

Mitigation of Fouling of Western Treatment Plant Desalination Membranes

Final Evaluation Report

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With the support of:
the Smart Water Fund

Name:	RMIT University
Project Description:	Mitigation of Fouling of Western Treatment Plant Desalination Membranes
Date of Report:	October 2008

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Executive Summary

Western Treatment Plant (WTP) treats approximately 52% of Melbourne's sewage, a total of approximately 485 million litres/day using a sequential activated sludge-lagoon (AS-lagoon) process. WTP employs two AS-lagoon systems (25W and 55E) from which the treated water is transferred to the head of the road storage pond (HORS) where it is disinfected prior to use as recycled water. The HORS can be supplied with treated water from either 25W, 55E, or a mixture of water from both systems. Melbourne Water currently supplies recycled water from WTP for various on-site and off-site uses and is working towards future schemes to meet the State Government's target of 20% water recycling by 2010. The salt level ($1,800 \mu\text{S cm}^{-1}$) is a limiting factor to the long term sustainable use of the recycled water and requires ongoing management; the State Government has committed to reducing this salt level by 40%. Trials have demonstrated that microfiltration (MF) or ultrafiltration (UF) can be used to pre-treat the effluent from the WTP prior to salt reduction via reverse osmosis (RO), however, it was observed that membrane fouling was a potential problem. The aim of this project is to develop an effective and practical strategy to overcome the MF and UF fouling problem which will support the future design and operation of a membrane salt reduction plant (MSRP) at WTP with high water recovery. The first step in achieving this aim is to characterise the membrane fouling potential of the treated water from the WTP.

The MF and UF membrane fouling potential of the treated water from the AS-lagoon system at WTP was monitored over a 2-year period and related to the water quality characteristics. As the major foulants of MF and UF membranes are organic compounds, in this case effluent organic matter (EfOM) in the treated water, this material was characterised in order to obtain an insight into the fouling mechanism of HORS water and hence to develop strategies for fouling control. A range of pre-treatments was investigated as a means of mitigating the membrane fouling. The major findings are summarised below.

- Clarifier effluent is not a suitable source as feed for the MSRP process due to its high fouling characteristics.
- MF and UF filterability of HORS samples varied over the collection period of October 06- September 08. In the warmer months, when algal blooms were most prevalent, the MF and UF filterability were low as turbidity, DOC, TDS and TSS were elevated. The sample collected on 19 March 07 during an algal bloom had significantly low MF and UF filterability, this markedly affected the average filterability of HORS over the sampling period.
- The MF and UF filterability of the treated water from 25W was higher than that from the 55E system. As HORS was supplied by a mixture of water from both systems for much of the sampling period, the MF and UF filterability was: $25W > \text{HORS} > 55E$.
- The relationships between the MF and UF filterability of HORS samples in terms of specific permeate volume at $40 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (V_M for MF and V_U for UF) and its turbidity (T), TSS (S), total algal count (A), DOC (O), TDS (D) and conductivity (C) using chemometrics were:

$$V_M = 1391 - 58.8 T - 57 O - 5.3 S$$

$$V_U = 1328 - 75.1 O - 18.6 T - 13.8 S$$

It was possible to predict the MF and UF filterability from these equations with 85% accuracy when all data were taken into account. Variation in the organic components such as humic-like materials and SMP content of the treated streams from 25W and 55E would explain the lower accuracy of prediction of the MF and UF filterability of the HORS stream.

- In terms of recommending a membrane process prior to RO, MF would be better than UF with regard to permeate flux, but, DOC removal by MF was significantly lower than that by UF. Thus UF leads to lower DOC levels in the permeate and so to reduced amounts of organic material potentially available to foul the subsequent RO membrane, either directly, or indirectly via biofouling through serving as a microbial growth substrate.

- The organic components of the 25W, 25E and thus of HORS streams were characterised and shown to vary with source and time.
- The major compounds detected in the fouling layers on both MF and UF membranes were proteins and polysaccharides. HPSEC analysis indicated that these are neutral, low UV-absorbing higher MW organic compounds.
- Extracellular organic matter (EOM) derived from an algal culture had a greater fouling effect than algal organic matter (AOM, which also contains intracellular organic matter) for MF, whereas their fouling propensity was similar for UF. This fouling was due largely to the hydrophilic fraction, although significant amounts of hydrophobic compounds were also removed. The hydrophilic fraction of AOM had a higher fouling propensity than that of EOM for MF, whereas the reverse held for UF. AOM led to greater irreversible fouling of both membrane types.
- Chemical coagulation treatment of HORS gave varying results for MF flux performance, depending on coagulant type and dosage. Alum performed better than ferric chloride for flux improvement at similar dosage (at same weight concentration or molar concentration of metal ion), and for both alum and ferric chloride increased coagulant dosage resulted in increased flux rate. The MF and UF performances of ACH and alum at the same dosage were similar. However, The use of aluminium chlorohydrate (ACH) is preferable to alum as ACH produces less sludge at equivalent dose, and leads to lower TDS increase in the treated water. Furthermore, the residual chloride ion is less problematic than sulfate in RO as the latter can lead to scale formation.
- Pre-treatment of the HORS water with a strong anionic exchange resin (10 mL L⁻¹) led to removal of up to 55% of DOC and good colour reduction, but did not improve the flux rate or reduce irreversible membrane fouling for either MF or UF. Indeed, there was increased irreversible fouling of the MF and UF membranes which would potentially lead to the need for more frequent chemical cleaning, and hence increased downtime and shortened membrane life. The low molecular weight and the negatively charged organic fractions removed by the resin did not greatly contribute to membrane fouling.
- Subsequent RO treatment of HORS after alum or ACH treatment prior to UF removed all humic-like, fulvic-like materials and SMPs but allowed passage of a small portion of the protein-like matter when HORS was treated with alum. For ACH-treated HORS, all protein-like matter was removed after RO. In general, the sequence of alum or ACH treatment and UF removes a significant proportion of the DOC from the HORS water and so reduces the potential for organic fouling in the subsequent RO step.

1. Background

Recycling wastewater is becoming imperative as demand on Melbourne's water resources due to population growth and drought is increasing. Western Treatment Plant (WTP) treats approximately 52% of Melbourne's sewage, a total of approximately 485 million litres/day, using a sequential activated sludge-lagoon (AS-lagoon) process. WTP employs two AS-lagoon systems (25W and 55E) in which sewage is treated by passing through anaerobic ponds and an activated sludge plant with anoxic and aeration zones where biodegradable matter is consumed by naturally-occurring bacteria. The biologically treated effluent then passes through a clarifier and a chain of lagoons before it is transferred to the head of the road storage pond (HORS) where it is disinfected prior to use as recycled water. The HORS can be supplied with treated water from either 25W, 55E, or a mixture of water from both systems, depending on water quality conditions of turbidity, ammonia concentration and the presence of algal blooms. The recycled water is currently used for various on-site and off-site purposes, however, due to catchment issues such as industrial waste input and saline aquifer infiltration, its salt content limits its long term sustainable use for some applications, such as agriculture, without additional management practices. Previous pilot-scale salt reduction trials at WTP, which utilised microfiltration (MF) or ultrafiltration (UF) as a pretreatment prior to reverse osmosis (RO), demonstrated that the product water was suitable for various applications including agriculture and domestic use.

Since the effluent from WTP contains algae and algal products from the lagoon process, as well as some residual products from the AS process, the resultant membrane fouling may be more problematic and differ from that arising from separate AS and lagoon processes. Membrane fouling leads to a decline in membrane permeability and thus reduces throughput and water recovery. Therefore, the nature and mechanisms of membrane fouling require investigation, and a strategy to mitigate fouling needs to be developed so that maximum water recovery can be achieved. As the microbial and algal populations tend to change with season, the effect of this change on the process also needs to be taken into account. The aim of this project was to develop an effective and practical strategy to reduce and optimise the management of MF and UF membrane fouling which will support the future design and operation of a membrane salt reduction plant (MSRP) at WTP.

Consequently, the membrane fouling potential of the treated water from the AS-lagoon system at WTP needed to be investigated. The designated feed for MSRP was water collected from HORS which holds recycled water from the AS-lagoon systems after its journey via an open channel and piped system of about 6 km length. The HORS water was considered an unusual feed for a membrane process as it had undergone several stages of biological treatment: anaerobic, activated sludge and lagoon processes. Furthermore, the lagoons are subject to periodic algal blooms and the seasonal influence of these on the membrane filterability was unknown. Therefore, the trends for a range of water characteristics for HORS water over an extended period needed to be established and their influence on its MF and UF filterability determined.

The major foulants of MF and UF membranes are organic compounds. The dissolved organic matter found in the effluent from wastewater treatment plants is commonly known as effluent organic matter (EfOM). EfOM comprises a wide range of heterogeneous compounds which can be classified as:

- refractory natural organic matter derived from drinking water
- synthetic organic compounds produced during domestic use and disinfection byproducts generated during water and wastewater treatment, and
- soluble microbial products derived from the biological wastewater treatment processes.

Characterisation of the EfOM was needed to obtain an insight into the fouling mechanism of HORS water and hence to develop strategies for fouling control. The engineering trial used preliminary screening for removal of particulates followed by either MF and RO, or ferric chloride pre-treatment prior to UF and RO. The aim of this work was to increase the productivity of the low pressure membrane process, and thus of the MSRP, by mitigation of the organic fouling of the membranes.

A commonly used approach for mitigation of fouling is feed pretreatment to remove/modify the components with high fouling potential (Shon et al., 2006). Chemical coagulation is widely used as a simple and effective means

for the removal of particulates, colloids and high molecular weight (MW) organic materials from water and wastewater. However, there are some cases where this has had negative effects on membrane performance (Karimi et al., 1999; Shorney et al., 2001). Overall, the effect of coagulation on membrane fouling is determined by factors such as coagulant type and dosage, properties of feed water and membrane type (Shon et al., 2005; Howe et al., 2006). Anion exchange resin has been investigated as a means of improving membrane performance by removing a significant fraction of organic matter from drinking water sources (Morran et al., 2004; Son et al., 2005; Fabris et al., 2007). However, its application in wastewater treatment has not been widely investigated; only one application was found where anion exchange resin was used in wastewater treatment, and this related to a submerged membrane bioreactor system with synthetic wastewater (Zhang et al., 2006). Hence, various pre-treatment methods including pre-filtration, chemical coagulation and anion exchange resin for improving MF and UF performance in the treatment of AS-lagoon effluent were evaluated in this work.

2. Description of Project

The original objectives of this work were to undertake a laboratory-based study to

- Investigate the fouling characteristics of the HORS effluent over a year to determine seasonality of the phenomenon
- Correlate the characteristics of the effluent, foulant and membrane performance
- Determine the efficacy of conventional fouling mitigation procedures, possible testing of these on extant pilot rigs at the WTP research facility
- Based on these results, undertake preliminary development of a more effective process.

Early in the study we were requested to explore the feasibility of the use of the clarifier overflow as feed to the membrane pre-treatment process. Furthermore, it was shown that the properties of the treated water from 25W and 55E process trains were different and thus affected the MF and UF filterability of HORS. Consequently, the investigation was broadened to:

- Investigate the fouling characteristics of clarifier overflow
- Investigate the fouling characteristics of the 25W and 55W system effluents to determine seasonal trends
- Correlate the characteristics of the effluent, foulant and membrane performance for these feed streams.

