
Information Collection Rule: Treatment Study Summary Report

**Broward County Office of Environmental
Services, Florida**

**District 2A WTP
BCOES Project No. 9520
July 1999**

ICR TREATMENT STUDY SUMMARY REPORT

Evaluation of Nanofiltration Using the Rapid Bench Scale Membrane Test Methodology for Compliance with the Information Collection Rule

Conducted during the period: March 1998 – April 1999

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Plant Name: Broward County District 2A Water Treatment Plant
Plant ICR #: 293

Four quarters of nanofiltration (NF) testing using pretreated Biscayne Aquifer water were successfully completed at the District 2A Water Treatment Plant (WTP) in Broward County, Florida. Cartridge filtration was the only NF pretreatment employed. Two NF membranes, the Koch-Fluid Systems TFC-SR membrane and the Hydranautics NTR7450 membrane, were used to complete Information Collection Rule (ICR) treatment study requirements using the Rapid Bench Scale Membrane Test (RBSMT) methodology.

The TFC-SR membrane achieved higher removals of total organic carbon (TOC), and precursor materials to trihalomethanes (THM) and haloacetic acids (HAA) compared to the NTR7450 membrane. For example, the highest recorded TOC concentration in the TFC-SR membrane permeate was 0.7 mg/L. In comparison, the highest TOC concentration measured in the NTR7450 membrane permeate was 2.5 mg/L.

Under the simulated distribution system (SDS) conditions employed, the highest SDSTTHM and SDSHAA(5) concentrations in the TFC-SR membrane permeate were 33 µg/L and 4.3 µg/L, respectively. However, the highest SDSTTHM and SDSHAA(5) concentrations in the NTR7450 membrane permeate were approximately 88 µg/L and 17 µg/L, respectively. For the TFC-SR membrane, SDSTTHM and SDSHAA(5) concentrations in permeate waters were always below the placeholders set by Stage II of the D/DBP rule (40 µg/L for TTHMs and 30 µg/L for HAA(5)), even when free chlorine was employed as the final disinfectant. For the NTR7450 membrane, however, only SDSHAA(5) concentrations in permeate waters were always below the placeholder set by Stage II of the D/DBP rule when free chlorine was employed as the final disinfectant.

In addition, the TFC-SR membrane achieved higher removals of a variety of inorganic water quality parameters compared to the NTR7450 membrane. For example, the average total hardness in the TFC-SR membrane permeate at 70% feed water recovery was 152 mg/L as CaCO₃. The average total hardness in the NTR7450 membrane permeate at 70% feed water recovery was 240 mg/L as CaCO₃.

Linear regression analysis suggests possible seasonal variations in fouling rates for both membranes. Using the RBSMT methodology, membrane chemical cleaning intervals ranged from approximately 115 hours to 700 hours at 70% feed water recovery and an average initial flux of approximately 14.0 gfd. However, more advanced NF membrane pretreatment may result in longer chemical cleaning intervals. In addition, more research may further establish the validity of the RBSMT methodology in terms of its ability to accurately predict membrane fouling rates (and cleaning intervals) observed in full-scale installations. Therefore, membrane fouling rates and cleaning intervals predicted by bench-scale experiments should be verified at the pilot-scale level.

Finally, because the concentrations of most water quality parameters in the TFC-SR and NTR7450 permeates increased with feed water recovery (at constant flux), the transport of dissolved solutes may be controlled by diffusion across these polymeric membranes.

Objectives. The primary objective of this Information Collection Rule (ICR) treatment study was to evaluate the ability of two nanofiltration (NF) membranes to remove

disinfection by-product (DBP) precursor materials and total organic carbon (TOC). Secondary objectives of this treatment study included the evaluation of inorganics rejection and membrane fouling. This report summarizes both membrane operation and permeate water quality data from bench-scale experiments conducted using the rapid bench scale membrane test methodology as specified in the *ICR Manual for Bench- and Pilot-Scale Treatment Studies* (EPA 814-B-96-003).

Existing water treatment processes. A simple schematic of the existing water treatment processes for the Broward County Office of Environmental Services Water Treatment Plant 2A is given in the flow diagram in Appendix A. This figure also illustrates chemical dosing points as well as chemical sampling points within the treatment train. The water for NF testing was obtained directly from the Biscayne Aquifer prior to any chemical addition. In Tables A.2 and A.3 of Appendix A, basic engineering and chemical feed data for each unit process are summarized.

Full-scale plant influent and finished water quality. Representative averages and ranges for various water quality parameters monitored regularly at the influent to Water Treatment Plant 2A are summarized in Table 1. All finished water quality parameters that are monitored at the full-scale plant have been summarized in Table 2. (No regular monitoring of THMs, HAAs, or UV₂₅₄ are currently undertaken in the distribution system.)

Table 1. Full-scale influent water quality data.

Parameter	Units	Average	Minimum	Maximum
Temperature	°C	26	25	27
pH	-	7.1	7	7.2
Turbidity	ntu	NA	NA	NA
Alkalinity	mg/L as CaCO ₃	235	220	270
Total Hardness	mg/L as CaCO ₃	270	240	310
Calcium Hardness	mg/L as CaCO ₃	262	230	310
TOC	mg/L	9.2	7	11

Table 2. Full-scale finished water quality data.

Parameter	Units	Average	Minimum	Maximum
Temperature	°C	26	25	27
pH	unit	9	8.8	9.2
Turbidity	ntu	0.27	0.2	0.35
TOC	mg/L	6.7	6	7.5
UV ₂₅₄	l/cm	NA	NA	NA
DS-THM4 ^a	µg/L	NA	NA	NA
DS-HAA5	µg/L	NA	NA	NA

^a DS represents distribution system

Section 3

Materials and Methods

ICR bench-scale treatment study apparatus. All bench-scale ICR experiments were conducted using the Rapid Bench Scale Membrane Test (RBSMT) methodology. For these tests, a pressurized cell using a flat membrane sheet was employed. This cell utilized feed and permeate spacers that are also used in spiral-wound elements. The feed water was pumped tangential to the membrane to maintain a shear stress on the membrane surface; thereby limiting concentration polarization. A schematic of the apparatus used to conduct the ICR bench-scale NF experiments is shown in Figure 1. The use of positive displacement gear pumps for both feed water and recycle water minimized pressure fluctuations. The feed pump head (Cole-Palmer, Vernon Hills, IL, model # 74011-11) was designed for use at high pressure and low flow. The recirculation pump head (Cole-Palmer, Vernon Hills, IL, model # 07002-23) was designed for use at low pressure and high flow. These pumps used helical gears made of Teflon, a low friction material, to reduce potential friction losses on the gears. Tubing, connections, and the membrane cell were fabricated of stainless steel. Dual float rotameters increased the accuracy of flow measurements. In addition, permeate and waste flows were manually measured using a graduated cylinder and a stopwatch.

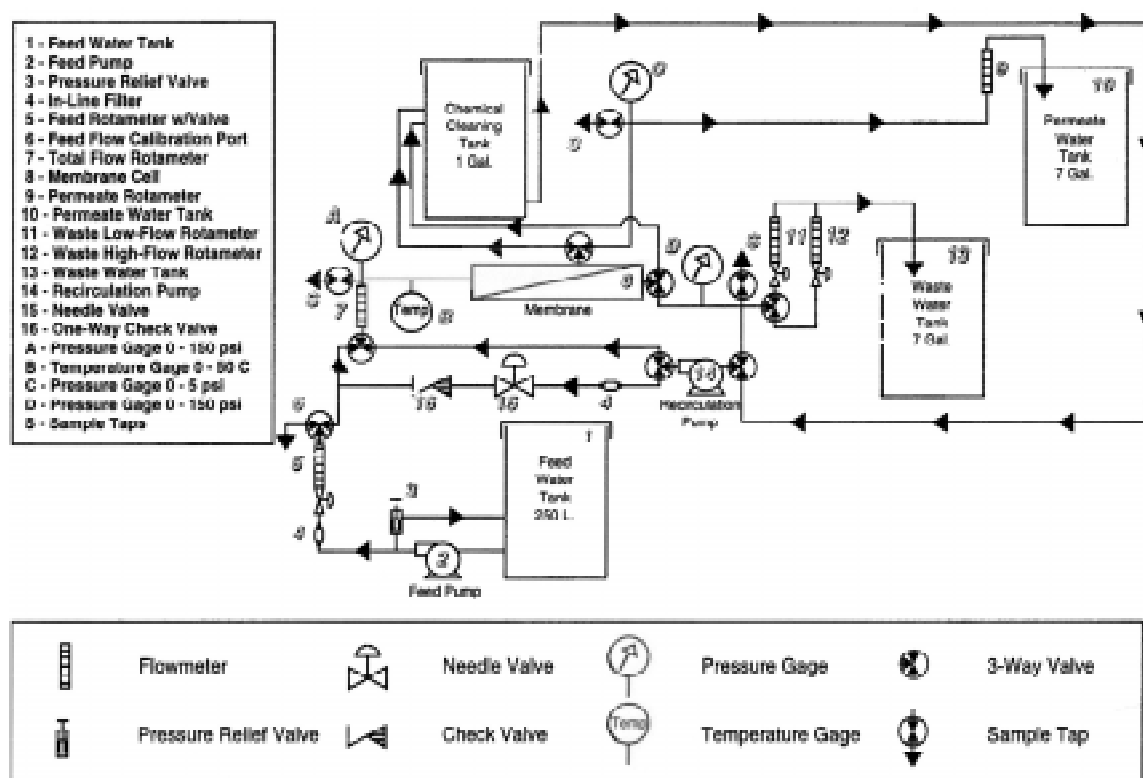


Figure 1. Schematic of the bench-scale NF apparatus

Membranes employed. ICR experiments were conducted using two NF membranes: NTR7450 (Hydranautics Corp., San Diego, CA) and TFC-SR (Koch-Fluid Systems Corp., San Diego, CA). Important characteristics for each membrane (as specified by the manufacturers) are summarized in Table 3.

