Australian Water Recycling
Centre of Excellence

Demonstration of robust water recycling:
Feedwater Report

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

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Demonstration of robust water recycling: Feedwater report

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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.

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Disclaimer

Executive Summary

The effluent quality from Self's Point Wastewater Treatment Plant (SPWWTP), which is the feed to the Davis Advanced Water Treatment Plant (DAWTP), was intensively sampled over a two week period. The water quality was measured for a range of parameters and compared against the Australian Drinking Water Guidelines (ADWG) for identification of which parameters needed on-going monitoring through the DAWTP, and to identify if large variations in feedwater quality were likely to make operation of the DAWTP difficult.

Generally only small variations in water quality parameters were observed over the 2 week period, with consistent patterns and values displayed. High true colour values of approximately 100 HU were observed, suggesting ozone consumption will be high. TOC values were generally between 8-10 mg/L, while TN values of up to 6 mg/L were detected. The make up of the organic matter appeared to vary diurnally from patterns in absorbance values. The absorbance values suggest that protein concentration was higher in the evenings and early morning.

It is recommended that:

- Metals only be monitored in the AWTP Self's Point feedwater and product water on a monthly basis because all values were less than the ADWG limits, apart from lead which was below the ADWG 96.3% of the time with only minor exceedances.
- UV absorbance be removed from the monitoring list, as these values are not used for critical control points or for identifying barrier performance.
- Assessment of Br and I disinfection by-products be undertaken.
- Further consideration of micro-contaminant removals achieved at Self's Point and how they may translate to Davis Station be given during the HACCP process.

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Objective

The feed water (the effluent before disinfection from Self's Point Wastewater treatment) to the Davis Advanced Treatment Plant (DAWTP) was sampled every one hour on weekdays and every three hours on weekends, for two weeks (18/8/14 to the 1/9/14). The intensive sampling was to characterise the feed water quality variation with time and to establish a baseline for plant control and monitoring. Furthermore, it was also used to identify if some contaminants could be removed from on-going monitoring given their low concentrations in the feed compared to the Australian Drinking Water Guideline (ADWG) limits.

As the plant is to operate at Davis Station on MBR effluent, the quality of the feedwater at Self's Point may alter the operation and performance of the DAWTP. Therefore, consideration of how the feedwater at Self's Point may be expected to differ from the performance of the DAWTP at Davis Station when fed MBR effluent was also undertaken.

Method

Samples were collected from the secondary effluent channel at Self's Point Wastewater Treatment Plant (SPWWTP) prior to UV disinfection and chlorine addition. Samples were collected both manually and with an automatic sampler. Samples collected during the day on week days (from approximately 8 AM to 3 PM) were collected manually, whilst samples taken overnight (from approximately 4 PM until 7 AM) and on week-ends were collected with an automatic sampler (Isco 3700). The automatic sampler used a peristaltic pump to collect 500 mL samples at one hour intervals, which were kept at ambient temperature until being processed the following morning. At the time of the sampling campaign, average overnight temperatures in Hobart were in the range of 5 – 10 °C, ensuring samples were well preserved. Over the week-end samples were taken every 3 hours and collected on Monday morning.

On site sample testing included measurement of pH, conductivity, true colour, bromine concentration and turbidity. From each hourly sample, 2 x 100 mL subsamples were taken (1 x glass amber and 1 x HDPE bottle) and sent to Victoria University for the analyses outlined in Table 1. Couriered samples were packed with ice packs to keep samples cool during transit, and upon receipt were stored in a fridge (4˚C) until tested.

Phosphorus and alkalinity were not part of the intensive feedwater sampling program because of the additional time required to undertake these measurements, and because neither have ADWG concentration limits. However, both can effect treatment plant performance, particularly with regard to fouling of the reverse osmosis membrane. Data was obtained for feedwater concentrations during the demonstration trials and this data is included in this report. Phosphorus was measured by ICP at Victoria University and alkalinity was determined by TasWater's NATA accredited analytical laboratory at Self's Point. The reverse osmosis (RO) system in the Advanced Water Treatment Plant (AWTP) was expected to remove both phosphorus and alkalinity, with final alkalinity in the product water being determined by efficiency of the calcite contactor.

The analytical techniques used for each water quality parameter are listed in Table 1. Difficulties with several of the tests arose during analysis, and the affected parameters are shown in red in Table 1. The issues and the responses taken to resolve them are outlined in Table 2.

Table 1: Water Quality analyses on DAWTP feedwater.

Parameter	Method to be Used	Location
Turbidity	Hand-held meter	On-site
Alkalinity	Titration	Self's Point laboratory (NATA accredited)
APHA Colour	Hach Method 8025 True colour – filtered samples	On-site/TasWater
Bromine	DPD Bromine – Hach Method 8016	On site – Samples cannot be preserved.
UV-254		Victoria University
UV-210		Victoria University
Total Organic Carbon	Combustion method – Method 5310 B from *Standard Methods*	Victoria University
Total Nitrogen	Digestion and oxidation with detection via chemiluminesce (Shimadzu TOC-TN instrument)	Victoria University
Ammonia	Salicylate Method – Hach Method 10031	Victoria University
Nitrate	Chromotopic acid - Hach Method 10020	Victoria University
Nitrite	Ferrous Sulphate – Hach Method 8153	Victoria University
Bromide	Ion Chromatography - Method 4110 from *Standard Methods*	Victoria University – Undertaken by Curtin University
Chloride		
Iodide		
Cyanide	Acid distillation followed by *Hach Method 8027*	Victoria University – no measurements made
Fluoride	Fluoride Ion Electrode - Method 4500-F^-C from *Standard Methods*	Victoria University
Aluminium	ICP – Method 3120A from *Standard Methods*	Victoria University (Arsenic, mercury and selenium measured by ICP-MS at the National Measurement Institute)
Antimony		
Arsenic		
Barium		
Beryllium		
Boron		
Cadmium		
Chromium		
Copper		
Iron		
Lead		
Manganese		
Mercury		
Molybdenum		
Nickel		
Phosphorus		
Selenium		
Silica		
Silver		
Sodium		
Tin		
Uranium		
Zinc		

Table 2: Water quality parameters for which the original sampling program was altered.

