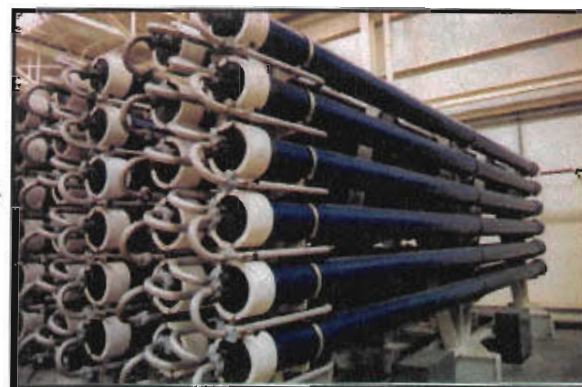


“Removal of Organics in Indirect Potable Reuse Systems:
A Comparison of Efficiencies of Long-term Soil-Aquifer
Treatment (SAT) and Best Available Technologies (BAT)”

FINAL REPORT



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EXECUTIVE SUMMARY

The scope of this study was directed to compare treatment technologies leading to indirect potable reuse of domestic effluent. Removal efficiencies for organics during long-term soil-aquifer treatment (SAT) (travel times > 6 months) and advanced membrane treatment using nanofiltration (NF) or reverse osmosis (RO) were studied using tertiary treated effluent from the Northwest Water Reclamation Plant Mesa, Arizona. The NF and RO membranes used in this study were chosen according to TOC rejection, and applicability in full-scale water reclamation facilities. The same set of analytical methods was applied for product water samples of SAT and membrane treatment including state-of-the-art bulk organic characterization techniques and GC-MS analysis for trace organics. Findings indicate that both systems, tertiary treatment followed by SAT and NF or RO can produce high quality water with DOC concentrations less than 1.3 mg/L in their product water. Based on the characterization techniques applied, bulk organics present in SAT product water resembled natural organic matter present in the original water supply or generated during wastewater treatment. Selected trace organics were substantially removed during travel through the subsurface. Due to the physical separation process of membrane treatment, remaining organic carbon concentrations in NF/RO permeates are comprised by low molecular weight carbon. Based on size exclusion chromatography results, more than 50 percent of the organic carbon in these permeates can be characterized as low molecular acids and neutrals. Wastewater indicator trace organics were not detected in both NF and RO permeates.

Results of this study revealed that both treatment alternatives currently practiced for indirect potable reuse can provide high quality water and are able to provide a reliable barrier for trace organics present in reclaimed water. Findings of the study underline that the final product of SAT and membrane treatment shares the same concern regarding the presence of polar and refractory micropollutants associated with a health concern which survive both treatments. Future research should be directed to the fate of these compounds in indirect potable reuse systems and potential human health effects associated with emerging compounds of concern.

CHAPTER 1

INTRODUCTION

Organics and Indirect Potable Reuse

An increasing number of municipalities have recognized recycled water as a new water resource and have developed a wide variety of options to reuse water. For indirect potable reuse, recycled water can either be discharged into surface water or infiltrated into the subsurface to augment in part a drinking water supply source. Infiltration into the subsurface can be accomplished by either direct injection into the aquifer or by surface spreading which provides additional soil-aquifer treatment (SAT) when water percolates through the subsurface. Indirect potable reuse projects currently established or proposed in the United States are using conventional tertiary treatment followed by surface spreading prior to SAT. For subsurface injection into the aquifer or for surface water augmentation projects, membrane treatment technologies such as microfiltration (MF) pre-treatment followed by nanofiltration (NF) or reverse osmosis (RO) are employed (National Research Council, 1998).

The success of establishing local water reuse systems is associated with a broad spectrum of potential health concerns, such as direct and indirect health effects and aesthetic quality issues (Drewes et al., 2000). The major concerns are that adverse health effects could result from the introduction of pathogens (bacteria, parasites, viruses), anthropogenic organic chemicals or nitrates into groundwater that is consumed by the public. Additionally, organic matter already present in drinking water or formed in the wastewater treatment process due to the decomposition of organic material might significantly influence total organic carbon (TOC) concentrations in groundwater at the point of recovery or can act as precursors for the formation of disinfection-byproducts (DBPs). Whereas concentrations of anthropogenic organic compounds are representing small fractions of a milligram or a few micrograms per Liter, concentrations of natural and effluent derived organic matter are orders of magnitude higher and in sum represent the unidentified bulk of residual DOC in reclaimed water. The State of California Department of Health Services (DHS) has proposed draft regulations addressing groundwater recharge with reclaimed water (Crook et al., 2000). In order to address potential human health risk associated with unidentified and unregulated organics present in reclaimed

water, DHS has selected TOC as a parameter to be monitored in reclaimed water. The bulk of organics present in reclaimed water can be quantified using parameters like TOC or dissolved organic carbon (DOC) after 0.45 μm filtration. The proposed regulations include a goal to achieve a concentration that does not exceed 1 mg TOC/L originating from reclaimed water in groundwater extracted by drinking water wells.

SAT systems and NF/RO treatment can be designed to recharge groundwater with treated wastewater. Both systems differ in the way how constituents are removed. Whereas soil-aquifer treatment takes advantage of adsorption and biodegradation processes which occur under unsaturated and saturated flow conditions and usually represents detention times of several month prior to abstraction, membrane treatment such as RO is designed to remove high molecular carbon compounds due to physical separation. Depending on the pretreatment, the type of membrane applied, and operating conditions, NF and RO membranes can also provide substantial removal of low molecular weight trace organics. Quality issues for residual organic compounds present in reclaimed water after NF/RO treatment are associated with polar, low molecular constituents not rejected during membrane treatment, which might survive travel through the aquifer after subsurface injection. Quality issues for residual organic compounds present in reclaimed water prior to surface spreading originate from their resistance to both sorption and biodegradation during wastewater treatment and subsequent soil-aquifer treatment which can lead to their presence in SAT product water. During the last 10 years, comprehensive pilot-scale and field studies were conducted at different sites in the U.S. to investigate performance of both systems regarding removal of organics (Freeman et al., 1996; Madireddi et al., 1997; Fujita et. al., 1996; Drewes & Fox, 1999; Fox et al., in press). Based on findings of these studies, both systems are able to achieve low TOC concentrations in their product water prior to dilution with native groundwater. However, uncertainties exist regarding removal efficiencies for bulk organics and unidentified and unregulated trace organics in both systems and regarding the character of remaining organics present in the product water of both treatments leading to indirect potable reuse.

pretreatment on DOC removal. The results demonstrated that the removal of DOC was independent of the DOC concentrations in the applied effluents. The residual DOC concentrations after simulated SAT correlated best with the DOC concentrations in the associated water supply (Drewes and Fox, 2000). At water reclamation facilities serving areas where surface water with high DOC concentrations were used for drinking water sources, up to 70 percent of reclaimed water DOC after simulated SAT was derived by drinking water DOC. Although, the majority of organic carbon is removed during the initial phase of SAT, field studies have shown that subsequent travel through the subsurface goes along with additional removal of organic carbon concentration and structural transformations of organic compounds (Drewes & Fox, 1999). At the Mesa and Rio Hondo sites, organic carbon concentrations observed in SAT product water (after travel > 4 weeks) were well below 2 mg/L DOC.

Extensive characterization of dissolved organic carbon in drinking water sources, applied effluents and samples from SAT systems was performed in previous studies using state-of-the-art analytical techniques (Fox et al., in press). The analytical techniques used focused on bulk organic carbon characteristics including hydrophobicity, molecular weight distribution, and organic carbon functional groups. According to spectroscopic analysis of organic matter from hydraulically corresponding samples of drinking water and reclaimed water after soil-aquifer treatment, dissolved organic carbon in SAT product water resembled natural organic matter present in drinking water sources (Fox et al., in press).

