

ICR Treatment Study Summary Report

Evaluation of Cross-Flow Micro-filtration Pretreatment and A Single Element Bench-scale Test Using A Desal DS5 Membrane Element For Compliance of the Information Collection Rule's Grandfather of A Previously Conducted Study

Information From USEPA Project Report # EPA/600/SR-92/023, April 1992.
Study conducted during the period of August 4, 1990 through January 27, 1991

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**South Water Treatment Plant,
ICR # - 283**

Attachments: 1 diskette containing the *Data Collection Spreadsheets (283MFDS5)* and
Summary Report

Section I: Conclusions and Recommendations

Conclusions

1. Several different membranes were able to produce a DBPFP below 0.10 mg/L as Cl^- during membrane selection at the surface water site. The DS5 and A15s were selected for further study because they were the most productive membranes, having the highest MTCs that reduced the DBPFP below 0.10 mg/L as Cl^- .
2. Pretreatment studies at the surface water site clearly demonstrated that conventional nanofiltration pretreatment, scaling control and prefiltration, or sand filtration in addition to conventional pretreatment were not adequate to enable the nanofilters to consistently produce water. Pretreatment studies of the surface water demonstrated that either alum coagulation, microfiltration or GAC filtration greatly reduced the fouling capacity of the surface water. Crossflow microfiltration followed by GAC filtration and alum coagulation was the indicated order of the pretreatment processes capable of reducing the rate of nanofilter MTC decline.
3. Long term operation of six different nanofiltration systems incorporating three different pretreatment systems and two different membranes demonstrated that any of the surface water site nanofiltration systems were capable of achieving consistent production for 16,770.8 of 17,994.5 hours or in excess of 93% of the operational time.
4. Long term operation at the surface water site demonstrated that any of six different nanofiltration systems consistently removed more than 98% of the raw water DBPFP and averaged 22 ug/L as Cl^- in the permeate stream.
5. The ratio of the TOXFP to the DBPFP, THMFP and HAFP was statistically equivalent for the raw, feed and permeate streams for each system at the surface water site. The distribution of brominated species was greater in the permeate stream than in the raw water or feed stream for the surface water systems. The concentration of chlorodibromomethane and dibromoacetic acid was typically the same or greater in the permeate stream, as opposed to the raw water and feed stream. DBPFP accounted for 37% of the TOXFP in the surface water site samples. The HAFP to THMFP ratio was equal in the raw, feed and permeate streams in all systems at the surface water site from October to February. The HAFP exceeded the THMFP, 4/3 ratio, at the surface water site from February to June.
6. The average NPDOC reduction by alum coagulation, microfiltration and GAC filtration was 66, 7 and 21% during the surface water site nanofiltration study.
7. The average MTC decline rates produced by pretreatment with alum coagulation, microfiltration and GAC filtration were $1.55\text{E}^{-4}/\text{d}^2$, $1.88\text{E}^{-4}/\text{d}^2$ and $4.14\text{E}^{-4}/\text{d}^2$. The average MTC decline rates produced by the DS5 and the A15s nanofilters were $1.63\text{E}^{-4}/\text{d}^2$ and $4.06\text{E}^{-4}/\text{d}^2$. Based on MTC decline rates, alum coagulation followed by the DS5 was the most effective pretreatment process and nanofilter combination.
8. The removal of DBP precursors by nanofiltration at the surface water site was independent of pressure and recovery variations and was determined to be sieving. DBP precursor rejection could feasibly be increased by a tighter membrane but would not be decreased by lower recovery or pressure.

9. There was a statistically significant difference between the THMs found using EPA methods 501.2 and 551 in the same samples from the surface water and groundwater sites. THM concentrations determined using EPA method 551 were found to be 80 % of the THM concentrations determined using the EPA method 501.2.

Recommendations

1. Two new pretreatment processes that should be investigated for fouling reduction from highly organic surface waters are bank filtration varying soil type and slow sand filtration.
2. Research involving the surface/liquid interface between the feed stream and membrane surface should be conducted to determine the effect of different membrane materials and feed stream chemical environments on mass transfer mechanisms in membrane processes. It is feasible that rejection of DBP precursors could be increased if a higher feed stream pH could be tolerated. Any ionization of DBP precursors would seemingly increase precursor rejection.
3. Additional research should be conducted on pretreatment processes such as coagulation, GAC filtration and microfiltration for fouling reduction in membrane processes. This and other works have demonstrated that groundwater have a fouling capacity that is several orders of magnitude less than surface waters with the same NPDOC concentrations. It is feasible that very low surface loading rates in filtration processes would reduce the fouling capacity of surface waters, since that is the natural process that recharges groundwater. Shallow well withdrawal from surface water sites is another feasible means of fouling reduction in surface waters.
4. The parallel and series combination of nanofiltration with other water treatment processes should be investigated in order to determine optimum methods of meeting DBP control levels. This research should include bypassing, blending, and series combination of different processes including nanofiltration.
5. Research should be conducted on the improvement of fouling indices that can quickly determine the fouling capacity of waters on membrane processes with pore sizes of 0.01 micron or less. Correlation of the rates of microfilter fouling to water quality, operating pressures and microfilter materials and devices should be determined using different indices and then the indices should be correlated to fouling in pilot or actual plant operation.
6. Model development should be pursued that investigates the effect of horizontal feed stream velocity, vertical feed stream velocity, recovery, feed stream water quality and pretreatment processes control parameters on mass transfer in membrane processes.
7. The effect of cleaning and feed water quality on the mass transfer characteristics of solutes and water on membranes of different materials should be investigated.
8. The comparative cost for construction and operation of membrane processes should be well documented by development of databases for engineering estimates and field verification of these estimates using newly constructed membrane plants.
9. Information regarding the comparative ease or difficulty of operation of water treatment plants using membrane processes should be developed. Membrane processes are more

automated and less subject to variation than conventional water treatment processes and should be significantly easier to operate and maintain, especially for small systems.

10. The effect of the NPDOC concentration in water should be investigated regarding chlorine demand, DBP formation, corrosion, bacterial integrity, and taste and odor in a distribution system. Adverse or beneficial effects on the system of interrelated water quality parameters should be investigated for finished waters from membrane systems. Additional benefits could justify the higher cost of membrane systems relative to conventional treatment.
11. The cost and associated water quality of concentrate disposal needs to be modeled and investigated. Concentrates from nanofiltration processes will not have a TDS concentration over 2000 mg/L and will not have the same adverse effects as concentrates from reverse osmosis processes. Testing methods for the effect of these concentrates should be developed so they can be disposed of within the regulatory environment.
12. A model needs to be developed that would incorporate the normal loss of productivity of membrane MTC to predict membrane replacement. The model should consider water quality, water production, power cost, element and system maintenance, as well as rate of MTC decline.
13. A comparison should be made involving several laboratories on THMFP using different waters analyzed by EPA methods 501.2 and 551. Any differences in this comparison should be fully explained or investigated through appropriate research.

Section II: Background Information

Introduction

The City of Melbourne, Florida utilizes a surface water source with an average TOC above 20 mg/L and serves a combined population of approximately 140,000. In accordance with the ICR the City of Melbourne must conduct pilot studies or grandfather an existing study. The attached forms, computer files and supporting documentation are from an existing membrane study submitted in compliance with the ICR grandfather clause.

The information contained within this report was summarized from membrane pilot studies conducted by the University of Central Florida for the USEPA Risk Reduction Engineering Laboratory, Cincinnati, OH. The results of these studies were published by USEPA in April of 1992 as EPA/600/SR-92/023 and was titled "*Reduction of Disinfection By-Product Precursors by Nanofiltration*". These studies were conducted with the direct objective of using a surface water source with advanced pretreatment and membrane technology to evaluate process capability for compliance with the disinfection by-product regulations proposed at the time. The studies were conducted on the source and finished waters to the South Water Treatment Plant (ICR-ID No. 283).

The City of Melbourne currently has two water treatment facilities. The South Water Treatment Plant treats approximately 10 MGD of surface water from Lake Washington using alum coagulation, flocculation, sedimentation, and PAC followed by filtration with sand and anthracite. The second facility, the RO Water Treatment Plant, is located adjacent to the surface water plant but uses a brackish groundwater as the source for its membrane process. The finished water from both facilities is disinfected using monochloramine prior to blending, storage and distribution.

