated from the dosed amount and measured concentration.

<sup>16</sup> Guidelines for validation treatment processes for pathogen reduction. Supporting Class A recycled water schemes in Victoria, Department of Health, Victoria, Feb 2013.



Figure 26: Free chlorine concentration in the sodium hypochlorite drum.

The chlorine dosing and contact system experienced many delays in becoming operational. These are listed in the robustness report and include: delayed arrival of parts for the chlorine sensors that left them inoperable for several months, the need to refine the SCADA control of the dosing and contact system once the sensors were operational, and syphoning from the contact tanks because of the discharge design at Selfs Point differing from how it will be at Davis Station (no syphoning possible from the tanks at Davis Station as there is no head difference).

These issues resulted in the chlorine dosing and contact system being inoperable for a large proportion of the trials and only limited data is available on its operational performance. However, the chlorination system was operational towards the end of the trial and Figure 27 shows data collected between 25/2/2015 and 4/5/2015 displaying the chlorine CT value achieved for water discharged from the system. The figure shows that once the chlorine dosing and contact system was operational, compliance was achieved. However, further operation is required to demonstrate the on-going reliability of the chlorine dosing and contact system, and operation for another 10-12 months is recommended.



Figure 27: Chlorination CT values achieved for each batch of water.

The RO permeate has very low DOC concentration (<0.2 mg/L), and the chlorine decay rate was close to zero. For a single batch of water, the chlorine dose at the completion of dosing and the start of the contact time was 1.07 mg/L free chlorine and at the completion of 50 minutes contact time it had remained at 1.07 mg/L free chlorine. Therefore, chlorine residual decay was very slow as expected for RO permeate.

### 4.10 Water quality

Water quality through the treatment process is shown in Appendix B. All metal ions in the product water were below the Australian Drinking Water Guideline (ADWG) values with the RO process being the most significant barrier for metals. DOC, P and TN were also low in the in the product water with the RO process again being the most significant barrier.

Microbiological analyses of water through the treatment process are shown in Table 5 and Appendix E. *E. coli* (30 samples) and somatic coliphage (5 samples) were effectively inactivated by the ozone system and no counts were detected after the ceramic MF. Coliforms (30 samples) were similarly removed by the ozone and ceramic MF, but they were also detected after the ceramic MF, BAC filter and on occasions in the RO permeate. No coliforms were detected after UV disinfection. The presence of coliforms and absence of *E. coli* and somatic coliphage after the ceramic MF suggests that coliforms do regrow in the system. This was confirmed by the development of a biofilm in the permeate lines that appeared green. Such regrowth does not present a health issue but does present a possible community acceptance issue if not managed appropriately. Given the green appearance for the film in the clear sight glass, it was suggested that it may have been an algal film. Since cleaning of the RO permeate lines there has been no regrowth over the following 11 weeks.

Disinfection by-product (DBP) data is reported in Appendix F (Curtin University Report), and shows that for the low, medium and high bromide and iodide concentrations the DBP values were all below the ADWG concentrations. The RO process was responsible for rejection of the disinfection by-products that were detected.

Concentrations of metals in the RO concentrate that is discharged to the environment were compared to the ANZECC Guideline values for pristine waters. Most of the metals measured (B, Ba, Fe, and Mn) have no identified guidance value for marine waters<sup>17</sup>, but Zn is identified as having a value of 15  $\mu$ g/L for the protection of 95% of species and 7  $\mu$ g/L for the protection of 99% of species. The concentration of Zn in the RO concentrate varied between 155 – 348  $\mu$ g/L (30 samples), which is 10-70 times higher than the guideline values. Similarly, P (1.2-10.5 mg/L) is high for discharge to pristine marine waters (0.01-0.02 mg/L P for pristine marine environments). It should be noted that ammonia concentrations post-BAC were between <0.1 – 0.13 mg/L (17 samples with 12 registering <0.1 mg/L) with one outlier of 3 mg/L. Hence, using a concentration of 0.43 mg/L of ammonia if the outlier is ignored, and this is below the guideline value of 0.91 mg/L for 99% protection of species in marine waters. These values are summarised in Table 12.

The concentrations of Zn and P at Davis Station are yet to be determined, and levels of Zn at Davis Station are expected to be low because there is little galvanised material or other sources of zinc at Davis Station. Additionally, MBRs generally have

<sup>17</sup> Australian and New Zealand Guidelines for Fresh and Marine Water Quality, Volume 1, The guidelines (chapters 1-7), National Water Quality Management Strategy, Paper no 4, Oct., 2000 (http://www.environment.gov.au/system/files/resources/53cda9ea-7ec2-49d4-af29-d1dde09e96ef/files/nw qms-guidelines-4-vol1.pdf).

filtrates lower in metals concentrations than other biological treatment processes<sup>18</sup>. Furthermore, bioassay and toxicity testing of the RO concentrate has shown it to be of lower biological impact than the feedwater (secondary treated sewage) because of the high removal of trace organic compounds (See Monitoring the levels of trace organic chemicals (TrOCs) in the 'Demonstration of Robust Recycling' Project report). Therefore the RO concentrate is of improved quality compared to the secondary treated effluent based on the bioassay and toxicity tests.

 Table 12: RO concentrate values, typical sewage treatment plant targets and

 ANZECC Guideline values for pristine water for DOC, Nitrogen, Phosphorus and

 Zinc.

Water quality	RO concentrate (mg/L)	STP Effluent (mg/L)	Pristine waters (mg/L)
Ammonia	0.43		0.91
Р	1.2-10.5	0.3	<0.02
Zn	0.15-0.35	N.A.	0.007-0.015

The high rejection of DBPs by RO results in elevated concentrations within the RO concentrate. As DBPs are not usually considered in wastewater treatment, there are no environmental discharge standards to compare with the RO concentrate values.

The microbiological quality of the RO concentrate was good. There were only 3 out of 10 samples above the limit of detection (<1 MPN/100 mL) for *E. coli*, with 2 samples registering 1 MPN/100 mL and the other 2 MPN/100 mL. The coliform concentrations were higher than the *E. coli* concentrations (12 – 435 MPN/100 mL), but given these arise from regrowth they are less likely to be of concern as these represent environmental bacteria.

<sup>18</sup> Santos, A. and Judd, S (2010) The fate of metals in wastewater treated by the activated sludge process and membrane bioreactors: A brief review., J. Environ. Monit., 12, 110-118.

### 5. Summary

The demonstration plant was operated for 12 months. As there was no formal handover of the plant it did not leave the commissioning stage until the last weeks of operation. Hence, demonstration of unattended operation could not be achieved for a significant length of time.

Early commissioning of the plant identified the ozone system as a potential weakness until the power of the ozone generation system was matched to the individual ozone cell. Prior to this occurring, there were several failures of the ozone system, but once the ozone generation power was limited to the capabilities of the specific cell in use, the ozone system operated reliably.

The feedwater characteristics did vary significantly over time, particularly when maintenance was undertaken on the SPWWTP settlers. Variations in ammonia and minor variability in DOC appeared not to affect the ozone system performance, but during periods of high turbidity the ozone system was unable to maintain ozone residual in the treated water. Native *E. coli* and somatic coliphage measurements across the ozone system over the demonstration period identified that LRV 2 could be achieved when the ozone dose was >11.7 mg/L, even when no ozone residual was measured. As a result, LRV of 2 for bacteria and virus is claimed across the ozone system provided the ozone dose is >11.7 mg/L. Currently the ozone system can measure ozone concentration in the gas phase, but an on-line instrument to measure gas flowrate requires installation.