Performance of NF/RO membranes

Since the late 1990's, the use of microporous membranes, such as ultrafiltration (UF) and microfiltration (MF), as the pretreatment for reverse osmosis has become the industry standard for indirect potable reuse applications. This improvement in pretreatment has favored thin-film composite membranes (such as polyamide membranes – PA), over cellulosic membranes (such as cellulose acetate – CA). Polyamide NF or RO membranes are superior to CA membranes in operating pressure and cost, removal efficiency, and operating life. Increasing competition between membrane manufactures has launched technical innovations that have further reduced membrane operating pressures, increased salt and organics rejection and decreased manufacturing costs.

Since NF and RO membranes are both successfully used in a wide range of applications leading to similar rejections of salts or/and organics, there is no clear distinction what separates a nanofiltration from a reverse osmosis membrane. Table 1.2 presents performance data from NF and RO membranes employed in previous pilot- and full-scale indirect potable reuse studies. Pretreatment of reclaimed water in these studies was either UF or MF.

All TOC concentrations reported in these studies for NF and RO treatment are below 2 mg/L. Due to the fact that most studies reported TOC results close to the detection limit of their TOC analyzer, it is difficult to precisely assess the performance of a specific membrane in terms of organics rejection. However, the introduction of high-sensitivity online TOC monitoring systems and improvements in membrane rejection had recently revealed that TOC concentrations in NF/RO permeates below 0.5 mg/L are feasible when reclaimed water is used as feed water.

Table 1.2 Summary of TOC levels in reclaimed water after NF/RO treatment

Site	Membrane	Permeate TOC (mg/L)	Reference
Polyamide Nanofiltration (thin-film composite)			
Scottsdale Pilot study	Koch Membrane Systems TFC-S	1.9	Freeman et al., 1996
Scottsdale Pilot study	DOW/FilmTec NF-70	0.8	Freeman et al., 1996
Cellulose Acetate Nanofiltration			
Scottsdale Pilot study	Koch Membrane Systems LP	2.0	Freeman et al., 1996
Polyamide Reverse Osmosis (thin-film composite)			
Scottsdale Water Campus	Koch Membrane Systems TFC-HR	< 0.3	Vernon & Alexander, 2000
Livermore		< 1.0	Geselbracht and Crook, 1996
OCWD Pilot study		0.1	Leslie et al., 2000
Livermore	DOW/FilmTec BW-30	< 1.0	Geselbracht and Crook, 1996
Scottsdale Pilot study		0.6	Freeman et al., 1996
Lake Arrowhead	DESAL SG, AG	0.85	Madireddi et al., 1997
Dublin San Ramon Services District	Hydranautics UAY ESPA	< 0.03	Salveson et al., 2000
Cellulose Acetate Reverse Osmosis			
OCWD Water Factory	Koch Membrane Systems ROGA	0.92	Fujita et al., 1996
Scottsdale Pilot study		0.9	Freeman et al., 1996

Objectives of this study

The intention of this study was to fill the gap between existing performance studies on organics rejection during membrane treatment (Reinhard et al., 1986; Fujita et al., 1996; Madireddi et al., 1997; Salveson et al., 2000) and studies addressing transport and fate of organics during SAT (Quanrud et al., 1998; Drewes & Fox, 1999; Fox et al., in press) by using the same reclaimed water source to feed both reuse systems. The primary objective was to compare organics removal efficiencies between long-term SAT (travel times > 6 month) and advanced membrane treatment (MF followed by either NF or RO) using reclaimed water from the Northwest Water Reclamation Plant in Mesa, Arizona. In addition, the study aims to examine mechanisms driving removal of organics in both treatment systems. The Mesa Northwest plant employs tertiary treatment and soil-aquifer treatment and has been in operation for more than 10 years. The membrane study using Mesa tertiary effluent was performed in a pilot-scale at the Water Quality Improvement Center (WQIC) operated by the U.S. Bureau of Reclamation (USBR) in Yuma, Arizona.

After discussions with USBR personnel, an intensive organic carbon characterization study was undertaken from July 2000 to March 2001 with the following major tasks:

1. The same set of analytical methods should be applied to study the performance of long-term SAT and NF/RO membrane treatment using the same reclaimed water.
2. In order to characterize organics present in long-term SAT product water and membrane treated water (after NF and after RO), bulk organic analyses using total organic carbon (TOC), UV absorbance (UVA), fluorescence spectroscopy, and size exclusion chromatography with online TOC and UVA detection were conducted.
3. State-of-the-art fractionation and isolation techniques were performed followed by solid-state carbon-13 nuclear magnetic resonance spectroscopy (^{13}C -NMR), and elemental analysis to characterize properties of organic matter.
4. Trace organics were screened and quantified by gas chromatography with mass spectroscopy detection (GC/MS) and the behavior of selected target compounds representing wastewater indicator were studied.

The major emphasis of this study was pilot-scale orientated. Field data with respect to soil-aquifer treatment reported in this study is a combination of long-term data and characterization work accumulated and performed during an AWWARF/EPA research study (Fox et al., in press) and short-term efforts by the study team during this research project.

CHAPTER 2

EXPERIMENTAL APPROACH

Study site and origin of reclaimed water

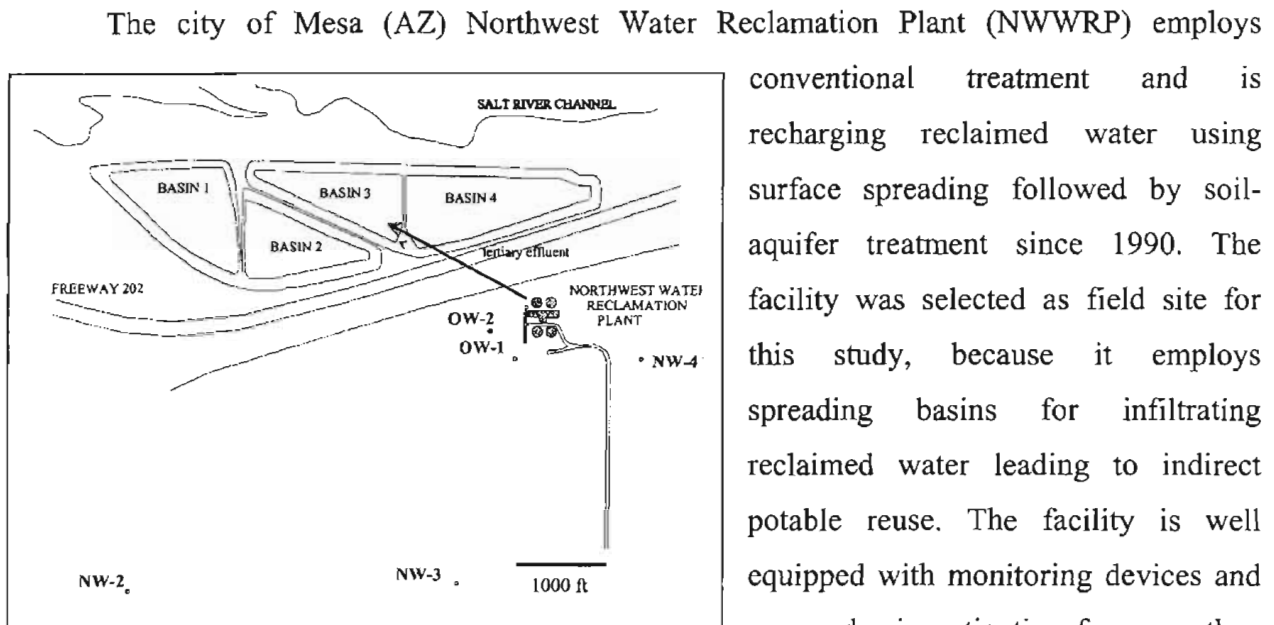


Figure 2.1 Location of recharge basins and monitoring wells at the Northwest Water Reclamation Plant Mesa, Arizona