Parameter	Issue	Resolution
Bromine	Bromine was measured according to the set frequency initially, but the measurements were below the detection limit of the technique.	Hence, sampling was reduced to once per day.
Bromide, Chloride and Iodide	There was insufficient time available to project staff to perform these analyses, as a new method required development for bromide.	A small number of samples were sent to Curtin University's Water Quality Research Centre. These samples comprised 5 AWTP feedwater samples and 5 product water samples. Given the low amount of variation identified in the concentration of other contaminants more extensive sampling was considered not to be required. Results in Table 5.
Cyanide	Unable to perform the analysis with ion chromatography method.	No analyses have yet been performed.
Arsenic, mercury and selenium	The ICP-OES was not sensitive enough to detect the concentrations below the ADWG values, and all concentrations were below the limit of detection for the VU instrument.	Analyses were performed on the RO concentrate, as arsenic, mercury and selenium should have a high rejection by RO. Again the concentrations were below the limit of detection for the VU ICP. Samples were sent to the National Measurement Institute (NMI) for analysis by ICP-MS. These samples comprised 5 AWTP feedwater samples and 5 product water samples. Given the low amount of variation identified in the concentration of other contaminants more extensive sampling was considered not to be required. Results are given in Table 4.
Phosphorus and alkalinity	Insufficient time to determine the phosphorus and alkalinity during the feedwater trials. Phosphorus required different standards for the ICP to metals.	Measured in the feedwater during the demonstration trials.

Results

Bromine

Detected bromine in the feed (see Table 3) showed the same value as the distilled water (control) and product water of the plant. This indicates that the bromine is under the detection limit of the meter. There is no ADWG value for bromine. However, there is an advanced oxidation (Ozone Barrier), which can oxidise bromine into Bromate (0.02 mg/L ADWG value). Therefore, bromate still needs to be monitored in the product and ozonated water.

Table 3: Bromine concentrations in demonstration plant feedwater.

Sampling day	**Time**	**Bromine (mg/L)**
1	3:00:00 PM	0.04
1	2:00:00 PM	0.02
1	1:00:00 PM	0.03
2	9:00:00 AM	0.04
3	11:00:00 AM	0.02
3	9:00:00 AM	0.05
4	2:00:00 PM	0.02
4	10:00:00 AM	0.04
10	10:00:00 AM	0.03
11	1:00:00 PM	0.03
11	10:00:00 AM	0.03
12	11:00:00 AM	0.02

Total Nitrogen (TN)

TN in the feed water varied from 1 to 6 mg/L, as shown in Figure 1. The lowest TN concentration achieved on each day was from 9 am to 3 pm, and highest TN concentration was achieved between 9 pm to 3 am, with a peak about midnight.

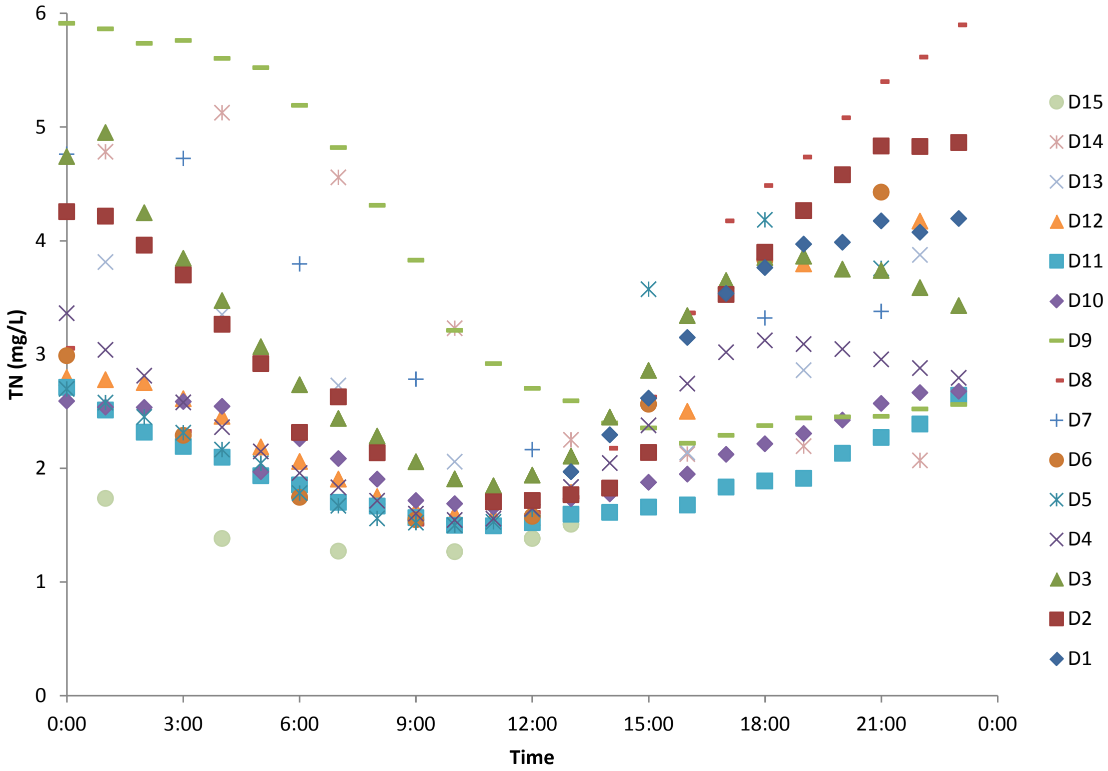

Figure 1: Diurnal variation of TN.

The Australia Drinking Water Guideline (ADWG) health values are 50 mg/L for Nitrate, 3 mg/L for Nitrite, and there are listed limits for ammonia. As specified by the ADWG, nitrite will be oxidised to nitrate rapidly, particularly across the first barrier of the DAWTP (ozonation). Therefore, based on the small likelihood of nitrite and a ratio of the ADWG/measured concentration (z) >5 for nitrate, both nitrite and nitrate were removed from the product wastewater monitoring.