The ceramic MF reliably achieved its PDT CCP. The ceramic MF did suffer from leaking valves during pressure decay testing for a short period of time, and a leak test was installed. This enabled identification of leaking valves and increased the reliability of the PDT. Backwashing and CEB effectively managed the fouling of ceramic MF, with no long term fouling observed over the demonstration period. The filtrate turbidity readings only became reliable at the end of the trials and further operation for 10 -12 months is required to demonstrate its reliability.

The BAC removed about 4 mg/L of DOC but the BDOC in the filtrate remained above 1 mg/L. This represents water that can maintain bioactivity, and an increase in the EBCT of the BAC above the 20 minutes of the demonstration plant should reduce the BDOC further. Iron, manganese and zinc were removed across the BAC likely because of oxidation and precipitation of these metals.

The RO membrane was able to reliably meet its conductivity and PDT CCPs. An aim of the project was to demonstrate prolonged operation of the RO system without the need for cleaning, however, CIPs were required every 4-5 months. Therefore, 2-3 CIPs would be required each year. The cartridge filter also required regular replacement at 2 week intervals. While this is a high rate of replacement, AAD were accepting of this.

Autopsies of the cartridge filter and RO membranes were undertaken. The cartridge filter was fouled by activated carbon coming from the BAC, so better design of the BAC by lower backwashing flowrates to reduce attrition or use of a harder media for filtration may reduce the amount of carbon fines being filtered on the cartridge filter. The RO membrane suffered from biofouling and a reduction in the BDOC from the

BAC would help reduce the biofouling on the RO membranes. This may be achieved by increasing the EBCT of water in the BAC.

Regrowth of coliforms was detect in the RO permeate after 5 months operation. This was cleaned and no regrowth observed after another 2 months operation. Consideration of how to automate the cleaning of these lines should be made, perhaps via sodium metabisulphite dosed into the permeate lines.

The UV system was reliable and there were no operational issues with its performance. The CCP was always met and the system required little attention.

The calcite filter also operated effectively with little maintenance, and required top-up every 600,000 L of treated water. The stability of the water post-calcite filter was passive to slightly aggressive as determined by the calculated CCPP and LSI values. An increase in the residence time within the calcite contactor (increase its size) may reduce the aggressiveness of the product water.

The chlorination system was operational for only a short period of the trial period. During its time in operation, the system was able to achieve the desired CCP. However, another 10-12 months operation is required to demonstrate its reliable performance. The chlorine decay rate of treated water was very low and could not be detected during the contact time required for chlorination. The CT value for the CCP was increased during the trials as the accuracy of the pH meter was downgraded. However, this only required a minor adjustment to the chlorine residual set point.

Decay in chlorine concentration of the stock sodium hypochlorite occurred over the demonstration period. This was measured weekly to correct the dosing required for CEBs and chlorine dosing. Accurate determination of the sodium hypochlorite concentration was difficult because of the large dilution factor required, which highlights the need for good operator training for this task. Alternatively a different dosing strategy could be used to set the hypochlorite flowrate and calculation of the stock hypochlorite concentration, thereby negating the need for operator determination of the stock hypochlorite solution concentration. Additionally, consideration could be given to using 8% sodium hypochlorite rather than 12.5% sodium hypochlorite to reduce the decay rate of the sodium hypochlorite.

Metals, DPBs, *E. coli* and virus in the product water were all below the ADWG. DOC, P and TN were also low in the product water. RO was the most effective barrier for metals, BPs, P, DOC and TN, while ozonation and ceramic MF effectively removed *E. coli* and somatic coliphage.

The RO concentrate at Selfs Point was high in Zn and P compared to ANZECC Guideline values for pristine waters. However the loads are low because of the low flowrate, and the total load is unchanged compared to what is currently disposed to the ocean. Furthermore, the removal of trace organic compounds will improve the environmental quality of the discharge, and bioassay and toxicity tests (see Monitoring the levels of trace organic chemicals (TrOCs) in the 'Demonstration of Robust Recycling' Project report) demonstrated much reduced levels of biological receptor activity and toxicity compared to the feedwater suggesting it is of lower environmental impact.

### 6. Recommendations

The prolonged commissioning stage for the AWTP meant that not all aspects of the plant could be demonstrated to operate reliably over an extended period of time. Hence, the following aspects of AWTP performance are recommended for further testing over the next 10-12 months of operation:

- The reliability of the plant in unattended operation mode be tested. The plant should be operated by the control system with only weekly water quality measurements and calibration of instruments being undertaken.
- An on-line instrument to measure ozone flowrate be installed and operated.
- The ceramic MF filtrate turbidity readings be monitored and the CCP alert value for turbidity be revised accordingly, as this sensor only became reliable at the end of the current trial period.
- The reliability of the chlorination system be tested as it was only fully operational in the last month of current operations.
- An alternative method of determining the stock sodium hypochlorite solution concentration be established, perhaps using the dose of hypochlorite and the free chlorine measurements, to avoid measurement of the stock solution by the operator.

The water quality at Davis Station will be different to that at Selfs Point. Therefore, there is the potential for the AWTP performance to alter and the following aspects of system operations should be monitored at Davis Station:

- Check the concentrations of Zn and other metals, P and DBP in the RO concentrate at Davis Station.
- Undertake a water quality review of the product water and other process streams as part of the re-commissioning process (ie. same level of TrOCs removal, are their different TrOCs at Davis Station).
- Verify the same water quality performance is achieved by each treatment barrier (ie. similar ceramic MF filtrate turbidity etc).
- Consider chlorinating water stored in the storage tanks prior to its distribution to the station. While recycled water from the AWTP is chlorinated, prolonged storage may result in regrowth within the storage tanks and re-chlorination will provide added security.

While operation of the plant was generally good, not all components of the design achieved the desired level of performance. If another plant is to be built, the following design changes should be considered:

- Increasing in the EBCT of the BAC above the current 20 minute design. This will allow further degradation of BDOC and increase the biological stability of the filtrate, and thus reduce fouling of the subsequent RO process.
- Consider including automated cleaning of the RO permeate lines to control biofilm growth.
- Increasing the residence time of the calcite contactor to improve the corrosion stability of the product water from mildly corrosive to stable.
- Construct pipework and fittings downstream of the chlorination dosing point in plastic or other material less prone to corrosion.

### Appendix A: Hydraulic Retention Time Measurements

Ozone system: Rhodamine WT HRT Test Data (flowrate = 20 L/min = design flowrate)



UV Hydraulic Retention Time Tests 1 & 2: Rhodamine WT, Flowrate = 14.4 L/min (design flowrate)



UV Hydraulic Retention Time Tests 1 & 2: Rhodamine WT, Flowrate = 12 L/min (design flowrate)





Figure B1a DOC concentrations in the feed and following each treatment unit (Log scale)



Figure B1b DOC concentrations in the feed and following each treatment unit (Linear scale)



Figure B2 Total Nitrogen (TN) concentrations in the feed and following each treatment unit



Figure B3 Boron concentrations in the feed and following each treatment unit



Figure B4 Barium concentrations in the feed and following each treatment unit



Figure B5 Iron concentrations in the feed and following each treatment unit



Figure B6 Manganese concentrations in the feed and following each treatment unit



Figure B7 Phosphorus concentrations in the feed and following each treatment unit



Figure B8 Zinc concentrations in the feed and following each treatment unit

### Appendix C: Accreditation of Metawater Ceramic Microfiltration



State of California—Health and Human Services Agency Department of Health Services



SANDRA SHEWRY Director ARNOLD SCHWARZENEGGER Governor

January 18, 2007

Dr. Yoshiho Tomita General Manager NGK Insulators, Ltd. 2-56 Suda-cho, Mizuho-ku Nagoya, 467-8530 Japan

Dear Dr. Tomita:

REVISION OF NGK CERAMIC MEMBRANE REPORT

Thank you for editing, revising, and resubmitting the original report and incorporating comments 1 through 5 from our February 21, 2006 letter of conditional acceptance. The conditions under which the NGK ceramic filtration technology has been accepted remain unchanged, with the exception of the flux and pathogen removal credit.