Table 3. Characteristics of membranes used during ICR testing.

Membrane designation	Manufacturer	Composition	MWCO ^a (Daltons)
NTR-7450	Hydranautics Corp.	polysulfone	~ 1,000
TFC-SR	Koch-Fluid Systems	polyamide	300

^a Denotes Molecular Weight Cut-Off

Membrane cleaning. Membrane cleaning was accomplished through the circulation of a sodium hydroxide solution in deionized water at a pH near 12. In many cases, when base cleaning was ineffective, a sulfuric acid solution in deionized water at a pH of approximately (but not less than) 2.5 was also used. Cleaning was conducted at a temperature of approximately 40°C. The cleaning solution was initially circulated for 15 minutes at a transmembrane pressure of less than 5 pounds per square inch (psi). The membrane was then soaked for 30 minutes. Finally, the cleaning solution was circulated again for 10 minutes at a transmembrane pressure of less than 5 psi. The crossflow velocity was maintained near 1 foot per second (fps) during the circulation portion of the cleaning cycle. A pressure-flux profile was established for both membranes, following chemical cleaning with deionized water. After the base cleaning, the membrane cell was physically removed from the RBSMT apparatus, dismantled, and rinsed with deionized water.

NF feed water and pretreatment. Three, thirty gallon drums were sent to the District 2A WTP each quarter for feed water sampling. Prior to sending the drums, they were chemically cleaned. A high pH sodium hydroxide solution was used to remove organics and biological contaminants. Next, a low pH sulfuric acid solution was used to remove possible metallic deposits. The barrels were thoroughly rinsed with tap water and then dried for a minimum of 24 hours prior to shipment.

As required by the ICR, water was sampled prior to the first point of continuous oxidant addition. For the District 2A WTP, sample water was taken directly from the Biscayne Aquifer. Prior to the RBSMT experiments, the only pretreatment applied to this water was filtration using a 5 µm cartridge filter (RyanHerco, Burbank, CA, Model #6711-505). A simple schematic of the pretreatment processes employed is given in Figure 2.

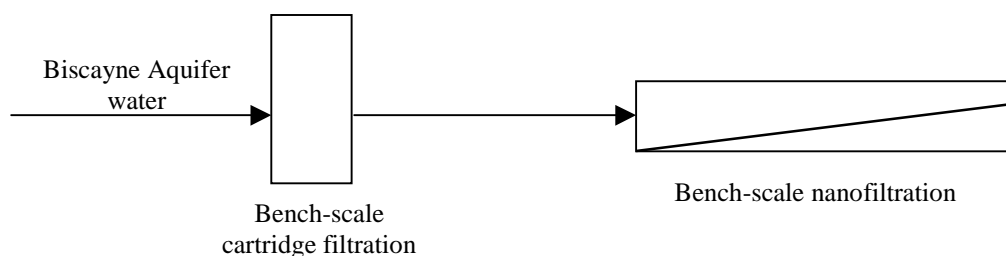


Figure 2. Simple schematic of the pretreatment used prior to bench-scale nanofiltration.

NF feed water samples were collected at the start of the first set of experiments and the end of the second set of RBSMT experiments. These samples were analyzed for a variety of physical, inorganic, and organic parameters. Table 4 summarizes membrane feed water quality for all four quarters of testing.

As shown in Table 4, after pretreatment, the NF feed water can be classified as a slightly alkaline hard water, having high concentrations of total organic carbon, simulated distribution system (SDS) haloacetic acid 5 (SDSHAA5¹), SDS haloacetic acid 9 (SDSHAA9²), and SDS total trihalomethanes (SDSTTHM³).

Table 4. Summary of NF membrane feed water quality for all four quarters of testing.

Parameter	Units	Quarter I	Quarter II	Quarter III	Quarter IV
Alkalinity	mg/L as CaCO ₃	229	330	443	217
Ca hardness	mg/L as CaCO ₃	248	268	260	237
Total hardness	mg/L as CaCO ₃	291	300	286	252
TDS	mg/L	270	286	333	305
Bromide	µg/L	62	85	190	170
Ammonia	mg NH ₃ -N/L	0.05	0.07	BMRL	BMRL
SDS Cl ₂ demand	mg/L	5.35	4.58	5.60	5.63
TOC	mg/L	6.10	6.65	6.75	5.90
TOX	µg/L	537.5	472.5	660	505
THM4	µg/L	190.6	202.2	235.8	192.3
HAA(5)	µg/L	90.9	58.1	66.3	56.2
HAA(9)	µg/L	98.4	60.6	79.65	61.1
UV ₂₅₄	cm ⁻¹	0.185	0.204	0.201	0.156
pH	-	8.48	7.86	7.57	8.10
Turbidity	NTU	0.13	0.20	0.28	0.15

^a Denotes Below Minimum Reporting Level

¹ SDSHAA5 denotes the sum of monochloro, dichloro, trichloro, monobromo and dibromo acetic acids.

² SDSHAA9 denotes the sum of HAA(5) and tribromo, chlorobromo, dichlorobromo, and chlorodibromo acetic acids.

³ SDSTTHM denotes the sum of chloroform, dichlorobromo methane, chlorodibromo methane and bromoform.

Membrane setting. Deionized water, characterized by a TDS concentration less than 1 mg/L, was filtered at the start of each set of RBSMT experiments for approximately 24 hours. This period is sometimes referred to as “membrane setting”. All experiments were conducted at room temperature (approximately 23°C). Therefore, any effects caused by seasonal variability in temperature were not reflected in the ICR experiments. A pressure-flux profile was conducted at the end of the first day or the beginning of the second day of testing, prior to switching to feed water. During these measurements, transmembrane pressure was changed in random order in the range of 0 to 80 psi to reduce systematic biases in calculating the membrane resistance. Results from pressure-flux profiles were modeled using Darcy’s law (Equation 1) where J denotes the permeate flux (m/s), R_m (m⁻¹) denotes the membrane resistance, P_{tm} is the transmembrane pressure (Pa), and μ (N-s/m²) denotes the absolute viscosity of water.

$$J = \frac{P_{tm}}{\mu R_m} \quad (1)$$

NF experiments using pretreated Biscayne Aquifer water. Table 5 summarizes the sampling and membrane operational dates for RBSMT experiments that were conducted for both membranes.

Table 5. Quarterly dates of RBSMT experiments.

Quarter	Sampling date	Dates of membrane operation	
		NTR-7450	TFC-SR
I	4/24/98	5/26/98-6/3/98	5/18/98-5/26/98
II	7/2/98	7/15/98-7/22/98	7/23/98-7/30/98
III	11/18/98	12/14/98-12/22/98	11/30/98-12/9/98
IV	3/9/99	3/31/99-4/7/99	3/23/99-3/30/99

During each quarter, experiments using pretreated Biscayne Aquifer water were conducted continuously with each membrane for a period of approximately 150 hours. The feed water recovery, R_f , for the first experiment (approximately 70 hours in duration) was maintained near 70%. This was followed by experiments where R_f was maintained at values near 90%, 50%, and 30%. As required under the ICR, these experiments were run without any cleaning when changing the feed water recovery. In Table 6, average experimental conditions including net driving pressure, permeate flux, and water mass transfer coefficients used for the NTR7450 membrane during the RBSMT are summarized. In Table 7, this information is given for the TFC-SR membrane.

Table 6. Summary of quarterly RBSMT experiments using NTR7450 membrane.

Quarter	Recovery (%)	Net driving pressure (psi)	Permeate flux (gfd)	MTC _w ^a (gfd/psi)
I	67	81.9	10.8	0.132
I	88	81.9	10.8	0.132
I	52	82.2	10.4	0.127
I	32	82.2	10.3	0.125
II	69	59.0	16.4	0.278
II	92	59.8	14.9	0.249
II	48	59.4	14.3	0.241
II	32	58.9	14.7	0.250
III	72	53.3	13.0	0.244
III	87	52.2	12.1	0.232
III	52	52.2	11.4	0.218
III	31	50.2	10.6	0.211
IV	69	61.3	15.1	0.246
IV	87	60.3	14.9	0.247
IV	49	60.5	13.6	0.225
IV	30	59.4	13.4	0.226

^a Denotes water mass transfer coefficient which is also referred to as the specific flux.

Table 7. Summary of quarterly RBSMT experiments using TFC-SR membrane.