conventional treatment and is recharging reclaimed water using surface spreading followed by soil-aquifer treatment since 1990. The facility was selected as field site for this study, because it employs spreading basins for infiltrating reclaimed water leading to indirect potable reuse. The facility is well equipped with monitoring devices and was under investigation for more than four years (Fox et al., in press). The Mesa Northwest Water Reclamation Plant is a nitrifying-denitrifying activated sludge treatment system followed by tertiary filtration with a capacity of 8 mgd (30,000 m³/d). Chlorinated tertiary effluent is used for recharge. Tertiary effluent is alternately discharged into the Salt River bed for 10 days and then fed into four recharge basins for five days occupying an area of 12 hectares. The spreading basins receive only reclaimed water. The location of recharge basins and groundwater monitoring wells located in the vicinity of the facility are indicated in Figure 2.1. Per the terms of the recharge permit, basins are flooded one at a time. The flooding-drying cycle varies for each basin and depends on basin specific infiltration rates and soil properties. Fine clay lenses result in low infiltration rates (6-12 cm/d) and therefore, the hydraulic resistance of a clogging layer is less than the resistance of the soil. On average, each basin experiences two complete wet/dry cycles per month. The vadose

zone below the basins is typically less than 1.6 m deep. The majority of flow occurs under saturated conditions as a consequence of the local hydrogeological conditions. The nitrifying-denitrifying system provides a consistent effluent quality, which is applied to the spreading basins with DOC concentrations of 5-7 mg/L and total nitrogen concentrations less than 10 mg-N/L. The majority of recharged water has not been recovered and a plume of reclaimed water extends greater than 2,000 meters downgradient from the recharge site. Regional groundwater flow is directed to the southwest. The reclaimed water plume is primarily contained in an upper alluvial unit approximately 30 m thick. Over twenty downgradient groundwater monitoring wells within the upper alluvial unit have been sampled during previous studies to characterize water quality changes in the reclaimed water plume (Fox et al., in press). Four of these monitoring wells representing different travel times were selected and sampled during this study.

Field sampling

For this study, four large composite samples (Pre, A, B, and C) of Mesa tertiary effluent were sampled (1,600 Liter each) over a course of four weeks in order to provide feedwater for subsequent membrane studies, to perform soil-column experiments simulating SAT, and to conduct advanced organic carbon characterization techniques. The tertiary effluent composite samples were collected after dechlorination prior to discharge to the Salt River bed. In addition, three downgradient groundwater monitoring wells within the upper alluvial unit were sampled to characterize water quality changes in the reclaimed water plume. Samples were collected at monitoring wells representing travel times of 6-12 months (OW2), 12-18 months (NW-2), and 6 years (6U), respectively. Due to groundwater modeling efforts and mixing calculations based on sulfate data, dilution with local background groundwater in these wells was less than 10 percent or negligible (Fox et al., in press). Additionally, a local groundwater well (OW2-200) not affected by reclaimed water was included in the study to represent local background quality. The samples were contained in 200 L-plastic carboys and directly delivered to the Arizona State University laboratory.

Laboratory studies

In the laboratory, adapted soil-column systems were employed to study DOC biodegradation and to simulate short-term SAT in a controlled environment. One 0.5-m column was used to simulate saturated aerobic redox conditions. The system was operated in a recycle mode to study the impact of time on organics removal in an aerobic environment. A second soil-column system was employed that simulated saturated, anoxic aquifer conditions in a series of four 1-m columns. A flow-through mode was established for the four anoxic columns simulating a hydraulic travel time of 21 days. Soil for both systems was collected from the Agua Fria River bed in Glendale, Arizona, which represents the composition of local aquifer material. The anoxic soil-column set-up is shown in Figure 2.2. Both laboratory column set-ups were initially biologically adapted using Mesa secondary effluent.

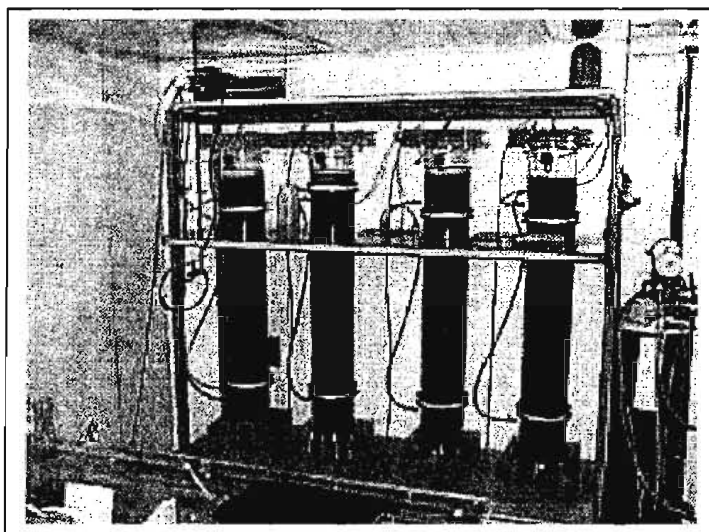


Figure 2.2 Experimental set-up of anoxic soil-column study to simulate short-term soil-aquifer treatment.

Membrane studies

In order to compare the performance of long-term SAT at the Mesa site with membrane treatment using NF and RO, a membrane pilot-scale unit was employed provided by the WQIC Yuma, Arizona to further treat Mesa tertiary effluent. Since the type of membrane and

operational conditions are driving factors for removal of organics, membranes and operational parameters for this study were selected according to TOC rejection considering existing or proposed full-scale field facilities for indirect potable reuse in the U.S. Table 1.2 summarized commonly used membranes in the field and rejection for organics reported for these facilities. For example, the selected RO membrane of this study is employed at the Scottsdale Water Campus (Arizona), a 10 mgd state-of-the-art facility for indirect potable reuse. The improvement of operational parameters such as fouling effects, pressure requirements, cleaning cycles or others were not subject of this study. The membrane studies were performed using four different Mesa tertiary effluents (Pre, A, B, C).

Microfiltration. The tertiary treated effluents sampled at the Mesa Northwest Water Reclamation Plant were additionally treated using microfiltration in order to avoid fouling of the NF and RO membranes due to presence of particular organic carbon. A mobile microfiltration unit (Osmonics/Desal EW4040F) was employed at Arizona State University with an active area of 8.36 m^2 . The microfiltration element (with a length of 40") was installed in one 4" diameter pressure vessel. The unit used is shown in Figure 2.3. The MF unit was mounted on a MF test skid and operated at 1 gpm (3.78 L/min) filtrate flow, at 2 gpm (7.57 L/min) concentrate flow, and a differential pressure of 3.1 psi (21.6 kPa).