The 200 gfd flux in the original draft was for an operating temperature of 25°C, which can be temperature corrected and has been adjusted to 175 gfd at 20°C in the final report. The WTC also noted the Table on pg. 2-3 contains a line for an "acceptable range of temperature," however; only one temperature value (60°F) is listed. The WTC also noted that the sample calculations in the addendum (Technical Memorandum [September 21, 2006] from S. Geno Lehman [MWH]) ranged from 41 to 77°F. The calculations were done within a narrower, but valid temperature range (the USEPA Final LT2 Membrane Filtration Guidance Manual (November 2005) notes that the ALCR equation, used in the addendum, is only valid for a temperature range of 32 to 86°F because that is valid range for the binomial fit used to for the viscosity ratio). At present the only temperature restriction will be to limit the operating range to 32 to 86°F, the valid range of the USEPA ALCR equation, recognizing that this temperature range is only valid as long as the pressure hold test is conducted at 20 psi and the UCL remains less than 0.20 psi/min.

While the WTC credited the NGK ceramic membrane with having demonstrated at least 3.5-log *Cryptosporidium*, 3.5-log *Giardia*, and 1-log virus removal under the conditions of testing, your addendum contained supplementary calculations detailing the application of the USEPA Final LT2 Membrane Filtration Guidance Manual (November 2005) integrity test equations for establishing the integrity test parameters to

Drinking Water Technical Programs Branch, 850 Marina Bay Parkway, Bldg P, 2<sup>nd</sup> Floor, Richmond, CA, 94804-1011 (510) 620-3474 FAX (510) 620-3455 DHS Internet Address: <u>www.dhs.ca.gov/ps/ddwem</u> Dr. Yoshiho Tomita Page 2 of 2 January 18, 2007

demonstrate a greater than 4.0 log removal value. This addendum is sufficient to increase the log removal credit for the NGK ceramic membrane to 4-log for *Giardia* and 4-log cryptosporidium. The increased pathogen removal credit is independent of coagulant use, i.e., the log removal credit applies whether a coagulant is used or not.

In addition, California requires an evaluation of any alternative filtration technology after one year of production. All utilities using the NGK ceramic membrane filtration technology are required to complete a first year engineering report (California Code of Regulations Title 22 Chapter 17 Article 2 Section 64653 (i)). This report is due 30 days after the first year of production. The report content should be discussed with our field staff prior to submittal.

Should you have any questions regarding the content of this letter, please feel free to contact me at (510) 620-3499.

Very truly yours,

RU # SJ

Richard H. Sakaji, PhD, PE Senior Sanitary Engineer

cc: WT Committee chron

Mr. Satoshi Fujiura Manager, Chief Engineer NGK-Locke, Inc. 28175 Haggerty Rd. Suite 108 Novi, MI 48377

Dr. Samer Adham and Mr. Geno Lehman MWH 300 N. Lake Ave., Suite 1200 Pasadena, California 91101

# Appendix D: Reverse osmosis membrane autopsy report

### 1. Introduction

The No. 3 RO membrane element of the 5 elements in series was pulled out for autopsy after the RO system had produced about 610,000 L of permeate in 3 months (23 September, 2014 - 23 December, 2014) and the normalised flux had dropped from 1.2 to 0.98 ( $L/m^2/h/bar$ ).

There were 3 pre-treatment processes upstream of the RO array, including ozonation, ceramic MF and BAC, and Pressure Decay Testing (PDT) was used to monitor the integrity of the RO membrane.

The autopsy was to study:

- If the frequent PDT will cause telescoping of the RO element
- What was the major fouling constituent on the RO membrane surface

### 2. Autopsy

### **2.1 Physical Properties**

The used wet element weighed about 3.8 kg compared to 3.6 kg for a clean wet membrane and 2.6 kg for a new, dry membrane element.

The side view of the element is shown in Figure D1. Although plant was shut down very frequently during the plant testing phase, and that several hundred PDTs were performed, no telescoping phenomenon was observed.



Figure D1. Side view of the RO element

The foulant on RO membrane surface formed a stripped pattern as shown in Figure D2.

Two pieces of membrane (9  $\times$  9 cm<sup>2</sup>) from the light and dark section were sampled, dried at 40°C in an oven for one hour, and then weighed to determine the weight of membrane with foulant loaded on. The specimen was subjected to cleaning with water and ultrasonic vibration, dried at 40 °C in the oven for one hour again and weighed to get the weight of the clean membrane. The difference of the weight was used to calculate the dry foulant load on the membrane surface and is shown in Table D1.



Figure D2. Patterns of foulant formed on the RO element surface

	Average foulant load (x10 <sup>-4</sup> g/cm <sup>2</sup> )
Light section	3.2
Dark section	5.0
Average	4.1

Table D1 Foulant load in different membrane sections

### 2.2 Characterisation of the foulant formed on membrane surface

The foulants were removed from the surface of a large piece of membrane, and dried at 80°C overnight in a pre-weighed crucible. The crucible had been preheated to 565°C in a muffle furnace for 2 hours to remove any organic material. The dried foulant was weighed and then loaded into a Muffle Furnace at 565°C overnight, cooled in a desiccator and weighed. The difference in weight was designated organic matter and the residue left after heating in the muffle furnace was designated inorganic material. The ratio of inorganic matter to the organic matter was 9:100 based on the measured mass difference.

The inorganic matter was digested with 5 wt% nitric acid for one hour at 60°C. The solution was filtered with 0.45  $\mu$ m PVDF filter which had been pre-weighed and preconditioned at 40°C. The filter was rinsed twice with deionised water and the rinsing solution was mixed with the filtered solution. The used filter was dried at 40 °C for 4 hours and weighed. The mass difference between the new and used filter was considered as the non-dissolvable inorganic matter, which was 44.5% by weight of the total inorganic matter. The total mass of the dissolvable elements of the inorganic matter measured by ICP and shown in Table D2 accounted for 81.7% of all dissolvable inorganic elements. Taking into account that most metal elements should be in oxide form, the total recovered mass listed in Table D2 would be higher than 99% (assuming metal elements to oxygen ratio is 1:1).

Elem	Wt%
AI	14.3
As	0.25
В	0.26
Ва	0.41
Be	0.02
Ca	23.1
Со	0.3
Cr	0.9
Cu	0.8
Fe	29.2
Mn	0.36
Ni	0.1
Р	25.4
Pb	0.55
Sr	0.14
V	0.11
Zn	3.63

Table D2 Element measured in the dissolvable inorganic

The non-dissolvable inorganic matter on the filter is measured by EDS as shown in Table D3 and Figure D3.

Table D3 EDS for the non-dissolved	inorganics	on 0.45	um	filter
------------------------------------	------------	---------	----	--------

Elem	Wt%	At%
С	16.89	26.88
0	40.02	47.82
Fe	12.33	4.22
Na	0.32	0.27
Mg	1.91	1.5
AI	6.72	4.76
Si	20.33	13.84
Ca	1.48	0.7
Total	100	100



Figure D3. EDS for the non-dissolvable inorganic matter on the filter

The EDS was also done for the fouled RO membrane surface, as shown in Figure D4 and Table D4.



Figure D4. EDS for the element on fouled membrane surface

Elem	Wt%	At%
С	53.84	68.87
0	27.29	26.21
Fe	1.82	0.50
Na	0.45	0.30
Mg	0.40	0.25
Al	1.15	0.66
Si	1.29	0.70
Ca	1.42	0.54
Total	100	100

Table D4 EDS for Fouled RO membrane surface

### 2.3 Normalised flux post CIP

The normalised flux trend is shown in Figure D5. The normalised flux increased greatly after CIP (alkali wash followed by acid wash), and was fully recovered to the original value.