Treatment Plant Description

The following section will describe the existing treatment process used by the South Water Treatment Plant (WTP). Figure 1 presents the process schematic of the WTP.

The membrane studies were conducted at the South WTP located northwest of the City of Melbourne, Florida, and adjacent to Lake Washington. The WTP uses the lake which is connected to the St. Johns River as its raw water source. The WTP uses alum coagulation followed by flocculation with the addition of polymer, sand filtration, and disinfection using chloramination. In addition it uses powdered activated carbon for odor control and lime for pH stabilization. The CFMF-DS5 study used the raw water from the WTP intake as the feed water to the micro-filtration unit.

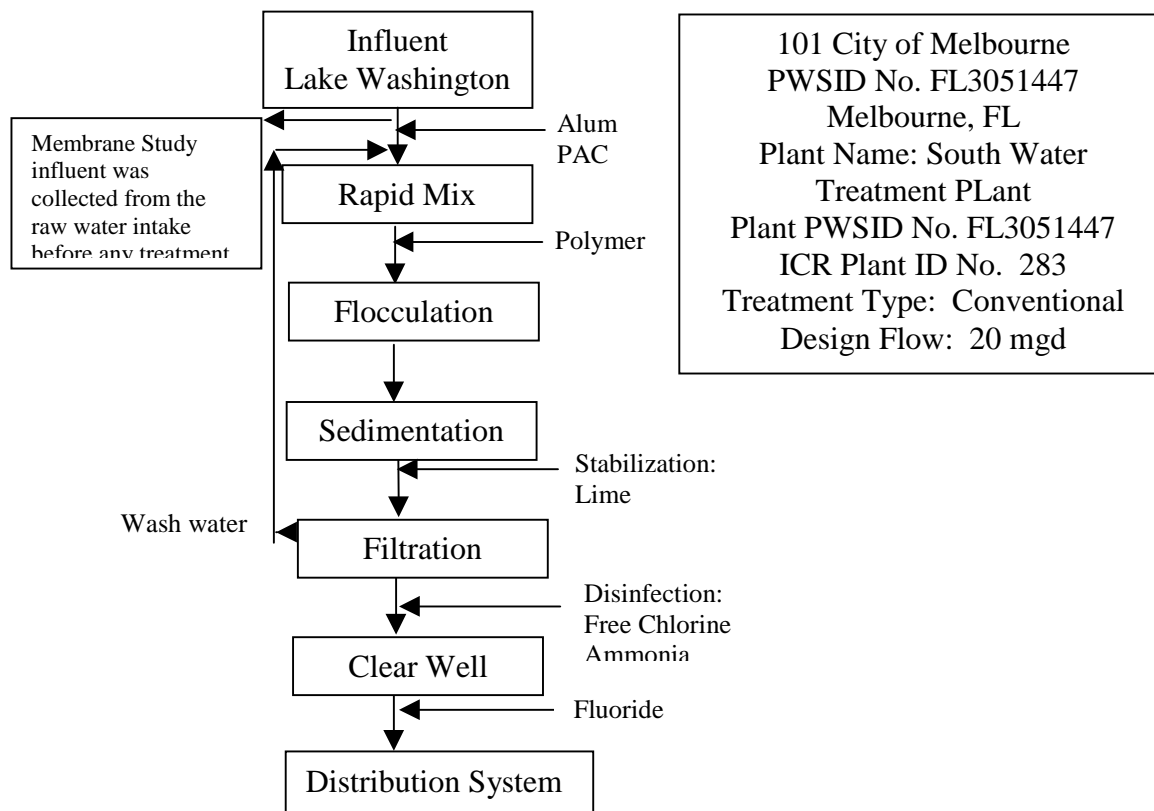


Figure 1: Process Schematic For The South WTP

Table 1 presents the South WTP process design and chemical addition parameters that were also documented in report forms A2 and A3 from the *ICR Sampling Manual* and submitted for the *ICR Water Utility Database System*. The period of time for the information reported in Table 1 was from 7/28/97 to 12/31/98.

The major challenge facing the utility will be to meet both the Surface Water Treatment and DBP Rules. It will take a carefully planned and concerted effort to reduce the DBP concentrations and maintain effective disinfection of the potable water system. The system currently blends with a brackish water reverse osmosis (RO) plant and uses chloramination to reduce the DBP level, which is mainly contributed by the South WTP. The current THM4 and HAA6 results of ICR monitoring indicate that they can meet phase I standards of 80/60; however, they may exceed the proposed phase II standards of 40/30 ug/L. Future plans provide for the expansion of the RO plant, however increases in disinfection “CT” requirements could off-set the DBP reduction benefits derived from the increased blending of the higher quality RO water. It is anticipated that advanced treatment processes for the reduction of the surface WTP finished water TOC and/or alternative disinfection will need further investigation to address anticipated “CT” and DBP requirements of proposed regulations.

Table 1: Process Design and Chemical Addition Parameters

Unit Process	Process Description	Quantity
Plant Information	Treatment Plant Name	South Water Treatment Plant
	ICR Treatment Plant ID	283
	Treatment Plant PWS ID	FL3051447
	Treatment Plant Category	Conventional
	State Approved Plant Capacity	16.5 MGD
	Historical Min. Water Temp.	8.0 deg. C
	Installed Sludge Handling Cap.	500,000 gpd
	Blending Indicator	N
Water Source	Water Source Name	Lake Washington-1
	Water Resource Type	Reservoir/lake
	Average Residence Time	13 days
	Intake Name	South Raw Water Intake
	Water Shed Control	Yes
	Hydrologic Unit Code	Lat. +28°8'46" (deg.,min.,sec.)
		Long. -80°44'14" (deg.,min.,sec.)
	Water Source Name	Lake Washington-2
	Water Resource Type	Reservoir/lake
	Average Residence Time	13 days
	Intake Name	North Raw Water Intake
	Water Shed Control	Yes
	Hydrologic Unit Code	Lat. +28°9'1" (deg.,min.,sec.)
		Long. -80°44'10" (deg.,min.,sec.)
Wash Water Return	Wash Water Treated	No
	24 hour Average Flow	0.82 MGD
Coagulation	Alum Dose*	126.5 mg/L Al ₂ (SO ₄) ₃ *14H ₂ O
	Powdered Activated Carbon*	24.1 mg/L
Clarification Solids Contact Unit	Polymer LC-211*	0.1 mg/L
	Surface Area	26,582 ft ²
	Volume	2,906,224 gal.
Stabilization	Calcium Oxide	19.4 mg/L CaO
	Surface Area	4,000 ft ²
	Volume	412,000 gal.
Filters	Surface Area	5,760 ft ²
	Liquid Volume	292,976 gal.
	Total Media Depth	328 in.
	Media Type	TRIM
	Min. Water Depth to Media	3.5 ft
	Top of media to top BW trough	3.0 ft
Disinfection	Chlorine Gas	11.10 mg/L Cl ₂
	Anhydrous Ammonia	3.00 NH ₃ A
Clear Well	Surface Area	8 665 ft ²
	Liquid Volume	741,500 gal.
	Min. Liquid Volume	246,076 gal
	Baffling Type	UN
	Short Circuiting Factor	N/A
	Covered Index Code	Y
	Hydrofluorosilic Acid	1.34 mg/L Na ₂ SiF ₆
	Calcium Oxide	19.3 mg/L CaO

Summary of Source and Finished Water Quality

The following section will present, in tabular form, the source and finished water quality of the South WTP for the reporting period of July 1990 to June 1991. In addition, it will report a summary of the source and finished water monitoring conducted for the ICR with respect to DBPs. Table 2 presents the source water and Table 3 presents the finished water monitoring conducted by the utility during the period of time the pilot study was conducted. Table 4 presents information that was collected for ICR monitoring between October 1997 and September 1998 and represents current conditions of DBP formation. The samples were collected from the “influent” to the South WTP and at the entry to the distribution system after blending of the RO and surface WTP finished waters (“finished”). The “Distribution System” THM4 and HAA6 results were collected at the farthest ICR sample location.