3. Samples and Methods

Samples were collected by Ecowise Environmental (Victoria) Pty Ltd. The sampling points were the overflow streams from clarifier 4 in the 55E system (55EC4) and the final ponds for each of the 25W and 55E systems (25WP10 and 55EP10), and the head of road storage pond (HORS). On receipt they were prescreened: 500 μm prior to MF and 130 μm prior to UF. Water quality parameters routinely measured included turbidity, pH, conductivity, total dissolved solids (TDS), total suspended solids (TSS), dissolved organic carbon (DOC), conductivity, and total algal counts, as well as filterability through both MF and UF membranes.

Filterability was determined using a bench-scale dead-end stirred cell rig which was operated at a constant pressure regulated using nitrogen gas and a magnetic stirrer at 430 rpm. The permeate flux was determined using a top-loading electronic balance with data logging function connected to a computer. PVDF membrane discs with a nominal pore size of 0.22 μm were used for MF, and PES membrane discs with an average molecular weight cut-off (MWCO) of 100 kDa were used for UF. A comparison of the filterability of selected samples with an MF membrane of smaller pore size (0.1 μm) was also undertaken. Filterability was reported as the specific permeate volume obtained on reaching a nominated flux rate of either 40 or 55 $\text{L m}^{-2} \text{h}^{-1}$. See Milestone 3 Report which may be obtained from SWF for further details.

A pilot scale MF/UF rig which utilised hollow fibre membranes (PVDF, 0.22 μm for MF; PAN with MWCO of 80 kDa for UF) in cross flow mode was used for treatment of the sample prior to RO. Reverse osmosis was

conducted with a polyamide RO membrane used in cross flow mode at 12 bar (see Milestone 7 Report which may be obtained from SWF for further details).

The organic components of the feeds and permeates were characterised by the bulk parameters of dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UVA). More extensive characterisation of selected samples was undertaken via determination of the molecular weight distribution by high performance size exclusion chromatography (HPSEC), rapid fractionation using non-ionic macroporous resins, determination of major groups of organics with excitation-emission matrix (EEM) fluorescence spectroscopy, identification of organic functional groups of the fouling layer on the membrane surface using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and determination of the morphological characteristics of foulants by environmental scanning electron microscopy (ESEM). Details of these methods can be obtained from Milestone Reports 5, 6 and 7 which are available from the SWF. The inorganic content of selected samples was determined by Inductively Coupled Plasma Mass Spectrometry (ICPMS).

4. Key Activities Completed

- The filterability of clarified activated sludge effluent was investigated with a view to its possible use as feed to the MF/UF pre-treatment process.
- The MF and UF filterability, and thus indication of fouling propensity, of HORS samples was conducted over 2 years (October 06-September 08).
- The water quality characteristics of HORS, 25W and 55E were correlated with their filterability.
- The relationship between the water quality parameters of the HORS stream and its MF and UF filterability were modelled with a view to prediction of performance and thus implementation of process control.
- The organic components of the HORS, 25W and 55E streams were characterised and monitored over several months.
- A range of techniques (FTIR, EEMs, HPSEC) was used to determine the major organic fractions which foul the MF and UF membranes, and those which pass through these membranes and so are available for fouling the RO membrane.
- The following methods for MF/UF fouling mitigation were investigated:
 - Alum coagulation
 - Ferric chloride coagulation
 - Aluminium chlorohydrate (ACH) coagulation
 - Anionic exchange resin
- The organic fractions which were removed by the various fouling mitigation techniques were determined.
- The following complete process trains were conducted for selected samples, and the various streams within each process were characterised in terms of organic and inorganic content:
 - MF/RO
 - UF/RO
 - Alum/MF/RO
 - Alum/UF/RO
 - ACH/UF/RO

5. Results Achieved

As will become clear the water quality parameters of the 25W, 55E and thus HORS streams varied, and so the results for different samples also varied. Consequently, the results reported herein should be considered within that context.

5.1 Investigation of Clarifier Effluent as Potential Feed for MF/UF Treatment

Comparison of the fouling potential of water from the clarifier overflow from the activated sludge step (sample taken from clarifier 55EC4), the treated water from the 55E lagoon system and HORS water was undertaken. Typically the HORS samples led to the lowest rate of fouling for both MF and UF, 55E gave a marginally greater rate of fouling, and the clarifier samples had the highest fouling potential. This was attributed to the relative contents of the TSS and hydrophilic organic compounds. The 55EC4 samples had the highest TSS and hydrophilic compound contents, and although 55E had lower TSS and turbidity than HORS, it tended to have a higher proportion of hydrophilic organics which have a high propensity for membrane fouling. Consequently, the lagoon-treated effluent was found to be more suitable as a source for salt reduction than clarifier effluent. Further details may be obtained in Milestone 3 Report, available from the SWF.

5.2 MF and UF Filterability of HORS

The MF and UF filterability, and thus indication of propensity for fouling, of the HORS sample varied over the sampling period (Figure 1). (Data for October 06-September 08 for UF at 200 kPa and 55 L m⁻² h⁻¹ are available in Milestone 9 Report available from the SWF). There were few strong or consistent trends for water quality characteristics and MF or UF filterability with season.

There was a severe algal bloom in March 07, this led to major increase in DOC, turbidity and TSS levels, and a major decrease in MF and UF filterability. Although there was another notable bloom in January-February 08, there was less impact on the turbidity and TSS, and little on the DOC levels, and little effect on the MF and UF filterability of the HORS sample. Although there were minor peaks in total algal count they were variously weakly positively correlated with DOC, TSS and turbidity. The averages and variability for the various water quality parameters and MF and UF filterability appear in Table 1. The variability was 41% for MF and 35% for UF, indicating that UF was more consistent and thus likely to be more predictable.

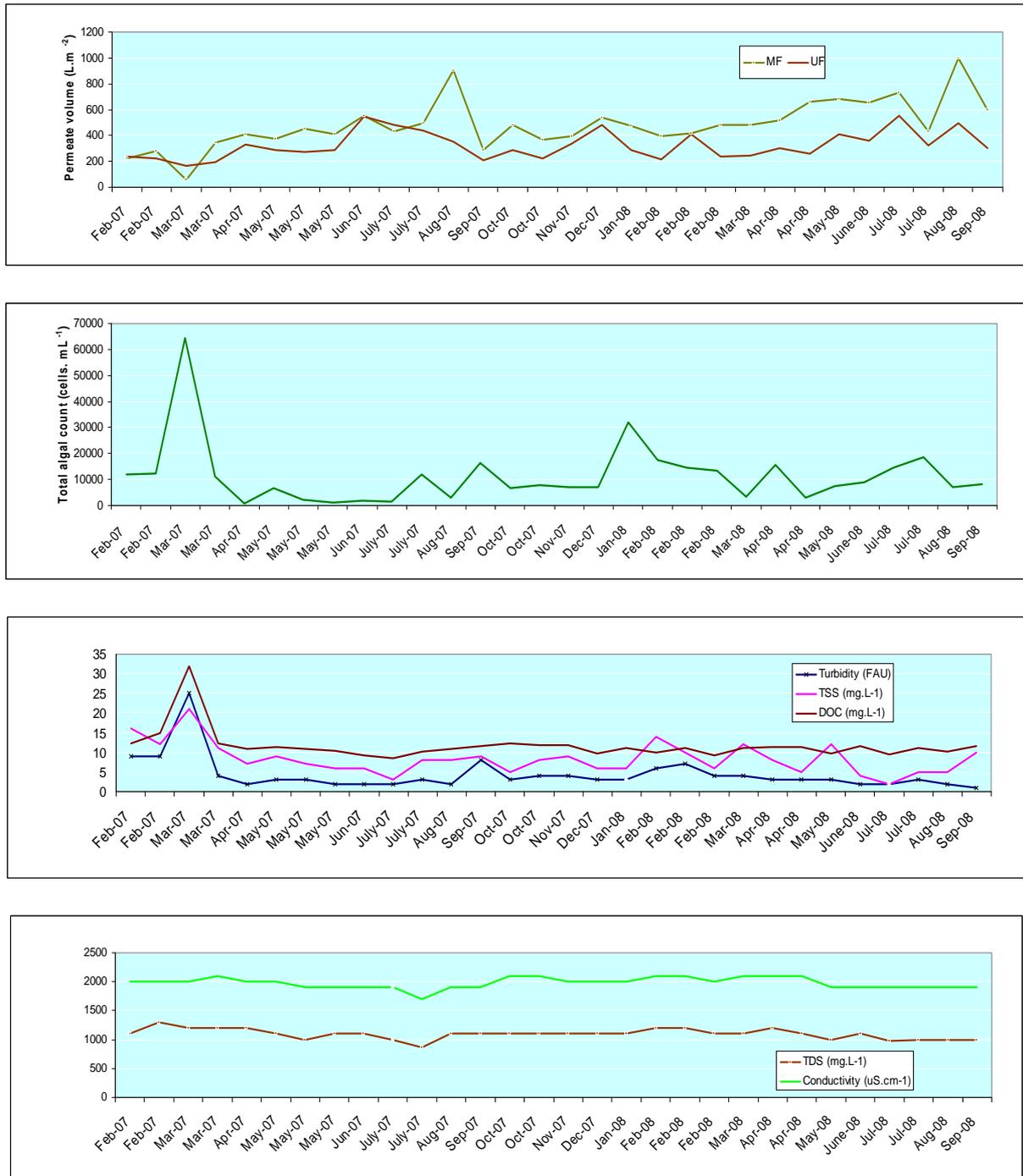


Figure 1. Variation of MF and UF filterability (measured as permeate volume at 40 L.m⁻².h⁻¹) and water quality parameters for HORS for February 07-September 08.

Table 1. Average values for water quality parameters, MF and UF filterability (measured at 40 Lm⁻²h⁻¹) for HORS for February 07-September 08. Second row gives values for which data for algal bloom in March 07 were excluded

Parameter (Average)	Average ± variation
Turbidity (FAU)	4.4 ± 4.7
Average excluding data for March 07	3.6 ± 2.2
TSS (mg.L ⁻¹)	8.4 ± 4.3
Average excluding data for March 07	7.9 ± 3.5
Total algal count (cells.mL ⁻¹)	11872 ± 12687
Average excluding data for March 07	9767 ± 6902
DOC (ppm)	11.8 ± 4.3
Average excluding data for March 07	11.0 ± 1.4
TDS (mg.L ⁻¹)	1091 ± 86
	1086 ± 85
Conductivity (µS.cm ⁻¹)	1992 ± 84
Average excluding data for March 07	1992± 86
MF filterability (Lm ⁻² at 40 L m ⁻² h ⁻¹)	491 ± 203
Average excluding data for March 07	508 ± 186
UF filterability (Lm ⁻² at 40 L m ⁻² h ⁻¹)	319 ± 112
Average excluding data for March 07	325 ± 109
MF filterability (Lm ⁻² at 40 L m ⁻² h ⁻¹)	491 ± 203
Ave excluding March 07 data	508 ± 186
UF filterability (Lm ⁻² at 40 L m ⁻² h ⁻¹)	319 ± 112
Ave excluding March 07 data	325 ± 109

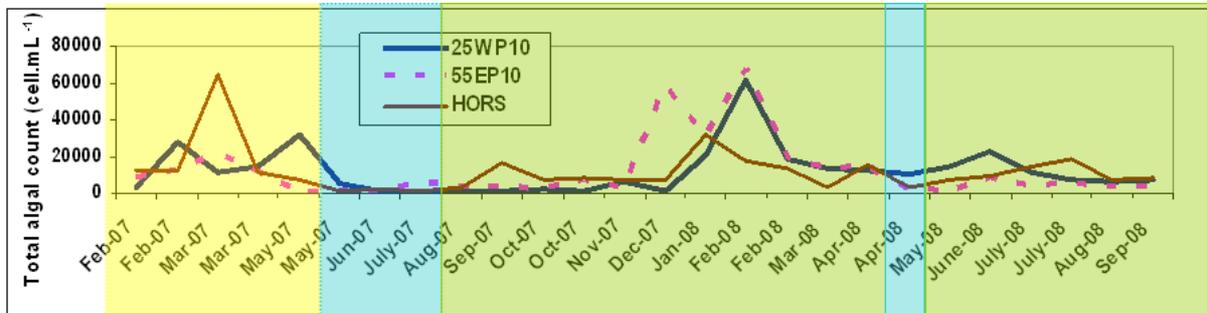
The following observations can be made:

- Algal blooms were most prevalent in the warmer months, ie., January-March
- Turbidity was reasonably consistent, but generally elevated with elevated algal count
- TSS levels seemed to be almost random, but were elevated with elevated algal counts
- DOC levels were fairly consistent, but markedly elevated during major algal bloom
- TDS tended to be elevated in warmer months
- There was elevated MF filterability in August 07 and 08.