### 3. Conclusion

- The major foulant loaded on membrane surface was organic matter, which was above 90% by weight of the total foulant.
- The major elements in inorganic foulant were iron, aluminium, calcium, and silica.

## Appendix E: Microbiological concentrations in the treatment system

#### Table E1: Microbial concentrations through the treatment system Total Coliforms Ecoli **Total Coliforms** Ecoli Somatic Coliphage Description date (MPN/100mL) (MPN/100mL) (MPN/100mL) (MPN/100mL) (pfu/100ml) 17/09/14 Feed >2419.6 1986.3 24/09/14 Feed >2419.6 1553.1 1/10/14 Feed >2419.6 1732.9 8/10/14 >2419.6 Feed 1553.1 15/10/14 Feed >2419.6 2419.6 22/10/14 >2419.6 2419.6 Feed 29/10/14 Feed >2419.6 2419.6 5/11/14 Feed >2419.6 2419.6 12/11/14 >2419.6 2419.6 Feed 19/11/14 Feed >2419.6 2419.6 26/11/14 165800 13500 Feed 2/12/14 435200 Feed 24300 10/12/14 1986300 290900 Feed 17/12/14 Feed 2419600 285100 834 21/01/15 Feed 2419600 770100 28/01/15 Feed 388000 53300 365400 90900 4/02/15 135400 Feed 18700 290900 62000 11/02/15 Feed >2419.6/est 2419.6 >2419.6/est 2419.6 18/02/15 488400 579400 150000 Feed 108100 25/02/15 Feed 115300 27500 151500 25300 3000 4/03/15 Feed 162400 28200 198900 28100 11/03/15 Feed 435200 70600 365400 74300 25/03/15 Feed 387300 39300 275500 48700 12000 Feed 1/04/15 74900 9700 8600 81600 15/04/15 79800 14800 95900 Feed 5200 22/04/15 4200 Feed 65700 3100 72700 5200 29/04/15 Feed 67000 9700 56500 7500 6/05/15 Feed 142100 16100 190400 14600 2500 20/05/15 Feed 1553100 133300 1859600 128650 27/05/15 222400 Feed >2419600 >2419600 178500 Post 17/09/14 ozonation 86.5 3.1 Post 24/09/14 ozonation 115.3 4.1 Post ozonation 1/10/14 35.9 5.2 Post 8/10/14 ozonation 21.6 4.1 Post 15/10/14 ozonation 151 2 Post ozonation 22/10/14 613.1 4.1

Post	20/10/11					
ozonation	29/10/14	35.5	1			
Post	5/11/14	73 3	3.1			
Post	5, 11, 11	13.3	5.1			
ozonation	12/11/14	68.4	4.1			
Post						
ozonation	19/11/14	45.5	1			
Post	26/11/14	20.0	1			
Post	20/ 11/ 1	20.9	1			
ozonation	2/12/14	61.3	2			
Post						
ozonation	10/12/14	54.8	4.1			
Post	17/12/14	1553 1	39.9			<1
Post		1555.1	59.9			
ozonation	21/01/15	325.5	24.3			
Post	20/01/15					
ozonation	28/01/15	127.4	7.5	95.9	12.2	
ozonation	4/02/15	172.3	12	172.2	97	
Post	1 - 1 -	172.5	12	172.2		
ozonation	11/02/15	127.4/est	12.1	325.5/est	21.6	
Post	10/02/15					
ozonation	18/02/15	172.3	37.9	>2419.6	72.3	
ozonation	25/02/15	770 1	15.8	53	3	1
Post	, ,	//0.1	10.0			1
ozonation	4/03/15	105.4	6.3	224.7	55.4	
Post	11/02/15	102.5	14.6	1412 6	24.6	
Ozonation	11/05/15	193.5	14.6	1413.0	24.6	
ozonation	25/03/15	107.1	2	387.3	10.8	7
Post						
ozonation	1/04/15	1986.3	4.1	272.3	18.9	
Post	15/04/15	75.2	2	50 °	1	
Post	13/04/13	13.2	2	32.8	1	
ozonation	22/04/15	152.9	7.5	58.3	1	5
Post						
ozonation	29/04/15	325.5	7.3	411.3	8.7	
Post	6/05/15	172 3	3	29.5	3.1	<1
Post	0,00,10	172.5	5	27.5	5.1	
ozonation	20/05/15	325.5	23.3	648.8	27.5	
Post	07/07/47					
ozonation	2//05/15	461.1	5.2	517.2	7.4	
MF filtrate	17/09/14	<1	<1			
MF filtrate	24/09/14	<1	<1			
MF filtrate	1/10/14	<1	<1			
MF filtrate	8/10/14	<1	<1			
MF filtrate	15/10/14	<1	<1			
MF filtrate	22/10/14	<1	<1			
MF filtrate	29/10/14	<1	<1			
ME filtrate	5/11/14	<1	<1			
ME filtrate	12/11/14	517.0	<1			
wir intrate	1-2/11/14	517.2	<1			

MF filtrate	19/11/14	<1	<1		
MF filtrate	26/11/14	<1	<1		
MF filtrate	2/12/14	<1	<1		
MF filtrate	10/12/14	<1	<1		
MF filtrate	17/12/14	<1	<1		<1
MF filtrate	21/01/15	209.8	<1		
MF filtrate	28/01/15	10.8	<1		
MF filtrate	4/02/15	2	<1		
MF filtrate	11/02/15	36.9/est	<1		
MF filtrate	18/02/15	119.8	1		
MF filtrate	25/02/15	3.1	<1		<1
MF filtrate	4/03/15	17.5	<1		
MF filtrate	11/03/15	1	<1		
MF filtrate	25/03/15	11	<1		<1
MF filtrate	1/04/15	<1	<1		~~
MF filtrate	15/04/15	1	<1		
MF filtrate	22/04/15	<1	<1		<1
MF filtrate	29/04/15	<1	<1		
MF filtrate	6/05/15	<1	<1		<1
MF filtrate	20/05/15	<1	<1		
MF filtrate	27/05/15	<1	<1		
BAC					
effluent	17/09/14	<1	<1		
BAC	24/09/14	31	~1		
BAC	,,	5.1	< <u>1</u>		
effluent	1/10/14	4.1	<1		
BAC	8/10/14	~1	~1		
BAC	0/10/14	<1	<1		
effluent	15/10/14	<1	<1		
BAC	22/10/14	1	-1		
BAC	22/10/14	1	<1		
effluent	29/10/14	22.6	<1		
BAC	5/11/14	17.5	.1		
BAC	5/11/14	17.5	<1		
effluent	12/11/14	12.1	<1		
BAC	10/11/14				
BAC	19/11/14	8.6	<1		
effluent	26/11/14				
BAC	2/12/11				
effluent BAC	2/12/14				
effluent	10/12/14				
BAC	17/12/14				
effluent BAC	1//12/14				<1
effluent	21/01/15				
BAC					
effluent	28/01/15				

BAC	1/02/15				
BAC	4/02/13				
effluent	11/02/15				
BAC	18/02/15				
BAC	10/02/13				
effluent	25/02/15				<1
BAC	4/02/15				
BAC	4/05/15				
effluent	11/03/15				
BAC	25/02/15				
effluent BAC	25/03/15				<1
effluent	1/04/15				
BAC	15/04/45				
effluent BAC	15/04/15				
effluent	22/04/15				<1
BAC	20/04/45				
effluent BAC	29/04/15				
effluent	6/05/15				<1
BAC	20/05/45				
effluent	20/05/15				
effluent	27/05/15				
RO	/				
concentrate	17/09/14	17.5	<1		
concentrate	24/09/14	49.6	<1		
RO					
concentrate	1/10/14	29.2	<1		
concentrate	8/10/14	12	<1		
RO					
concentrate	15/10/14	26.2	<1		
KO concentrate	22/10/14	12.1	1		
RO					
concentrate	29/10/14	260.3	2		
concentrate	5/11/14	142.1	<1		
RO					
concentrate	12/11/14	435.2	1		
RO concentrate	19/11/14	43.1	<1		
RO					
concentrate	26/11/14				
KO concentrate	2/12/14				
RO	, ,				
concentrate	10/12/14				
KO concentrate	17/12/14				
RO	,, _ 1				
concentrate	21/01/15				
RO concentrate	28/01/15				
concontiate	-,, -0				