Total Organic Carbon (TOC)

TOC in the feed water varied from 7.5 to 10 as shown in Figure 2. However, it did not show any specific relationship to time throughout the day. There is no specific ADWG value for TOC. However, TOC is an indicator for the ozone demand and performance of the BAC barrier so it remains a parameter for regular monitoring. It is also a surrogate indicator of the presence of trace organic chemicals of concern.

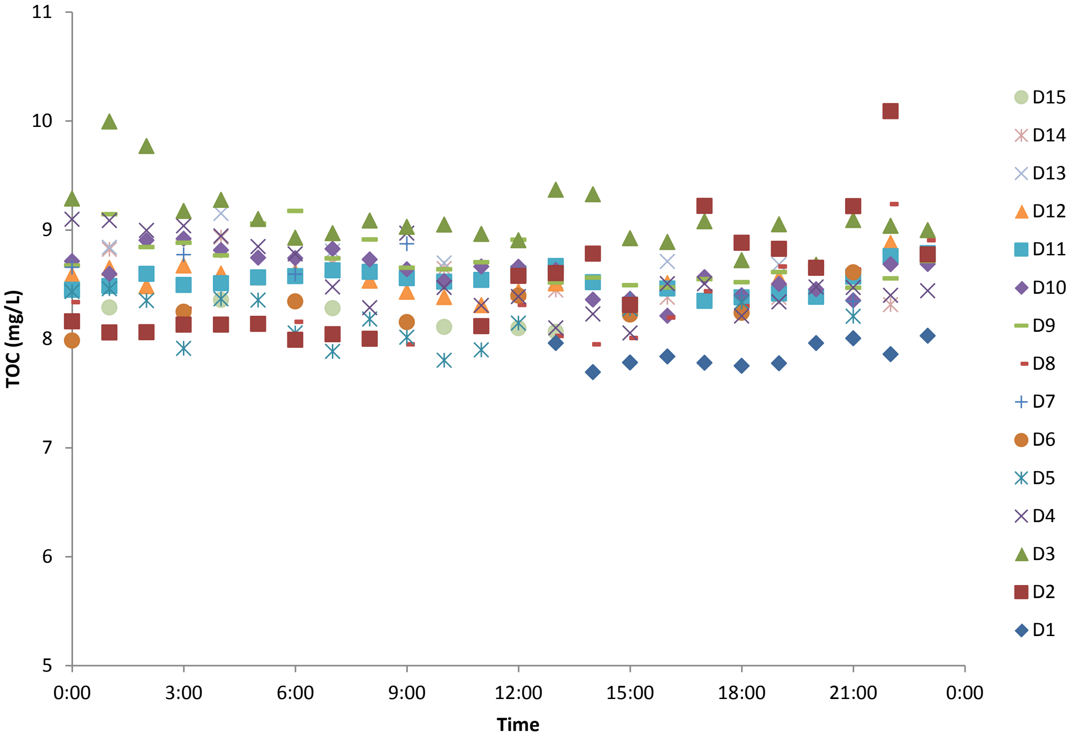

Figure 2: Diurnal variation of TOC.

Fluoride

Fluoride varied from 1.5 to 3.5 mg/L in the feed water and did not show any specific relationship to the time of day as shown in Figure 3. Since the ADWG value is 1.5 mg/L, and the feedwater fluoride ratio of the ADWG/measured concentration (z) <1, as such, the product water needs to be monitored.

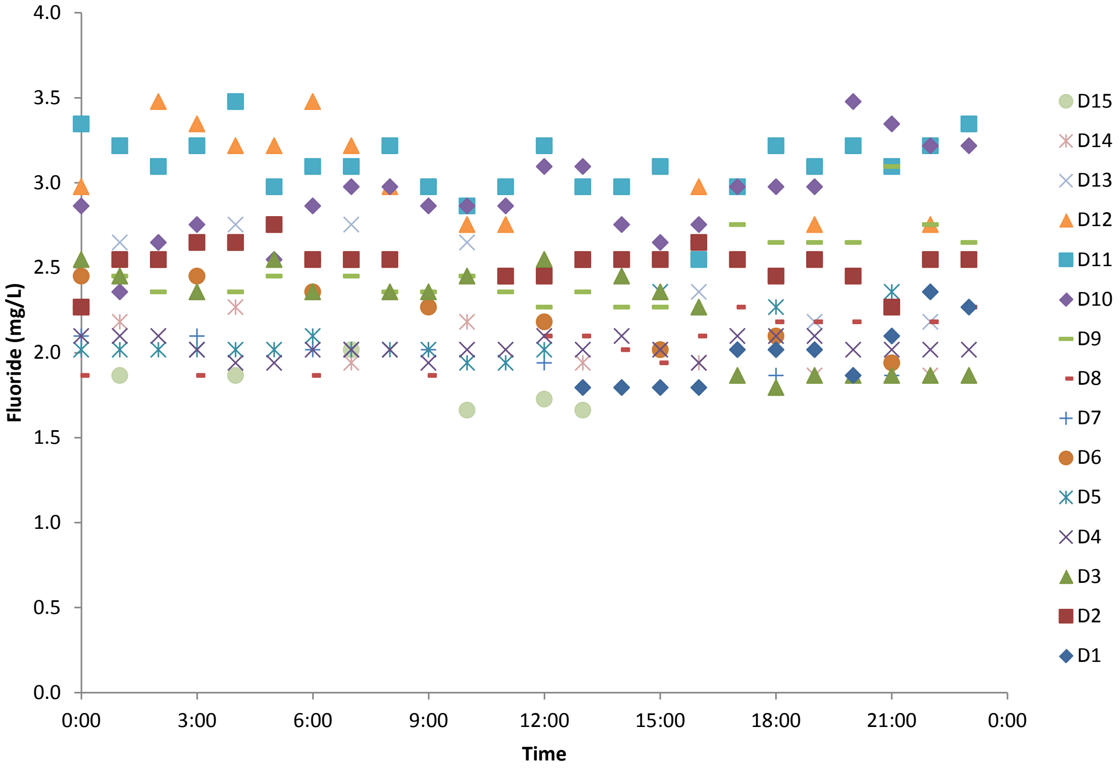

Figure 3: Fluoride variations throughout the day.