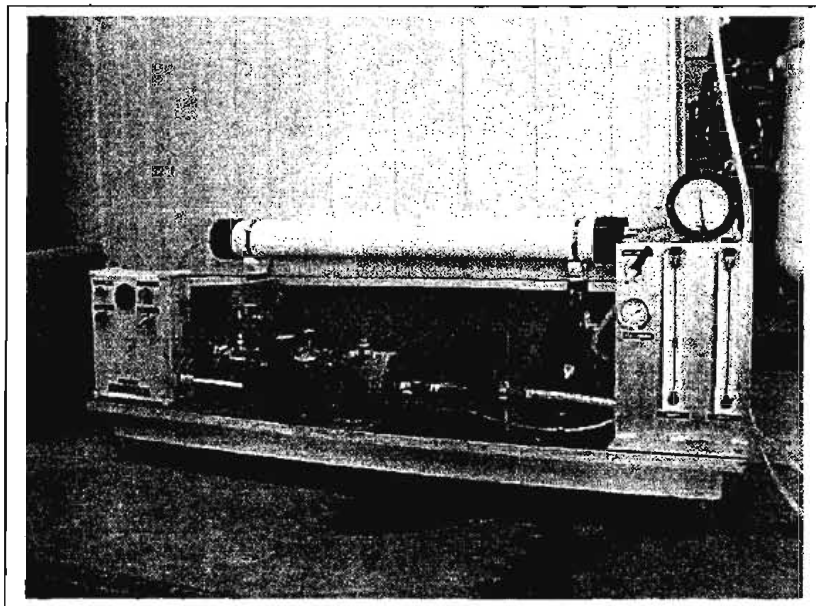


Figure 2.3 Osmonics/Desal Microfiltration unit used during this study

Filtrate flow declined slightly during the 2 hours of operation to generate a total filtrate volume of 900 L. The same day, the microfiltered reclaimed water sample were shipped to the WQIC in Yuma, Arizona.

Nanofiltration. Two different polyamide nanofiltration membranes were selected for this study: a DOW/FilmTec NF-90 2540 and a Koch Membrane Systems TFC-S 2540. The membrane elements used had a diameter of 2.5'' and a length of 40''. Specifications of the membranes are listed in Table 2.1. The NF-90 was employed during the first three experiments (Pre, A, and B) and the TFC-S was used during the last experiment (C). Two elements of each NF were installed in one 2.5'' diameter pressure vessel with a length of 80''. The set-up allowed to individually sample permeate of each single element. The NF elements were specified as 1A and 1B.

Reverse Osmosis. The thin-film polyamide TFC-HR 2540 membrane manufactured by Koch Membrane Systems served as reverse osmosis membrane. The RO elements used had a diameter of 2.5'' and a length of 40''. Specifications are listed in Table 2.1.

Table 2.1 Specifications of NF and RO membranes used during this study

Type	Manufacturer	Active area	Molecular weight cutoff (MWCO)	Rejection of inorganics	Typical operating pressure
NF90-2540	DOW/FilmTec	26 ft ² 2.5 m ²	~ 200 Dalton	85 – 95 % (Cl ⁻) >97 % (hardness)	75 – 150 psi 517-1035 kPa
TFC-S 2540	Koch	27ft ² 2.5 m ²	~ 200 Dalton	90 – 92 % (Cl ⁻) 98 – 99 % (hardness)	75 – 150 psi 517-1035 kPa
TFC-HR 2540	Koch	27ft ² 2.5 m ²	~ 100 Dalton	99.5 % (Cl ⁻) 99.8 % (hardness)	200 – 400 psi 1380-3105 kPa

The RO membrane was used in all four experiments (Pre, A, B, and C) in parallel to the NF membranes. Two RO elements were installed in one 2.5'' diameter pressure vessel with a length of 80''. The set-up allowed to individually sample permeate of each single element. The RO elements were specified as 2A and 2B.

Prior to the test, all membranes were intensively flushed with RO permeate available onsite, and permeate quality was analyzed for conductivity, UV absorbance and TOC concentrations. The rinse water provided onsite had a conductivity varying between 230 and 250 $\mu\text{S}/\text{cm}$, an average UV absorbance of 0.45 l/m, and a TOC concentration which varied between 0.15 and 0.8 mg/L. During the pre-test, the membrane element released a significant amount of organic carbon resulting in DOC concentration of 117 mg/L in the rinse water. Based on a low SUVA of 0.05 L/mg m, the released carbon was dominated by non-aromatic compounds. It was decided, to intensively flush the MF element with RO permeate for 6 days. After this intensive rinsing, no further release of carbon was detected.

The NF and RO membranes showed only slightly higher DOC concentrations during the initial rinse of the new elements. After processing 100 L RO permeate rinse water, DOC concentration and UV absorbance of the NF and RO permeates did not differ to concentrations measured in the rinse water.

Membrane operation. A flowscheme of the membrane pilot plant used at the WQIC is illustrated in Figure 2.4. The so called “clean water system (CWS)” is shown in Figure 2.5.