RO concentrate	4/02/15				
RO					
concentrate	11/02/15				
RO	18/02/15				
RO	10/02/13				
concentrate	25/02/15				
RO	4/02/15				
concentrate PO	4/03/15				
concentrate	11/03/15				
RO					
concentrate	25/03/15				
KO concentrate	1/04/15				
RO					
concentrate	15/04/15				
RO	22/04/15				
RO					
concentrate	29/04/15				
RO	6/05/15				
RO	0/03/13				
concentrate	20/05/15				
RO	27/05/15				
concentrate	27/05/15				
permeate	17/09/14	<1	<1		
combined					
permeate	24/09/14	<1	<1		
permeate	1/10/14	<1	<1		
combined					
permeate	8/10/14	<1	<1		
combined	15/10/14	<1	<1		
combined		~1	<b>\1</b>		
permeate	22/10/14	<1	<1		
combined	20/10/14	1	-1		
combined	23/10/14	1	<1		
permeate	5/11/14	<1	<1		
combined	17/11/14	2			
combined	12/11/14	2	<1		
permeate	19/11/14	9.8	<1		
RO					
combined	10/12/14	~1			
combined	10/12/14	<1			
permeate	17/12/14	1			
combined	21/01/15	(10.0			
combined	CT/UT/T2	048.8			
permeate	28/01/15	7.5			
combined	1/02/15				
permeate	4/02/15	3.1			
combined	11/02/15	4.8/est			

permeate					
combined					
permeate	18/02/15	2.6			
combined	25/02/15	4.1			
combined	23/02/13	4.1			
permeate	4/03/15	3.1			
combined					
permeate	11/03/15	<1			
combined	25/03/15	2			
combined	23/03/13	2			
permeate	1/04/15	12.1			
combined					
permeate	15/04/15	4.7			
combined	22/04/15	<1			
combined		< <u>1</u>			
permeate	29/04/15	<1			
combined					
permeate	6/05/15	1			
permeate	20/05/15	<1			
combined	, ,				
permeate	27/05/15	1			
Post UV	17/09/14	<1	<1		
Post UV	24/09/14	<1	<1		
Post UV	1/10/14	<1	<1		
Post UV	8/10/14	<1	<1		
Post UV	15/10/14	<1	<1		
Post UV	22/10/14	<1	<1		
Post UV	29/10/14	<1	<1		
Post UV	5/11/1/	<1	<1		
Post UV	12/11/14	<1	<1		
Post UV	12/11/14	<1	<1		
Post UV	19/11/14	<1	<1		
product water	17/09/14	<1	<1		
product	, ,	<u></u>			
water	24/09/14	<1	<1		
product	1/10/14	1	4		
water	1/10/14	<1	<1		
water	8/10/14	<1	<1		
product					
water	15/10/14	<1	<1		
product	22/10/14	<1	-1		
nroduct	22/10/14	<1	<1		
water	29/10/14	<1	<1		
product					
water	5/11/14	<1	<1		
product	12/11/14	~1	~1		
product	+ <u>+</u> , +1, 14	<u></u>	<u></u>		
water	19/11/14	<1	<1		
product					
water	26/11/14	<1	<1		

product water	2/12/14	<1	<1		
product water	10/12/14	<1	<1		
product water	17/12/14	<1	<1		
product water	21/01/15	<1	<1		<1
product water	28/01/15	<1	<1		
product water	4/02/15	<1	<1		
product water	11/02/15	<1/est	<1		
product water	18/02/15	<1	<1		
product water	25/02/15	<1	<1		<1
product water	4/03/15	<1	<1		
product water	11/03/15	<1	<1		
product water	25/03/15	<1	<1		<1
product water	1/04/15	<1	<1		
product water	15/04/15	<1	<1		
product water	22/04/15	<1	<1		<1
product water	29/04/15	<1	<1		
product water	6/05/15	<1	<1		<1
product water	20/05/15	1	<1		
product water	27/05/15	<1	<1		

### **Appendix F: Disinfection by-product report**

### Bromide and lodide sampling program of the Water Recycling Plant

#### 1. Aim and Scope

The aim of this work was to study the behaviour of bromide (Br<sup>-</sup>) and iodide (I<sup>-</sup>) through the Advanced Water Treatment Plant (AWTP) to ensure the mitigation of potentially harmful DBPs is efficient in providing safe water. Three different concentrations of bromide and iodide were spiked in the plant feed before any oxidative process, where chlorination was the final disinfection process. Thereafter, the distribution of bromate (BrO<sub>3</sub><sup>-</sup>), iodate (IO<sub>3</sub><sup>-</sup>), Adsorbable Organic Halides (AOCI AOBr and AOI), trihalomethanes (THMs) and haloacetic acids (HAAs) at different sampling points (8 in total) in the treatment plant was quantified.

#### 2. Samples

Twenty-four water samples (stored in amber bottles) were received on 26 February 2015. Any ozone residual in Post ozone and Post MF samples were already quenched with sodium sulphite during sampling. Upon receipt of samples, samples taken as Product Water were analysed for chlorine residual (measured values ranging from 1.0 to 1.6 mg.L<sup>-1</sup>) and subsequently quenched accordingly for the different analyses required. Samples were stored at 4°C for less than a week until further analyses were performed. Bromide and iodide concentrations of the feed were provided as followed:

Dosing	Bromide (µg.L <sup>-1</sup> )	lodide (µg.L⁻¹)
Low	~200 (Natural feed)	9
Medium	490	37
High	693	63

The sampling points in the AWTP were: Plant Feed, Post Ozone, Post MF, Post BAC, RO Feed, RO Concentrate, RO Permeate and Product Water

### 3. Materials and Methods

All chemicals used in this study were of the highest grade purity and were used without further purification. Reagents were prepared using ultra-pure water produced from an ELGA purification system with a resistivity of 18.2 m $\Omega$ .cm and TOC of approximately 0.1 mgC. L<sup>-1</sup>.

### a. Bromide, lodide, Bromate and lodate

Halides (Br<sup>-</sup> and l<sup>-</sup>) and oxyhalides (BrO<sub>3</sub><sup>-</sup> and IO<sub>3</sub><sup>-</sup>) were analysed using a Dionex ICS3000 ion chromatograph (IC) system, equipped with an anion exchange column (Dionex IonPac® AS9-HC 4 x 250 mm) and sodium carbonate as the eluent. 500  $\mu$ L of filtered sample was injected and the anions were measured simultaneously using both conductivity and UV detectors<sup>1</sup>. The detection of Br<sup>-</sup> and l<sup>-</sup> was determined with the conductivity detector while BrO<sub>3</sub><sup>-</sup> and IO<sub>3</sub><sup>-</sup> was obtained by an online postcolumn reaction (using acidified potassium iodide, catalysed by heptamolybdate) with UV/Vis detection of I<sub>3</sub><sup>-</sup> at 288 nm. The IC system was calibrated with either sodium or potassium salts of bromide, iodide, bromate and iodate. The limit of detection (LOD) for these anions is shown in Table F1 and duplicate measurements were carried out for each sample.