UV_{210} and UV_{254}

UV_{210} absorbance of the feed water is shown in Figure 4, and varied from 0.6 to 1.8. The lowest absorbance for each day was between 9 am to 3 pm, and highest absorbance achieved between 9 pm to 3 am at around mid-night. UV_{210} is sensitive to protein concentration, although it is also influenced by humic acids present in solution.

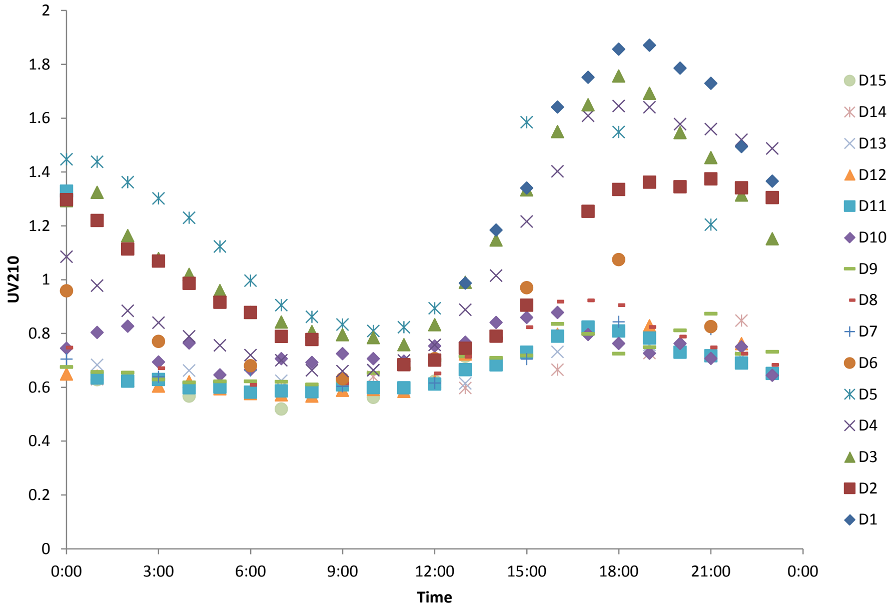

Figure 4: UV 210 absorbance variations with time.

UV_{254} absorbance varied from 0.19 to 0.25 and showed a similar trend to that of the UV_{210} absorbance, but the variation was of lower magnitude.

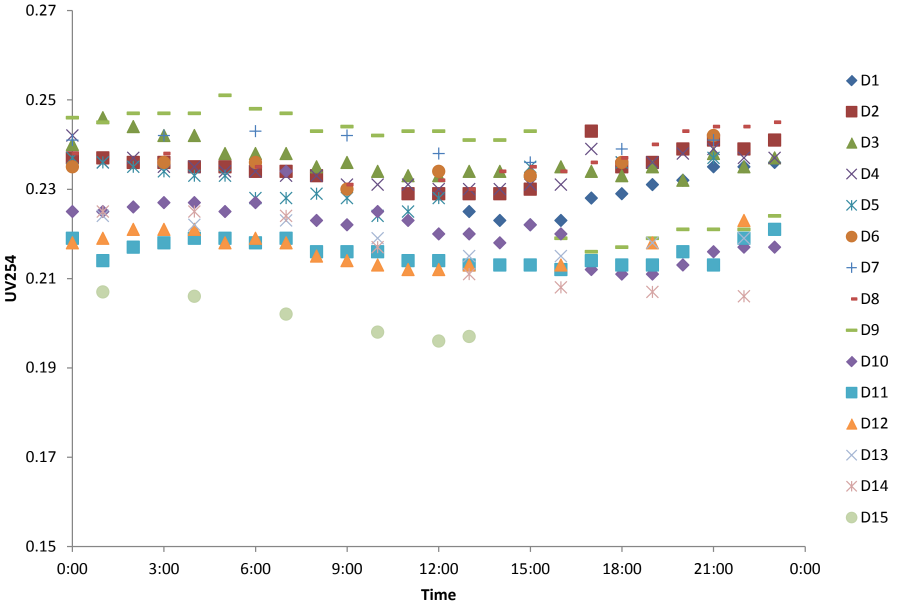

Figure 5: UV 254 absorbance varies with time.

There is no specific ADWG value for the UV absorbance, although they are indicators for organic compounds in the water. UV_{254} is more sensitive to humic acids and aromatic compounds than proteins, and is more sensitive to the detection of aromatic compounds than UV_{210}. UV_{210} is sensitive to protein concentrations, although it is also influenced by humic acids present in solution. These results suggest that the humic compounds are constant throughout the day, while protein concentrations may vary according to the patterns shown in Figure 4.

Colour

True colour of the feed water varied from 30 to 120 HU, and did not show a specific relationship with the time of day. Furthermore, most of data was distributed between 70 and 110 HU, as can be found in Figure 6.

There is no health related values for colour in ADWG, and the ozonation barrier can reduce the colour to below 15 HU, which is the Aesthetic Value in ADWG.