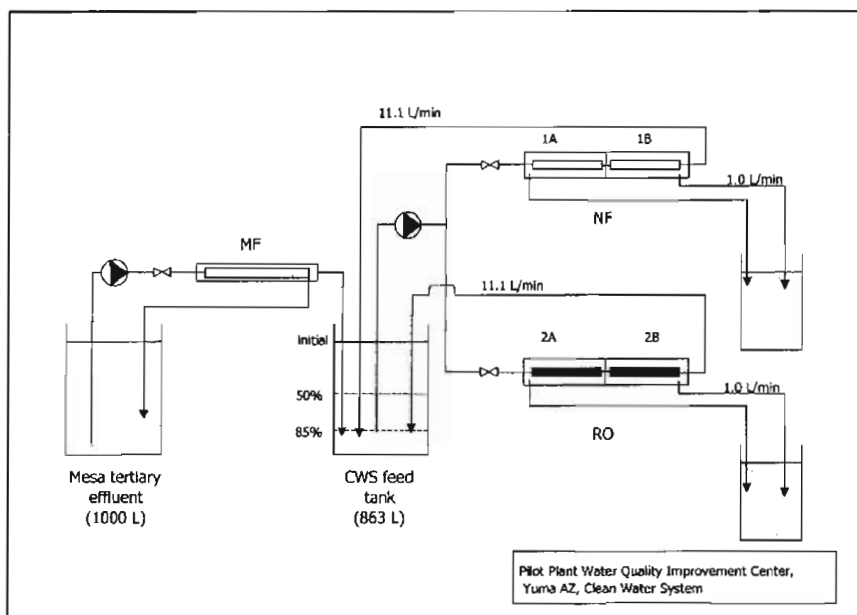


Figure 2.4 Flowscheme of the clean water system (CWS) at the WQIC, Yuma, Arizona

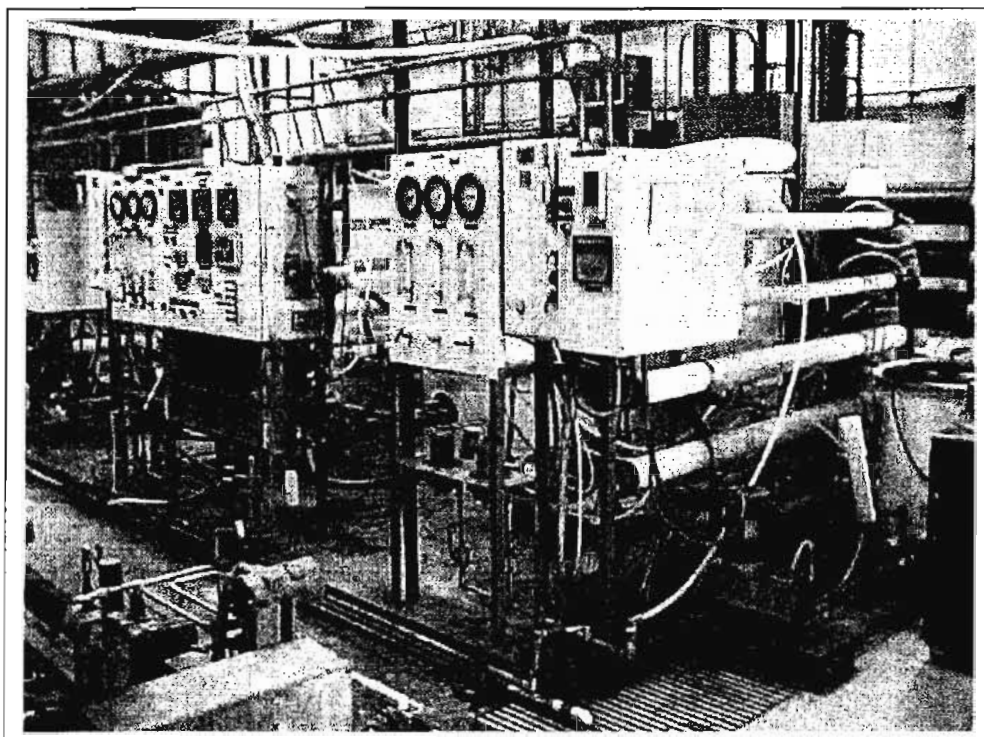


Figure 2.5 Clean water system at the WQIC, Yuma Arizona

The microfiltered Mesa tertiary effluent was adjusted using concentrated hydrochloric acid to a pH of 6 and fed to the NF membrane and a RO membrane vessel aligned in parallel (Figure 2.4). Both vessels were arranged in a recycle pass mode in order to achieve a rate of recovery between 80 to 90 %. Each set of vessels was equipped with inlet and outlet control valves for independent control of the transmembrane pressure. The vessels were operated in a constant flux with variable pressure mode. A permeate flux of ~ 1.0 Liter/min was implemented for all membranes considering an average flux of approximately 14 gfd (34.2 m/h) as applied in full-scale facilities (AWWA, 1999). The NF and RO operation was established in recycle mode. Reject of both membranes were pumped back into the feed container. Due to this operation, the feedwater concentration constantly increased simulating increasing feed concentration over a series of membrane stages. A dosage of anti-scalent chemicals was not applied due to the short time of operation and to avoid interference during subsequent organics analyses.

In order to generate sufficient permeate volume for advanced chemical characterization, each test was performed for 4-5 hours. During each test, NF and RO permeates were collected continuously in 50 L-carboy drums. The operation mode of recycling the reject allowed to collect permeate samples as a function of increasing feedwater concentrations representing the initial phase of the experiment, the phase of 50 percent remaining feed volume, and the phase of 85 percent remaining feed volume. During these phases, permeate and feed water sample were collected for TOC, UV absorbance and conductivity analyses to monitor quality changes. In order to collect a representative sample for the subsequent advanced organics analyses, 150 Liter composite samples of the NF and RO permeates were prepared composed of similar aliquots representing the initial phase, 50 percent remaining feed volume, and 85 percent remaining feed volume of the NF/RO treatment process.

Sampling Program

The sampling effort during this study focused on four tertiary effluent sampling events at the Mesa Northwest Water Reclamation Plant in September and October 2000 in order to provide feedwater for the subsequent membrane studies, soil-column experiments, and advanced organic carbon characterization efforts. In addition, a total of five monitoring wells at the Mesa

site were sampled to provide background and long-term SAT field samples. The sampling program conducted during this study is - differentiated into various analyses - presented in Table 2.2.

Table 2.2 Samples generated and analyses performed during this study

Sample	Date	Physical-chemical (T, pH, conductivity)	Anions	Cations	TOC	UVA	Trace Organics	LC-OCD	Advanced organics characterization
Mesa tertiary effluent Pre	9/25/00	X			X	X			
After MF	9/25/00	X			X	X			
NF permeate	9/26/00	X			X	X			
RO permeate	9/26/00	X			X	X			
NF/RO concentrate	9/26/00	X			X	X			
Mesa tertiary effluent A	10/10/00	X	X	X	X	X	X	X	X
After MF	10/11/00	X	X	X	X	X	X	X	
NF permeate	10/11/00	X	X	X	X	X	X	X	X
RO permeate	10/11/00	X	X	X	X	X	X	X	X
NF/RO concentrate	10/11/00	X	X	X	X	X			
Soil-column aerobic	10/10/00	X	X	X	X	X			
Soil-column anoxic	10/10/00	X	X	X	X	X	X		
Mesa tertiary effluent B	10/19/00	X	X	X	X	X	X	X	
After MF	10/19/00	X	X	X	X	X			
NF permeate	10/20/00	X	X	X	X	X	X	X	
RO permeate	10/20/00	X	X	X	X	X	X	X	
NF/RO concentrate	10/20/00	X	X	X	X	X			
Mesa tertiary effluent C	10/24/00	X	X	X	X	X	X	X	X
After MF	10/24/00	X	X	X	X	X			
NF permeate	10/25/00	X	X	X	X	X	X	X	X
RO permeate	10/25/00	X	X	X	X	X	X	X	X
NF/RO concentrate	10/25/00	X	X	X	X	X			
Monitoring wells:									
OW2-90'	3/15/00	X	X	X	X	X	X	X	X
OW2-200'	3/15/00	X	X	X	X	X	X	X	
NW-2	9/6/00	X	X	X	X	X	X		X
NW-4	12/18/00	X	X	X	X	X	X		X
6U	4/11/00	X	X	X	X	X	X	X	X

X: analyses performed

Due to limited access and ongoing construction at the Mesa site, groundwater wells OW2 and 6U were already sampled during spring of 2000. Monitoring wells NW-2 and NW-4 were sampled in September and December of 2000, respectively. The first test (Pre) using microfiltered Mesa effluent was designed as a pre-experiment in order to adjust operational conditions and to proof performance of each single element. No samples were collected from this experiment for advanced organics analyses.

Fractionation and Isolation of organic matter using reverse osmosis and XAD resins

Fractionation techniques currently applied in the field of organic carbon characterization are not only operational defined but also in a steady process of ongoing improvement. To address this dynamic, especially where it is driven by efforts to improve recoveries, three different fractionation and isolation techniques were applied in this study. The purpose of doing this was to be consistent with the most commonly used approach in the field, which allows to compare findings to studies reported in the literature, and additionally to improve the recovery of particular organic carbon fractions. Since this study is dedicated to compare removal efficiencies of organics of two alternative technologies leading to indirect potable reuse, higher recoveries are generating more organic carbon for the scope of advanced characterization techniques applied.