The water quality shows that the source has yearly average TOC concentrations above 27 mg/L. The finished water from the South WTP in 1990 before the RO plant was built removed approximately 70 % of the TOC to an average of 8 mg/L. Table 4 shows that blending with the RO plant has reduced the TOC of the finished water to below 5 mg/L. DBP results indicate that the THM4 and HAA6 concentration can currently meet the phase I levels of 80/60 ug/L, but may not meet the proposed phase II limits of 40/30 ug/L. In addition, bromide concentrations measured in the source water could eliminate ozone as an alternative option for disinfection.

Table 2: Source Water Quality Summary For South WTP (1990-91)

Water Quality Parameter	Average Yearly Concentration	Standard Deviation	Maximum Yearly Average	Minimum Yearly Average
Temperature (°C)	24.5	4.32	32.8	13.3
PH	7.98	0.06	8.38	7.57
Turbidity (ntu)	45.6	4.3	564	38.4
Alkalinity (mg/L CaCO ₃)	69	1.8	75	64
Calcium Hardness (mg/L CaCO ₃)	104	14	144	88
Total Hardness (mg/L CaCO ₃)	137	19	192	113
NPDOC (mg/L C)	27.7	3.06	36.3	19.6

Table 3: Finished Water Quality Summary For The South WTP (1990-91)

Water Quality Parameter	Average Yearly Concentration	Standard Deviation	Maximum Yearly Average	Minimum Yearly Average
Temperature (°C)	24.9	4.3	32.8	13.3
PH	7.84	0.04	8.13	7.60
Turbidity (ntu)	0.24	0.10	0.96	0.10
TOC (mg/L C)	8.24	0.31	10.9	6.6
THM	15	2	11	20

Table 4: Current Source and Distribution Water Quality (1997-98)

Water Quality Parameter	Average Yearly Concentration	Standard Deviation	Maximum Yearly Average	Minimum Yearly Average
<u>Influent</u>				
Bromide(mg/L)	0.19	0.12	0.44	0.035
UV-254 (cm ⁻¹)	0.770	0.108	0.922	0.544
TOC (mg/L C)	21.2	3.6	27	11
<u>Finished</u>				
PH	8.0	0.3	8.7	7.6
UV-254 (cm ⁻¹)	0.092	0.015	0.117	0.066
TOC (mg/L C)	4.2	0.9	6.1	2.7
THM4 (µg/L)	25.2	14.4	48	11.1
HAA6 (µg/L)	21.3	8.0	30.6	13.6
<u>Distribution System</u>				
Distribution System THM4 (µg/L)	42.3	18.6	69.5	22.8
Distribution System HAA6 (µg/L)	15.4	10.1	30.7	3.5

Section III: Methods and Materials

Integrated Membrane System

A flow diagram of the CFMF-DS5 system, sampling locations and points for monitoring flow and pressure is shown in Figure 2. The membrane treatment study was conducted using the raw surface water supplied to South WTP. From a tap in the raw water collection main, prior to entry into the plant the water was pumped to the membrane pilot unit.

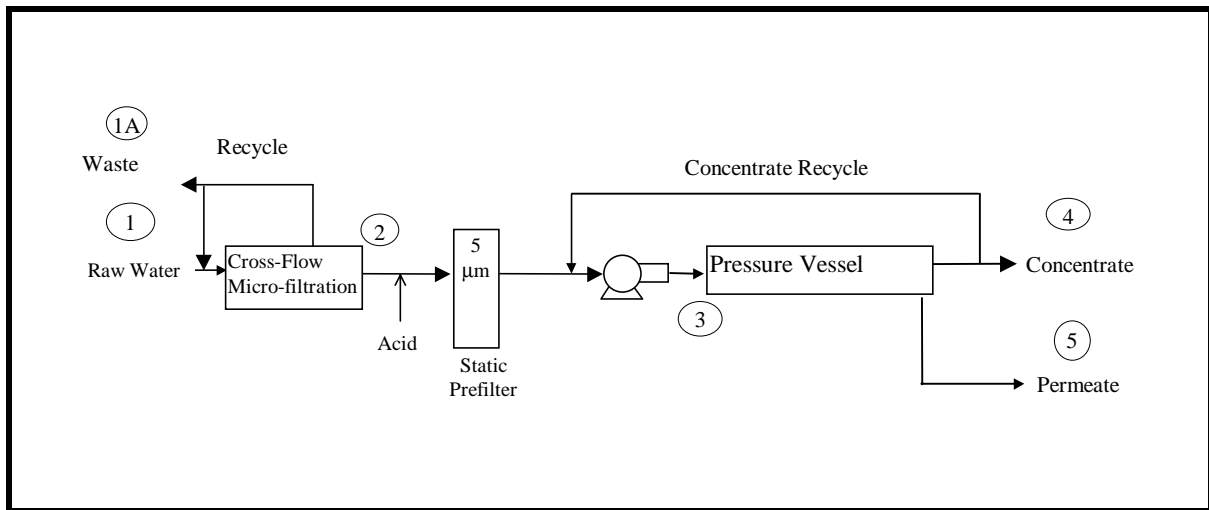


Figure 2: CFMF-DS5 Single Element Bench Unit Flow Diagram

The single element bench-scale unit was operated with a Memcor cross-flow micro-filter (CFMF) as the advanced pretreatment to control nanofiltration fouling. The CFMF unit contained 53.75 ft² of membrane surface area in the form of hollow polypropylene fibers. The fibers had a pore size of 0.2 microns and flow was from the outside to the inside of the fiber. A four horsepower Lowara pump pressurized the raw water from 15 to 25 psi. A crossflow of approximately 30 gpm was maintained across the feed/concentrate side of the membranes at all times. The unit could be automatically pneumatically backwashed every 10 to 60 minutes. Three 100 psi blasts of air reversed the flow through the membranes and discharged 3 to 5 gallons of backwash water containing dislodged particles. This one minute long backwash cycle extended operation times between chemical cleanings. Due to the high fouling nature of the source water the backwash cycle was set for every 10 minutes. The filtrate stream from the MF entered the single element bench-scale unit. The concentrate stream was discharged to the sewer system. Recoveries were maintained at approximately 60 to 70 percent. Table 5 presents a summary of some of the pretreatment design parameters.

As shown by Figure 2, the filtrate from the CFMF was acidified, directed to a Harmsco 5 micron cartridge filter, pressurized and passed into the single element pressure vessel. Sulfuric acid injection lowered the pH of the CFMF filtrate to approximately 6.0. The bench scale unit contained a single 4040 Desal DS5 (DS5) nanofiltration membrane.

The DS5 contained 90 ft² of membrane surface area. The manufacturer reported membrane characteristics are presented in Table 6.

Table 5: Membrane Pilot Unit Pretreatment Design Parameters

Unit Process	Process Description
Cross-flow Micro-filter	Memcor Unit
	Hollow Fibers
	Membrane Surface Area (μm): 53.75
	Pore Size (μm): 0.2
Scale Control (Pilot-Scale)	
	Chemical Type: Sulfuric Acid
	Adjust pH: 6.0
Cartridge Filtration (Pilot-Scale)	
	Total Surface Area (ft ²): 0.55
	Nominal Pore Size (μm): 5
	Filter Material: Wrapped Polypropylene Yarn

Cleaning Procedures

The CFMF was chemically cleaned when the trans-membrane pressure (TMP) reached 15 psi. Initially TMPs were 1 to 4 psi. A solution of sodium hydroxide and EDTA was used to remove organic foulants from the membrane surface. The filtrate valve was closed and cleaning solution was pumped across the surface of the membranes at 30 gpm for approximately one to two hours. The cleaning solution was then replaced with city water and the unit was backwashed five to fifteen times. This removed additional organic matter and flushed the cleaning solution from the membranes.

Chemical cleaning of the bench scale unit occurred at the end of each operational setting. The DS5 membrane was cleaned using a solution of high phosphate commercially available detergent and sodium hydroxide. The permeate valve was closed and cleaning solution was recirculated across the feed/concentrate side of the membrane for approximately one hour.