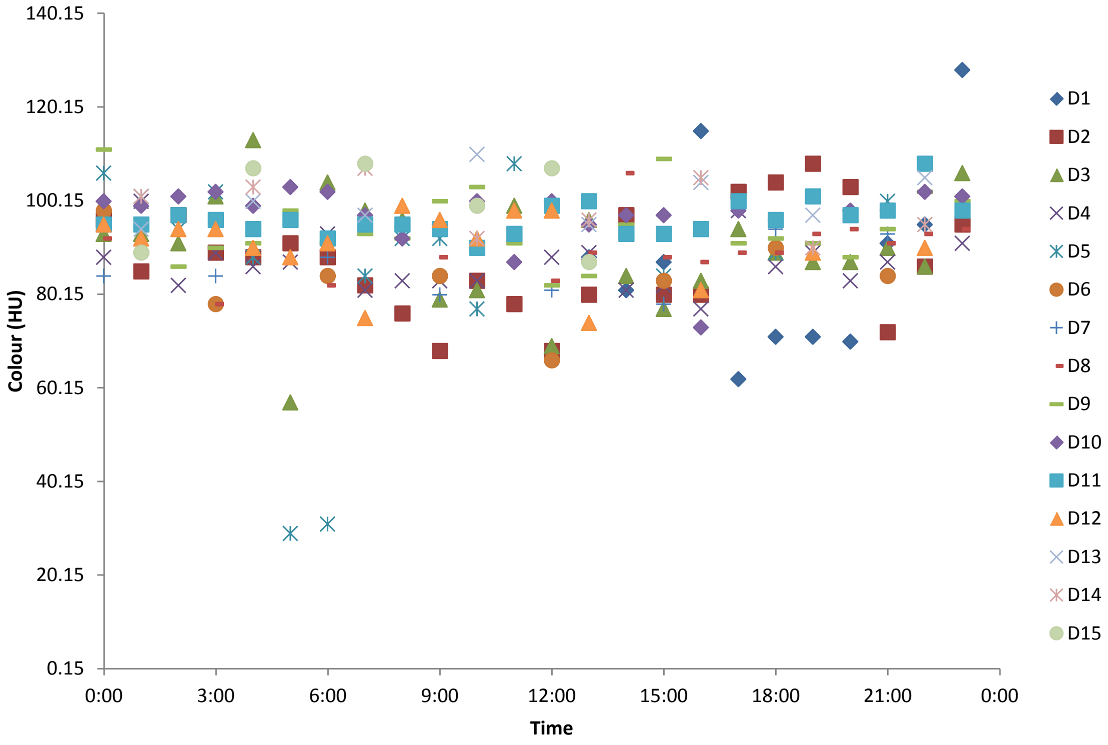

Figure 6: Colour variations with time.

Conductivity

Conductivity of the feed water varied from 530 to 620 µS/cm, and the highest values were achieved between 9:00 am to 3:00 pm as shown in Figure 7. There is only an aesthetic value of 600 mg/L TDS (about 1200 µS/cm) listed in the ADWG, and the variations in conductivity with time are minor for the performance of most operating units. However, conductivity is a critical control point for the RO system, so further monitoring should continue.

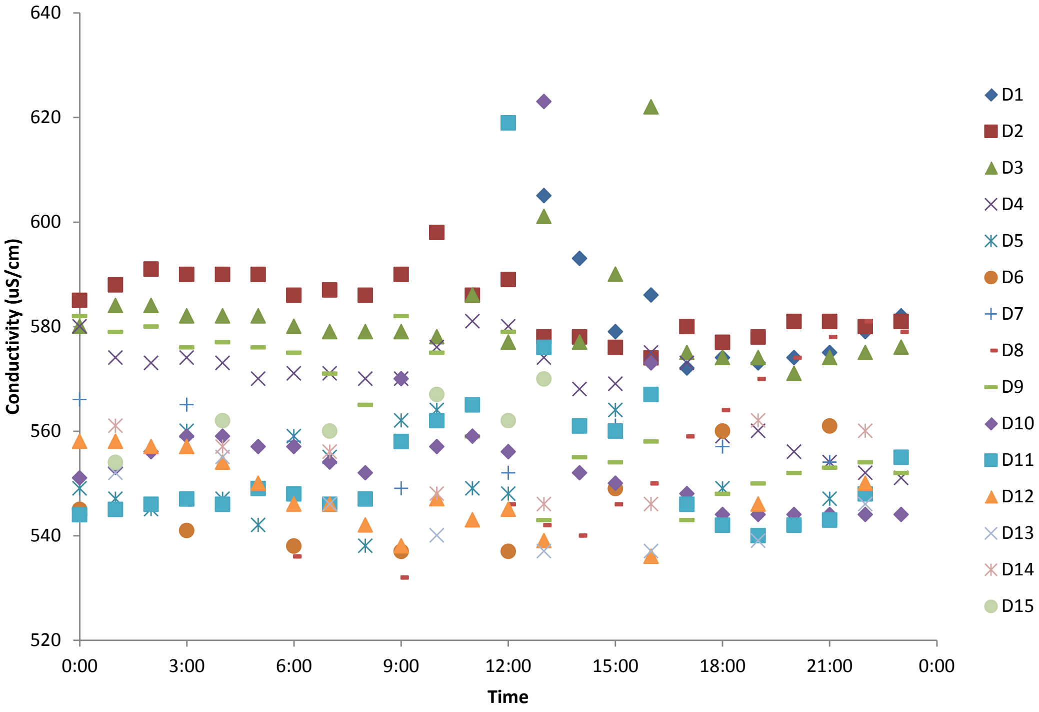

Figure 7: Conductivity variations with time.

Turbidity

The turbidity of the feed water varied from 0.5 to 7 NTU, as shown in Figure 8. The turbidity was lower during the day than during the night, which probably reflects the attenuation of the peak diurnal flowrates (reduced HRT) through SPWWTP. Furthermore, most of the data are distributed from 1 to 2.5 NTU. There is only an aesthetic value for turbidity in ADWG, but it is a critical control point for the microfiltration barrier and it may also affect the ozone process. Therefore, it should continue to be monitored.