### b. Specific Adsorbable Organic Halides (AOCI, AOBr and AOI)

Specific adsorbable organic halides (AOCI, AOBr and AOI), which is a bulk parameter to represent overall organic halogenated compounds formed after oxidation, were analysed using a Mitsubishi AQF-100 combustion unit, coupled with the Dionex ICS3000 IC system<sup>2</sup>. 50 mL of samples were first acidified to pH 2, followed by passing through two activated carbon columns in series. The activated carbon columns were then transferred to ceramic boats and combusted using a Mitsubishi AQF-100 system. Hydrogen halide gases produced from the combustion was collected into MilliQ water and subsequently analysed in the IC system with a conductivity detector using an anion exchange column (Dionex IonPac® AS19-HC 4 x 250 mm) and potassium hydroxide as the eluent. AOCI, AOBr and AOI concentrations, respectively. Trichlorophenol, tribromophenol and iodophenol standards were used to calibrate the specific adsorbable organic halogens (AOX) measurement. The LODs for this analysis are shown in Table F2 and duplicate measurements were carried out for each sample.

c. THMs

Ten trihalomethanes (including iodinated THMs) were analysed using head-space solid phase micro-extraction (SPME), followed by gas chromatography separation and mass spectroscopy detection (GC-MS). The detection of the analytes was carried out according to a previously published method<sup>3</sup>. Calibration was carried out by making standard solutions from the neat compounds of the ten trihalomethanes. The LODs for the THMs are shown in Table F3 and duplicate measurements were carried out for each sample.

### d. HAAs

Nine haloacetic acids were measured using liquid-liquid extraction (LLE) with methyltert-butyl-ether (MtBE), subsequent derivatisation with acidic methanol and then quantified using GC-MS in electron impact (EI) mode<sup>4</sup>. Calibration was carried out by making standard solutions from a commercial standard mixture that contained the nine haloacetic acids. The LODs for the HAAs are shown in Table F2 and duplicate measurements were carried out for each sample.

Disinfection by-product (DBP) Class	Species analysed
Trihalomethanes (THMs)	Chloroform (CHCl <sub>3</sub> ), Chlorodibromomethane
	(CHBr <sub>2</sub> Cl), Bromodichloromethane (CHBrCl <sub>2</sub> ),
	Bromoform (CHBr <sub>3</sub> ), Chlorodiiodomethane (CHCll <sub>2</sub> ),
	Dibromoiodomethane (CHBr <sub>2</sub> I),
	Bromochloroiodomethane (CHBrCll),
	Dichloroiodomethane (CHCl <sub>2</sub> I), Bromodiiodomethane
	(CHBrl <sub>2</sub> ), lodoform (CHl <sub>3</sub> )
Haloacetic Acids (HAAs)	Chloroacetic acid (MCAA), Dichloroacetic acid (DCAA),
	Trichloroacetic acid (TCAA), Bromoacetic acid
	(MBAA), Dibromoacetic acid (DBAA), Tribromoacetic
	acid (TBAA), Bromochloroacetic acid (BCAA),
	Chlorodibromoacetic acid
	(CDBAA), Bromodichloroacetic acid (BDCAA)

## e. Dissolved organic carbon (DOC) and Specific Ultraviolet Absorbance at 254 nm (SUVA<sub>254</sub>)

Dissolved organic carbon (DOC) concentration was measured for all samples and specific ultraviolet absorbance at 254 nm (SUVA<sub>254</sub>), a surrogate parameter for aromatic content of organic matter (i.e., strong reactive sites), were determined for the Plant Feed and Post Ozone samples. DOC measurement was carried out using

the UV/persulfate oxidation method according to the standard method 5310C with a Shimadzu TOC-Vws Total Organic Carbon analyser<sup>5</sup>. The ultraviolet absorbance at 254 nm (UV<sub>254</sub>) of all samples was measured using Cary 60 UV-Vis Spectrophotometer (Agilent Technologies, California, USA) with a 1 cm quartz cell. SUVA<sub>254</sub> is defined as UV absorbance measured at 254 nm divided by DOC<sup>6</sup>. The LOD of DOC is shown in Table F1, with the DOC concentration taken as an average of the best three out of five measurements per sample. Single measurement was performed for UV<sub>254</sub> for each sample.

#### 4. Results

The concentrations of DOC, halide and oxyhalide ions are shown in Table F1. The concentrations of specific adsorbable organic halides (AOX) together with HAAs formed in the samples are presented in Table F2, and the concentrations of different species of THMs measured can be found in Table F3. Measurements of DOC concentration across the treatment processes and the molar distribution of inorganic and organic bromine species in all samples are also illustrated in Figure F1 and F2a-c, respectively.

LOD (µg.L <sup>-1</sup> )	0.2 mg.L <sup>-1</sup>			1	3	0.2	0.2
Concentration (ug.L <sup>-1</sup> )	DOC (ma.L <sup>-1</sup> )	UV <sub>254</sub> (cm <sup>-1</sup> )	SUVA <sub>254</sub> (L.mg <sup>-1</sup> .m <sup>-1</sup> )	Br <sup>-</sup> (µa/L)	r (ya/L)	BrO3 <sup>-</sup> (µa/L)	lO <sub>3</sub> <sup>-</sup> (µɑ/L)
Low Dosing		(- )	( 3 /				
L3037L Plant Feed	8.0±0.07	0.201	2.5	179±0.4	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3044L Post Ozone	6.1±0.04	0.064	1.0	152±1.3	<lod< td=""><td>37±0.1</td><td>28±0.1</td></lod<>	37±0.1	28±0.1
L3084L Post MF	5.7±0.01			155±1.9	<lod< td=""><td>38±0.8</td><td>28±0.2</td></lod<>	38±0.8	28±0.2
L3096L Post BAC	3.9±0.02			150±2.5	<lod< td=""><td>32±0.9</td><td>25±0.6</td></lod<>	32±0.9	25±0.6
L3122L RO Feed	5.4±0.01			236±2.9	<lod< td=""><td>45±0.0</td><td>33±0.1</td></lod<>	45±0.0	33±0.1
L3147L RO Concentrate	9.8±0.06			479±5.3	<lod< td=""><td>94±0.3</td><td>71±1.7</td></lod<>	94±0.3	71±1.7
L3155L RO Permeate	<lod< td=""><td></td><td></td><td>3±0.0</td><td><lod< td=""><td>0.6±0.0</td><td>0.2±0.0</td></lod<></td></lod<>			3±0.0	<lod< td=""><td>0.6±0.0</td><td>0.2±0.0</td></lod<>	0.6±0.0	0.2±0.0
L3206L Product Water	0.3±0.00			<lod< td=""><td><lod< td=""><td>0.9±0.0</td><td>0.4±0.0</td></lod<></td></lod<>	<lod< td=""><td>0.9±0.0</td><td>0.4±0.0</td></lod<>	0.9±0.0	0.4±0.0
Medium Dosing							
L3037M Plant Feed	8.2±0.06	0.203	2.5	408±0.4	13±0.9	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3044M Post Ozone	5.8±0.03	0.066	1.1	352±2.0	<lod< td=""><td>68±2.3</td><td>58±0.2</td></lod<>	68±2.3	58±0.2
L3084M Post MF	5.7±0.04			350±0.7	<lod< td=""><td>66±0.4</td><td>57±0.1</td></lod<>	66±0.4	57±0.1
L3096M Post BAC	3.9±0.02	1		186±1.1	<lod< td=""><td>35±0.1</td><td>38±0.7</td></lod<>	35±0.1	38±0.7
L3122M RO Feed	5.5±0.02			254±4.9	<lod< td=""><td>50±0.6</td><td>41±0.6</td></lod<>	50±0.6	41±0.6
L3147M RO Concentrate	9.8±0.04			513±10.6	<lod< td=""><td>101±0.6</td><td>80±0.2</td></lod<>	101±0.6	80±0.2
L3155M RO Permeate	<lod< td=""><td></td><td></td><td>4±0.0</td><td><lod< td=""><td>0.8±0.0</td><td>0.4±0.0</td></lod<></td></lod<>			4±0.0	<lod< td=""><td>0.8±0.0</td><td>0.4±0.0</td></lod<>	0.8±0.0	0.4±0.0
L3206M Product Water	0.3±0.03			<lod< td=""><td><lod< td=""><td>1.1±0.0</td><td>0.5±0.2</td></lod<></td></lod<>	<lod< td=""><td>1.1±0.0</td><td>0.5±0.2</td></lod<>	1.1±0.0	0.5±0.2
High Dosing							
L3037H Plant Feed	8.0±0.03	0.203	2.5	609±3.0	29±0.1	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3044H Post Ozone	6.4±0.03	0.071	1.1	501±5.7	<lod< td=""><td>125±1.9</td><td>105±0.5</td></lod<>	125±1.9	105±0.5
L3084H Post MF	5.7±0.02			506±0.2	<lod< td=""><td>119±1.9</td><td>106±1.1</td></lod<>	119±1.9	106±1.1
L3096H Post BAC	3.9±0.03			275±1.3	<lod< td=""><td>50±0.3</td><td>87±0.0</td></lod<>	50±0.3	87±0.0
L3122H RO Feed	5.6±0.02			296±3.1	<lod< td=""><td>59±1.5</td><td>84±0.3</td></lod<>	59±1.5	84±0.3
L3147H RO Concentrate	9.8±0.05			619±1.3	<lod< td=""><td>118±3.6</td><td>168±0.8</td></lod<>	118±3.6	168±0.8
L3155H RO Permeate	<lod< td=""><td></td><td></td><td>5±0.1</td><td><lod< td=""><td>0.8±0.0</td><td>0.9±0.1</td></lod<></td></lod<>			5±0.1	<lod< td=""><td>0.8±0.0</td><td>0.9±0.1</td></lod<>	0.8±0.0	0.9±0.1
L3206H Product Water	0.3±0.00			<lod< td=""><td><lod< td=""><td>1.3±0.0</td><td>0.9±0.1</td></lod<></td></lod<>	<lod< td=""><td>1.3±0.0</td><td>0.9±0.1</td></lod<>	1.3±0.0	0.9±0.1