Table 6: Membrane Design Parameters

General Information	
Membrane manufacturer	Osmonics Desal
Membrane trade name	DS5
Membrane element model number	DK 4040F
Molecular weight cutoff (Daltons)	150 – 300
Membrane material (e.g., PVD, polyamide, etc.)	Proprietary
Membrane construction (e.g., thin-film composite)	Thin Film Composite
Membrane hydrophobicity	Hydrophilic
Membrane charge (e.g., negative, highly negative, neutral, etc.)	Negative
Design Parameters	
Element size (e.g., 2.5" x 40", 4" x 40", etc.)	4" x 40"
Active membrane area of membrane element used, A (ft ²)	90.0
Design flux, F_W (gfd)	20
Net driving pressure at the design flux, NDP (psi)	100.0
Water mass transfer coefficient, MTC_W (gfd/psi)	0.2
Temperature at which the MTC_W was determined, T°C (°C)	25.0
Maximum flow rate to the element, $Q_{I, \max}$ (gpm)	Max ΔP = 10 psi
Minimum flow rate to the element, $Q_{I, \min}$ (gpm)	6.25
Total width of all membrane envelopes in the element, w (ft)	16.0
Feed spacer thickness, T (ft)	0.0028
Active membrane area of an equivalent 8" x 40" element (ft ²)	350.0
Purchase price for an equivalent 8" x 40 " element (\$)	1500.00
Additional Information	
Design cross-flow velocity (fps)	
Required influent flow to permeate flow rate ratio, $Q_i:Q_p$	5
Maximum element recovery (%)	20
Variability of design flux (%)	±15
Rejection of reference solute and conditions of test(e.g., solute type and concentration)	98% of 2000 mg/L solution of MgSO ₄
Variability of rejection of reference solute (%)	
Standard testing recovery (%)	10
Standard testing pH	7.0
Acceptable range of operating pressures	70 – 500 psig
Acceptable range of operating pH values	2 - 11
Typical pressure drop across a single element (psi)	<10
Maximum permissible SDI	5
Maximum permissible turbidity (ntu)	1
Chlorine/oxidant tolerance (e.g., < 0.1 mg/L for extended use, etc.)	1000 ppm - hours

Experimental Design

Table 7 presents the overall schedule of operation and the experimental design associated with each of the pilot unit combinations. The CFMF-DS5 bench-scale study was one of six different pilot- and bench-scale unit combinations to be operated at the South WTP. The pilot-scale studies included combinations of 2 pretreatment (Alum coagulation, sedimentation, Sand filtration and filtration with GAC) and two membrane elements (Desal DS5 and Dupont A15S) used in a 2-stage (nine elements total) pilot unit). The bench-scale studies used combinations of 2 pretreatment (cross-flow or direct flow micro-filtration) and

one membrane type, the Desal DS5. As is shown in Table 7 the CFMF was operated from August 1990 to the end of January 1991. Table 7 also shows the scheduled dates for water quality monitoring which was once a month for a total of six sample sets.

Table 7: Experimental Plan and Schedule For Membrane Studies

PILOT-SCALE ACSSF-NF & GAC-NF MEMBRANE PILOT PLANT SYSTEM												
System	Oct-90	Nov-90	Dec-90	Jan-91	Feb-91	Mar-91	Apr-91	May-91	May-03	May-10	May-16	May-23
Sample Date	Oct-05	Nov-10	Dec-02	Jan-02	Feb-07	Mar-05	Apr-03	May-06	May-06	May-13	May-17	May-27
ACSSF-A15S												
10gsfd-65%R	1											
15gsfd-65%R		1										
10gsfd-45%R			1									
15gsfd-45%R				1								
ACSSF-DS5												
10gsfd-65%R					1							
15gsfd-65%R						1						
10gsfd-45%R							1					
15gsfd-45%R								1				
GAC-A15S												
10gsfd-65%R					1							
15gsfd-65%R						1						
10gsfd-45%R							1					
GAC-A15S												
10gsfd-20%R									1			
15gsfd-45%R										1		
15gsfd-20%R											1	
10gsfd-45%R												1
GAC-DS5												
10gsfd-65%R	1											
15gsfd-65%R		1										
10gsfd-45%R			1									
15gsfd-45%R				1								
BENCH-SCALE MF-NF PILOT PLANT SYSTEM												
SAMPLE PERIOD	31-Aug	28-Sep	21-Oct	27-Nov	15-Dec	09-Jan	02-Feb	28-Feb	24-Mar	07-Apr	19-Apr	02-May
Sample Date	13-Sep	05-Oct	27-Oct	02-Dec	27-Dec	21-Jan	07-Feb	02-Mar	30-Mar	14-Apr	02-May	16-May
CFMF-DS5												
50gsfd-15%R		1										
50gsfd-24%R			1									
75gsfd-15%R				1								
75gsfd-24%R					1							
100gsfd-15%R						1						
100gsfd-24%R	1											
DFMF-DS5												
50gsfd-15%R							1					
50gsfd-24%R								1				
75gsfd-15%R									1			
75gsfd-24%R										1		
100gsfd-15%R											1	
100gsfd-24%R												1

Analytical Methods

The following section presents a summary of the analytical methods used for the water quality analysis of samples collected during the membrane studies conducted at the City of Melbourne South WTP.

The City of Melbourne does use chloramination for disinfection. However, the DBP formation potential conditions were selected to simulate DBP formation in the distribution if the City used a free chlorine residual. The distribution system is extensive and has a relatively long detention time. The conditions for DBP formation potential were selected to provide a conservative SDS formation for this system. These conditions were set at an incubation pH of 7.6, temperature of 22°C, a reaction time of 96 hours at doses of 5 mg/L for the permeate samples, 100 mg/L for the raw and 50 mg/L for the microfilter filtrate. The free chlorine residuals after the 96 hours for the permeate samples were no less than 0.2 mg/L CL_2 .

The DBPs for the long term membrane pilot studies were measured using the USEPA 501, 551 and 552 methods which included the measurement of 26 different compounds. While the University of Central Florida was conducting membrane research for the USEPA project titled "*Reduction of Disinfection By-Product precursors by Nanofiltration*", (EPA/600/SR-92/023, April 1992) it was required to participate in DBP analytical methods comparison. The comparison was associated with the THM4 methods EPA 501.2 and EPA 551. These studies were conducted in anticipation of the adoption of both EPA 551 and 552 methods. Included with the request for approval to grandfather information was a paper titled "*Comparison of THM Analyses by EPA Method 501.2 and 551*". This paper was presented during an AWWA WQTC conference, (Orlando, 1992) and summarizes the results of the comparison of THMs by EPA 501.2 and 551. The THMs for this study were analyzed by both EPA 501.2 and 551 methods.

Overall, the value determined by method 501.2 was higher than method 551. The combined EPA project data showed that total THMs as determined by method 551 overall approximately 80% of the value determined by method 501.2. Similarly, chloroform as determined by method 551 was 78% of the value by method 501.2. Dichlorobromomethane and chlorodibromomethane as determined by method 551 were approximately 90% of the value by method 501.2. Only the values for bromoform as determined by 551 were higher than those by method 501.2. Bromoform averaged 113% of 501.2 bromoform. Due to the low levels of bromoform detected, an accurate regression could not be made for some data types. Table 8 presents the results of regression statistics applied to the results of samples collected during the studies conducted at the South WTP.

In this report all values discussed for THMFP were determined by method 551 unless otherwise specified. If the corresponding THMFP value by method 501.2 is desired, an approximate conversion from method 551 can be made using the factors described in the previous paragraph.

**Table 8: Individual And Total THMFP Regression Of EPA Method 551 (Y)
And EPA Method 501.2 (X)**

DATA TYPE	Regression Species	EQUATION	n	R-Squared	F	Alpha
MELBOURNE PERMEATE DATA						
	Total	y=1.139x	49	0.978	2136	<1E-15
	Chloroform	y=0.927x	64	0.286	25	<1E-5
	Dichlorobromomethane	y=0.926x	64	0.965	1722	<1E-15
	Chlorodibromomethane	y=0.968x	74	0.969	2320	<1E-15
	Bromoform	y=1.339x	64	0.956	1356	<1E-15
MELBOURNE FEED DATA						
	Total	y=0.798x	32	0.980	1528	<1E-14
	Chloroform	y=0.771x	49	0.976	1989	<1E-14
	Dichlorobromomethane	y=0.937x	53	0.944	884	<1E-14
	Chlorodibromomethane	y=1.052x	48	0.953	955	<1E-15
	Bromoform	#N/A	#N/A	#N/A	#N/A	#N/A
MELBOURNE RAW DATA						
	Total	y=0.768x	31	0.971	1021	<1E-15
	Chloroform	y=0.748x	35	0.952	679	<1E-15
	Dichlorobromomethane	y=0.941x	32	0.979	1418	<1E-15
	Chlorodibromomethane	y=1.097x	33	0.708	78	<1E-9
	Bromoform	#N/A	#N/A	#N/A	#N/A	#N/A

This membrane study evaluated the water quality of the flow streams for more parameters than the ICR protocol requires. However, there were 2 parameters that were not measured during this study that are required of a proposed ICR study, bromides and UV-254. These parameters have been presented for the South WTP source and finished water in the previous section. In addition, instead of measuring total organic carbon (TOC) this study analyzed for non-purgeable dissolved organic carbon (NPDOC).