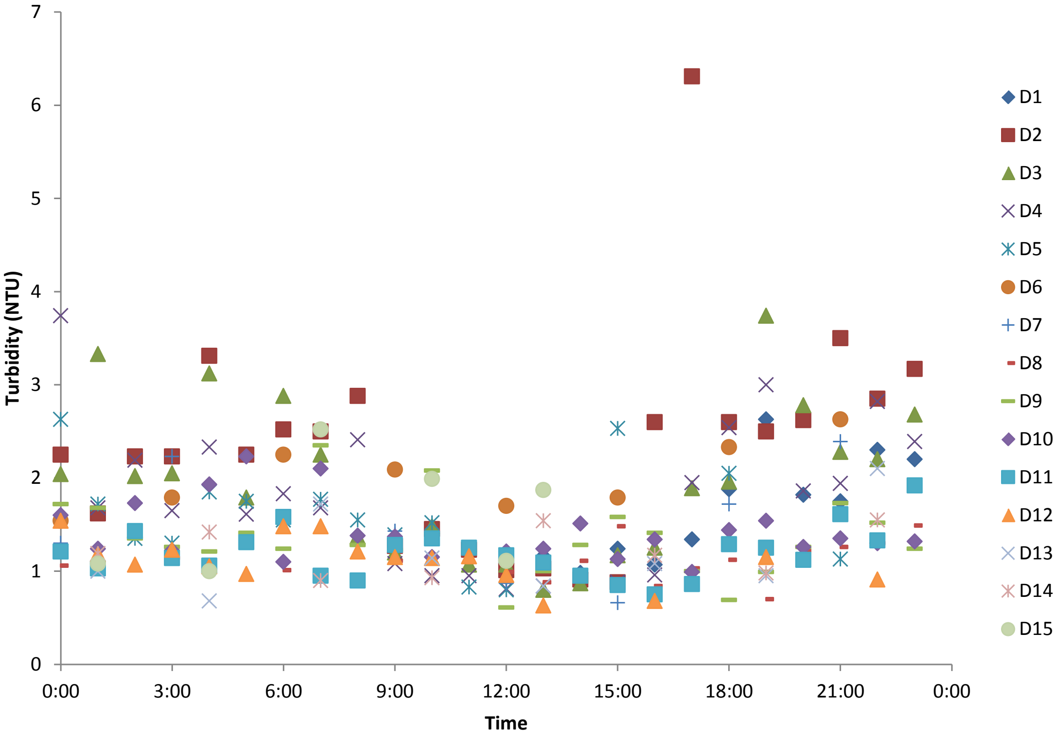

Figure 8: Turbidity variations with time.

pH

pH of the feed water varied from 6.4 to 7.5 as shown in Figure 9. On weekends, pH did not show a specific relationship with time. However, on weekdays, pH showed the lowest value from 9:00 am to 6:00 pm. The discontinuity in the pH trend at 9.00am coincides with the change in sampling from the auto-sampler to manual sampling. This discontinuity suggests that sampling with the auto-sampler may have led to increased pH values upon standing due to biological activity.

The AWDG only provides an aesthetic range of values of 6.5 - 8.5 for pH, but it is the critical control point for feedwater quality (an indication that the biological process is operating well) and for the calcite filter barrier, so it should continue to be monitored.

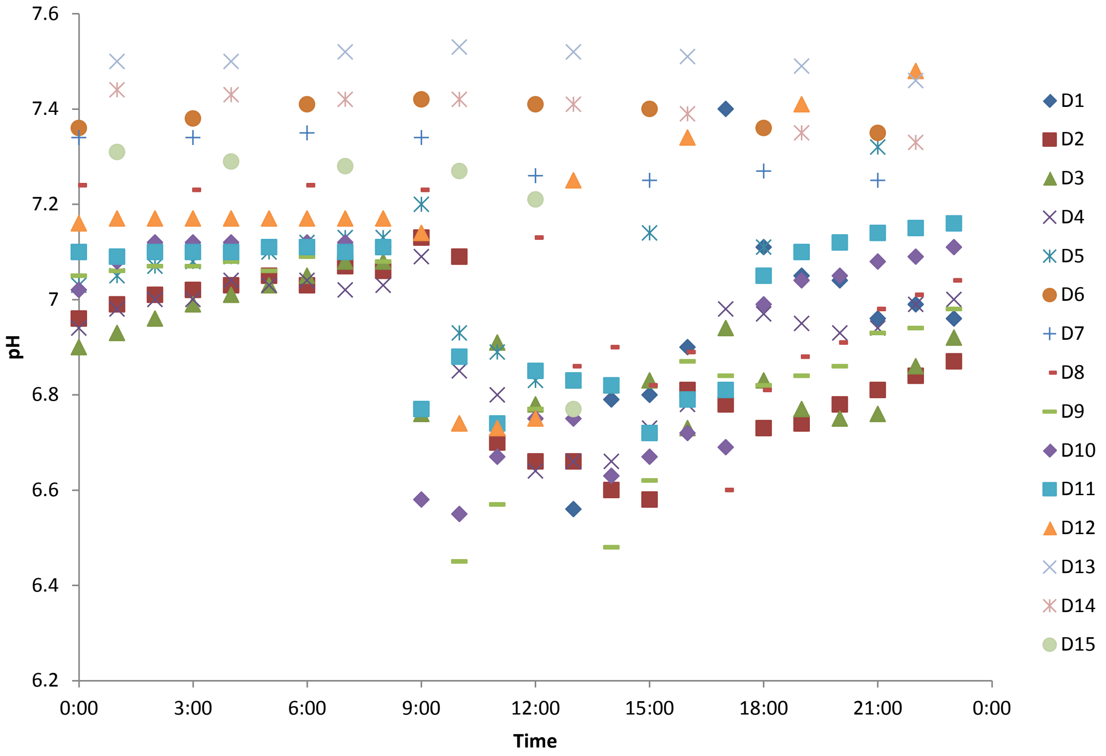

Figure 9: pH variations with time.

Others

The other chemical elements or components also measured, except phosphorus and alkalinity, are shown in Table 4. All measurable values met the ADWG values, except for lead (Pb). There were 9 samples of the more than 300 samples that were greater than the 0.01 mg/L ADWG limit. Additionally, there were three elements, As, Hg and Se, which could not be confirmed to be below the ADWG by ICP-OES. Monthly checking of metals in the product water and feed water is recommended to confirm the RO rejection of different elements.

Table 4: Comparison of the ADWG values with measured values in the feed water.