A combination of reverse osmosis, Amberlite® XAD-4 and XAD-8/4 resin adsorption was employed to concentrate and isolate organic matter from water samples. Sorption characteristics of non polar acrylic ester XAD-8 and low polar styrene divinylbenzene XAD-4 resins are dependent on the average pore diameter (XAD-8/XAD-4) 250/50 Å, the specific surface area 140/750 m²/g, and the specific pore volume 0.82/0.99 cm³/g (Aiken et al., 1992). XAD-resin fractionation also allows to operational differentiate into different fractions of polarity (Thurman et al., 1985). Leenheer (1981) divided the bulk of organic carbon in water samples into three major fractions, hydrophobic organic carbon adsorbing onto XAD-8 resin containing acids, bases and neutrals, and transphilic organic carbon adsorbing onto XAD-4 resin containing acids, bases and neutrals. The remaining fraction, which neither adsorbs onto XAD-8 nor XAD-4, was defined as hydrophilic organic carbon. Organics adsorbed onto XAD-resins can be recovered by either establishing a caustic pH or by using an organic solvent. The recovery

during NaOH elution is usually limited to recover only hydrophobic and hydrophilic acids. Hydrophobic and hydrophilic neutrals remain on the resin. Employing XAD-8/4 resin for surface water and wastewater samples, Aiken et al. (1992), Malcolm (1990, 1992) and Drewes et al. (1999) recovered only 50-70 % of total organic carbon. Neutrals can be recovered by organic solvents, such as acetone or acetonitrile. Another issue associated with organic carbon characterization is the fact that most of the advanced state-of-the-art characterization tools require a minimum amount of organic carbon, which requires for low-TOC samples a concentration step in order to provide sufficient mass. Recently, nanofiltration and reverse osmosis membranes were employed to concentrate organics from surface and groundwater samples (Sun et al., 1995; Croue et al., 2000). However, the drawback of this promising technique, especially where high TDS waters are processed, is that salts are concentrated along with the organics which potentially interfere in subsequent organic carbon characterization techniques. In order to address the issue of recovery, the following three fractionation and isolation approaches were applied during this study:

- (1) adsorption onto XAD-8/4 resin in series and desorption with NaOH,
- (2) RO concentration followed by XAD-4 resin adsorption and backelution with acetonitrile, and
- (3) RO concentration followed by XAD-8/4 resin adsorption in series and backelution with acetonitrile.

For the RO/XAD-4 and the RO/XAD-8/4 resin approach acetonitrile was used to also recover the neutral fraction in order to achieve higher recoveries. The different operational defined organic carbon fractions and the characteristics of the chemical isolation protocol are summarized in Table 2.3.

Table 2.3 Polarity groups during XAD fractionation (adopted from Aiken et al., 1992)

Hydrophobic fraction		Transphilic fraction		Hydrophilic fraction
Acids	Neutrals	Acids	Neutrals	
Adsorbed onto XAD-8 resin at pH 2, desorbed with acetonitrile or NaOH at pH 13	Adsorbed onto XAD-8 resin at pH 2. Recovered by acetonitrile, not recovered at pH 13 using NaOH	Adsorbed onto XAD-4 resin at pH 2 desorbed with acetonitrile or NaOH at pH 13	Adsorbed onto XAD-4 resin at pH 2. Recovered by acetonitrile, not recovered at pH 13 using NaOH.	Not adsorbed onto XAD-8 or XAD-4 resin at pH 2, therefore present in the XAD-remainder

The methods employed consist of the following steps:

- (1) **Pre-concentration** of organic matter by reverse osmosis,
- (2) **Adsorption** of organic matter onto XAD-8 and XAD-4 resin in series to separate organic from inorganic matrix
- (3) **Back elution** of organics with either acetonitrile or NaOH (pH 13)
- (4) **Purification** of isolated organic matter by rotorevaporation, and finally
- (5) **Freeze drying** to provide solid-state isolate.

Isolates were subsequently used for solid-state carbon-13 nuclear magnetic resonance spectroscopy (^{13}C -NMR) and elemental analysis. Table 2.4 provides an overview on the characterization protocol performed for various samples during this study. A detailed description of each isolation method is presented in the following section.

Table 2.4 Overview on fractionation and isolation protocol performed for various samples during this study (recovery of organics was performed by either using acetonitrile or NaOH as indicated)

Sample	Date	RO/ XAD-4 (Acetonitrile)	RO/XAD8/4 (Acetonitrile)	XAD8/4 (NaOH)
Mesa tertiary effluent A	10/10/00	X		
Mesa tertiary effluent A	10/10/00		X	
Mesa tertiary effluent A	10/10/00			X
Mesa tertiary Effluent C	10/25/00			X
Monitoring well 6U	04/11/00	X		
Monitoring well 6U	04/14/99			X
Monitoring well OW-2 90 ft	03/15/00	X		
Monitoring well NW-4	12/19/00		X	
Nanofiltration A	10/10/00		X	
Nanofiltration C	10/25/00		X	

Pretreatment

All samples for subsequent organic carbon characterization were filtered through 0.45-micron and 0.1-micron filters in series at a flow rate of 1 liter per minute to remove particular matter. For this step, 100-25-DH and 100-25-AH filters manufactured by Whatman/Balston were used. After the filtration process all samples were softened by passing the sample through a sodium saturated ionexchange cartridge (Amtek) prior to the RO concentration step to avoid scaling on the RO membrane. All samples were stored at 4°C pending resin isolation.

Another very important aspect for all resin adsorption techniques is the pH dependency of the chemical properties of the functional groups. At low pH weak acids are protonated and adsorb onto XAD-8/4 resin, at high pH weak acids are ionized therefore desorption is favored. Therefore, all samples were acidified to pH 2 with concentrated HCl prior to adsorption.

Pre-concentration of Organics using Reverse Osmosis

A laboratory-scale RO unit was employed to concentrate organics. The RO unit consisted of one Koch TFC-HR 2540 reverse osmosis element (2.5'' diameter, 40'' length). This membrane is characterized as a low-pressure thin-film composite polyamide membrane. The

manufacturer reported a molecular weight cut off (MWCO) of 100 Dalton, and a pH tolerance of 4 and 11. Additional specifications of this membrane are reported in Table 2.1. The membrane was operated in a recycle regime where the concentrate was fed back into the feed container until a desired concentration was reached. Pressure settings of 100-120 psi (690 – 830 kPa) were chosen and the unit was operated with constant pressure and decreasing permeate flux. A flowscheme of the laboratory unit is presented in Figure 2.6. A volume of 90 - 150 liters of the filtered and softened sample were processed. Volumes processed for specific samples differed and are reported in Table 2.5.

Table 2.5 Volume of initial sample processed and final retentate volume in Liter

Sample	Feed (L)	After RO (L)
Mesa tertiary effluent A 10/10/00	100	15
Monitoring well OW-2 90', 3/15/00	180	15
Monitoring well 6U, 4/11/00	195	7
Monitoring well NW-4, 12/18/00	180	11.3
NF permeate A, 10/11/00	200	9.8
NF permeate C, 10/25/00	200	10

The achieved concentration volumes varied between 7 and 15 Liter. The final RO concentrate was acidified with HCl to pH 4 and stored at 4°C pending subsequent resin isolation.

In order to clean the membrane from potential adsorbed organics, 3 liter of a 0.01 N NaOH solution were processed through the membrane element at a pressure setting of 100 psi (690 kPa) in recycle mode. The initial and the final TOC concentrations of the rinsing solution were measured and considered for mass balance calculations. Thereafter, distilled water was processed for approximately 30 minutes at 100 psi (690 kPa) to rinse the membrane prior to a subsequent experiment. During the washing process, samples were collected and the DOC and UVA of the rinse water were monitored to assure that the membrane was free of organic matter.