The UCF ESEI Laboratory conducted all of the analysis associated with the membrane studies. The UCF ESEI laboratory was certified by the State of Florida and participated in USEPA performance evaluations during these studies. The City of Melbourne Utilities Laboratory and their contract laboratory (Environmental Health Labs) conducted the more recent analysis reported as associated with the ICR Monitoring requirements. The sample analysis related to ICR monitoring was used to produce Table 4, which presents the most recent source and blended finished water quality for the South WTP.

A summary of the analytical methods and detection limits for the UCF ESEI Laboratory analysis associated with the membrane studies is presented in Table 9. The contact personnel and information for the three laboratories are presented in Table 10.

Table 9: Summary Of Analytical Procedures

Procedure	Description	Reference	Reporting Level
Alkalinity	Acid titration	SM 403	2 mg/L
Chloride	Argentometric	SM 407A	1 mg/L
Chlorine Residual	Amperometric titration DPD Ferrous titrimetric	SM 408C SM 408D	0.1 mg/L 0.1 mg/L
Color	Spectrophotometric	SM 204B	0.5 cpu
Fluoride	SPADNS	SM 413C	0.05 mg/L
Hardness, Total Ca ⁺⁺	EDTA titration	SM 314B	2 mg/L
		SM 311C	2 mg/L
Metals, General	Plasma Emission	SM 305	Fe = 10 µg/L
PH	Meter	SM 429	N/A
Sulfate	Turbidimetric	SM 426C	1 mg/L
Total Dissolved Solids	Gravimetric	SM 209B	1 mg/L
Turbidity	Ratio turbidimeter	SM 214	0.05 NTU
Silica	Heteropoly Blue	SM ¹⁹ 4500-SiE	1 mg/L
Sodium	Plasma Emission	SM 305	1 mg/L
Non-purgeable dissolved Organic Carbon	Persulfate-Ultraviolet Oxidation	SM 505B	0.3 mg/L
Disinfection By-Products	Micro-extraction, GC-ECD	EPA551,552*	1 µg/L Individual
Trihalomethane	Liquid-Liquid extraction	EPA 501.2	1 µg/L Individual
Total Organic Halide	Adsorption-Pyrolysis, Titrimetric	SM 506	2 µg/L
Formation Potential	Chlorination followed by 501.2, 551, 552, and TOX Analysis	TEXT	N/A

*EPA 551 analyzed the base-neutral function, while EPA 552 analyzed the haloacetic fraction.

SM = 16th Edition of Standard Methods. SM¹⁹ = Referenced under 19 th edition of Standard Methods.

EPA = U.S. Environmental Protection Agency

Table 10: Laboratories Conducting Analysis For Report

Laboratory	ICR I.D.	Contact	Address	Phone
City of Melbourne Utilities	FL-051	Yvonne Gonsalves Chief Lab Tech.	6055 Lake Washington Rd Melbourne, FL 32934	Phone – (407)-255-4622 FAX – (407)-255-4636
Environmental Health Labs	IN-004	Richard Radclift		
UCF Environmental Systems Engineering Institute	N/A	Dr. James S. Taylor, Director	University of Central Florida CEE Department 4000 Central Florida Blvd. Orlando, FL 32816- 2450	Phone – (407)-823-2785 FAX – (407)-823-6562

Section IV: Results And Discussions

Operations Description

The flow diagram of the CFMF-DS5 integrated membrane system was presented in Figure 2. The actual schedule of operation for the CFMF-DS5 system is shown in Table 11. There were seven periods of operation in which the nanofiltration membrane flux was initially set at either 10 or 15 gsfd and 15 or 24% recovery except for the first period of operation when the flux and recovery were 13 gsfd and 22%. The recovery is based on only the incoming flow to the nanofiltration unit which did not include recycle and was used to define operating conditions. Since recycle flow around the nanofiltration unit was used to maintain the relatively constant 4 gpm required by the NF high pressure pump the recovery based on total flow to the nanofiltration unit would be lower because recycle is included. The CFMF flux was controlled at 100, 75 and 50 gsfd and recovery was either 60 or 70%. The 60% recovery was only used in conjunction with the 50 gsfd for the CFMF. The CFMF flux was purposely varied but recovery was maximized given the NF operating conditions. Higher recoveries could have been realized in a multi-stage NF system.

Table 11: Schedule Of Operation For The CFMF-DS5 Integrated Membrane System

Run #	Hours Of Operation	Microfilter		Nanofilter	
		Recovery (%)	Flux (GSFD)	Recovery (%)	Flux (GSFD)
1	0.0-566.3	70	100	22	13
2	566.3-857.8	70	100	24	15
3	857.8-1382.5	60	50	15	10
4	1382.5-1920.0	60	50	24	15
5	1920.0-2268.3	70	75	15	10
6	2268.3-2715.5	70	75	24	15
7	2715.5-3936.3	70	100	15	10

A time balance was developed from the CFMF-DS5 operation log and is presented in Table 12. The CFMF-DS5 system was available for operation a total of 4223.8 hours which was subdivided into 155.1 hours of unavoidable downtime, 1187.5 hours of avoidable downtime and 3036.3 hours of actual operation. The CFMF-DS5 system was operating 95% of time based on runtime and unavoidable downtime. The hours and percent of unavoidable downtime were low pressure shut-off (11.5 hr-8%), membrane cleaning (30.1 hr-8%), CFMF fouling (33.0-21%), South WTP shutdown (64.9 hr-21%), filter backwash (5.1 hr-3%) and repair or maintenance (10.5 hr-7%). The pumps supplying the sand filtered water and the raw water were powered through a common supply. This interconnection resulted in the operation of the CFMF being discontinued when the filter was backwashed. The largest category of avoidable downtime is the preparation of the CFMF-DS5 system for each planned period of operation and the elapsed time following the cessation of operation due to fouling of either membrane before project personnel could arrive at the plant to clean the system.

Table 12: Time Balance For The Operation Of The CFMF-DS5 Integrated Membrane System

Classification	Item	Time (Hours)
Unavoidable	Low Pressure Shut Off	11.5
Unavoidable	Membrane System Cleaning	30.1
Unavoidable	Fouled Memcor Unit	33.0
Unavoidable	WTP Shut Down	64.9
Unavoidable	Filter #2 Backwash	5.1
Unavoidable	Repair/Maintenance	10.5
	Total Unavoidable Downtime	155.1
Avoidable	Setup Runs/Membrane Cleaning	832.9
Avoidable	Pump/Line Modifications	7.7
Avoidable	Fouled Memcor Unit	191.8
	Total Avoidable Downtime	1032.4
	Total Downtime	1187.5
	Total Downtime	1187.5
	Run Time	3036.3
	Total Time	4223.8

Water Production

All recorded observations of flow and pressure during the CFMF-DS5 unit operation are presented in the computer file and the Appendix. Recovery, flux and MTCs for water were determined for each observation of pressure and flow and are also presented in the files and Appendix. All of the physical observations in these tables are correlated to date, time of recording, and run time.

The water MTC decline is shown in Figure 3 for all hours and conditions of operation for the CFMF-DS5 system. The NF MTC is relatively constant with time of operation except at the end of period 1, during period 2 and 5. The MTC decline at the end of period 1 and during period 2 suggest that a raw water quality change may have been responsible for the MTC decline, otherwise the decline would have been seen at the beginning of period 1. The MTC decline in period 5 occurred at a CFMF flux of 75 gsfd, the optimum CFMF flux in the pretreatment study, and the lowest NF flux and recovery.