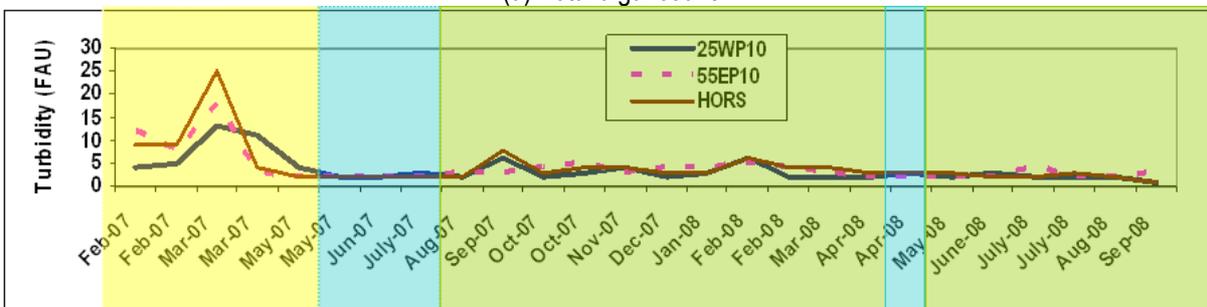
The elevated MF filterability of the August samples could not be explained in terms of the chosen water quality parameters. It may be due to the presence of supra-colloidal particles in these samples (Ricker and Hunter, 1971). These particles are colloids with particle size of 1-100 µm such as protozoa, algae, organic debris, cell fragments, and biomass/microbial aggregates produced during biological treatment and which are not removed from the treated water in the final clarifier.

5.3 Relationship of MF and UF Filterability of HORS, 25E and 55E Treated Water

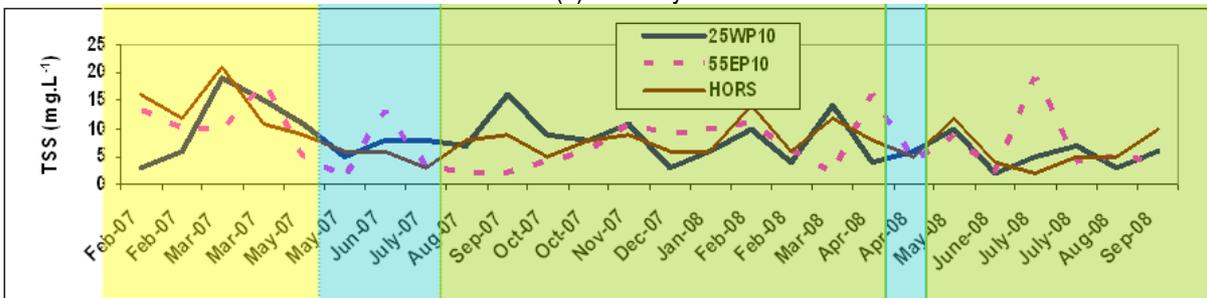
The feed to HORS is supplied by 25W or 55E, or a mixture of both, depending on operational issues such as turbidity, ammonia concentration and the presence of algal blooms. The variation of MF and UF filterability with water quality parameters of HORS, 25W and 55E is shown in Figure 2.



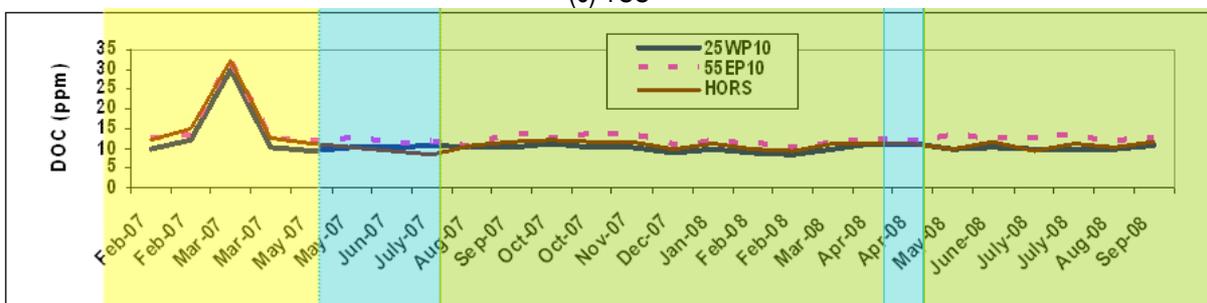
(a) Total algal count



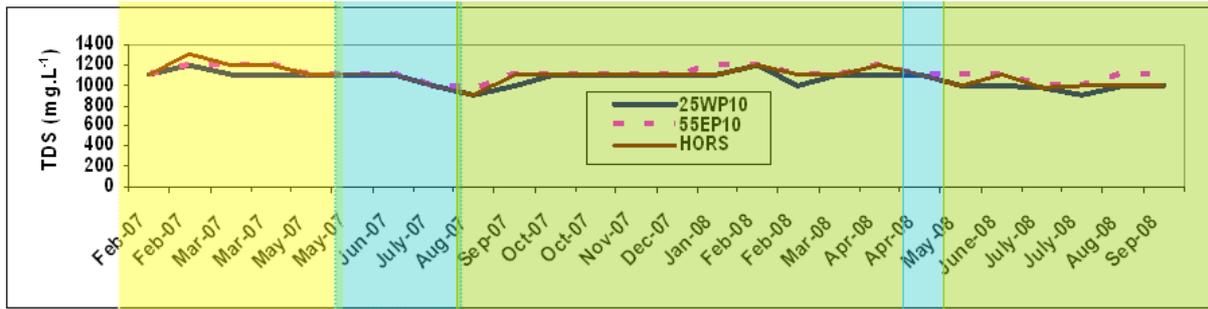
(b) Turbidity



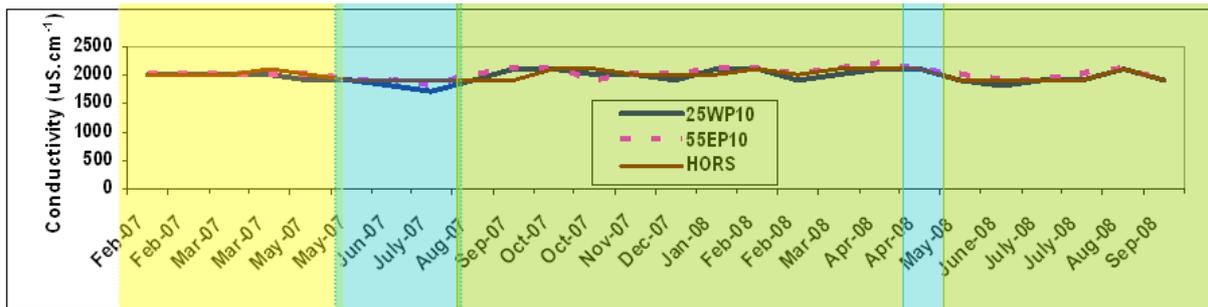
(c) TSS



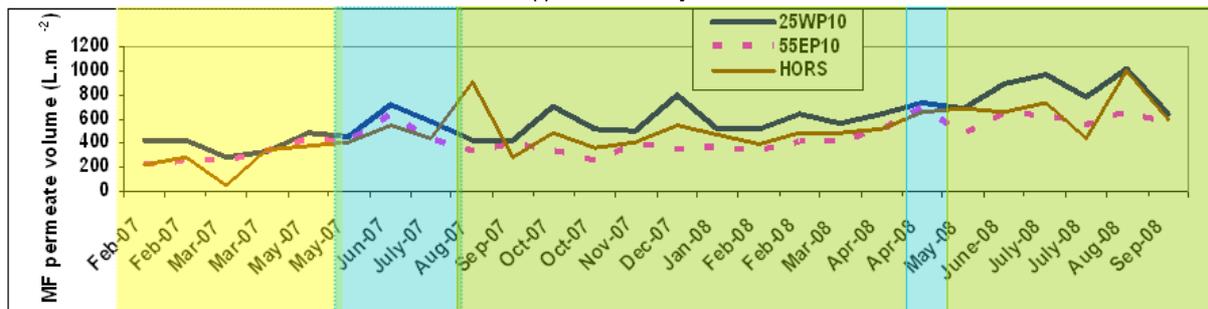
(d) DOC



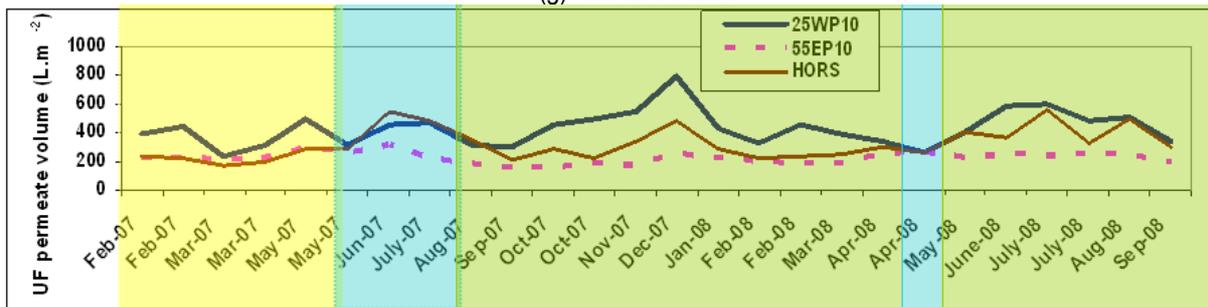
(e) TDS



(f) Conductivity



(g) MF at 70 kPa



(h) UF at 110 kPa

Figure 2. The variation of MF and UF filterability with water quality parameters of HORS, 25W and 55E. The yellow zone denotes that HORS was supplied by 55E, blue by 25W, and green by various ratios of 55E and 25W.

The average values and variations for these parameters are given in Table 2 (the HORS data has been included for ease of comparison). The average values for turbidity, TSS, total algal counts, TDS and conductivity are fairly similar for the three sample types. However, the variations for turbidity, TSS and total algal counts are very large, and, as expected there is some correlation between these parameters. It is interesting to note that the turbidity and the TSS of the HORS sample were occasionally higher than that of the source lagoons. According to Melbourne Water this is usually due to start up of pump station ERW1, or very occasionally, to wind action in the reuse channel carrying the water to HORS.

There is a clear difference in the DOC levels of the treated water from 25W and 55E, the former being significantly lower.