Quarter	Recovery (%)	Net driving pressure (psi)	Permeate flux (gfd)	MTC _w (gfd/psi)
I	72	53.7	10.9	0.203
I	90	66.8	10.6	0.203
I	50	66.7	11.5	0.172
I	29	66.8	11.5	0.172
II	69	43.0	15.9	0.370
II	89	42.8	14.8	0.346
II	51	42.7	15.4	0.361
II	30	41.9	15.1	0.360
III	67	32.4	10.7	0.330
III	85	31.5	9.4	0.298
III	51	31.9	11.1	0.348
III	32	33.6	12.0	0.357
IV	69	54.6	13.2	0.242
IV	87	53.1	10.0	0.188
IV	49	56.9	6.1	0.107
IV	29	57.7	6.1	0.106

Membrane fouling analysis. Membrane fouling was analyzed using the 70% feed water recovery experiment for both membranes. This experiment was selected because of its extended operation time (approximately 78 hours) compared to the other three recovery rates (approximately 24 hours). Since the rate of fouling appeared to be highly dependent on the feed water recovery, using data from all four recoveries in each quarter resulted in very low regression coefficients. In addition, full-scale plants would be operated at one fixed feed water recovery based either on pilot-scale tests or previous design experience. Therefore, fouling rates were calculated using linear regression of permeate flux data obtained at 70% recovery. Results from this analysis were modeled using the equation for a straight line given in Equation 2.

$$J = -mt + b \quad (2)$$

where J = permeate flux at room temperature (gfd)
 m = fouling rate (gfd/h)
 t = time (h)
 b = initial permeate flux (gfd)

From Equation 3, cleaning intervals (t_{clean}) were calculated assuming a 20% drop in initial specific flux.

$$t_{\text{clean}} = \frac{0.2b}{m} \quad (3)$$

Similar calculations can be made for 10% and 15% initial flux declines based on manufacturer recommendations or pilot-scale results for full-scale operation.

Monitoring. Routine monitoring for membrane operation and water quality was conducted according to the recommended minimum EPA requirements described in Tables 8 and 9 respectively. Flow, pressure, and temperature measurements for feed, permeate, concentrate, and influent were recorded hourly during each recovery. TDS, pH, and UV₂₅₄ were monitored at least three times per day for permeate, feed, and concentrate samples. On most occasions, ICR requirements were exceeded and TDS, UV₂₅₄, and pH were monitored hourly for permeate, feed, and concentrate samples.

Table 8. ICR recommended minimum monitoring frequencies for the RBSMT.

Routine RBSMT Study Monitoring Requirements					
Parameter	Feed	Permeate	Concentrate	Influent	Recycle
Flow	none	6xD	6xD	6xD	none
Pressure	none	none	6xD	6xD	none
Temperature	none	none	none	6xD	none
TDS	1xD	3xD	1xD	none	none
pH	1xD	3xD	1xD	none	none
UV ₂₅₄	1xD	3xD	1xD	none	none

1xD – one time per 24 hours

3xD – three times per 24 hours

6xD – six times per 24 hours

Water quality parameters listed in Table 9 were analyzed on composite samples collected for each recovery.

Table 9. RBSMT water quality monitoring requirements established by the ICR.

Water Quality Parameters to be Evaluated at Each Recovery			
Parameter	Feed	Permeate	Concentrate
pH	TPR	FTPR	FTPR
Total Hardness	TPR	FTPR	FTPR
Calcium Hardness	TPR	FTPR	FTPR
Alkalinity	TPR	FTPR	FTPR
Total Dissolved Solids	TPR	FTPR	FTPR
Turbidity	TPR	FTPR	FTPR
Total Organic Carbon	TPR	FTPR	FTPR
UV ₂₅₄	TPR	FTPR	FTPR
Bromide	TPR	FTPR	none
SDS-THM4	TPR	FTPR	none
SDS-HAA6	TPR	FTPR	none
SDS-TOX	TPR	FTPR	none
SDS-Cl ₂ demand	TPR	FTPR	none

TPR – two times per run

FTPR – five times per run

Simulated distribution system tests. One of the important components of ICR treatment studies is the simulated distribution system (SDS) testing of NF feed and permeate waters. Backup permeate samples were collected overnight during the 70% recovery experiment. These samples were used to conduct a trial chlorine demand

experiment with at least two different chlorine doses. Using the predetermined quarterly SDS conditions of temperature, pH, and holding time, the samples were analyzed for chlorine concentrations using the DPD method. Based on these trial SDS experiments, appropriate chlorine dosages were determined for the actual SDS testing. During this test, the sample water was dosed with free chlorine after pH adjustment to obtain a free chlorine residual near 1 mg/L at the conclusion of the incubation period. The samples were then incubated under conditions that closely simulated “average” conditions of the existing distribution system. Following incubation, the chlorinated waters were sampled for THMs, HAAs, and TOX. The SDS conditions employed during the four quarters of testing are summarized in Table 10.

Table 10. Simulated distribution system test conditions used in this study.

Parameter	Quarter I	Quarter II	Quarter III	Quarter IV
Disinfectant	Free chlorine	Free chlorine	Free chlorine	Free chlorine
Temperature (°C)	25	25	25	24
pH	9	9	9	9.0
Holding time (hour)	24	24	24	24
Free chlorine residual (mg/L)	~1	~1	~1	~1

Analytical methods and laboratories involved. A list of analytical methods and their corresponding minimum reporting levels is given in Table 11. All analyses were performed using the methods and QA/QC procedures described in *DBP/ICR Analytical Methods Manual* (EPA 814-B-96-002, April 1996).

All analytical measurements were made by the operator conducting the RBSMT experiments or by Montgomery Watson Laboratories. Laboratory information is provided in Table 12.

Table 11. Summary of analytical methods and MRLs used in this study.

Analyte	Method	Units	Minimum Reporting Level
Alkalinity	SM 2320 B	mg/L as CaCO ₃	2
Ammonia	EPA 350.1	mg/L	0.05
Bromide	EPA 300	µg/L	40
Calcium hardness	SM 3500 Ca D	mg/L as CaCO ₃	5
Total hardness	SM 2340 C	mg/L as CaCO ₃	5
Chlorine residual	SM 4500 Cl G	mg/L	0.5
pH	SM 4500 H ⁺ B	-	-
TDS	SM 2510 B (probe)	mg/L	10
Temperature	SM 2550 B	°C	-
Turbidity	SM 2130 B	NTU	0.05
TOC	SM 5310 C	mg/L	0.50

Table 11 (continued). Summary of analytical methods and MRLs used in this study.

Analyte	Method	Units	Minimum Reporting Level
UV ₂₅₄	SM 5910 B	cm ⁻¹	0.009
CHCl ₃ , BDCM, DBCM, CHBr ₃	EPA 524.2	µg/L	1 for each analyte
MCAA, DCAA, TCAA, MBAA, DBAA, TBAA, BCAA, BDCAA, DBCAA	SM 6251 B	µg/L	2, 1, 1, 1, 1, 4, 1, 1, and 2 respectively
TOX	SM 5320 B	µg Cl ⁻ /L	25

Table 12. Laboratory information.

Laboratory	Service dates	Analyses performed	Contact information
Field site	April 1998 – April 1999	Alkalinity, calcium and total hardness, pH, Cl ₂ residual, TDS, temperature, turbidity, UV ₂₅₄	Dr. Shankar Chellam Montgomery Watson 560 Herndon Pkwy #300 Herndon, VA 20170
Montgomery Watson Laboratories	April 1998 – April 1999	Bromide, Ammonia, TOC, HAA, THM, TOX	ICR ID #: CA013 Dr. Andrew Eaton 555 E. Walnut St. Pasadena, CA 91101 Phone: (626) 568-6425 Fax: (626) 568-6324

Section 4

Results and Discussion

MEMBRANE OPERATION

Clean membrane resistances and cleaning. Results from pressure-flux profiles conducted at the start of the experiments using new NTR7450 and TFC-SR membranes are given in Figures 3 and 4 respectively. The linearity of the pressure-flux profiles suggests that compaction effects were negligible for these membranes in the range of pressures tested.

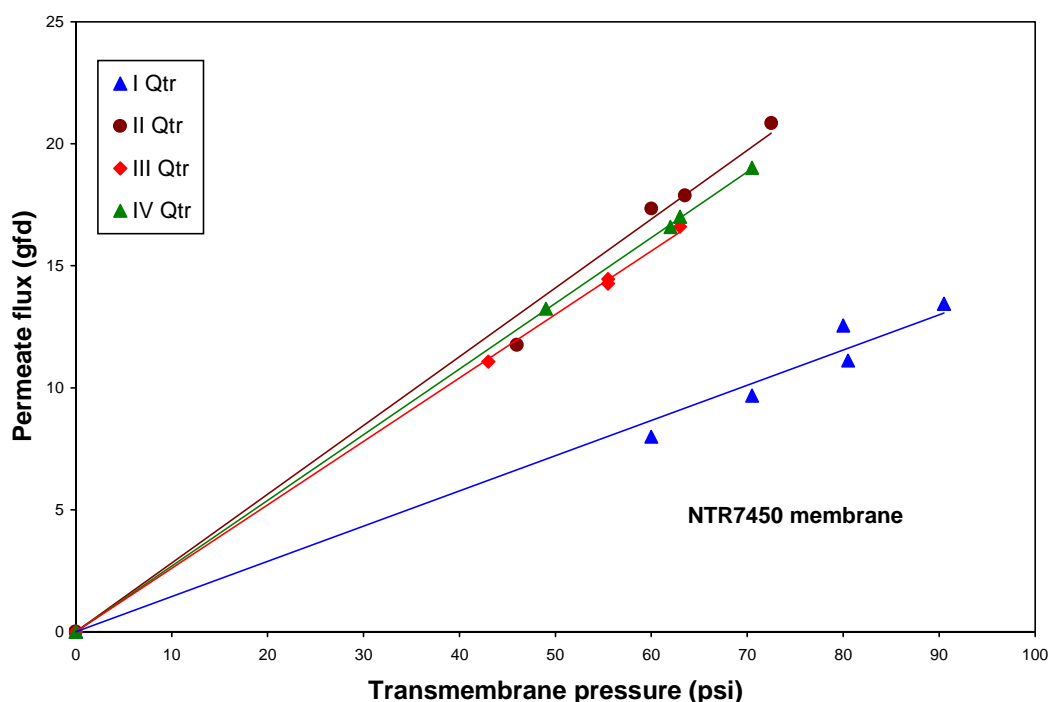


Figure 3. Resistances of the new NTR-7450 membranes used for each quarter of testing.