The USEPA project involved one year of membrane operations at a groundwater site and the operation of six different membrane systems at the South WTP. Due to large scope of this project certain concessions had to be made as to monitoring. This particular system did not include the monitoring of the temperature on regular basis nor the water quality and pressure of the concentrate stream. Due to the nature, location and weather associated during the operation of this system the temperature was maintained at approximately 25 °C. The

hydraulics of the system was such that the concentrate pressure of the system would be very near the feed and therefore the spreadsheet data was input as the feed pressure. This would average the feed stream pressure to be the measured input feed. The osmotic pressure of the system was very low because of the low TDS which would average out to be approximately 5 psi there for 5psi was used as the delta osmotic pressure in the calculation of the specific flux. These assumptions would be consistent with all of the data points and do not adversely effect the trend of the specific flux decline. The specific flux is presented in units of gsfd to confirm the input of data into the ICR data spreadsheets. However, the report evaluated the specific flux in units of day-1 which is derived by dividing gsfd by 17.253.

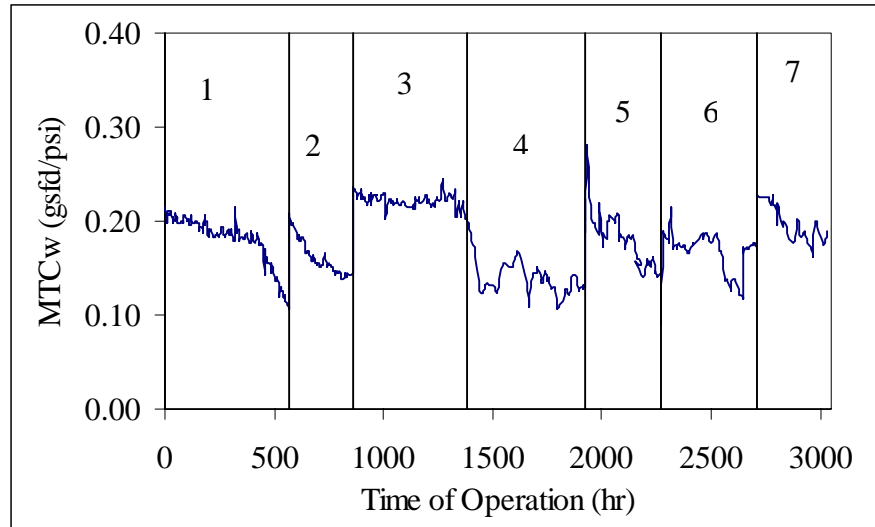


Figure 3: CFMF-DS5 Nanofiltration Water Production

The MTCs for each operational period were regressed with time and the results of the statistical analysis are presented in Table 13. The lowest rate of NF MTC decline was $0.000037/d^2$ and occurred for CFMF flux, NF flux and recovery, (operating conditions), of 50 gsfd, 15 gsfd and 15%. The highest rate of NF MTC decline occurred at 75 gsfd, 10 gsfd and 15% R and was $0.000284/d^2$. The average rate of NF MTC decline during these studies was $0.000189/d^2$. These results indicate that CFMF does reduce NF fouling relative to conventional pretreatment which fouled the membrane in a few hours during pretreatment studies. The lowest rate of NF MTC decline was recorded at the lowest recovery (highest surficial NF velocity), lowest NF flux (velocity through the NF) and lowest CFMF flux (velocity through the CFMF). Generally the rate of MTC decline appears to decrease as the CFMF flux and NF flux and recovery decrease. However, the much lower rate of MTC decline produced during groundwater site studies indicate that something in addition to CFMF flux or NF flux and recovery is responsible for NF MTC decline at this surface water site.

Table 13: MTC Regression With Time Of Operation For The NF Membrane Using The CFMF-DS5 System

Run #	Run Hour	NF Recovery (%)	NF Flux (Gsfd)	MF Recovery (%)	MF Flux (Gsfd)	Slope (1/Day ²)	Alpha	R ²	Raw Avg. Color (CPU)	Raw Avg. NPDOC (mg/L C)	Avg. Temp. (F)
1	0.0	22	13	70	100	-0.000162	.0000	.74	94.1	23.5	85.3
2	566.3	24	15	70	100	-0.000252	.0000	.86	332.9	34.4	84.5
3	857.8	15	10	60	50	-0.000037	.0000	.32	252.2	29.7	80.8
4	1382.5	24	15	60	50	-0.000100	.0000	.35	232.9	29.6	73.6
5	1920.0	15	10	70	75	-0.000284	.0000	.70	200.9	29.1	66.7
6	2268.3	24	15	70	75	-0.000081	.0040	.15	178.0	29.1	67.3
7	2715.5	15	10	70	100	-0.000189	.0000	.66	162.6	28.2	70.2

Water Quality

There were a total of seven sets of water quality samples collected and analyzed for the CFMF-DS5 system over the 3036.3 hours of operation. The high, low and average raw, feed (CFMF filtrate) and NF permeate from the CFMF-DS5 system are presented in Table 14. The concentrate was not monitored for water quality.

The DS5 nanofilter reduced the TOXFP by 99% from 5017 ug/L as Cl⁻ to 47 ug/L as Cl⁻. The THMs were reduced by 97%, from 1036 ug/L as species in the microfilter filtrate to 32 ug/L in the nanofilter permeate on average. Two permeate samples had THMs at 81 and 74 while the other five samples were measured below 24 ug/L as the species. HAA5s were reduced by the nanofilter on average 99% with the permeate average concentration at 13 ug/L as the species.

The inorganic water quality, in addition to the TOXFP and the NPDOC is presented in Table 14. The CFMF is seen to decrease the average turbidity, HPC and iron from 8.8 to 0.17 NTU, 2380 to 403 CFU/ml and 298 to 179 ug/L. The iron reduction is probably due to the removal of absorbed or entrained iron since microfiltration through a 0.2 micron pore would not be expected to remove dissolved iron. The microfilter would be expected to and did achieve very effective turbidity or microorganism removal. The remaining parameters listed in Table 14 were either affected very little or not at all by the microfiltration process. The DS5 nanofilter is seen to reduce the average TDS from 359 to 228 mg/L, sodium from 44 to 32 mg/L, total hardness from 137 to 56 mg/L and alkalinity from 142 to 85 mg/L. Inorganic solute removal in a nanofiltration system is a diffusion controlled process and to some degree organic solute removal may be diffusion controlled.

The CFMF-DS5 system is seen to remove 99% of the DBPFP at the surface water site and produce water 95% of the operational time. No adverse water quality effects were found to occur for either the CFMF or NF process. The calcium and alkalinity of the permeate stream could be increased by higher recovery, higher MWC or alkalinity recovery by CaO addition as previously discussed. Some inorganic solute removal was observed and significant turbidity and HPC reduction was achieved by the CFMF.

Table 14: Water Quality For The CFMF-DS5 Integrated Membrane System

Parameters	Units	Raw			Feed			Permeate		
		High	Low	Avg.	High	Low	Avg.	High	Low	Avg.
THMFP*	(ug/L)	1487	170	906	1622	421	1036	81	9	32
HAA5	(ug/L)	2090	631	1402	1724	680	1293	34	2	13
TOXFP	(ug/L as Cl ⁻)	7120	3700	5174	6920	3300	5017	62	24	47
COLOR	(CPU)	340	80	230	250	60	191	2	0	0.6
NPDOC	(mg/L)	34	18	28	28	18	25	0.5	0	0.2
TDS	(mg/L)	570	310	391	560	130	359	380	66	228
Sodium	(mg/L)	68	32	44	70	30	44	59	12	32
Total Hardness	(mg/L as CaCO ₃)	190	120	137	180	120	137	97	4	56
Calcium Hardness	(mg/L as CaCO ₃)	150	85	107	140	90	102	88	7	53
Chloride	(mg/L)	160	75	97	160	74	96	140	63	85
Sulfates	(mg/L)	3	0	1	2	0	0.9	2	0	1
Alkalinity	(Mg/L As Caco ₃)	570	84	160	560	0	142	380	18	88
PH		7.90	7.10	7.55	7.90	7.30	7.69	8.00	6.10	6.51
Iron	(ug/L)	500	94	298	260	25	179	14	0	3
Turbidity	(NTU)	8.8	1.1	3.2	0.28	0.11	0.17	0.64	0	0.12
Heterotrophic Plate Count	(CFU/ml)	4400	1200	2380	750	140	403	680	2	351

* Method USEPA 501.2

Impact of Seasonal Variability

The seasonal change in Central Florida is relatively small compared to the upper U.S. During this testing from August 1990 to February 1991, the average feed water temperature only ranged from 67 to 85 °F. In addition, the pilot unit design and location further reduced the variability of the temperature. The data presented in Table 13 for MTC decline and the water quality analysis did not indicate any adverse effects based on the season changes experienced during this study.