	ADWG required value (mg/l)	Measured value in feed water (mg/L)	Z (ADWG conc / measured conc)
Al	0.1	Under detection limit	>10
Ammonia	0.5	0.3	>1
Antimony	0.003	Under detection limit	>1
Arsenic	0.01	Not measurable by ICP-OES	
Barium	2	<0.014	>10
Beryllium	0.006	<0.0028	>2
Boron	4	<0.084	>4
Cadmium	0.002	Under detection limit	>1
Chromium	0.05	<0.01	>5
Copper	2	<0.021	>10
Iron	0.3	<0.14	>2
Lead	0.01	9/242 samples with detectable value >0.01 maximum 0.056	<1 (for only 3.7% of time)
Manganese	0.1	<0.042	>2
Mercury	0.001	Not measurable by ICP-OES	
Nickel	0.02	Under detection limit	>1
Nitrite	3	<0.2 (based on TasWater Lab)	>10
Nitrate	50	total N <6 mg/L	>8
Selenium	0.01	Not measurable by ICP-OES	
Silica	80	About 4.5 mg/L	>10
Silver	0.1	Under detection limit	>1
Zinc	3	<0.12	>10

ICP-MS results for mercury, selenium and arsenic are shown in Table 5. The samples were taken following ozonation and ceramic MF in the DAWTP, as well as from the DAWTP product water. All samples were below both the ADWG values and the detection limit.

Table 5: ICP-MS results for Hg, Se and As.

Sample Description	Sampling Date	Mercury (mg/L)	Selenium (mg/L)	Arsenic (mg/L)
Post Ozonation and MF	29/10/2014	<0.001	<0.001	<0.001
Post Ozonation and MF	05/11/2014	<0.001	<0.001	<0.001
Post Ozonation and MF	12/11/2014	<0.001	<0.001	<0.001
Post Ozonation and MF	19/11/2014	<0.001	<0.001	<0.001
Post Ozonation and MF	26/11/2014	<0.001	<0.001	<0.001
Product Water	29/10/2014	<0.001	<0.001	<0.001
Product Water	05/11/2014	<0.001	<0.001	<0.001
Product Water	12/11/2014	<0.001	<0.001	<0.001
Product Water	19/11/2014	<0.001	<0.001	<0.001
Product Water	26/11/2014	<0.001	<0.001	<0.001

Anion concentrations were measured by Curtin University using ion chromatography, and the results are shown in Table 6. They indicate low chloride concentrations, bromide concentrations that may lead to issues with bromate formation and iodide that was detectable on occasions. Further analysis of bromide and its oxidised products, as well as iodide and its oxidised products is warranted during operation of the DAWTP at Self's Point, as iodide and bromide entering the wastewater at Davis Station is considered possible. \

Table 6: Anion concentrations.

Feedwater Sample	Cl- (±0.1) (mg/L)	Br- (±7) (□g/L)	I-(±2) (□g/L)
D1S7	69.2	185	<5
D4S18	66.6	170	6
D8S12	64.2	168	<5
D12S00	62.8	162	8
D14S01	56.8	179	7

Phosphorus and alkalinity concentrations in the feedwater from September 2014 to May 2015 are shown in Figures 10 and 11. The average feedwater phosphorus concentration was 0.98 mg/L with a standard deviation of 0.68 mg/L, and the average feedwater alkalinity concentration was 150 mg/L $CaCO_3$ with a standard deviation of 15 mg/L $CaCO_3$. Neither phosphorus nor alkalinity have concentration limits defined by the ADWG, but were measured as part of the routine feedwater characterisation during the demonstration trials as they can affect treatment processes within the AWTP. The variations in these parameters during the trials period was small and should not have led to any plant upsets because of spikes in the feedwater.

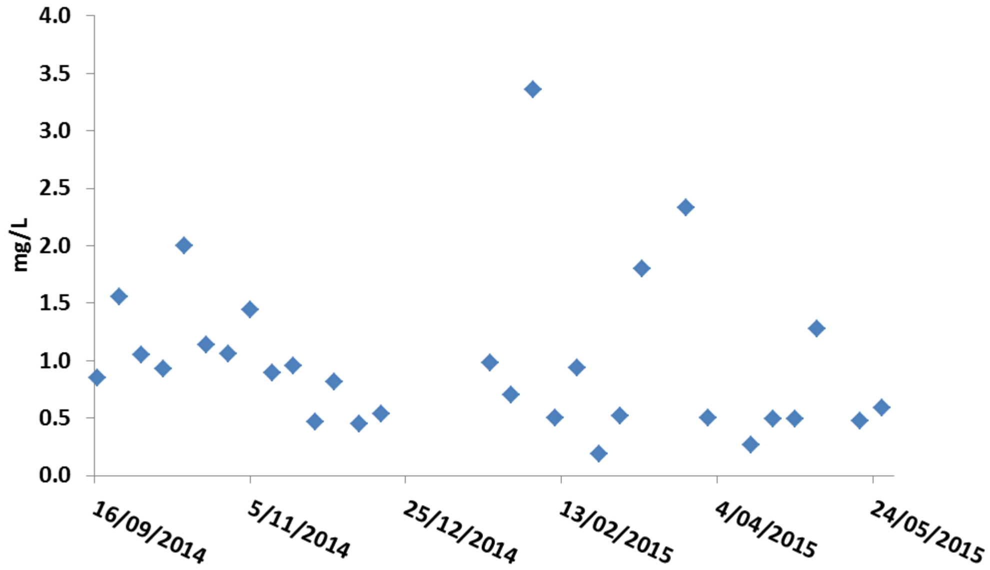

Figure 10: Feed water phosphorus concentrations during the demonstration trials.