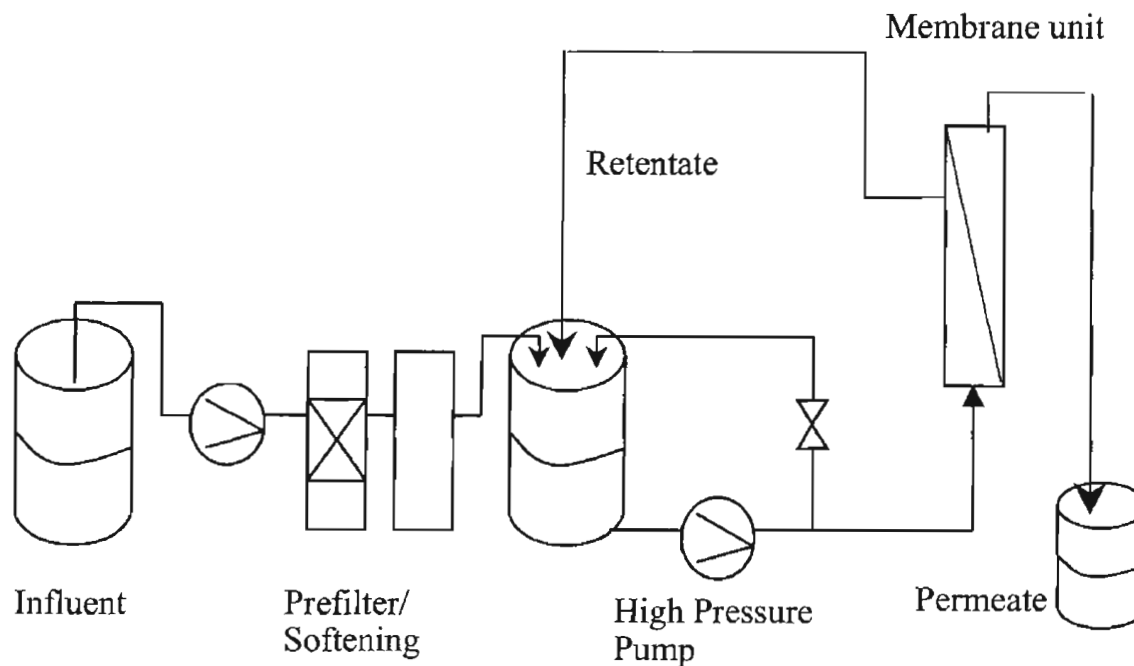


Figure 2.6 Flow scheme of laboratory RO unit to concentrate organics

Fractionation Techniques

Resin Preparation and Cleaning. The Amberlite® XAD 8/4 resin was obtained from Rohm and Haas, PA. Prior to the initial use, the resins were cleaned to remove contaminants and unpolymerized monomers. Therefore, resins were placed in a Soxhlet apparatus and extracted using acetonitrile and methanol alternately for three days. After the extraction process, the resins were filled into two chromatographic glass columns (115 cm high, 6.35 cm in diameter) as resin-methanol slurry. The columns were connected with Teflon tubings and fittings in order to minimize adsorption of organic matter onto tubing and to avoid contamination by desorption of plasticizers. The sample was fed to the resin columns using two peristaltic pumps. The resin columns were then rinsed with distilled water for 24 hours to flush out remaining methanol. The final rinse water was analyzed for TOC.

For the XAD-8/4 resin approach using NaOH, a standard washing procedure was performed after each sample consisting of 6 bedvolumes 0.1 N sodiumhydroxide and 6 bedvolumes 0.1 N hydrochloric acid. The columns were left in the acid phase prior to sample adsorption. Between the alternately base and acid rinse two bedvolumes of distilled water were

passed through to avoid a high pH gradient between the acid and the base rinse. Where acetonitrile was used to recover organics from the XAD-resins, the cleaning procedure was limited to one rinsing step including 200 bedvolumes of d.i. water. The final rinse water was analyzed for TOC.

Capacity factor. The adsorption efficiency of the adsorption step depends on operational parameters. According to Thurman et al. (1978), the capacity factor is defined as the distribution coefficient that represents the ratio between the mass of solute on the resin and the mass of solute present in the void volume (Equation 1).

$$k' = \frac{\text{mass of solute on the resin}}{\text{mass of solute present in the void volume of the resin}} \quad \text{Equation 1}$$

The capacity factor can be used to determine the relationship between the sorbent and the sample volume. Leenheer (1981) defined Equation 2 representing a retention factor of 50 percent of total carbon mass.

$$V_{0.5r} = 2 * V_0 * (1 + k') \quad \text{Equation 2}$$

V_0 is determined as the void volume of the resin determined by taking into account 65 percent pore volume and the volume of the resin (580 ml) (Malcolm, 1990). For the XAD-8/4 approach, a k' of 50 was chosen, which is in accordance with studies performed by Malcolm (1990). However, by applying a k' of 50 almost 50 percent of the total mass of carbon passed the resins and could not be retained. Therefore, to improve recovery rates a lower k' of 2 was selected for all experiments where acetonitrile was used to recover organics from the XAD resins.

XAD-8/4 – resin fractionation. For the XAD-8/4 resin approach the following protocol was applied. Two columns filled with XAD-8 and XAD-4 resin were set up in series. The fractionation scheme of XAD-8/4-resin fractionation including adsorption and resorption step employed in this study is illustrated in Figure 2.7.

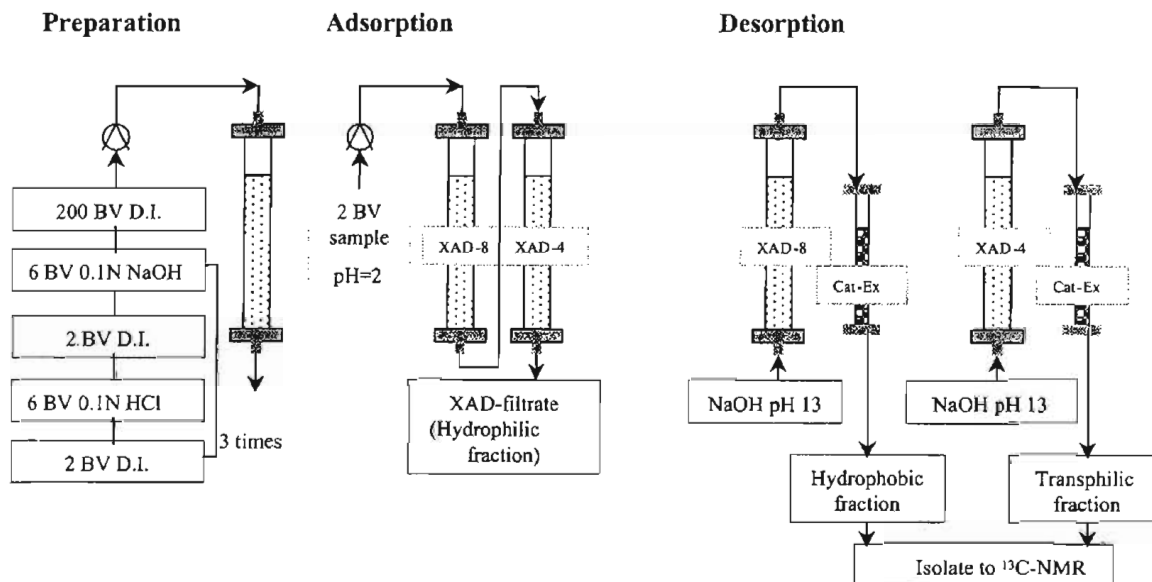


Figure 2.7 Schematic of XAD-8/XAD-4 resin fractionation

The sample (pH 2) was passed through both resins with a flow rate of 10 bedvolumes/h (BV/h). For the adsorption process, a mass balance regarding DOC and UVA was performed in order to quantify the amount of organic material adsorbed by the resins. Therefore, 30 mL were collected on an hourly basis from the XAD-8 and XAD-4 column effluent. After the completed adsorption, the system was rinsed with 3 BV of d.i. water at five cation exchange-BV/h to flush the resins from remaining sample.