Cost Information

Estimated Capital and O & M costs for microfiltration pretreatment are reported in Table 15. The microfiltration unit could filter approximately 13 MGD of raw water resulting in 12 MGD of filtrate for feed to the nanofiltration system. This flow would require 24 individual microfiltration units, each with 60 membrane elements and a total of 6460 ft² of surface area per unit. Each membrane element consists of hollow polypropylene fibers with a 30 micron inner diameter, 60 micron outer diameter, and 0.2 micron pore diameter. The microfiltration unit also contains a pneumatic backwash system, which cleans the elements for a one minute duration after ten minutes of operation. The entire unit would be shipped together and installed for a capital cost of \$7,200,000. No additional process equipment would be required. Instrumentation and electrical components of the system were estimated at \$900,000, and process and connecting piping to the membrane system at \$1,000,000. The total construction cost for the microfiltration pretreatment option would be \$9,980,000, or \$0.32/Kgal of nanofilter product water.

Labor requirements for the microfiltration unit include three head operators at \$25,000/year and four operators at \$20,000/year, for an estimated total cost of \$160,000/year. The power requirement of \$65,000/year was determined using a feed pressure of 15 psi to the unit, 95% recovery, a water flux of 75 gsf/d, and \$0.075/kwh. The process power requirement of \$44,000 was increased by 25% to cover building and pumping requirements. Membrane replacement costs were figured using a membrane life of 2 years and \$700/element, for a total maintenance cost of \$720,000/year. The chemical supply cost of \$45,000/year reflects the purchase of cleaning chemicals, and cleaning every two weeks. The total yearly operation and maintenance cost of microfiltration pretreatment is \$998,000, or \$0.27/Kgal of nanofilter product water.

From the total estimated capital cost for the microfiltration pretreatment option is \$9,980,000. The major cost component is the microfiltration unit, at 72% of the total capital cost. The amortized capital cost, 20 years at 10%, is \$0.32/Kgal. The total O & M cost was estimated as \$998,000/year, or \$0.27/Kgal. The major O & M cost component is maintenance representing 72% of the total O & M cost. The estimated total cost for microfiltration pretreatment is \$0.59/Kgal of nanofilter product water.

The microfiltration pretreatment system and DS5 membranes showed a $1.88 \times 10^{-4}/d^2$ MTC decline. This rate of decline corresponds to a 4.6 day cleaning frequency. Four additional operators at \$20,000/year were estimated to cover cleaning requirements. This additional labor cost was added to the base cost of \$195,000/year for a total labor cost of \$275,000/year. Cleaning chemicals were estimated at \$59,511/year and added to base

chemical supply costs of \$197,000/year for a total cost of \$260,000/year. Membrane life with the microfilter option was assumed to be 2.5 years to estimate replacement costs at \$1,332,250/year. Maintenance costs for this option included membrane replacement, controls and pump maintenance, but no prefilter replacement. Total maintenance costs were estimated at \$1,400,000/year. O & M costs for the membrane system with the microfiltration option is \$2,514,000/year or \$0.69/Kgal of finished water.

Table 15: Cost Estimate For 12 Mgd (Permeate) Microfiltration Plant

Category	Cost
<u>Capital Cost</u>	
Land	\$30,000
Site Work	\$150,000
Building	\$700,000
Process Equipment	
Microfiltration Unit	\$7,200,000
Instrumentation and Electrical	\$900,000
Process Piping and Pumps	<u>\$1,000,000</u>
Total:	\$9,980,000
\$/Kgal (20 years at 10%)	\$0.32
<u>O & M (per year)</u>	
Wages	\$160,000
Power	\$65,000
Chemical Supplies	\$45,000
Maintenance	\$720,000
Other	<u>\$8,000</u>
Total:	\$998,000
\$/Kgal	\$0.27
Total \$/Kgal	\$0.59

Table 16 presents capital and O & M cost estimates for the nanofiltration system associated with the surface water scenario using pretreatment. This estimates only includes costs related to the nanofiltration facilities and excludes the advanced pretreatment cost presented earlier. The nanofiltration capital cost for the site with microfiltration pretreatment does not include the purchase of prefilter apparatus, because no prefiltration is required with this pretreatment option. The surface water membrane system was designed to operate at 85% recovery, a 100 psi feed pressure and a water flux of 10 gsf. This design requires 13 membrane skids, each producing 0.8 MGD, for 12 duty and 1 standby skid. The additional membrane skids also require additional process piping and instrumentation. For the microfiltration pretreatment option, the nanofiltration capital cost is estimated as \$20,557,250 or \$0.66/Kgal of finished water.

Table 16: Cost Estimate For 10 Mgd Nanofiltration Plant For Surface Water

Category	Microfiltration, Nanofiltration
<u>Capital</u>	
Land	\$35,000
Site work	\$300,000
Buildings	
Membrane	\$1,400,000
Chemical Feed	\$224,000
Bulk Chemical Storage	\$168,000
Chlorine Feed	\$168,000
Clearwell and pumps	\$244,000
Administration and Lab	\$140,000
Power Vault	\$15,000
Process Equipment	
Membranes and pumps	\$7,580,000
Chemical Feed	\$115,000
Chlorination	\$100,000
Aerator	\$400,000
Storage	\$1,600,000
Process Piping	\$1,639,000
Instrumentation and electrical	\$1,229,250
High Service Pumps	\$200,000
Deep Well	
Injection Well	\$3,000,000
Unlined Lagoon Back-up	\$200,000
Monitoring System	\$950,000
Transport Pipeline	<u>\$850,000</u>
Total:	\$20,557,250
\$/Kgal (20yrs at 10%)	\$0.66
<u>O & M (per year)</u>	
Wages	\$275,000
Power	\$500,000
Chemical Supplies	\$260,000
Maintenance	\$1,400,000
Telephone	\$12,000
Deep Well	\$15,000
Other	<u>\$52,000</u>
Total:	\$2,514,000
\$/Kgal	\$0.69
Total Cost \$/Kgal	\$1.35
Total Cost With MF	\$1.94

Section V: QA/QC Summary

The following section will present a summary of the quality assurance and quality control results compiled during the membrane pilot studies

Solute Mass Balances

The USEPA project involved one year of membrane operations at a groundwater site and the operation of six different membrane systems at the South WTP. Due to the large scope of this project certain concessions had to be made as to monitoring. This particular system did not include water quality and pressure monitoring of the concentrate stream. Therefore mass balance calculation cannot be accomplished.

Precision

Precision was the reproducibility observed between duplicate analyses. Duplicates were two determinations of a given parameter for the same sample by repeating the analytical procedure. The precision was expressed as percent relative deviation for each pair of analyses and was calculated by the following formula:

$$\% \text{ RSD} = \left(\frac{S}{\bar{X}} \right) \times 100$$

where:

S = standard deviation

\bar{X} = mean (average for a pair)

The standard deviation (S) for a data pair was calculated using the following equation:

$$S = \sqrt{\frac{(X_1 - X_2)^2}{2}} \cdot 0.89$$

where: X_1 and X_2 were individual observations.