These data were used in Equation 1 to calculate new membrane resistances and are summarized in Table 13. Table 13 also summarizes membrane resistances calculated following chemical cleaning. New NTR7450 membrane resistance values were in the range of 5.18×10^{13} to $1.01 \times 10^{14} \text{ m}^{-1}$ with an average value of $6.58 \times 10^{13} \text{ m}^{-1}$. New R_m values for the TFC-SR membrane ranged from 3.91×10^{13} to $8.46 \times 10^{13} \text{ m}^{-1}$ with an average value of $5.46 \times 10^{13} \text{ m}^{-1}$. Table 13 shows the TFC-SR membrane resistances before and after cleaning were less than 10%. However, large increases in NTR7450 membrane resistances were sometimes observed following chemical cleaning. These data suggest that the cleaning procedure employed was effective only in removing TFC-SR membrane foulants present in the Biscayne Aquifer water. Different cleaning protocols may need to be developed for the NTR7450 membrane.

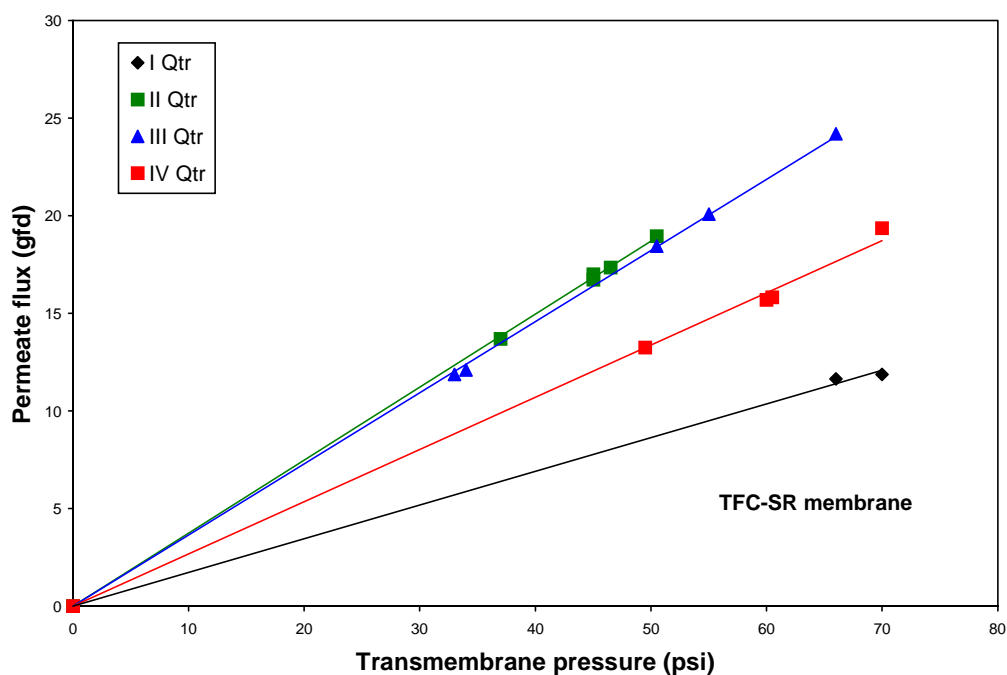


Figure 4. Resistances of the new TFC-SR membranes used for each quarter of testing.

Table 13. Summary of new membrane resistances and after membrane cleaning.^a

Qtr	Membrane	Initial R_m (m^{-1})	R_m after base cleaning (m^{-1})	R_m after acid cleaning (m^{-1})	Change (%)	Cleaning solution
I	NTR7450	1.01×10^{14} $\pm 6.8 \times 10^{12}$	1.23×10^{14} $\pm 2.0 \times 10^{12}$		22	NaOH
I	TFC-SR	8.46×10^{13} $\pm 5.1 \times 10^{12}$	8.24×10^{13} $\pm 1.3 \times 10^{12}$		-3	NaOH
II	NTR7450	5.18×10^{13} $\pm 2.8 \times 10^{11}$	6.08×10^{13} $\pm 1.3 \times 10^{12}$		17	NaOH
II	TFC-SR	3.91×10^{13} $\pm 3.0 \times 10^{11}$	3.35×10^{13} $\pm 1.1 \times 10^{12}$		-14	NaOH
III	NTR7450	5.62×10^{13} $\pm 8.0 \times 10^{11}$	7.38×10^{13} $\pm 1.5 \times 10^{12}$	5.76×10^{13} $\pm 2.4 \times 10^{12}$	2	NaOH & H_2SO_4
III	TFC-SR	4.01×10^{13} $\pm 4.0 \times 10^{11}$	4.02×10^{13} $\pm 9.0 \times 10^{11}$		0	NaOH
IV	NTR7450	5.43×10^{13} $\pm 3.0 \times 10^{11}$	6.95×10^{13} $\pm 1.1 \times 10^{12}$	9.78×10^{13} $\pm 2.7 \times 10^{12}$	80	NaOH & H_2SO_4
IV	TFC-SR	5.46×10^{13} $\pm 1.9 \times 10^{12}$	1.25×10^{14} $\pm 2.0 \times 10^{12}$	5.82×10^{13} $\pm 8.0 \times 10^{11}$	7	NaOH & H_2SO_4

^a All cleanings were conducted at a temperature of approximately 40°C.

Specific flux profiles. Normalized specific flux profiles for the length of the experiments are depicted in Figures 5 and 6 for each membrane. It was observed that both membranes experienced an initial decline in flux and a decline during the 90% recovery experiment. However, the flux appeared to stabilize for the duration of the remaining experiments at 30% and 50% recoveries (with the exception of the TFC-SR membrane during Quarter IV testing). Overall, both membranes experienced relatively stable operation throughout the duration of the experiment. The dramatic drop in TFC-SR membrane normalized specific flux during Quarter IV testing at 90% recovery suggests that foulants were irreversibly deposited. Thus, it may not be feasible to achieve this high value of feed water recovery unless advanced pretreatment (other than cartridge filtration) is employed.

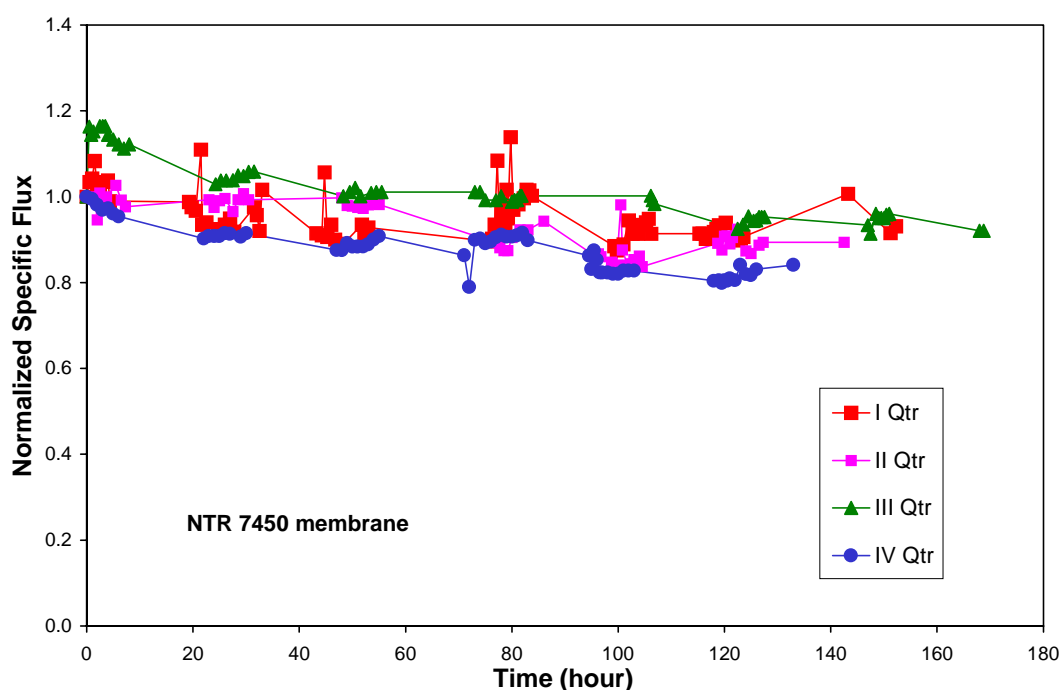


Figure 5. Normalized specific flux profiles for 4 quarters using the NTR7450 membrane