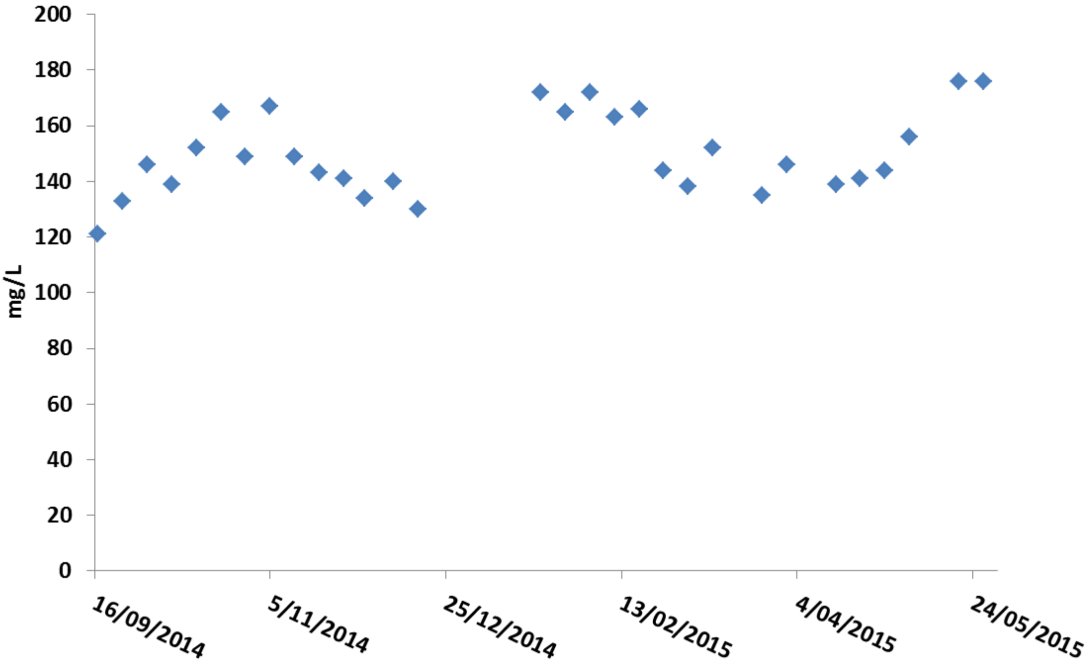

Figure 11: Feedwater alkalinity as measured over the trials period.

Comparison with MBR and Davis Wastewater

Water quality data for Davis Station's MBR is not available, as the MBR is yet to be commissioned. However, water quality from MBRs is expected to be significantly lower in turbidity (<0.2 NTU) and also TOC due to removal of flocs that may be carried over and also rejection of high molecular weight biopolymers. The preferential removal of the biopolymers via the MBR will both reduce the amount of organic material and alter the organic composition of effluent at Davis Station compared those at Self's Point. Given that ozone-BAC is known to be an efficient process for micro-contaminant removal, and that the kinetics of organics break down will alter with a change in composition and concentration of organic material, the extent of micro-contaminant removal may vary between Self's Point and Davis Station. Therefore, further consideration should be given to the removal of micro-contaminants at Self's Point and how these may be translated to performance at Davis Station.

The higher turbidity and TOC concentrations anticipated at Self's Point will provide a greater challenge for pathogen inactivation at Self's Point than at Davis Station, so inactivation performance at Self's Point is expected to be conservative with regard to pathogens.

Table 7 shows the raw wastewater concentrations of various elements in the Davis Station wastewater. Arsenic, barium, chromium, fluoride and silica are all below the Australian Drinking Water Guideline (ADWG) values before MBR treatment. For several elements, there were no wastewater concentrations available (antimony, beryllium, boron, mercury, and silver), while several other elements had concentrations above or occasionally above the ADWG values (aluminium, cadmium, iron, lead, manganese, nickel and selenium). These concentrations will be reduced once the wastewater is treated biologically through the MBR, and the reverse osmosis process will reject the metal ions.

However, higher concentrations of some of these elements may change the operation and performance of the DAWTP. Specifically, higher concentrations of manganese and iron may lead to manganese and iron oxidising bacteria in the BAC. The presence of higher concentrations of iron and aluminium may also serve as catalysts during ozone oxidation.

In terms of pathogen inactivation, these variations in water quality will have little impact. However, they may have some impact on micro-contaminant reductions via changes to the bacterial population in the BAC and oxidation pathways during ozonation.

Table 7: Raw wastewater contaminant concentrations at Davis Station.

Element	Davis Station* (mg/L)	ADWG required value (mg/l)	Less than ADWG
Aluminium	0.2-5.7	0.1	X
Antimony		0.003	-
Arsenic	<0.01	0.01	
Barium	0.02-0.44	2	
Beryllium		0.006	-
Boron		4	-
Bromide	<1	none	
Cadmium	<0.009	0.002	?
Chromium	0.003-0.155	0.05	-
Copper	0.1-3.3	2	-
Fluoride	<0.5	1.5	
Iron	0.5-12.1	0.3	X
Lead	0.012--0.14	0.01	X
Manganese	0.04-0.79	0.1	X
Mercury		0.001	
Nickel	0.01-0.11	0.02	X
Selenium	<0.015	0.01	?
Silica	3-10	80	
Silver		0.1	-
Zinc	0.25-5.45	3	?

*Data from a water quality report on wastewater, conducted on the 14/5/13

Recommendations

The variations in water quality parameters were quite small over the 2 week period, with consistent patterns and values displayed. The colour is quite high being about 100 HU. TOC was of reasonable value (8-10 mg/L) as was TN (up to 6 mg/L). The absorbance values suggested that the make-up of the organic matter varied with a diurnal pattern, and the protein concentration was higher in the evenings and early morning.

Grab samples for lead were occasionally above the ADWG (3.7%) but were predominantly below the detection limit (96.3%). Therefore, based on the characterisation of the feedwater quality, it is recommended that:

- Metals only be monitored in the feedwater and product water on a monthly basis, as these values were all below the ADWG, apart from lead, which was below the ADWG values for 96.3% of the time with only minor exceedances.
- UV absorbance be removed from the monitoring list, since those characteristics are neither critical control points nor the parameters providing direct reference of the barriers' performance.
- Analysis for Br and I disinfection by-products be undertaken.
- Further consideration of micro-contaminant removals achieved at Self's Point and how they may translate to Davis Station be given during the HACCP process.