Precision of a given analytical method was continuously determined by using the mean range and variance determinations. The range was the difference between the two duplicates. The normalized mean range, \bar{R} , was calculated using the following equation:

$$\bar{R} = \frac{\sum_{n=1}^N R}{N}$$

where:

$$\sum_{n=1}^N R = \text{sum of the relative standard deviations}$$

$$N = \text{number of data pairs}$$

The variance, S_R^2 , was calculated by:

$$S_R^2 = \frac{\sum_{n=1}^N R^2 - (N \bar{R}^2)}{(N-1)}$$

where:

$$\sum_{n=1}^N R^2 = \text{sum of the relative standard deviations}$$

$$\bar{R}^2 = \text{square of the mean range}$$

$$N = \text{number of data pairs}$$

The warning limits (WL) and control limits (CL) were calculated by the following equations:

$$WL = \bar{R} + 2S_R$$

$$CL = \bar{R} + 3S_R$$

where:

$$\bar{R} = \text{mean range}$$

$$S_R = \text{square root of variance}$$

Data was assessed by interpreting the mean range (also referred to as the central line), with regard to the warning and control limits. A graph of concentration versus sample occurrence or number was used to facilitate the interpretation. The mean range, WL and CL were shown as horizontal lines on the graph. The results of an individual paired duplicate analysis were entered on the graph and interpreted by where they fell within the boundaries on the graph. A minimum of twenty pairs of duplicate analyses were used to construct the graph.

Table 17 and 18 lists the compilation of the precision data obtained for the parameters monitored during the project and the percentage of the time that the data was within the ninety-five percent confidence interval.

Table 17: Precision For Organic Parameters

Parameter	Precision RSD	Std. Dev	Mean	UWL	UCL	%C.I.
Chloroform	0 - 23	6	4	12	18	98
Bromodichloromethane	0 - 16	5	3	9	14	100
Dibromochloromethane	0 - 44	10	4	20	30	93
Bromoform	0 - 16	4	3	8	12	80
Monochloroacetic acid	0 - 110	28	22	55	83	90
Monobromoacetic acid	0 - 95	24	18	49	73	98
Dichloroacetic acid	0 - 94	29	25	58	87	98
Dibromoacetic acid	0 - 48	15	14	29	44	93
Trichloroacetic acid	0 - 129	34	29	69	103	98
Color	0 - 9	3	2	6	9	100
NPDOC	0 - 14	4	4	8	12	98
TOX	0 - 15	4	6	9	13	98

Table 18: Precision For Inorganic Parameters

Parameter	RSD Precision	Std. Dev.	Mean	UWL	UCL	%C.I.
Alkalinity	0 - 4	1	1	2	4	100
Turbidity	0 - 17	4	6	9	13	93
TDS	0 - 13	4	4	8	12	98
Total Hardness	0 - 12	4	2	8	12	100
Ca Hardness	0 - 9	2	2	5	7	93
Chloride	0 - 11	3	2	7	10	93
Sulfate	0 - 75	20	8	41	61	93
Fluoride	0 - 16	5	4	11	16	100
Silica	0 - 8	3	1	5	8	100
Sodium	0 - 7	2	2	4	6	98
Iron	0 - 8	3	2	5	8	100

Accuracy

The data obtain through spike analyses was used as a measure of accuracy, the degree of difference between observed and known values. Known concentrations were added to samples and the following equation used to determine the recovery of the specific parameter:

$$\% \text{ Recovery} = \left(\frac{(Z - X)}{T} \right) \times 100$$

where:

Z = observed spike concentration

X = concentration of unspiked sample

T = True concentration of spike

The percent recovery, the mass of the spike, spiked and unspiked sample concentration were reported on quality control report forms. As with the duplicates, the mean, variance, warning and control limits were calculated using at least twenty data points. For the spikes, percent recovery was used instead of relative standard deviation; and as with the duplicates the mean, variance, warning and control limits were calculated using the previously cited equations. One additional difference between the presentation of the spike and duplicate data is that the warning and control limits were expressed in terms of plus or minus standard deviations. The upper limits were positive deviations. The lower limits were negative standard deviations. A graph of the data and the statistically calculated control were developed. This graph was used to assess the acceptability of the data in the same manner as previously described for the duplicate analyses. Table 19 and 20 list the compilation of accuracy data for the parameters monitored in this study and the percentage of time that the data was within the ninety-five percent confidence interval.

In addition to the duplicate and spike data, purchased reference check samples were also used to assess analytical quality. The samples came with preparation instructions, a true value, and a ninety-five percent confidence interval that was computed by the manufacturer. These samples were used for the inorganic analyses, since most of the samples could be maintained and reanalyzed on a daily basis for three months if refrigerated. Sample analysis was not to take place if the results of the reference analysis were outside the given confidence interval. Additionally some analyses made use of a check sample that was prepared by the laboratory staff to monitor analytical performance.

Table 19 Accuracy For Organic Parameters

Parameter	Accuracy	Std. Dev.	Mean	Warning Limit	Control Limit	% C.I.
Chloroform	52 - 104	15	83	±31	±46	98
Bromodichloromethane	76 - 112	8	91	±16	±24	100
Dibromochloromethane	76 - 178	15	96	±30	±45	93
Bromoform	83 - 128	9	93	±18	±27	80
Monochloroacetic acid	16 - 190	39	63	±79	±118	93
Monobromoacetic acid	25 - 180	41	74	±83	±124	98
Dichloroacetic acid	20 - 196	44	77	±87	±131	100
Dibromoacetic acid	22 - 230	42	68	±85	±127	95
Trichloroacetic acid	6 - 74	20	33	±40	±60	98
NPOC	86 - 110	7	98	±14	±21	100
TOX	90 - 120	10	108	±20	±30	100

% C.I. refers to % of time analysis is within 95% confidence interval.

Table 20: Accuracy For Inorganic Parameters

Parameter	Accuracy	Std. Dev.	Mean	Warning Limit	Control Limit	% C.I.
Alkalinity	92 - 111	5	100	±11	±16	100
Total Hardness	88 - 106	6	99	±11	±17	100
Ca Hardness	89 - 105	5	99	±10	±15	100
Chloride	88 - 112	6	101	±11	±17	100
Sulfate	89 - 127	10	106	±21	±31	100
Fluoride	106 - 128	9	113	±18	±27	100
Silica	92 - 110	6	101	±11	±17	100
Sodium	86 - 115	9	98	±17	±26	100
Iron	93 - 110	6	100	±13	±19	100

USEPA Performance Evaluation

Eight performance evaluation studies were performed during the course of the project. The results of the evaluations are summarized in Table 21.

Table 21: USEPA Performance Evaluation Summary

Parameter	Units	WS020	WS021	WS022	WS023	WS024	WS025	WS026	WS027
Chloroform	µg/l	19.6 56	13.1 76.6	44.9 24.3	37.5 45.1	9.9 67.8	83.8 28.7	6.7 51	87.3
Bromoform	µg/l	44 20.5+	67.1 27.8	56.7 25.7	70 15.9	11 60.8	49.4 10.2	16 92	25.5
Bromodichloromethane	µg/l	22.6 73	10.4 39.7	18.6 61.5	12 65.4	22.1 59.9	76.5 9.7	24 58	35.4
Dibromochloromethane	µg/l	63.7 30.2+	44.3 16.4	69 15.7	26.9 44.7	8.1 80.2	48.4 16.5	21 86	33.6
Total THM's	µg/l	149.9 179.7	134.9 160.5	189.2 127.2	146.8 171.1	51.1 268.7	258.1 65.1	67.7 287	181.8
Residual Free Chlorine	mg/l	0.64 1.42		0.31 1.13	0.35 1.26	0.7 1.18	0.54 1.47	0.89 0.27	0.36
Turbidity	NTU	4.4 0.7						5.83 1.28	0.99 0.7
Fluoride	mg/l			0.72 1.55	0.27+ 1.32	1.39 1.77	2.46 1.44	3.43 1.33	4.32
Calcium (as CaCO ₃)	mg/l	116		152				122	138
pH	Units	9.11						9.04	9.21
Alkalinity (as CaCO ₃)	mg/l	34.9		51.0+				40.6	37.9+
Sodium	mg/l							15.6	-15.3
Sulfate	mg/l							22.8 8.79	13.9
Dibromoacetic acid	µg/l								4.4
Dichloroacetic acid	µg/l								6.3
Monobromoacetic acid	µg/l								3.5
Monochloroacetic acid	µg/l								7.1
Trichloroacetic acid	µg/l								9.5

- = Value outside acceptable range on the low side

+ = Value outside acceptable range on the high side

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Appendix

Data Collection Spreadsheets