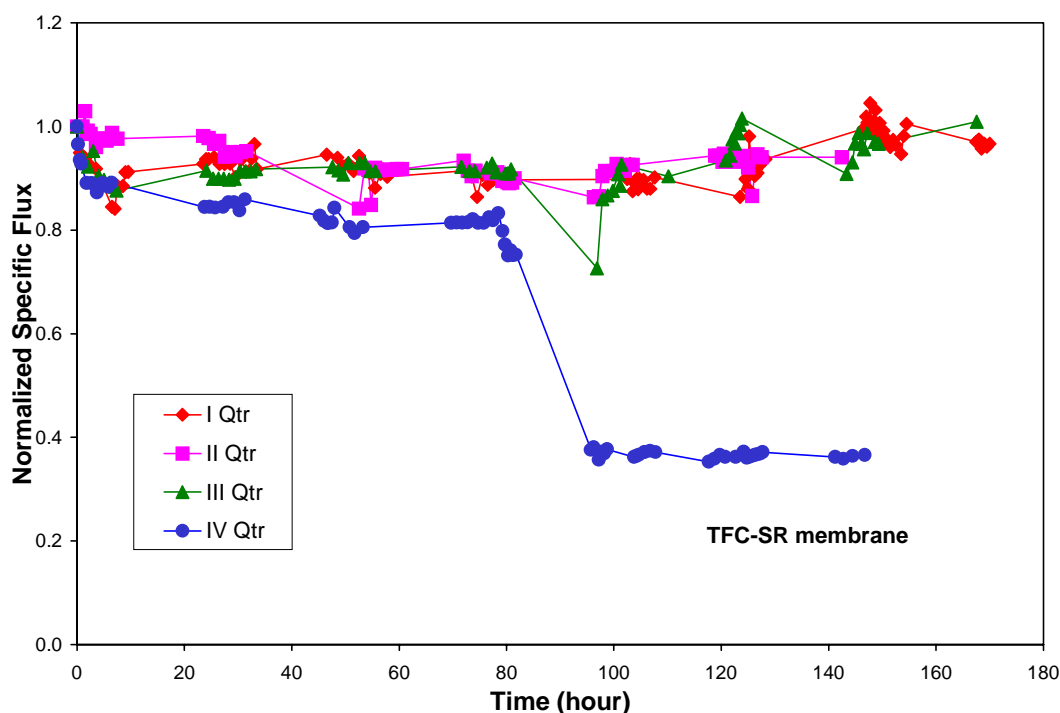


Figure 6. Normalized specific flux profiles for 4 quarters using the TFC-SR membrane

Table 14 summarizes the average permeate flux during membrane setting as well as the lowest recorded permeate flux for each experiment. It was observed that the initial permeate flux ranged from 10.3 to 17.7 gfd with an average value of 14.6 gfd. The lowest recorded permeate flux ranged from 5.8 to 14.2 gfd with an average value of 10.8 gfd. This constituted a decrease of approximately 26% in flux from the membrane setting period to the lowest recorded permeate flux, which always occurred at 90% recovery.

Table 14. Summary of worst case permeate fluxes.

Quarter	Membrane	DI water permeate flux (gfd)	Lowest permeate flux ^a (gfd)
I	NTR7450	10.34	9.9
I	TFC-SR	11.71	10.2
II	NTR7450	17.03	14.2
II	TFC-SR	17.71	14.3
III	NTR7450	13.52	10.6
III	TFC-SR	15.29	8.3
IV	NTR7450	16.34	13.0
IV	TFC-SR	15.33	5.8

^a The lowest recorded permeate flux always occurred at 90% recovery.

Fouling analysis and cleaning intervals. Fouling rate parameters obtained from Equation 2 for the RBSMT experiments conducted at 70% recovery are listed in Table 15. These data were obtained by linear regression analysis (the 95% confidence intervals are shown following the \pm sign). Better straight-line fits were obtained for the NTR7450 membrane compared to the TFC-SR membrane. The coefficient of regression ranged from 0.31 to 0.67 for the NTR7450 membrane. The corresponding cleaning intervals were obtained using Equation 3 and ranged from 86 to 365 hours. Poor straight-line fits were observed (low R^2 values) for the TFC-SR membrane. Longer chemical cleaning intervals were sometimes calculated using Equation 3. Therefore, it appears that under the conditions employed, membrane cleaning needs to be conducted every 7 days of operation at 70% recovery for the NTR7450 membrane and every 14 days of operation for the TFC-SR membrane. However, it should be understood that no attempt was made to “optimize” membrane operation or increase the duration between cleanings by pH adjustment, anti-scalent addition, or by incorporating more advanced pretreatment processes such as micro- or ultrafiltration. (It is not the intent of the ICR to determine optimum operating conditions for NF.)

Table 15. Summary of statistical fits to specific flux profiles at 70% recovery.

Quarter	Membrane	Fouling rate (gfd/h)	Initial flux (gfd)	R^2	Cleaning interval (h)*
I	NTR7450	0.0199 ± 0.0075	11.45 ± 0.28	0.46	115
II	NTR7450	0.0091 ± 0.0059	16.59 ± 0.22	0.31	365
III	NTR7450	0.0326 ± 0.0110	14.01 ± 0.45	0.55	86
IV	NTR7450	0.0233 ± 0.0061	16.20 ± 0.30	0.67	139
I	TFC-SR	0.0031 ± 0.0037	10.89 ± 0.16	0.09	376
II	TFC-SR	0.0189 ± 0.0044	16.52 ± 0.20	0.69	175
III	TFC-SR	0.0059 ± 0.0038	11.10 ± 0.18	0.19	703
IV	TFC-SR	0.0225 ± 0.0051	14.33 ± 0.23	0.72	127

* Cleaning interval was calculated assuming a 20% drop in initial flux. Some R^2 values were low (< 0.2), suggesting that these cleaning intervals should be interpreted with caution.

PERMEATE WATER QUALITY

Composite sample collection. Permeate water quality was monitored frequently to establish a “steady-state” before collecting composite permeate and concentrate samples. Upon switching recoveries for each experiment, permeate water samples were collected every 20 minutes and analyzed for TDS and UV_{254} . Once consistent readings were achieved and the experiment reached “steady-state” conditions, composite samples were collected. These composite samples were analyzed for a variety of organic and inorganic water quality parameters. SDS testing was performed on the composite permeate samples and the feed water.

Section 4 – Results and Discussion

Tables 16 and 17 provide a summary of all physical, organic and inorganic permeate water quality parameters obtained using the NTR7450 and TFC-SR membranes at 70% feed water recovery for all four quarters of testing.

Table 16. NTR7450 permeate water quality for all quarters of testing at 70% recovery.^a

Parameter	Units	Quarter I	Quarter II	Quarter III	Quarter IV
Alkalinity	mg/L as CaCO ₃	178	258	364	201
Ca hardness	mg/L as CaCO ₃	178	247	227	221
Total hardness	mg/L as CaCO ₃	210	290	235	225
TDS	mg/L	236	260	308	280
Bromide	µg/L	61	80	215	160
Ammonia	mg NH ₃ -N/L	BMRL	0.13	BMRL	BMRL
SDS Cl ₂ demand	mg/L	0.55	1.50	1.37	1.50
TOC	mg/L	0.95	2.05	1.30	1.45
TOX	µg/L	79	140	115	90.5
THM	µg/L	33.45	71.75	74.85	61.1
HAA(5)	µg/L	7.15	14.85	8.70	9.35
HAA(9)	µg/L	10.15	17.15	15.45	20.45
UV ₂₅₄	cm ⁻¹	0.020	0.048	0.029	0.028
pH	-	8.24	8.14	8.09	8.20
Turbidity	NTU	0.12	0.09	0.19	0.07

^a BMRL denotes Below Minimum Reporting Level.

Table 17. TFC-SR permeate water quality for all 4 quarters of testing at 70% recovery.^a

Parameter	Units	Quarter I	Quarter II	Quarter III	Quarter IV
Alkalinity	mg/L as CaCO ₃	165	231	189	99
Ca hardness	mg/L as CaCO ₃	157	164	125	58
Total hardness	mg/L as CaCO ₃	167	197	175	67
TDS	mg/L	190	216	149	129
Bromide	µg/L	63	77	170	78
Ammonia	mg NH ₃ -N/L	0.07	BMRL	BMRL	0.23
SDS Cl ₂ demand	mg/L	1.26	0.87	1.24	2.45
TOC	mg/L	0.5	0.50	BMRL	BMRL
TOX	µg/L	47.5	29	26	BMRL
THM	µg/L	10.45	15.15	17.7	8.45
HAA(5)	µg/L	0.6	2.55	1.85	0
HAA(9)	µg/L	0.6	2.55	3.05	0
UV ₂₅₄	cm ⁻¹	BMRL	BMRL	BMRL	BMRL
pH	-	7.97	7.86	7.86	8.60
Turbidity	NTU	0.06	0.21	0.21	0.08

^a BMRL denotes Below Minimum Reporting Level.