Table 2. Average values for water quality parameters, MF and UF filterability for HORS, 25W and 55E samples collected over Feb 07-Sept 08. Second row gives values for which data for algal bloom in March 07 were excluded

Parameter (Average)	25WP10	55EP10	HORS
Turbidity (FAU)	3.6 ± 2.8	4.1 ± 3.6	4.4 ± 4.7
Ave excluding March 07 data	3.2 ± 2.1	3.5 ± 2.6	3.6 ± 2.2
TSS (mg.L ⁻¹)	7.9 ± 4.4	7.7 ± 5.2	8.4 ± 4.3
Ave excluding March 07 data	7.5 ± 3.8	7.6 ± 5.3	7.9 ± 3.5
Total algal count (cells.mL ⁻¹)	12031 ± 13201	11895 ± 16699	11872 ± 12687
Ave excluding March 07 data	12058 ± 13473	11492 ± 16915	9767 ± 6902
DOC (ppm)	10.9 ± 4.0	13.0 ± 4.0	11.8 ± 4.3
Ave excluding March 07 data	10.1 ± 0.8	12.2 ± 1.0	11.0 ± 1.4
TDS (mg.L ⁻¹)	1060 ± 77	1106 ± 67	1091 ± 86
Ave excluding March 07 data	1058 ± 78	1102 ± 65	1086 ± 85
Conductivity (µS.cm ⁻¹)	1965 ± 109	2001 ± 92	1992 ± 84
Ave excluding March 07 data	1964 ± 111	2004 ± 93	1992 ± 86
MF filterability (Lm ⁻² at 40 L m ⁻² h ⁻¹)	599 ± 118	428 ± 137	491 ± 203
Ave excluding March 07 data	612 ± 180	435 ± 135	508 ± 186
UF filterability (Lm ⁻² at 40 L m ⁻² h ⁻¹)	429 ± 122	220 ± 39	319 ± 112
Ave excluding March 07 data	437 ± 118	221 ± 39	325 ± 109

Microfiltration

The average MF filterability of 25W was much higher (by 40%) than of 55E, and had much less variability. As would be expected the filterability for HORS was intermediate between these, but there was markedly higher variability. When the data for the algal bloom event were excluded, there was a small increase in filterability for all, and the variability in percentage terms was fairly similar for all. These results show that for MF the 25W system is the preferred source of treated water on the basis of higher flux rate and consequential higher productivity.

Ultrafiltration

Similarly, the average UF filterability of 25W was much higher (by 95%) than of 55E, but had markedly greater variability. When data for the March 07 algal bloom were excluded, there was a marginal increase in filterability, and the variability was effectively unchanged for all water types. The values for HORS were intermediate between those of 25W and 55E, as expected, but as for MF, the variability was higher. The higher UF filterability of 25W may be attributed to its lower DOC content. As for MF, these results show that the 25W system is the preferred source of treated water.

5.4 Prediction of the MF and UF Filterability of HORS Samples

The relative filterability for the samples within a sample batch, ie., from 25W, 55E and HORS, collected on the same day could be explained in terms of their water quality parameters.

MF: As a general observation, elevated TSS and turbidity (which may also occur with elevated total algal cell count) led to lower MF filterability, whereas

UF: elevated DOC levels led to lower UF filterability.

To further investigate the influence of the water quality parameters on MF and UF filterability, the data for the HORS samples were pooled and subjected to simple regression analysis. For

MF: the effects, in decreasing order of influence, were TSS > turbidity > DOC > total algal count > TDS, where the R² values for TSS and turbidity were 0.44 and 0.41, respectively.

UF: The order was DOC > TSS > TDS > turbidity where the R² values for DOC and TSS were 0.39 and 0.31, respectively.

Although these correlations are not strong, these results indicate that the interactions of particulate matter with the membrane are the main determinant of MF filterability, and the interaction of the EfOM with the membrane is the main determinant of UF filterability.

Statistical correlation between the water quality parameters such as turbidity, DOC, TSS, total algal count, conductivity and TDS and the filterability of HORS water was used to identify the relative importance of these parameters in influencing the fouling propensity of HORS water in low-pressure membrane filtration.

Two series of HORS samples which were collected at different times each month over Mar 07-Sept 08 were used for the development and evaluation of the models: the first series was used for the development of models, while the second series, which was collected separately over this sampling period, was employed to determine the prediction accuracy of the models.

Using multiple linear regression (MLR) the correlation between water quality parameters and MF filterability of HORS water was:

$$V_M = 1603 - 54.3 T - 48.6 O - 4.5 S - 0.278 D - 0.008 C - 0.65 A \quad (1)$$

where:

- V_M = MF permeate volume (L m⁻²)
- T = Turbidity (FAU)
- O = Dissolved organic carbon, DOC (mg L⁻¹)
- S = Total suspended solids, TSS (mg L⁻¹)
- D = Total dissolved solids, TDS (mg L⁻¹)
- C = Conductivity (μS cm⁻¹)
- A = Total algal count (10³ cells mL⁻¹)

The prediction accuracy of this model was evaluated using the second series of 12 samples which were not employed in the development of the model. The agreement between the experimental and the predicted values calculated from Model 1 was 84.9%. Conductivity (C), algal count (A) and TDS (D) can be omitted from Model 1 with very little change in the prediction accuracy (from 84.9% to 84.8%). Therefore, a suitable model for prediction of MF filterability of HORS water was:

$$V_M = 1391 - 58.8 T - 57 O - 5.3 S \quad (2)$$

For UF, the MLR model for HORS water with highest prediction accuracy was:

$$V_U = 1505 - 70.3 O - 13.8 S - 14.6 T - 0.115 C - 1.57 A \quad (3)$$

The agreement between the experimental and the predicted values calculated from Model 3 was 85.1%. There was little change in the prediction accuracy of Model 3 when algal count (A), conductivity (C) and TDS (D) were removed (the accuracy changed from 86.7% to 86.4%), therefore a suitable model for the UF filterability of HORS water was:

$$V_U = 1328 - 75.1 O - 18.6 T - 13.8 S \quad (4)$$

As shown in Model 2 and Model 4, turbidity, DOC and TSS were the key factors affecting the MF and UF filterability of HORS water. The extent of the influence of these water quality parameters on the accuracy of the models was different. Turbidity was the dominant factor affecting the accuracy of the MLR model for MF, and DOC was the major factor affecting the accuracy of the model for UF. As turbidity, DOC and TSS can be determined on-line (van den Broeke et al., 2006), Model 2 and Model 4 would be useful for rapid prediction of the MF and UF filterability, respectively, of HORS water.

Comparisons of the experimental and predicted values calculated from Models 2 and 4 for the filterability of the second series of samples of HORS water (which was not used for the development of the models) are shown in Figure 3. For most samples, the predicted values for MF filterability were higher than the experimental values, except for sample 4 which had an experimental value significantly higher than the predicted value (Figure 3a). The predicted and experimental values for UF filterability were fairly similar, except for samples 7 and 9 for which the predicted values were considerably higher (Figure 3b). The differences between the experimental and the predicted values in Figures 3 may be due to the MF and UF filterability of the HORS water being not only influenced by basic water quality parameters such as turbidity, DOC and TSS as shown by the developed models, but also by other factors such as the presence of supra-colloidal particles in the feed water (te Poele et al., 2004; Soffer et al., 2004), variation of the organic components in the feed water, and the chemical and physical interactions of organic components and the MF and UF membranes (Hong and Elimelech, 1997). These factors, which were not included in the development of the models, would affect the prediction accuracy of the models for MF and UF filterability. The effect of these factors on the accuracy of the developed models requires further investigation.

As fresh membranes were used for each filterability test the influence of biofouling was not investigated in this study. The effect of biofouling on the accuracy and applicability of the models should be considered in longer term trials at pilot-scale.

Note: This work has been accepted for publication in the journal *Water Science and Technology*. Nguyen et al., "Identification of key water characteristics affecting the filterability of biologically treated effluent in low-pressure membrane filtration".

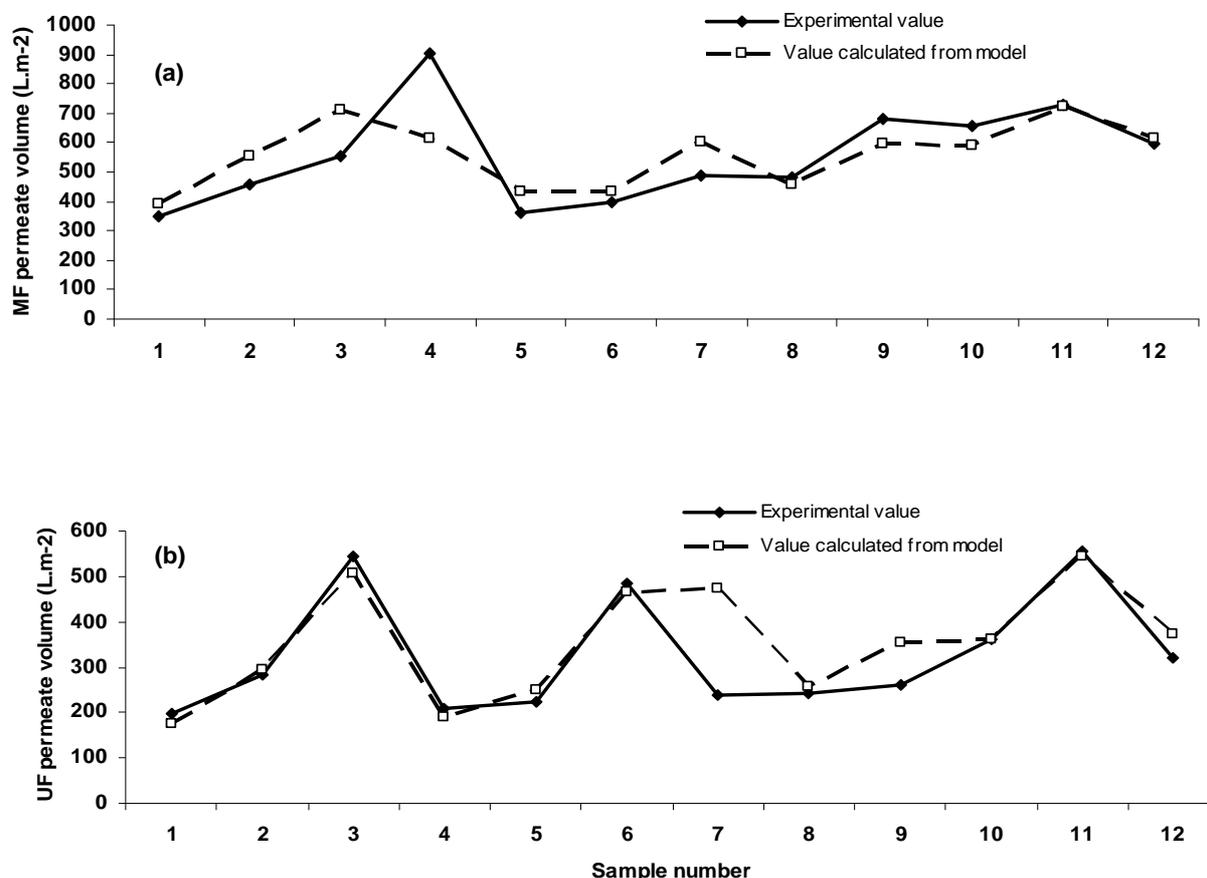


Figure 3. The trends for the experimental and predicted results for (a) MF and (b) UF filterability of HORS water.