Table F1. Mass concentrations of DOC, halide and oxyhalide ions

LOD (µg.L <sup>-1</sup> )	2	2	1	0.2	0.6
Concentration (µg.L-1)	AOCI	AOBr	AOI	DCAA	DBAA
Low Dosing					
L3037L Plant Feed	78±3.3	11±0.3	20±0.4	0.2±0.02	<lod< td=""></lod<>
L3044L Post Ozone	38±1.0	4±0.4	14±0.2	1.1±0.08	<lod< td=""></lod<>
L3084L Post MF	39±2.9	5±0.0	13±0.9	0.6±0.03	<lod< td=""></lod<>
L3096L Post BAC	21±0.1	2±0.1	6±0.4	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3122L RO Feed	29±1.2	5±0.6	8±0.4	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3147L RO Concentrate	57±0.6	9±0.6	17±1.7	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3155L RO Permeate	2±0.3	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3206L Product Water	3±0.4	<lod< td=""><td><lod< td=""><td>0.3±0.02</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.3±0.02</td><td><lod< td=""></lod<></td></lod<>	0.3±0.02	<lod< td=""></lod<>
Medium Dosing					
L3037M Plant Feed	73±0.0	11±0.2	20±0.9	0.3±0.01	<lod< td=""></lod<>
L3044M Post Ozone	34±0.1	6±0.4	18±0.1	1.0±0.06	<lod< td=""></lod<>
L3084M Post MF	34±0.7	5±0.0	17±0.9	0.4±0.06	<lod< td=""></lod<>
L3096M Post BAC	22±0.6	5±0.3	7±0.1	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3122M RO Feed	31±0.7	5±0.3	12±1.2	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3147M RO Concentrate	54±0.7	9±0.1	21±0.6	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3155M RO Permeate	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3206M Product Water	<lod< td=""><td><lod< td=""><td><lod< td=""><td>0.3±0.00</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>0.3±0.00</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>0.3±0.00</td><td><lod< td=""></lod<></td></lod<>	0.3±0.00	<lod< td=""></lod<>
High Dosing					
L3037H Plant Feed	68±0.9	9±0.3	50±0.5	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3044H Post Ozone	35±0.9	25±0.2	41±1.2	1.0±0.07	1.3±0.20
L3084H Post MF	33±0.4	10±0.1	36±0.7	0.2±0.00	<lod< td=""></lod<>
L3096H Post BAC	21±2.6	6±0.2	14±0.9	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3122H RO Feed	30±2.2	6±0.2	21±0.1	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3147H RO Concentrate	59±0.9	11±0.2	43±0.9	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3155H RO Permeate	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
L3206H Product Water	2±0.1	2±0.2	<lod< td=""><td>0.4±0.13</td><td><lod< td=""></lod<></td></lod<>	0.4±0.13	<lod< td=""></lod<>

### Table F2. Mass concentrations of specific adsorbable halides (AOX) and HAAs

LOD ( $\mu g.L^{-1}$ )	0.05	0.02	0.01	0.01	ng.L <sup>-1</sup>	ng.L <sup>-1</sup>	
Concentration (µg.L-1)	CHCl <sub>3</sub>	CHBrCl₂	CHBr₂CI	CHBr₃	CHBr <sub>2</sub> I (ng.L <sup>-1</sup> )	CHBrl <sub>2</sub> (ng.L <sup>-1</sup> )	
Low Dosing							
L3037L Plant Feed	1.4±0.01	<lod< td=""><td><lod< td=""><td><lod< td=""><td>8±0.1</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>8±0.1</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>8±0.1</td><td><lod< td=""></lod<></td></lod<>	8±0.1	<lod< td=""></lod<>	
L3044L Post Ozone	1.1±0.17	0.03±0.00	<lod< td=""><td><lod< td=""><td><lod< td=""><td>9±2.3</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>9±2.3</td></lod<></td></lod<>	<lod< td=""><td>9±2.3</td></lod<>	9±2.3	
L3084L Post MF	1.2±0.02	0.03±0.00	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3096L Post BAC	2.1±0.01	0.1±0.00	<lod< td=""><td>0.01±0.00</td><td><lod< td=""><td>9±0.4</td></lod<></td></lod<>	0.01±0.00	<lod< td=""><td>9±0.4</td></lod<>	9±0.4	
L3122L RO Feed	2.7±0.28	0.1±0.01	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3147L RO Concentrate	4.7±0.12	0.2±0.01	0.01±0.00	0.01±0.00	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3155L RO Permeate	1.1±0.14	0.1±0.00	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3206L Product Water	1.4±0.05	0.4±0.01	0.2±0.00	0.04±0.00	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
Medium Dosing							
L3037M Plant Feed	1.1±0.04	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3044M Post Ozone	1.3±0.14	0.03±0.00	<lod< td=""><td>0.01±0.00</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	0.01±0.00	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3084M Post MF	1.3±0.22	0.02±0.00	<lod< td=""><td>0.01±0.00</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	0.01±0.00	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3096M Post BAC	2.1±0.15	0.1±0.00	<lod< td=""><td>0.01±0.00</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	0.01±0.00	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3122M RO Feed	2.6±0.00	0.1±0.00	<lod< td=""><td>0.01±0.00</td><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	0.01±0.00	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3147M RO Concentrate	3.9±0.18	0.2±0.00	0.01±0.00	0.01±0.00	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3155M RO Permeate	1.1±0.05	0.1±0.01	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3206M Product Water	1.4±0.05	0.5±0.02	0.30±0.00	0.1±0.00	7±0.3	<lod< td=""></lod<>	
High Dosing							
L3037H Plant Feed	1.1±0.05	<lod< td=""><td><lod< td=""><td><lod< td=""><td>8±0.2</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>8±0.2</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>8±0.2</td><td><lod< td=""></lod<></td></lod<>	8±0.2	<lod< td=""></lod<>	
L3044H Post Ozone	1.3±0.01	0.03±0.00	<lod< td=""><td>0.1±0.00</td><td>8±0.2</td><td><lod< td=""></lod<></td></lod<>	0.1±0.00	8±0.2	<lod< td=""></lod<>	
L3084H Post MF	1.3±0.10	0.03±0.00	<lod< td=""><td>0.04±0.00</td><td>7±0.0</td><td><lod< td=""></lod<></td></lod<>	0.04±0.00	7±0.0	<lod< td=""></lod<>	
L3096H Post BAC	2.2±0.36	0.1±0.00	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3122H RO Feed	2.5±0.26	0.1±0.01	0.01±0.00	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3147H RO Concentrate	4.3±0.18	0.2±0.00	0.01±0.00	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3155H RO Permeate	1.0±0.00	0.1±0.00	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>	
L3206H Product Water	1.3±0.03	0.5±0.03	0.3±0.00	0.1±0.00	8±0.7	<lod< td=""></lod<>	