Total organic carbon removal. Of the two membranes tested at the bench-scale, the TFC-SR membrane achieved higher rejections of total organic carbon. This is illustrated in Figure 7. In Table 18, permeate TOC concentrations using the TFC-SR membrane are given. All concentrations were below the minimum reporting level of 0.5 mg/L with the exception of two measurements. The highest recorded permeate TOC concentration using this membrane was 0.7 mg/L. Thus, the lowest TOC removal percentage using the TFC-SR membrane was 89%. In contrast, the NTR7450 membrane achieved lower TOC removal, as shown in Table 19. The highest recorded permeate TOC concentration using this membrane was 2.5 mg/L. Therefore, the lowest TOC removal percentage using the NTR7450 membrane was 62%.

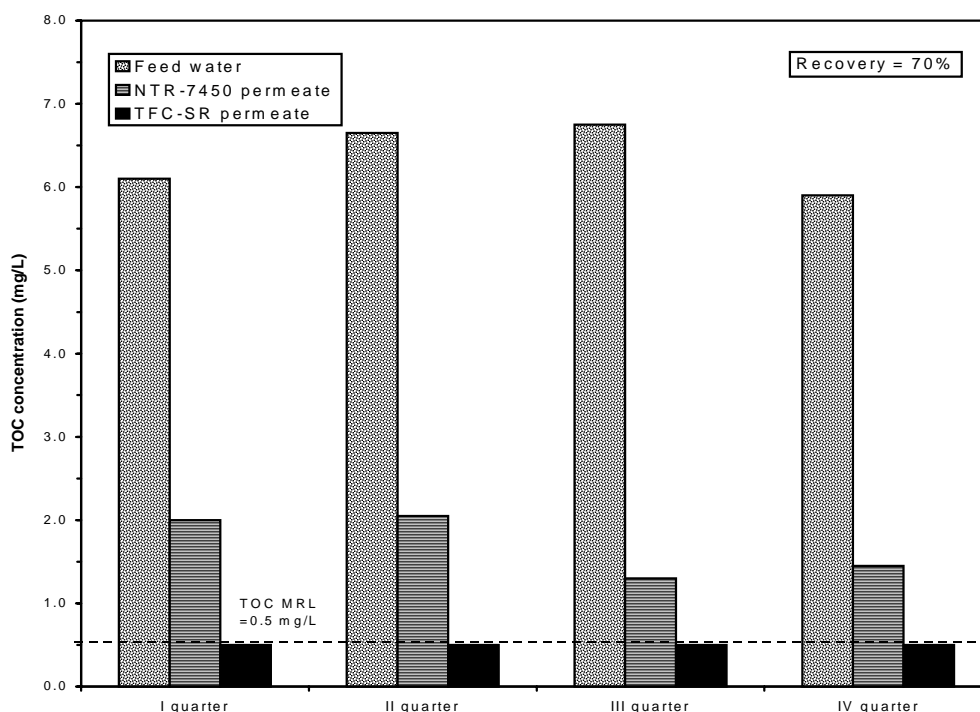


Figure 7. Comparison of TOC removal by the TFC-SR and NTR7450 membranes at 70% recovery.

Table 18. Summary of TOC concentrations in the permeate water using the TFC-SR membrane.

Recovery (%)	Quarter I		Quarter II		Quarter III		Quarter IV	
	Concentration (mg/L)	Removal (%)	Concentration (mg/L)	Removal (%)	Concentration (mg/L)	Removal (%)	Concentration (mg/L)	Removal (%)
30	BMRL ^a	> 92	0.6	91	BMRL	> 93	BMRL	> 92%
50	BMRL	> 92	BMRL	> 92	BMRL	> 93	BMRL	> 92%
70	BMRL	> 92	BMRL	> 92	BMRL	> 93	BMRL	> 92%
90	0.60	90	0.7	89	0.50	93	BMRL	> 92%

^a Calculated using 0.5 mg/L as the TOC minimum reporting level.

Table 19. Summary of TOC concentrations in the permeate water using the NTR7450 membrane.

Recovery (%)	Quarter I		Quarter II		Quarter III		Quarter IV	
	Concentration (mg/L)	Removal (%)	Concentration (mg/L)	Removal (%)	Concentration (mg/L)	Removal (%)	Concentration (mg/L)	Removal (%)
30	0.7	89	1.4	79	0.7	90	0.8	86
50	0.8	87	1.2	82	1.0	85	0.9	85
70	1.0	84	2.1	68	1.3	81	1.5	75
90	1.3	79	2.5	62	1.7	75	1.7	71

Disinfection by-product precursor removal. The highest SDSTTHM and SDSHAA(5) recorded concentrations using the TFC-SR membrane were approximately 33 µg/L and 4.3 µg/L, respectively. Compared to the TFC-SR membrane, higher concentrations of organic constituents were observed in the NTR7450 membrane permeate water. The highest SDSTTHM and SDSHAA(5) concentrations for this membrane were approximately 88 µg/L and 17 µg/L, respectively.

Under the SDS conditions employed, SDSHAA(5) concentrations in both membrane permeate waters were always below the place holder set by Stage II of the D/DBP rule (30 µg/L for HAA(5)). Further, the TFC-SR membrane also always reduced SDSTTHM precursor concentrations to below the place holder set by Stage II of the D/DBP rule (40 µg/L for TTHMs). However, on most occasions, the SDSTTHM concentrations in the NTR7450 membrane permeate were greater than 40 µg/L.

HAA(5) and TTHM precursor removals from pretreated Biscayne Aquifer water (at 70% recovery) are summarized in Figures 8 and 9, respectively.

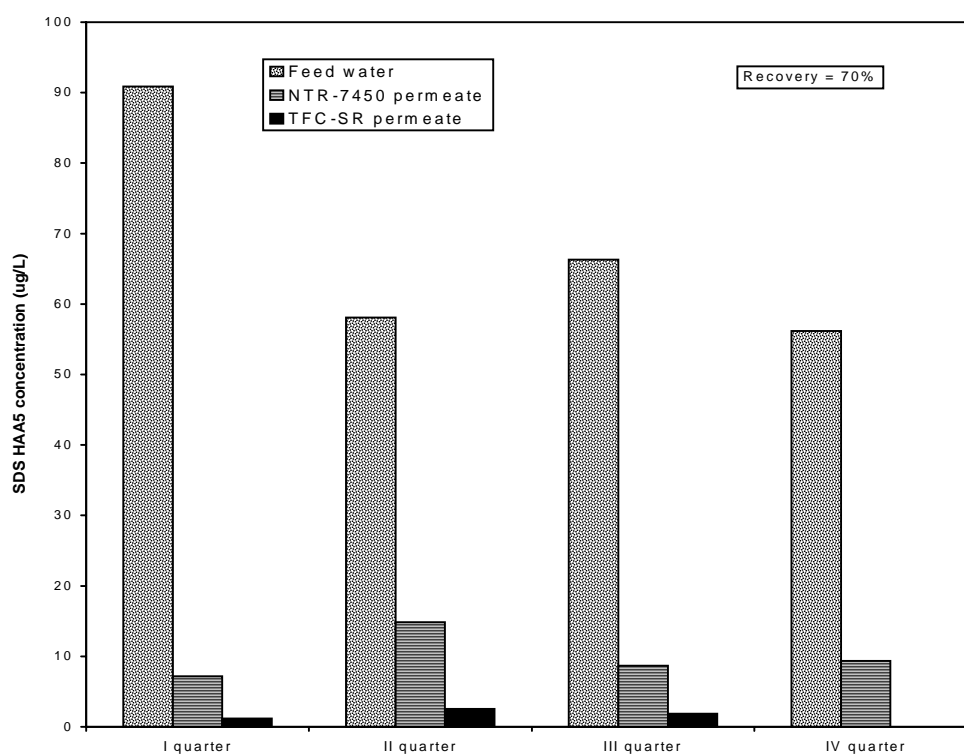


Figure 8. HAA5 precursor removals by both membranes employed in this study.