5.5 Relationship of Aromaticity and Filterability of the HORS Sample

The degree of aromaticity of the effluent organic matter (EfOM) in the HORS sample was estimated by specific UV absorbance (SUVA), the ratio of the UVA 254 nm to DOC (Figure 4). There was a trend of compositional change in the EfOM, the aromaticity being lower in September and higher in February-March. For HORS samples having the same dissolved organic contents ($11.3 \pm 0.2 \text{ mg.L}^{-1}$), the permeate volumes at a final flux rate of $40 \text{ Lm}^{-2}\text{h}^{-1}$ increased with increasing SUVA values, indicating that the higher the aromaticity, the greater the filterability. This suggests that the lower the aromaticity, the greater the hydrophilic neutral content of the EfOM, and thus the lower the filterability. This effect was greater for UF than MF filterability with R^2 values of 0.69 and 0.29, respectively.

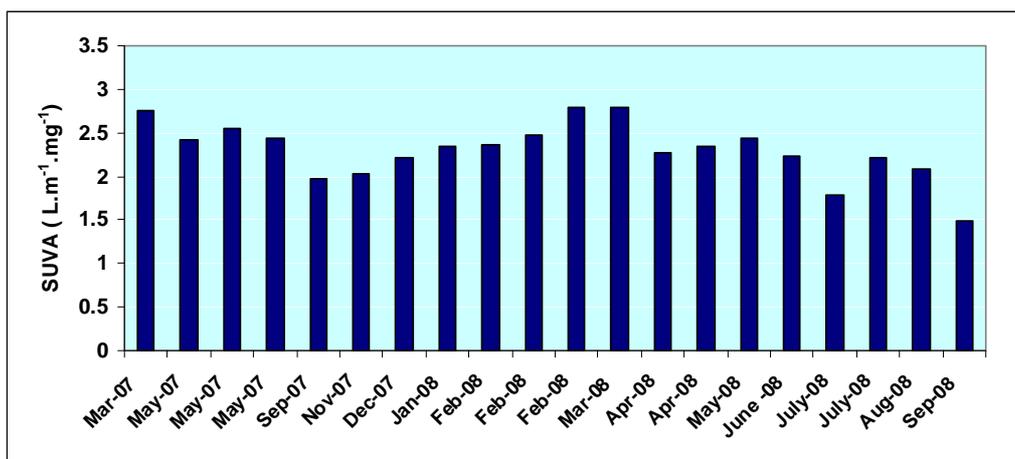


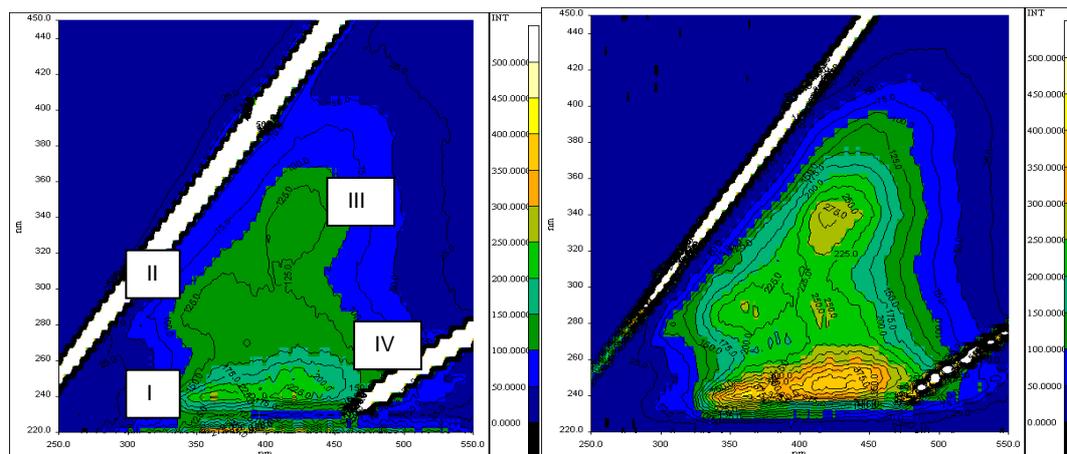
Figure 4. SUVA values for HORS samples for March 07- September 08

5.6 Variation of the Organic Composition of HORS Water

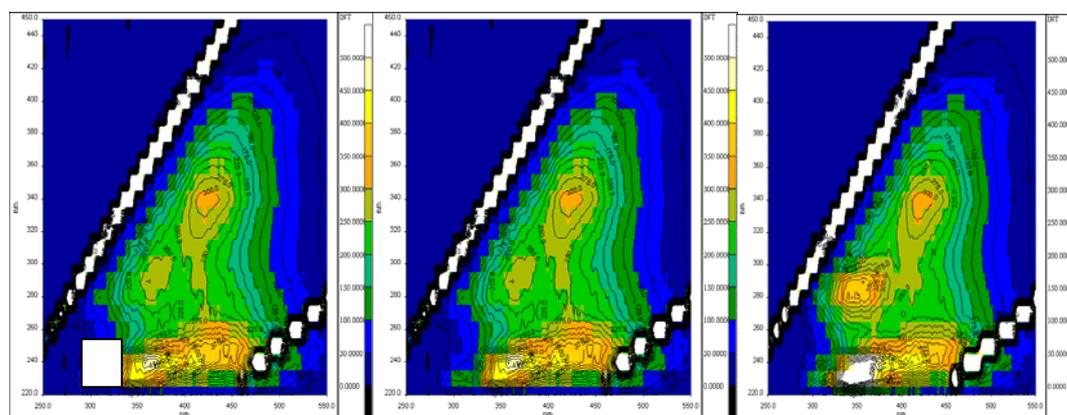
Emission-excitation matrices (EEMs) provide 3-dimensional plots of the intensity of molecular excitation and emission in the UV-visible wavelength range. It is a useful analytical tool that can be used for providing a “fingerprint” of organic compounds dissolved in water. Four regions of high fluorescence intensity may be observed: peak I at 225/340-350 nm; peak II at 280-285/340-350 nm, peak III at 330-350/420-430 nm, and peak IV (240-250/420-460 nm). Peak I is associated with protein-like extracellular organic matter which contains aromatic amino acids, peak II is attributed to soluble microbial products (SMP), peak III contains humic-like fluorophores (Sheng and Wu, 2006) and peak IV is associated with more fulvic-like material (Nguyen *et al.*, 2005).

The EEM spectra of HORS samples of similar DOC levels but collected on different dates can differ markedly in terms of component content (Figure 5(a)). As noted previously, there are some differences in the content of the treated effluents from 25W and 55E; difference in the organic components (protein-like content and SMPs) is clearly shown in the EEM spectra of the 25WP10 and 55EP10 samples collected on 5 February 2007 (Figure 8(b)), even when DOC level is taken into account. The spectra for 25W and HORS are similar as HORS was supplied entirely by the 25W system. For the sample collected on 5 February 2008 HORS was supplied by both 25WP10 and 55EP10 at water ratio of 2:3. Despite the lower DOCs for these samples, it is clear that there is a marked difference in the organic composition of these samples (Figure 5(c)) which were taken one year later than those in Figure 5 (b).

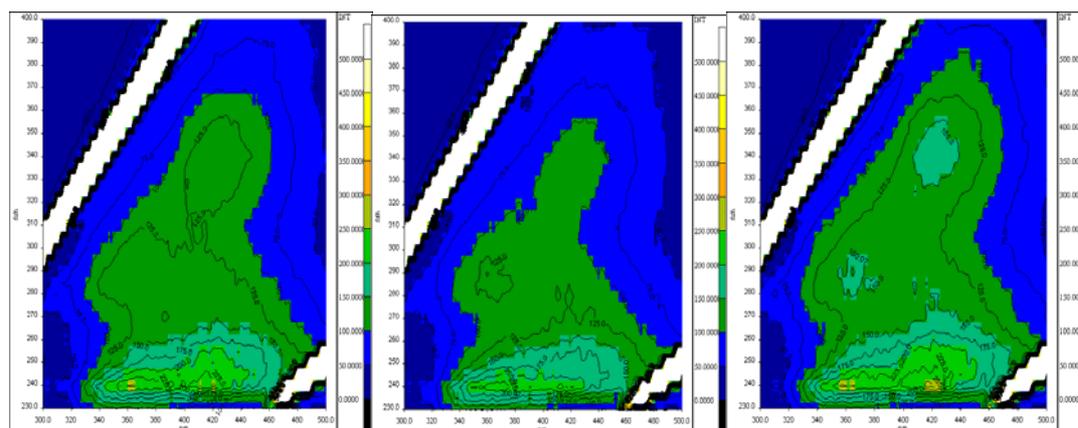
This variation in the organic components, particularly of the humic-like material, and as shown later of the SMP content, of the treated streams from the 25W and 55E systems would explain some of the difficulty in establishing models to predict the MF and UF filterability of the HORS stream.



HORS (DOC = 10 ppm) HORS (DOC = 10.1 ppm)
 (a) Samples collected 5 Feb 08 and 12 August 08



HORS (DOC = 12.3 ppm) 55E (DOC = 12.4 ppm) 25W (DOC = 10.6 ppm)
 (b) Samples collected 5 February 07



HORS (DOC = 10 ppm) 25W (DOC = 8.7 ppm) 55E (DOC = 11.1 ppm)
 (c) Samples collected 5 February 08

Figure 5. Comparison of the EEMs for (a) different HORS samples with similar DOC level (b) HORS, 25W and 55E samples when HORS supplied by 25E, and (c) HORS, 25W and 55E samples when ratio in HORS of 25W and 55E was 2:3, respectively. I denotes extracellular protein-like matter, II soluble microbial products, III humic-like matter, IV fulvic-like matter.

These data were confirmed by resin fractionation in which the organic components were separated into hydrophobic (humic-like), transphilic (fulvic-like) and hydrophilic (SMP and protein-like extracellular matter) by use of macroporous resins, as exemplified in Figure 6.

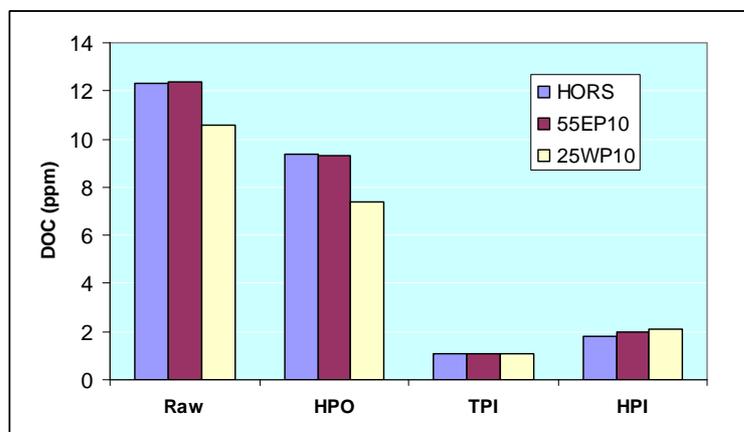


Figure 6. Organic fractions of samples collected on 5 February 2007
HPO denotes hydrophobic, TPI transphilic and HPI hydrophilic.

5.7 Characterisation of the Foulant Layer on MF and UF Membranes

Typically, DOC removals of 2-4% and 25-28% were obtained by MF and UF filtration, respectively. Fractionation of the permeate showed that there appeared to be greatest removal of the hydrophilic fraction, but as little DOC was removed by MF, no firm conclusions could be drawn regarding the relative removals of the fractions when experimental error was taken into account. For UF, the bulk of the DOC retained on the filter (37%) belonged to the hydrophobic (humic substances) fraction, followed by the hydrophilic (polysaccharides, protein-like matter) fraction (25%) and then the transphilic fraction (11%). These results were confirmed by EEM spectra.