### Table F3. Mass concentrations of THMs

#### Notes/Comments

- Error values are the standard deviation (SD) of duplicate analyses
- Other trihalomethanes and haloacetic acids analysed but not shown in the table, were not detected in any of the samples
- Spiked iodide concentration was under-recovered in plant feed matrix (highlighted in yellow)
  - Iodide was <LOD in low dosing plant feed sample, iodide detected in medium and high dosing plant feed samples were also less than expected
    - ✓ Possibly due to matrix effects; further lab tests confirmed that iodide spiked into this sample was under-recovered
    - ✓ Low dosing plant feed spiked with 10 µg/L iodide recovered ~6 µg/L while with 40 µg/L iodide recovered 26 µg/L=> recovery ~60-65%
  - > There was co-elution with another peak just beside it



Figure F1. The concentration of DOC across the treatment processes for the three Br/I feed concentrations







Figure F2a-c. Molar concentration of bromine species (Br<sup>-</sup>, BrO<sub>3</sub><sup>-</sup> and AOBr) in sample with low, medium and high bromide and iodide concentrations.

### 5. Discussions

- The quality of RO permeate is really good and quite consistent, with concentrations of bromate, chloroform and bromodichloromethane detected for all three bromide/ iodide feed concentrations well below the drinking water guidelines.
- The average removal of bromide through the RO process was around 98%; the concentrations of bromide left in the RO permeate were around 3-5 μg.L<sup>-1</sup>.
- A large fraction of bromide was removed through BAC filtration, particularly for the medium and high bromide/ iodide feed concentrations with an approximate 46% removal. During ozonation, bromide is guickly oxidised to bromine (HOBr+BrO<sup>-</sup>)  $(k=160 \text{ M}^{-1}\text{s}^{-1})$ . Thereafter, bromine is slowly oxidised to bromate. Since the oxidation of bromine to bromate is slow, bromine is stable in the waters. With around 10-14% of initial bromide converted to bromate after ozonation, it is postulated that the remaining bromide was in the form of bromine (but analysed as bromide since the samples were quenched and bromine was reduced to bromide). Therefore, during BAC treatment, HOBr/ BrO were scavenged by reaction BAC. with NOM adsorbed onto the This led to the formation of adsorbable organic bromine (AOBr). This AOBr was actually adsorbed onto the BAC and thus led to a decrease of the bromide concentration after BAC.
- The BAC treatment was found to be efficient in reducing bromate and DOC concentrations. This is common for new BAC filters, however the efficiency in reducing bromate and DOC will drastically decrease when the filter gets older.
- Very low concentrations of regulated chemical species such as the four conventional THMs (chloroform, chlorodibromomethane, bromodichloromethane and bromoform), dichloroacetic acid and bromate were detected in the Product water after UV and chlorination treatments; dibromoiodomethane, which was found in low concentrations (nanograms per litre) was the only iodinated THMs found in the Product water for the medium and high bromide/ iodide feed concentrations.
- The concentrations of bromate, dichloroacetic acids (DCAA) and total trihalomethanes (TTHMs) detected in all Product Water samples were below the Australian Drinking Water Guideline (ADWG6 2011; last updated in Dec 2014); Guidelines are 0.02 mg.L<sup>-1</sup> for bromate, 0.10 mg.L<sup>-1</sup> for DCAA and 0.25 mg.L<sup>-1</sup> for TTHMs.
- Overall, very low concentrations of THMs and HAAs were detected through the treatment process, and the majority of the disinfection by-products formed postozonation were bromate and iodate. Formation of bromate and iodate after ozonation was higher with higher bromide/ iodide feed concentrations, with around 10-14% of initial bromide converted to bromate during ozonation.
- Chloroform (CHCl<sub>3</sub>) was found to increase after BAC for all bromide/ iodide feed concentrations. This is probably due to the saturation of the BAC filters that caused a release of previously absorbed CHCl<sub>3</sub> to leach back out from the filters.
- No/very low detection of iodinated THMs were detected after ozonation. From a kinetic point of view, iodide (I) is expected to be oxidised rapidly to hypoiodous acid (HOI) and then further oxidised to iodate (IO<sub>3</sub><sup>-</sup>) very quickly with ozonation (less than milliseconds). This is why IO<sub>3</sub><sup>-</sup> was the major iodine compound detected in all samples after ozonation.
- Even though the DOC concentration of the Plant feed is high (approximately 8 mgC.L<sup>-1</sup>) the formation of bromate (BrO<sub>3</sub><sup>-</sup>) after ozonation is high. The oxidation of HOI to IO<sub>3</sub><sup>-</sup> is fast and in contrast to Γ, the formation of hypobromous acid (HOBr)
from oxidation of bromide (Br<sup>-</sup>) is fast but the oxidation of HOBr to  $BrO_3^-$  is relatively slow which leads to a competition between NOM and ozone for reaction with HOBr. Therefore, for high DOC concentration a high formation of AOBr (from the reaction of HOBr with NOM) is expected. Furthermore, one can expect that ozone will be rapidly consumed by the DOC, resulting in lower bromate formation. This shows that the NOM in the plant feed was poorly reactive.

- SUVA<sub>254</sub> of the Plant feed (2.5 L.mg<sup>-1</sup>.m<sup>-1</sup>) showed that the NOM in the Plant Feed was not very aromatic, confirming that it was poorly reactive. Therefore, low concentrations of DBPs are expected. This is why not much of the THMs and HAAs, including bromoform, were formed.
- There was a decrease in DOC concentrations after both ozonation and BAC, as the mineralisation/removal of DOC to a certain extent is expected for these two treatment processes.
- The increase in DOC concentration in RO Feed samples was the result of recycling of the RO Concentrate back to make up part of the RO feed.
- UV<sub>254</sub> decreased after ozonation resulting in lower values of SUVA<sub>254</sub>, which indicated the effective removal of highly reactive aromatic compounds (UV absorbing compounds) by ozone.
- All parameters analysed were detected at approximately twice the concentration in the RO Concentrate than in the RO Feed for all three Br/l feed concentrations; from this, the conversion through the RO process was estimated to be about 50% i.e. 100% feed sample is converted to 50% product water.
- In general, there was a decreasing trend for specific AOXs due to the stripping of volatile halogenated organic compounds except for the high bromide dosing samples. High bromide concentrations resulted in higher formation of HOBr that led to higher AOBr formation from the reaction of HOBr with NOM.

## 6. References

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