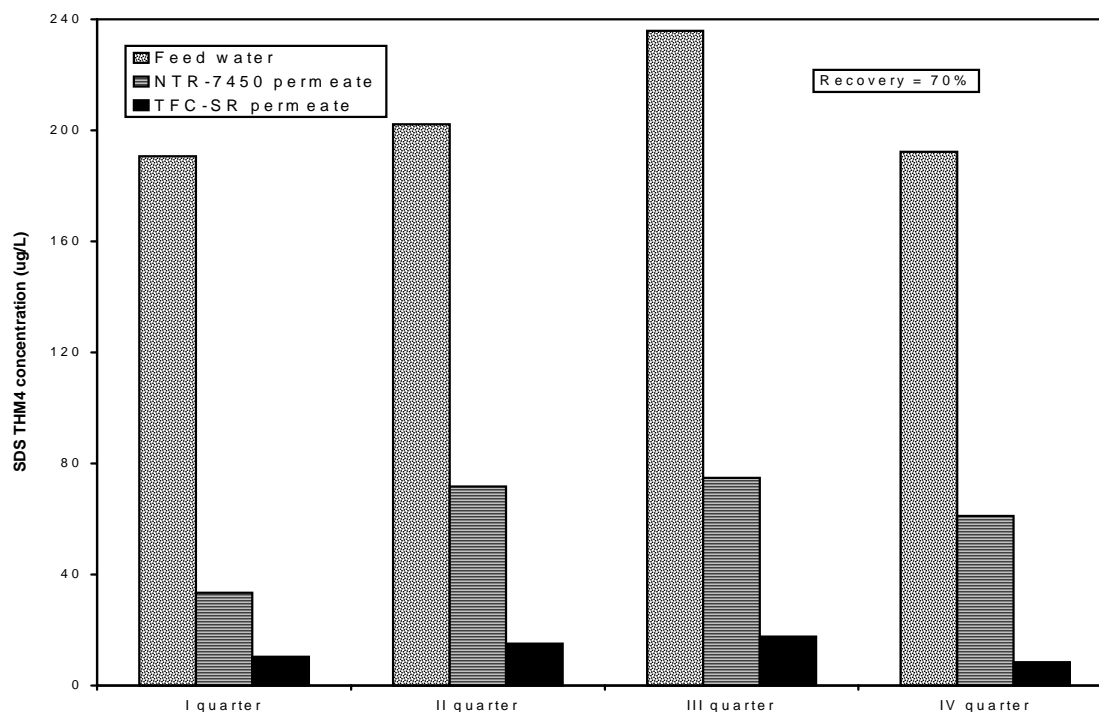


Figure 9. THM precursor removal by both membranes employed in this study.

Effect of nanofiltration on THM speciation. As described in the previous sections, the NF membranes employed achieved high TOC removals. However, these membranes achieved essentially no bromide ion rejection. It appears these membranes were completely permeable to the bromide ion. Hence, the ratio of the concentration of bromide ion concentration to TOC concentration increased dramatically in the NF permeate water compared to the NF feed water. At the same time, SDS experiments were conducted by employing similar free chlorine concentration to TOC concentration ratios in the feed and permeate waters to achieve a similar free chlorine concentration (approximately 1 mg/L) at the end of the SDS incubation period.

Because of these SDS experimental conditions, large changes in the relative concentrations of the individual THM species were detected in the NF feed and permeate waters. This phenomenon is depicted in Figure 10 by expressing each THM species as a mole fraction. As shown, chloroform was the dominant specie in the NF feed water. However, as the ratio of the concentration of bromide ion concentration to TOC concentration increased dramatically, chlorodibromo methane, dichlorobromo methane and bromoform increased in relative concentrations in the NF permeate water.

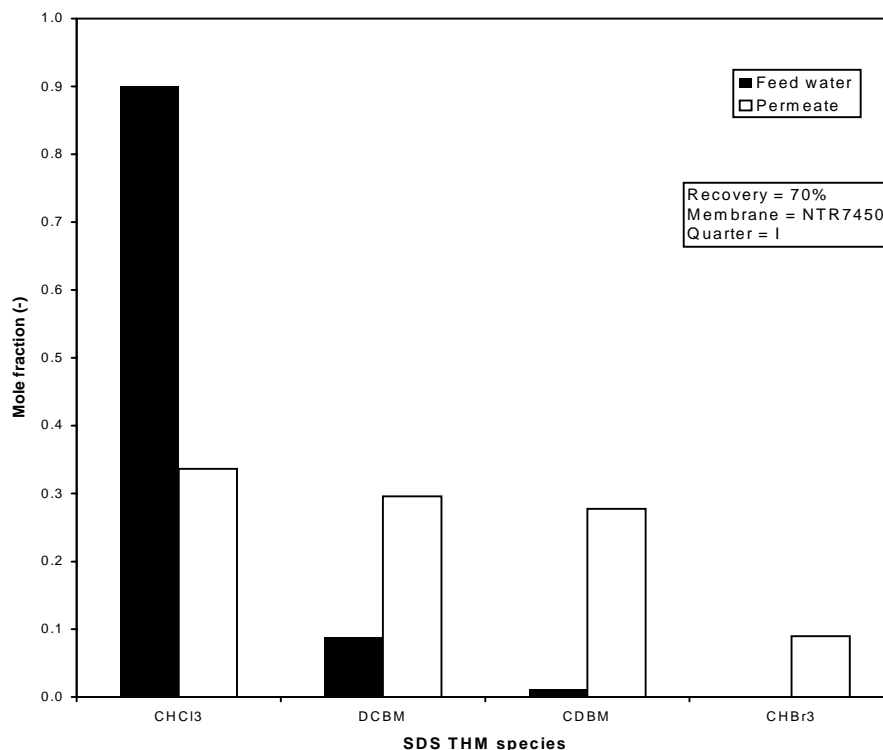


Figure 10. Changes in THM speciation expressed as a mole fraction upon nanofiltration (data from Quarter I experiments at 70% feed water recovery and NTR-7450 membrane).

Inorganics removal. Although the NTR7450 membrane achieved only approximately 20% TDS rejection, the TFC-SR membrane was able to remove approximately 53% TDS from the Biscayne Aquifer water. In addition, the TFC-SR membrane removed an average of approximately 45% of total hardness (at 70% recovery). The NTR7450 membrane removed only 15% of total hardness from the membrane feed water (at 70% recovery). None of the membranes utilized in this study were able to achieve substantial removal of the bromide ion, resulting in large changes in trihalomethane and haloacetic acid speciation between the permeate water and the feed water.

Effect of feed water recovery on rejection. The concentrations of a variety of inorganic and organic permeate water quality parameters were dependent on feed water recovery for both membranes. Table 20 summarizes the effects of recovery on the rejection of selected water quality parameters by the NTR7450 membrane. In Table 21, these data are given for the TCR-SR membrane. These data were obtained by averaging data from all quarters of testing. The median and range for each parameter are also listed. In general, permeate concentrations increased with increasing feed water recovery, suggesting that the transport of many water quality constituents across these polymeric membranes is controlled by diffusion.

Figure 11 depicts the effects of feed water recovery on permeate TDS concentrations and TDS removal using the NTR7450 and the TFC-SR membranes for the first quarter of testing. It can be observed that permeate TDS concentrations increased exponentially

with feed water recovery (R_f) for both membranes. The following empirical fits were obtained using the first quarter data:

TFC-SR membrane: Permeate TDS (mg/L) = $1,728 \exp(0.0040R_f)$ ($R^2 = 0.88$)

NTR7450 membrane: Permeate TDS (mg/L) = $237 \exp(0.0015R_f)$ ($R^2 = 0.87$)

Empirical correlations relating other organic and inorganic permeate water quality parameters to feed water recovery can be derived using linear regression techniques if necessary.

Table 20. Effect of feed water recovery on rejection of selected water quality parameters using the NTR7450 membrane.

Parameter	Units	30% recovery		50% recovery		70% recovery		90% recovery	
		Median	Range	Median	Range	Median	Range	Median	Range
Ca hardness	mg/L as CaCO ₃	206	196-226	216	204-236	222	176-254	246	238-314
Total hardness	mg/L as CaCO ₃	221	214-268	236	214-278	228	196-294	271	246-332
Alkalinity	mg/L as CaCO ₃	205	186-318	238	188-336	212	175-370	290	208-432
TDS	mg/L	257	226-278	270	228-287	273	227-309	283	247-325
Bromide	mg/L	113	56-180	115.5	58-180	160	60-240	122.5	63-190
Ammonia	mg NH ₃ -N/L	BMRL	BMRL	0.06	BMRL-0.06	0.13	BMRL-0.13	0.08	BMRL-0.09
SDS Cl ₂ demand	mg/L	0.97	0.57-1.47	1.13	0.5-1.53	1.44	0.55-1.5	1.52	1.15-1.9
TOC	mg/L	0.8	0.7-1.4	1.0	0.8-1.2	1.4	0.9-2.2	1.7	1.3-2.5
SDSTOX	µg/L	64.5	49-84	76.5	67-100	99	74-150	115	95-180
SDSTTHM	µg/L	41.5	24.2-53.9	52.5	27.5-78.4	64.3	32.4-81.0	66.5	42-88
SDSHAA(5)	µg/L	5.3	4.1-9.0	7.4	5.0-12.5	9.0	6.5-14.9	13.1	12.0-16.7
SDSHAA(9)	µg/L	12.8	7.5-17	16.9	8.8-21	20.5	11.1-25.3	26.0	23.4-28.3
UV ₂₅₄	cm ⁻¹	0.011	0.010-0.028	0.015	0.014-0.029	0.029	0.018-0.048	0.033	0.027-0.070

Refer to Table 12 for minimum reporting levels of water quality parameters.

Table 21. Effect of feed water recovery on rejection of selected water quality parameters using the TFC-SR membrane.