HPSEC showed that both the MF and UF membranes allowed passage of the lower apparent MW molecules which, according to Levine *et al.* (1985), in biologically treated sewage effluent comprise mainly lower MW humic substances and proteins, chlorophyll and vitamins. When UV detection is used molecules which absorb radiation of 260 nm are revealed (Figure 7a), whereas when DOC detection is used, all organic molecules are revealed (Figure 7b). In this case, the lower MW components appeared in both chromatograms, but only some of the higher MW components which appeared with DOC detection were apparent with UV detection since they do not all absorb UV radiation. Using DOC detection, non UV-absorbing molecules of 40-70 kDa were shown to contribute to the fouling of the MF membrane (Figure 7b). According to Levine *et al.* (1985) these organic materials would be macromolecules such as polysaccharides, higher MW humic acids and proteins, nucleic acids and lipids. For UF, molecules in the 40-70 kDa apparent MW range, a large proportion of which were UV-absorbing, contributed a significant proportion of membrane fouling. Furthermore, the organic fraction within the size range 100 kDa (0.01 μ m), representing organic macromolecules and small colloids, contributed a significant proportion of UF membrane fouling.

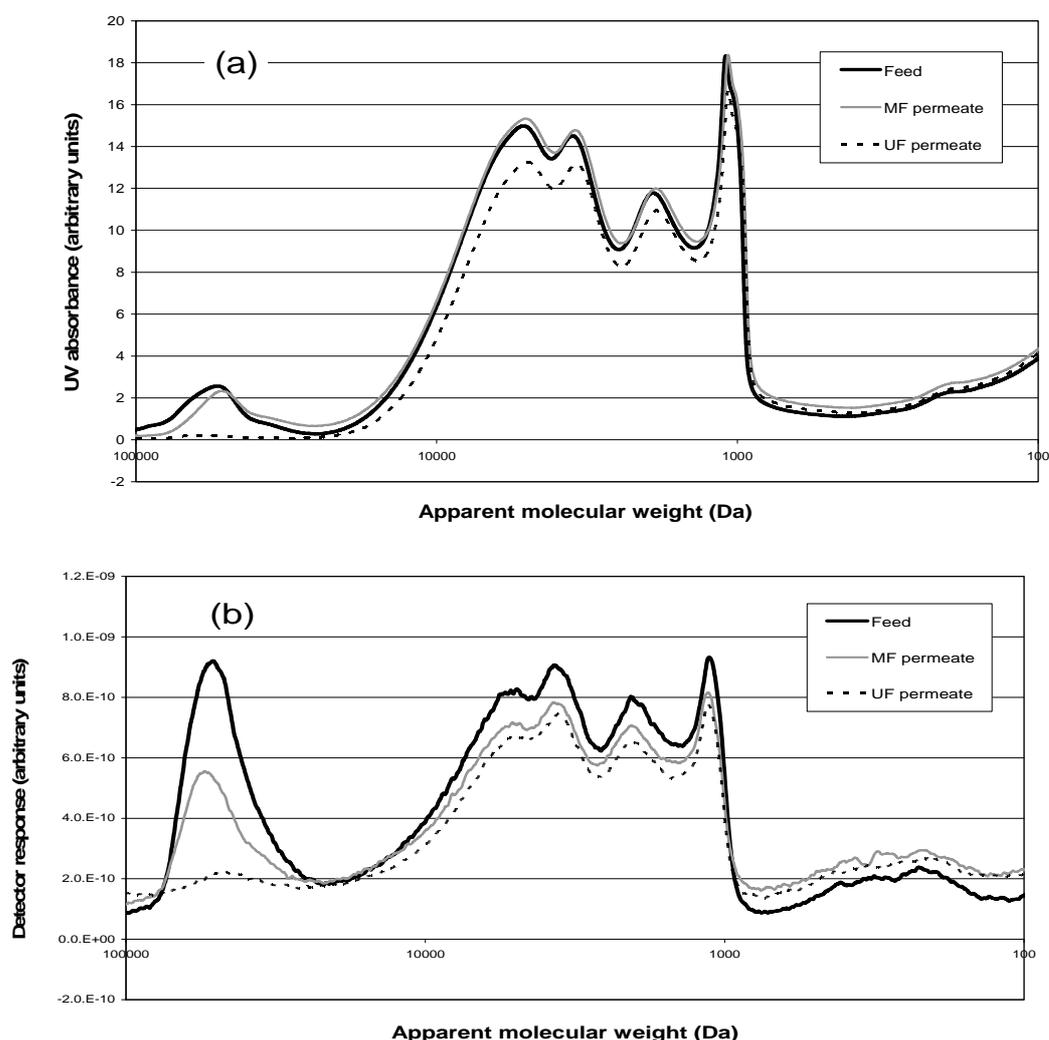


Figure 7 (a) SEC-UV and (b) SEC-DOC chromatograms for feed, MF permeate and UF permeate

ATR-FTIR analysis of fouled MF and UF membranes showed similar spectra for all samples which indicated that proteins, polysaccharides and/or aminosugars were possible foulants. Evidence of fouling due to humic and fulvic substances was also noted.

Overall, the major compounds detected in the fouling layers on both MF and UF membranes were proteins and polysaccharides. This finding was consistent with those of Jarusutthirak et al. (2002), Her et al. (2004) and Shon et al. (2006).

Details of these results can be found in Milestone Reports 5 and 6, available from the SWF.

Results for algal preparations were consistent with these findings. Experiments with extracellular organic matter (EOM) which is secreted by algae during growth, and algal organic matter (AOM) which is released on algal death by a blue green alga, showed that EOM had greater fouling effect than AOM for MF, whereas the fouling rates were similar for UF.

MF removed mainly hydrophilic compounds from both the EOM and AOM solutions, indicating that the proteins and polysaccharides in this fraction were the main contributors to the fouling of the membrane. UF removed a greater amount of hydrophilic compounds than MF, and although EOM had a higher hydrophilic content than AOM, a similar amount of hydrophilic material passed through the membrane for both. There was significant removal of hydrophobic material for both EOM and AOM, and as for the hydrophilic matter, a similar amount of

hydrophobic matter appeared in the permeate for both sample types. The smaller, slightly charged transphilic compounds were not retained by either the MF or UF membrane.

The hydrophilic fractions of the EOM and AOM (obtained by resin fractionation) were subjected to MF and UF. For MF, the reduction in flux was greater for the feed than for the hydrophilic fractions for both EOM and AOM, suggesting that the hydrophilic components were not the only factor involved in the fouling. The fouling rate for the AOM-derived fraction was greater than for the EOM-derived fraction. For UF, as for MF, the flux decline was lower for the hydrophilic fractions than for the whole feed, however, the fouling rate for the EOM-derived fraction was greater than for the AOM-derived fraction. When the surfaces of the fouled membranes were surface washed and then backwashed with MilliQ water, markedly higher flux recoveries were obtained for EOM than for AOM, for both MF and UF. Further details can be obtained from Milestone 9 Report which is available from the SWF.

5.8 Utilisation of 0.1 µm Microfiltration Membrane

Comparison of MF membranes of smaller pore size (0.1 µm) with the standard MF membrane (0.22 µm) showed that the filtration time could be fairly similar or much greater (depending on the sample), but the specific permeate volume, DOC removal (3-5%), and types of organic fractions removed were fairly similar for the two MF membranes. In comparison, for UF the permeate volumes were approximately half those for MF, and the DOC removals (14-17%) were markedly higher for the two samples tested. Further details can be obtained from Milestone 9 Report which is available from the SWF.

5.9 Influence of Pre-treatment on MF and UF Filterability

As there was little removal of organic matter by filtration alone, various pre-treatments of HORS were investigated as a means of increasing the material removed and thus reducing the amount of organic material potentially available to foul the subsequent RO membrane, either directly, or indirectly via biofouling through serving as a microbial growth substrate. Furthermore, pre-treatment can reduce the external fouling by pore plugging and internal/irreversible fouling of the MF/UF membrane, and so enhance the flux, as well as extend the service time before membrane cleaning is required. Coagulation with aluminium ion (Al^{3+}) as alum and aluminium chlorohydrate (ACH), coagulation with ferric ion (Fe^{3+}), and treatment with an anion exchange resin was investigated. Standard jar testing procedure and aluminium and ferric ion concentrations within the range of 0-10 mg L^{-1} metal ion were used.

5.9.1 Pre-treatment with Alum, Ferric Chloride and Aluminium Chlorohydrate

Comparison of alum and ferric chloride coagulation as a pre-treatment for MF showed that, overall, alum performed better than ferric chloride for flux improvement at similar dosage (same weight concentration or molar concentration of metal ion), and for both alum and ferric chloride increased dosage resulted in increased flux rate. With regard to external fouling, ESEM showed that the alum-treated foulant layer was more porous and less gel-like compared with the ferric chloride foulant layer on the membrane surface. Particle size analysis showed that the ferric chloride-treated water had a higher proportion of smaller particles than the alum-treated water. The smaller particles would result in more direct blockage of the membrane pores and formation of a denser cake layer on the membrane surface, making it less permeable than for the alum-treated water.

There was only a small improvement in MF flux after settling of alum-treated water compared with filtration of the treated water without settling. In contrast, pre-filtration of the treated water with a 1.6 µm filter (equivalent to micro-media filtration) significantly enhanced the flux. This implied that a media filtration process following coagulation would greatly enhance the productivity of the MF/RO system. However, the benefit of this additional step would need to be traded off against the added capital and running costs.

Coagulation with 2 mg L^{-1} Fe^{3+} or Al^{3+} reduced internal MF fouling almost as well as with 5 mg L^{-1} metal ion, however, alum dosage at 5 mg L^{-1} was more effective for removal of organic matter (7%), maintaining a higher

flux and providing greater mitigation of internal membrane fouling (total DOC removal of 15%). Improvements in flux recovery of 34-55% were obtained after use of the pre-treatments.

Similar results were obtained for UF: coagulation with alum and ferric chloride enhanced the flux and reduced internal fouling, alum being more effective. Total DOC removal with an alum dosage of 5 mg L⁻¹ was 20%, which resulted in the highest improvement in flux recovery of 35%.

The use of aluminium chlorohydrate (ACH) is preferable to alum as (Gebbie, 2001): residual aluminium in the treated water can be maintained at low levels (0.01-0.05 mg.L⁻¹), it works well at low raw water temperature and over a broader pH range (pH 5-8) compared with alum (pH 5.5-6.5), produces less sludge at equivalent dose, and leads to lower TDS increase in the treated water. Furthermore, the residual chloride ion is less problematic than sulfate in RO as the latter leads to scale formation (Chong and Sheikholeslami, 2001). Comparison of alum and ACH at 2.5 mg L⁻¹ Al³⁺ showed removals of 3% DOC from HORS by coagulation alone, of 15% by UF alone, and of 21% and 20% by alum/UF and ACH/UF, respectively. There was a marginal difference in the removals of the different types of organics as shown by the EEM spectra, and this was reflected in the marginal difference in the filterability of the two treated samples, alum having slightly greater removal of organic material and filterability (4%). The filterability of the treated samples was markedly higher (approximately 70%) than for the untreated sample.

As the difference in performance was slight and within experimental error, the use of ACH would be preferable to that of alum for the pre-treatment of HORS water. Further details may be obtained in Milestone Report 9, available from the SWF.

5.9.2 Pre-treatment with Anion Exchange Resin

As strong anionic exchange resins have been shown to remove large proportions of organic matter from drinking water, this type of resin was evaluated as a pre-treatment to increase organic matter removal and so reduce membrane fouling and thus enhance flux. Pre-treatment of the HORS water with a strong anionic exchange resin (10 mL L⁻¹) did not improve the flux rate or reduce irreversible membrane fouling for either MF or UF, despite the removal of up to 55% of DOC and good colour removal. Indeed, there was increased irreversible fouling of the MF and UF membranes which would potentially lead to the need for more frequent chemical cleaning, and hence increased downtime and shortened membrane life. The low molecular weight and the negatively charged organic fractions removed by the resin did not greatly contribute to membrane fouling.

When sequential alum and anion exchange resin treatment was used, compared with untreated water, considerably higher flux and lower irreversible fouling was obtained, similar to the results obtained for alum coagulation alone. Resin fractionation showed that alum treatment removed some of the hydrophobic and hydrophilic fractions, whereas the anion exchange resin removed large proportions of the hydrophobic and transphilic fractions, but not the hydrophilic fraction. HPSEC-UV-DOC showed that the high molecular weight hydrophilic organic compounds (SMPs such as polysaccharides, proteins) were the major cause of the flux decline and irreversible fouling in the MF/UF of the HORS sample.

The shortcomings of the anionic exchange resin pre-treatment may be overcome by using alum coagulation prior to the resin. This sequence leads to significant improvement in MF and UF flux rates, reduced irreversible fouling and better quality feed water for a subsequent RO process. However, the increased capital and operating costs would need to be taken into account.

Further details of each of these treatments can be obtained in the Milestone Reports available from the SWF: coagulation with alum and ferric chloride (#5, #6), anion exchange resin (#6).

5.10 Investigation of Sequential HORS Pre-treatment and Reverse Osmosis

The impact of MF or UF alone, MF or UF with alum pre-treatment, and UF with ACH pre-treatment prior to RO was investigated. The water quality of selected streams within these processes was determined to establish the effectiveness of the various unit operations. A pilot scale MF/UF rig was used to obtain sufficient pre-treated water for the RO step (Figure 8).

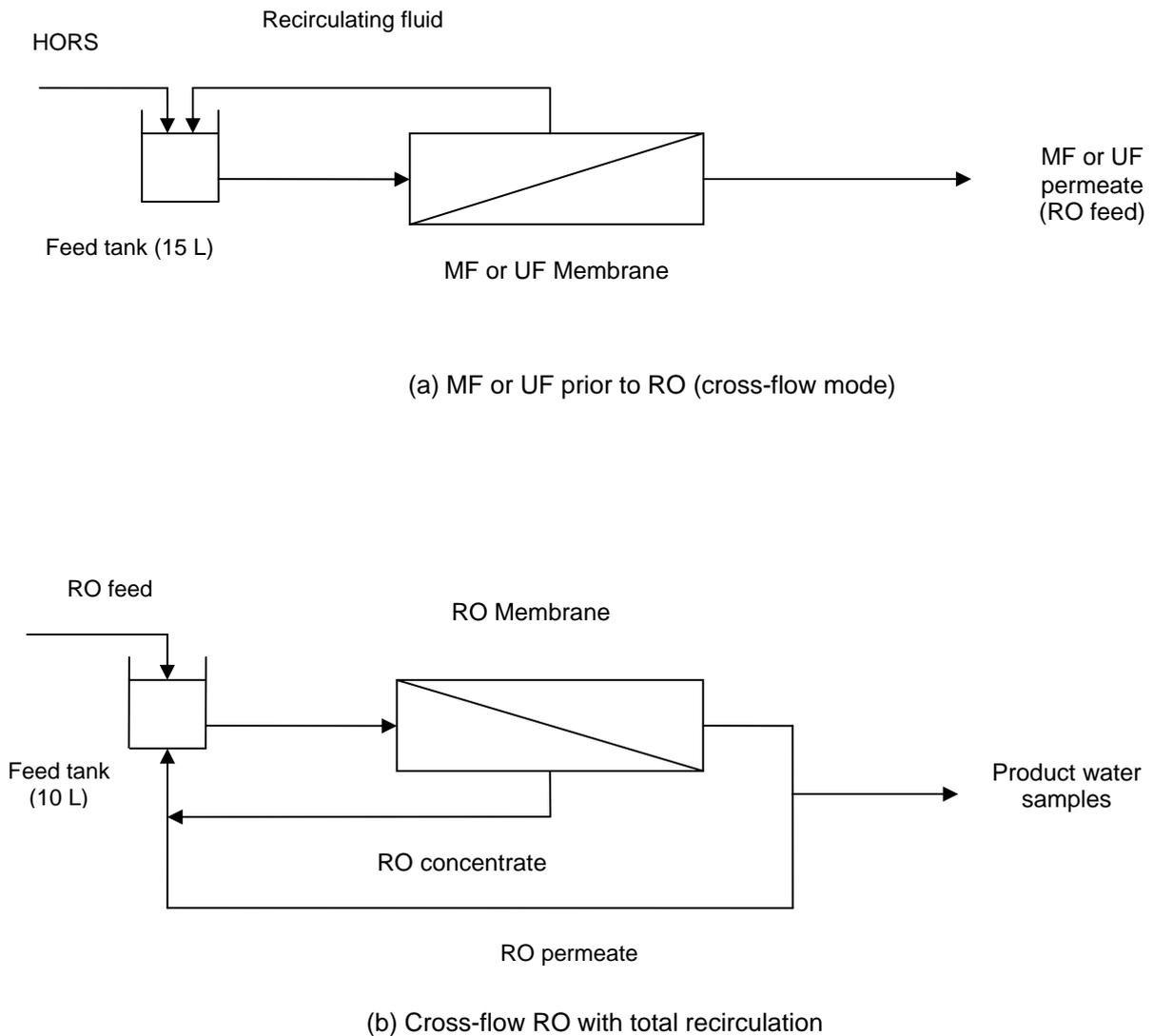


Figure 8. Schematic diagram for the sequential MF or UF and RO process

5.10.1 Alum Pre-treatment

Alum pre-treatment at a dosage of $10 \text{ mg Al}^{3+} \text{ L}^{-1}$ followed by settling removed 3-4% DOC from raw HORS water. However, when used without settling prior to MF and UF, it significantly improved the flux and reduced irreversible fouling at both bench and pilot scale (DOC removals were 19% and 28% for pilot scale). After alum pre-treatment, the amount of product collected in one hour in the pilot system for MF and UF was 150% and 170%, respectively, compared with the untreated sample. Furthermore, the fluxes for the alum-treated samples were higher than those that would require a backflush cleaning operation, whereas the membranes used for the untreated water required cleaning. A cleaning regime of backwash with tap water, sodium hypochlorite and thorough rinsing with tap water for the UF membrane led to high flux recoveries of 97% and 90% for the alum-treated and untreated water, respectively.

Minimisation of turbidity, microbe numbers and DOC reaching the RO membrane is desirable, hence maximisation of their removal by MF or UF is required in order to extend the operational time of the RO membrane. As there was greater DOC removal for UF at both bench and pilot scale, it would be the process of choice prior to RO. Although alum treatment improved the flux and thus the productivity for the UF step, there was no consequential improvement of the flux for the subsequent RO process.

EEM spectra showed that MF or UF, with and without alum pre-treatment, reduced the levels of humic-like and fulvic-like materials, soluble microbial products (SMPs) and protein-like matter in the treated HORS water. There was slightly greater removal of all organic component types by the alum treatment. Subsequent RO treatment removed all humic-like, fulvic-like materials and SMPs but allowed passage of a small portion of the protein-like matter. Thus the sequence of alum treatment and UF removes a significant proportion of the DOC from the HORS water and so reduces the potential for organic fouling in the subsequent RO step. The conductivity and DOC level of the RO permeate were both reduced by 98%. ICPMS analysis of the treated water showed that aluminium, iron, nickel, copper, zinc and barium were not detected indicating 100% removal, and that there was 97-99% removal of sodium, magnesium, potassium and calcium for all the RO-treated samples. Further details may be obtained from Milestone 8 Report, available from the SWF.

Alum pre-treatment prior to MF or UF led to greater DOC removal, improved flux and lower internal fouling, and thus increased the productivity of the pre-treatment step. UF is the preferred membrane treatment process prior to RO since there is greater DOC removal and thus less potential for organic fouling of the subsequent RO membrane.

5.10.2 ACH Pre-treatment

ACH pre-treatment of HORS prior to UF followed by RO was evaluated. A dose of 2.5 mg L⁻¹ Al³⁺ was selected based on earlier data and its effectiveness in aiding ultrafiltration of municipal effluent according to Qin et al., (2004). Although the DOC removal due to ACH treatment alone was low (3%), the UF flux rate in the pilot scale rig was markedly higher than for untreated water. For the subsequent RO process DOC removals were 19% and 23% for untreated and ACH-treated water, respectively.

The RO flux for untreated HORS was slightly lower than for the ACH-treated HORS for the first 32 h, after which they were similar until the experiment was terminated at 48 h. Examination of the resultant RO permeate showed that there was 98% reduction in conductivity and DOC, and 97% reduction in turbidity, the results being very similar for both the untreated and ACH-treated water. No fluorescent organic matter was detected in EEM spectra of the RO permeate.

ACH pre-treatment prior to RO is recommended.

6. Issues Arising

The results show that water treated in the 25W system has consistently lower DOC content, and consistently higher MF and UF filterability, than the water treated in the 55E system. Hence when choosing a feed water, to maximise MF and UF membrane productivity, the 25W system is the feed of choice for the RO process. However, HORS is supplied from either or both systems, according to operational issues. From an operational viewpoint, 25W is preferred as the water is gravity fed via the channel to HORS whereas pumping is required for the transfer of 55E water to HORS. However, other factors also affect the choice of feed system for HORS. These include: the prevailing westerly winds which can lead to increased turbidity; the ammonia content needs to be taken into account with regard to the subsequent chlorination process (ie., chloramination vs. chlorination), and the periodic presence of algal blooms.

MF was approximately 40% better than UF in terms of water productivity, however, the MF filterability of HORS was less predictable than the UF filterability. This reduced predictability makes it more difficult to implement process control. UF gives better virus removal (99.9% removal for a membrane with MWCO of 100 000 Da (Bechtel et al., 1988) and 99.2-99.999% rejection of seeded poliovirus by UF-RO (Sorber), both cited by Madaeni et al. (2004)), and so provides another barrier and reduces the load on the subsequent disinfection process.

Smaller pore size MF membranes (0.1 μm) are increasingly being used for water treatment. However, this study indicated that there was no advantage in using this pore size in place of the 0.22 μm membrane as there was no improvement in water quality and there was a decrease in productivity. There may be an advantage with regard to the greater removal of some microbes, however the perceived advantage of this is small.

Coagulation of HORS leads to enhancement of MF and UF flux, and reduction of irreversible membrane fouling, and thus greater productivity. This enhancement is greater if media filtration occurs before the MF or UF process. However, this means addition of a further unit operation, and the consequent capital and operating cost needs to be investigated.

The long term impact (months) of the different pre-treatment methods on RO fouling was not evaluated due to the experiments being conducted only at bench scale, and because access to the pilot scale plants at WTP was not possible.