Parameter	Units	30% recovery		50% recovery		70% recovery		90% recovery	
		Median	Range	Median	Range	Median	Range	Median	Range
Ca hardness	mg/L as CaCO ₃	144	52-148	144	60-162	154	58-175	209	96-268
Total hardness	mg/L as CaCO ₃	159	60-162	161	66-180	167	64-226	220	104-290
Alkalinity	mg/L as CaCO ₃	157	90-168	174	100-188	174	96-232	220	118-316
TDS	mg/L	205	121-229	206	131-260	202	128-250	238	159-299
Bromide	mg/L	75.5	57-160	77.5	59-170	77.5	63-170	91.5	65-190
Ammonia	mg NH ₃ -N/L	0.12	BMRL-0.12	0.18	BMRL-0.18	0.15	BMRL-0.23	0.15	BMRL-0.15
SDS Cl ₂ demand	mg/L	0.92	0.31-1.9	0.80	0.43-2.02	1.25	0.87-2.45	1.07	0.4-2.05
TOC	mg/L	0.39	0.190.60	0.31	0.21-0.36	0.42	0.3-0.5	0.55	0.27-0.70
SDSTOX	µg/L	33	BMRL-40	30.5	BMRL-32	29	BMRL-58	38	BMRL-44
SDSTTHM	µg/L	10.55	8.1-13	11.8	7.2-23	13.1	8.2-18	22.7	14-33
SDSHAA(5)	µg/L	1	BMRL-1.2	1.3	BMRL-1.8	1.85	BMRL-2.8	2.45	1.2-4.3
SDSHAA(9)	µg/L	1	BMRL-1.2	1.3	BMRL-1.8	2.1	BMRL-3	3.65	1.2-6.7
UV ₂₅₄	cm ⁻¹	BMRL	BMRL	BMRL	BMRL	BMRL	BMRL	BMRL	BMRL-0.009

Refer to Table 12 for minimum reporting levels of water quality parameters.

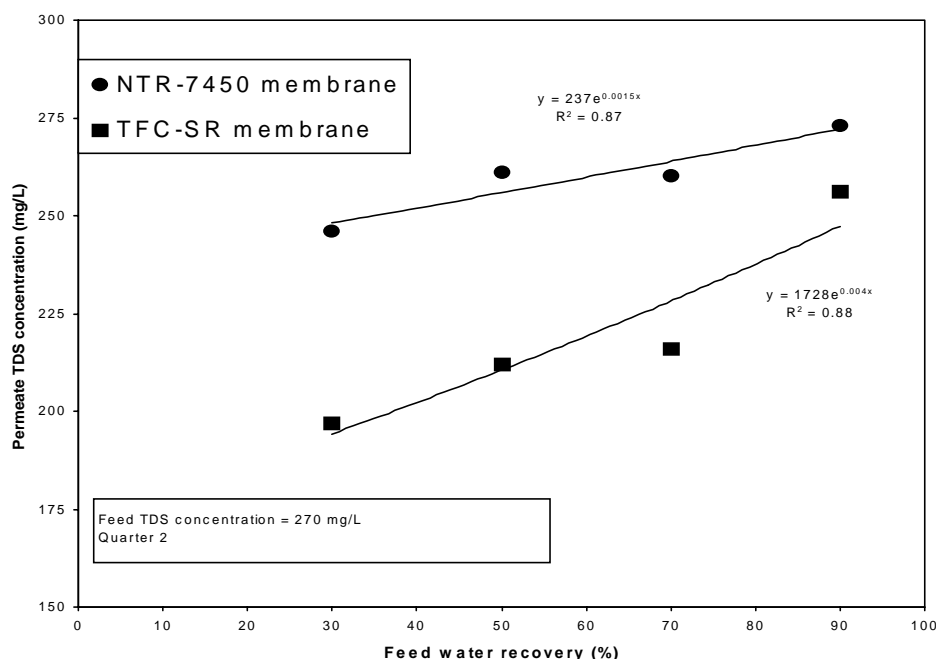


Figure 11. Effect of feed water recovery on permeate TDS concentration.

Permeate and feed water blending. Because of the high rejection capabilities of some nanofiltration membranes employed in water treatment, the concentrations of many water quality parameters in permeate waters are often much lower than regulatory maximum contaminant levels. This may allow the possibility of blending NF feed water with NF permeate, thereby reducing membrane area and/or energy requirements for the full-scale membrane plant.

It should be noted, however, that the concentrations of THM and HAA9 precursor materials in the NF feed water (average feed water SDSTTHM concentration = 205 µg/L, average feed water SDSHAA9 concentration = 86 µg/L) were relatively high. If free chlorine is employed as the disinfectant, blending is not expected to be a feasible alternative when Stage II concentrations of the Disinfectant/Disinfection By-Products Rule is considered.

Problems encountered. In general, ICR experiments conducted for the District 2A WTP were executed smoothly. Waste flow rates occasionally dropped by approximately 2 to 8% when the RBSMT apparatus was left unattended during overnight operation, particularly during the 90% feed water recovery experiment. In addition, it was not always possible to accurately buffer the SDS samples at a pH equal to 9.0.

Section 5

QA/QC Summary

Laboratory analyses. For this study, samples were shipped to Montgomery Watson Laboratories in Pasadena, California, an ICR certified laboratory. The tables presented in Section 5 summarize the QA/QC information provided by Montgomery Watson Laboratories in the format required by the ICR.

Quality assurance and quality control (QA/QC) summary data from Montgomery Watson Laboratories reflects ICR samples for Broward County and other bench-scale test utilities. These data are presented in support of an agreement with Mr. Steve Allegeier, ICR Technical Coordinator.

ICR RBSMT data collection spreadsheets. To ensure the integrity of the data collected and reported in this treatment study, we have already undergone one preliminary review of the ICR Treatment Study Data Collection Spreadsheets by the United States Environmental Protection Agency (USEPA). The comments generated by EPA during this preliminary review process are given in Appendix B. The Data Collection Spreadsheets reflect these comments. Detailed responses to these comments are described below:

Global Comments Applicable to Both Membrane Worksheets:

1. Missing information in Field 1 has been provided.
2. Cost of an 8x40 TFC-SR membrane element is not available from manufacturer.
3. No water quality parameters (including potential foulants) were measured prior to pretreatment because they were not required under the ICR.
4. Cartridge filtration was the only membrane pretreatment employed.
5. Cost data have been provided.

TFC-SR Membrane 1st Quarter:

1. The relatively low MTC_w values were verified and found to be correct. No changes made.
2. Feed bromide concentrations and HAA concentrations were verified and found to be as reported by Montgomery Watson Laboratories. No changes were made.
3. Alkalinity, TDS, total and calcium hardness values were all verified and found to be correct. No changes made.
4. TDS concentrations at various recoveries were verified and found to be correct. No changes made.

TFC-SR Membrane 2nd Quarter:

1. Feed TOX, THM, and HAA concentrations were verified and found to be as reported by Montgomery Watson Laboratories. No changes were made.
2. Alkalinity, total hardness, and calcium hardness values were verified and found to be correct. No changes were made.

TFC-SR Membrane 3rd Quarter:

1. Missing date and time for the concentrate sample (run 3) has been provided.
2. Feed TOX, THM, and HAA concentrations were verified and found to be as reported by Montgomery Watson Laboratories. No changes were made.
3. All water quality parameters for the 70% and 90% recovery experiments were verified and found to be correct. No changes were made.
4. THM concentrations at 70% recovery were verified and found to be correct. No changes made.

TFC-SR Membrane 4th Quarter:

1. Missing time for the concentrate sample (run 1) has been provided.
2. Pretreatment information has been entered.
3. Major drop in MTC_w was probably caused by membrane fouling. All operational data were verified and found to be correct. No changes made.
4. All TDS values were verified and found to be correct. No changes made. It is possible that fouling resulted in changes in TDS rejection.
5. Feed TCAA concentrations were verified and found to be correct. No changes made.
6. All water quality parameters for the 90% recovery experiment were verified and found to be correct. No changes made.
7. It is possible that the major fouling that occurred during this quarter resulted in changes in rejection characteristics compared to the previous quarters of testing.

NTR7450 Membrane 1st Quarter:

1. The relatively low MTC_w values were verified and found to be correct. No changes made.
2. Total hardness values were verified and found to be correct. No changes made.

NTR7450 Membrane 2nd Quarter:

1. Feed TOX, THM, and HAA concentrations were verified and found to be as reported by Montgomery Watson Laboratories. No changes were made.
2. All water quality parameters for the 90% recovery experiment were verified and found to be correct. No changes made.

3. THM4 and CHCl_3 concentrations were verified and found to be correct. TDS, alkalinity, and bromide concentrations at 70% recovery were also verified and found to be correct. No changes were made.

NTR7450 Membrane 3rd Quarter:

1. Concentrate sampling date and time for run 1 has been provided.
2. Sampling time for permeate and concentrate waters have been corrected for run 2.
3. Bromide concentration for 70% recovery was verified and found to be correct. No change was made.

NTR7450 Membrane 4th Quarter:

1. The pH meter malfunctioned during these experiments. Therefore, no pH values were measured.
2. Feed TCAA concentrations were verified and found to be correct. No change made.
3. TOC concentrations verified and found to be correct. No change made.

Section 6

Acknowledgments

The laboratory testing and analysis component of this ICR treatment study would not have been completed without the assistance of Jennifer Abrajano, Dan Bush, Andy Eaton, Jim Hein, and Jason Radgowski. Dr. Dan Askenaizer and David Wilkes provided valuable comments during review of this summary report. Jennifer McMahon served as the project manager.

Jerry Baker of the Broward County Office of Environmental Services assisted in sampling efforts at the District 2A Plant. In addition, he provided background data required for the completion of ICR treatment study spreadsheets.

Appendix A

Appendix B