7. Conclusions

- Clarifier effluent is not a suitable source as feed for the membrane salt reduction process due to its high fouling characteristics.
- MF and UF filterability of HORS samples varied over the collection period October 06-September 08. In the warmer months, when algal blooms were most prevalent, the MF and UF filterability were low as turbidity, DOC, TDS and TSS were elevated. The sample collected on 19 March 07 during an algal bloom had significantly lower MF and UF filterability, which markedly affected the average filterability of HORS over the sampling period.
- The MF and UF filterability of the treated water from 25W was higher than that from the 55E system. As HORS was supplied by a mixture of water from both systems for much of the sampling period, the MF and UF filterability was: 25W > HORS > 55E.
- The relationships between the MF and UF filterability of HORS samples in terms of specific permeate volume at 40 L.m⁻².h⁻¹ (V_M for MF and V_U for UF) and its turbidity (**T**), TSS (**S**), total algal count (**A**), DOC (**O**), TDS (**D**) and conductivity (**C**) using chemometrics are:

$$V_M = 1391 - 58.8 T - 57 O - 5.3 S$$

$$V_U = 1328 - 75.1 O - 18.6 T - 13.8 S$$

It is possible to predict the MF and UF filterability from these equations with 85% accuracy when all data are taken into account. Variation in the organic components such as humic-like materials and SMP content of the treated streams from 25W and 55E would explain the lower accuracy of prediction of the MF and UF filterability of the HORS stream.

- In terms of recommending a membrane process prior to RO, MF would be better than UF with regard to permeate flux, but, DOC removal by MF was significantly lower than that by UF. Thus UF leads to lower DOC levels in the permeate and so to reduced amounts of organic material potentially available to foul the subsequent RO membrane. Fouling can take place either directly, or indirectly via biofouling by serving as a microbial growth substrate.
- The organic components of the 25W, 25E and thus of HORS streams were characterised and shown to vary with source and time.
- The major compounds detected in the fouling layers on both MF and UF membranes were proteins and polysaccharides. HPSEC analysis indicated that these are neutral, low UV-absorbing higher MW organic compounds.
- Extracellular organic matter had a greater fouling effect than algal organic matter for MF, whereas their fouling propensity was similar for UF. This fouling was due largely to the hydrophilic fraction, although significant amounts of hydrophobic compounds were also removed. The hydrophilic fraction of algal organic matter had a higher fouling propensity than that of extracellular organic matter for MF, whereas the reverse held for UF. Algal organic matter led to greater irreversible fouling of both MF and UF membranes.
- Chemical coagulation treatment of HORS gave varying results for MF flux performance, depending on coagulant type and dosage. Alum performed better than ferric chloride for flux improvement at similar dosage (at same weight concentration or molar concentration of metal ion), and for both alum and ferric chloride increased coagulant dosage resulted in increased flux rate. The MF and UF performances of ACH and alum at the same dosage were similar. However, the use of aluminium chlorohydrate (ACH) is preferable to alum as ACH produces less sludge at equivalent dose, and leads to lower TDS increase in

the treated water. Furthermore, the residual chloride ion is less problematic than sulfate in RO as the latter leads to scale formation.

- Pre-treatment of the HORS water with a strong anionic exchange resin (10 mL L^{-1}) led to removal of up to 55% of DOC and good colour reduction, but did not improve the flux rate or reduce irreversible membrane fouling for either MF or UF. Indeed, there was increased irreversible fouling of the MF and UF membranes which would potentially lead to the need for more frequent chemical cleaning, and hence increased downtime and shortened membrane life. The low molecular weight and the negatively charged organic fractions removed by the resin did not greatly contribute to membrane fouling.
- Subsequent RO treatment of HORS after alum or ACH treatment prior to UF removed all humic-like, fulvic-like materials and SMPs but allowed passage of a small portion of the protein-like matter when HORS was treated with alum. For ACH-treated HORS, all protein-like matter was removed after RO. In general, the sequence of alum or ACH treatment and UF removes a significant proportion of the DOC from the HORS water and so reduces the potential for organic fouling in the subsequent RO step.

7. References

- Bechtel M. K., Bagdasarian A., Olson W. P. and Estep T. N., Virus removal or inactivation in haemoglobin solutions by ultrafiltration or detergent/solvent treatment, *Biomaterials, Artificial Cells and Artificial Organs*, 16(1988), 123-128
- Chong T. H. and Sheikholeslami R., Thermodynamics and kinetics for mixed calcium carbonate and calcium sulfate precipitation. *Chem. Eng. Sci.*, **56** (2001), 5391-5400.
- Fabris R., Lee E.K., Chow C.W.K., Chen V., Drikas M., Pre-treatments to reduce fouling of low pressure micro-filtration (MF) membranes *J. Mem. Sci.*, 289 (2007), 231-240
- Fan L., Harris J. L., Roddick F.A. and Booker N. A., Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes. *Water Res.*, 35(2001), 4455-4463
- Fan L., Harris J. L., Roddick F.A. and Booker N. A., Fouling of microfiltration membranes by the fractional components of natural organic matter in surface water. *Water Sci. Tech.: Water Supply*, 4 (2004), 129-139
- Gebbie P., Using polyaluminium coagulants in water treatment, *64th Annual Water Industry Engineers and Operators' Conference*, Bendigo, 5th and 6th September 2001, 39-47
- Her N., Amy G., Park H.-R., Song M., Characterizing algogenic organic matter (AOM) and evaluating associated NF membrane fouling. *Water Res.* 38 (2004), 1427-1438
- Hong S. and Elimelech M. (1997). Chemical and physical aspects of natural organic matter (NOM) fouling of nanofiltration membranes. *Journal of Membrane Science*, **132**, 159-181
- Howe K. J., Marwah A., Chiu K-P and Adham S. S., Effect of coagulation on the size of MF and UF membrane foulants. *Environ. Sci. Technol.*, 40(2006), 7908-7913
- Jarusuthirak, C., Amy, G and Croué, J.-P., Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes. *Desalination* 145 (2002), 247-255
- Karimi A.A., Vickers J.C., Harasick R.F., Microfiltration goes Hollywood: the Los Angeles experience, *J. AWWA* 91 (1999), 90-103
- Levine A.D., Tchobanoglous G., Asano T., Characterization of the size distribution of contaminants in wastewater: treatment and reuse implications, *J. Water Pollut. Control Fed.*, 57 (1985), 805-816
- Madaeni S. S., Fane A. G. and Grohmann, Virus removal from water and wastewater using membranes. *J. Mem. Sci.*, 102 (1995), 65-75
- Morran J.Y., Drikas M., Cook D., Bursill D.B., Comparison of MIEX treatment and coagulation on NOM character, *Water Sci. Tech.: Water Supply*, 4 (2004), 129-139
- Nguyen M. L., Westerhoff P., Baker L., Hu Q., Esparza-Soto M., and Sommerfeld M., Characteristics and reactivity of algae-produced dissolved organic carbon, *J. Environ. Eng.*, 131 (2005), 1574- 1582
- Qin J.-J., Oo M. H., Lee H. and Kolkman R., Dead-end ultrafiltration for pretreatment of RO in reclamation of municipal wastewater effluent. *J. Mem. Sci.*, 243(2004), 107-113
- Rickert D.A. and Hunter J. V., General nature of soluble and particulate organics in sewage and secondary effluent. *Water Res.*, 40 (2006), 1233-1239
- Sheng G.-P., and Yu H.-Q., Characterization of extracellular polymeric substances of aerobic and anaerobic sludge using three-dimensional excitation and emission matrix fluorescence spectroscopy *Water Res.*, 40 (2006), 1233-1239
- Shon H.K., Vigneswaran S., Ngo H.H., Ben Aim R., Is semi-flocculation effective as pretreatment to ultrafiltration in wastewater treatment? *Water Res.*, 39 (2005), 147-153
- Shon H.K., Vigneswaran S., Snyder S.A., Effluent organic matter (EfOM) in wastewater: constituents, effects and treatment. *Critical Reviews Environ. Sci. Technol.*, 36 (2006), 327-374
- Shon, H. K., Vigneswaran, S., Kim, In S., Cho, J. and Ngo, H. H., Fouling of ultrafiltration membrane by effluent organic matter: A detailed characterization using different organic fractions in wastewater *J. Mem. Sci.*, 278 (2006), 232-238
- Shorney H.L, Vernon W.A., Clune J., Bond R.G., Performance of MF/UF membranes with in-line ferric-salt coagulation for removal of arsenic from a southwest surface water, in: *Proc. 2001 AWWA Membrane Technology Conference, San Antonio, TX (2001)*
- Soffer, Y., Adin, A. and Gilron, J. (2004). Threshold flux in fouling of membranes by colloidal iron. *Desalination*, **161**, 207-221.

- Sorber C. A., "Virus Rejection by the Reverse Osmosis-Ultrafiltration Processes", Ph. D Dissertation, University of Texas, Austin, TX.
- Son H.J., Hwang Y.D., Roh J.S., Ji K.W., Sin P.S., Jung C.W., Kang L.S., Application of MIEX registered pre-treatment for ultrafiltration membrane process for NOM removal and fouling reduction, *Water Sci. Tech.: Water Supply*, 5 (2005), 15-24
- te Poele, S., Roorda, J. H. and van der Graaf, J. H. J. M. (2004). Influence of the size of membrane foulants on the filterability of WWTP-effluent. *Water Science and Technology*, **50**(12), 111-118.
- van den Broeke, Langergraber G. and Weiingartner A.(2006). On-line and in-situ UV/vis spectroscopy for multi-parameter measurements: a brief review. *SpectroscopyEurope*, **18**(4), 1-4.
- Zhang R., Vigneswaran S., Ngo H.H., Nguyen H., Magnetic ion exchange (MIEX®) resin as a pre-treatment to a submerged membrane system in the treatment of biologically treated wastewater. *Desalination*, 192 (2006), 296-302

8. Publications and Dissemination of the Project Findings

International Refereed Journal papers

Nguyen, T, Fan, L, Roddick, F A and Harris, JL A comparative study of microfiltration and ultrafiltration of activated sludge-lagoon effluent. *Desalination* 236 (2009), 208-215

Fan, L., Nguyen, T., Roddick F.A. & Harris J. L. (2008) Low-pressure membrane filtration of secondary effluent in water reuse: Pre-treatment for fouling reduction, *Journal of Membrane Science*, 320 No. 1-2, 135-142

Nguyen, T, Fan, L, Roddick, F A and Harris, JL Identification of key water quality characteristics affecting the filterability of biologically treated effluent in low-pressure membrane filtration, *Water Science and Technology*, (accepted 4 June 2010)

International Conference Presentations

Roddick, F. A. Nguyen, T., Fan, L. and Harris, J. L. (2008) Impact of seasonal water quality changes on low pressure membrane filtration of an activated sludge-lagoon effluent. Presented at ICOM 08 (International Congress on Membrane Processes), Honolulu, July.

Nguyen, T., Fan, L., Roddick, F.A. and Harris, J. L. (2007) A comparative study of microfiltration and ultrafiltration of activated sludge-lagoon effluent. IMSTEC07 (International Membrane Science and Technology Conference), New South Wales, November

Domestic Conference Presentations

Stork, D., Nguyen, T., Roddick, F.A. and Harris, J.L. (2007) Membrane pretreatment of clarifier and lagoon effluents for reverse osmosis. AWA Membranes Specialty Conference II Melbourne, February. (Plus Proceedings CD-ROM)

Roddick, F.A., Nguyen, T., Fan, L. and Harris J. L.(2007) Gaining an understanding of the fouling of microfiltration and ultrafiltration membranes. AWA Victorian Branch Regional Conference, Traralgon, October. (Plus Proceedings).

Thesis

Stork, D. Mitigation of membrane fouling from algae-containing waters. Master thesis, School of Civil, Environmental and Chemical Engineering, RMIT University.