Prior to resorption, the HCl-saturated AG-MP-50 ion exchange resin was rinsed with d.i. water at a flow rate of 10 BV/h until the conductivity was lower than 10 μ S/cm. Then, a parallel backflush of XAD-8/4 resins was performed with 0.1 N sodium hydroxide solution at five cation-exchange-BV/h to desorb the organic compounds from the resin. The eluates were directly passed through a hydrogen-saturated cation exchange resin to retain cations which might interfere during subsequent analysis. Both eluates were monitored using an on-line VWR

conductivity meter 2025. Once an increasing conductivity was observed, the fraction was separately collected until conductivity returned back to original level. Finally, the recovered XAD-isolates were lyophilized.

RO-XAD-4 adsorption procedure. RO concentrated samples were acidified to a pH of 2 using concentrated HCl before samples were applied to the XAD-4 columns at a flow rate of 0.5 L/h and with a capacity factor k' of 2 in downstream modes. The schematic of the XAD-4 approach is illustrated in Figure 2.8. After the adsorption process, formic acid was passed through the columns to remove residual salts. Conductivity was recorded by using a VWR flow through conductivity cell. At conductivities of less than $1,000 \mu\text{S}/\text{cm}$, the formic acid rinse was stopped and the columns were rinsed with one bedvolume super Q-water. For the resorption process, two bedvolumes of a solution composed of 75 percent acetonitrile and 25 percent super Q-water were passed through the resins. The eluted fraction was collected in 1 liter acid cleaned glass bottles. Acetonitrile was removed by rotoevaporation using a Buechi Rotavapor R153 (Brinkmann, Switzerland). The cooling water temperature was set $+3^\circ\text{C}$, and the water bath at $32\text{--}35^\circ\text{C}$. The remaining sample volume was lyophilized at a temperature of -145°C using liquid nitrogen to obtain organic carbon in solid state.

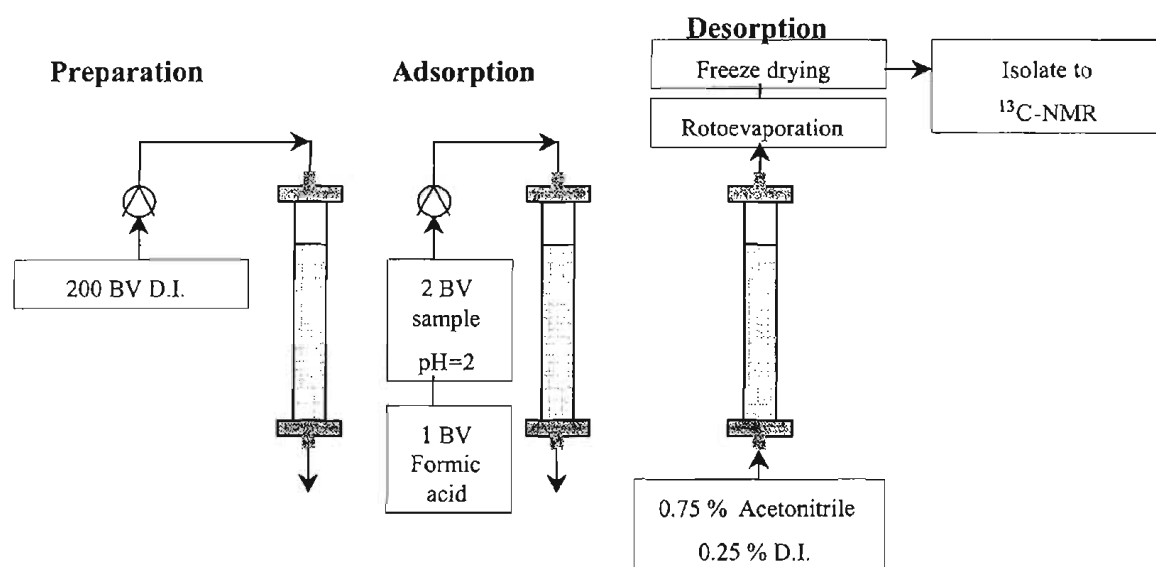


Figure 2.8 Schematic of RO/XAD-4 resin approach

RO-XAD-8/4 fractionation. Additionally, RO concentrates were applied to the RO-XAD-8/4 resins in series in order to differentiate between more hydrophobic and hydrophilic carbon. Prior to adsorption, samples were acidified to a pH of 2. Samples were applied to the XAD-8/4 columns at a flow rate of 0.5 L/h in downstream mode. The approach is illustrated in Figure 2.9. Considering a constant conductivity, formic acid was passed through the resin to remove residual salts. At conductivities of less than $1,000 \mu\text{S}/\text{cm}$ the formic acid rinse was stopped and the columns were rinsed with one bedvolume super Q-water. For the desorption process, two bedvolumes of a solution composed of 75 percent acetonitrile and 25 percent super Q-water were passed downstream through the resin. The eluted fraction was collected in 1 liter acid cleaned bottles. As described earlier, rotorevaporation and lyophilization were final steps to obtain solid-state isolates.

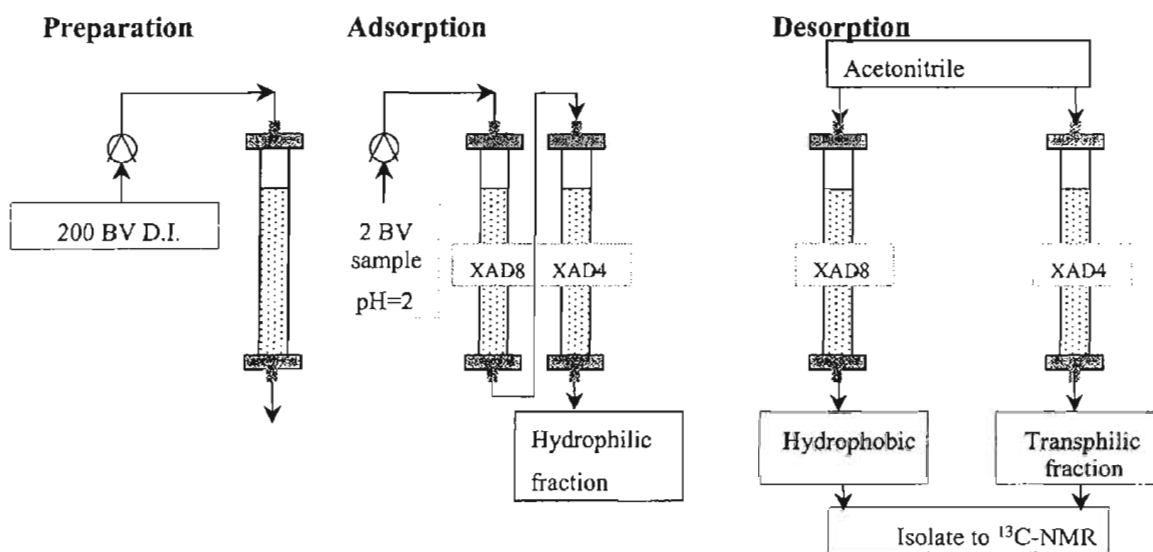


Figure 2.9 Fractionation scheme for the RO-XAD8/4 resin approach

In order to illustrate consequences of applying different approaches, Mesa tertiary effluent A was fractionated using the conventional XAD-8/-4 resin approach with NaOH desorption and using an improved approach employing reverse osmosis to concentrate organics followed by fractionation on either XAD-8/-4 resins or XAD-4 resin only with acetonitrile desorption. The most important difference between the three approaches was the capacity factor k' applied. The proportions of hydrophobic, transphilic and hydrophilic carbon using different

capacity factors are presented in Figure 2.10. Based on this comparison, the proportion of hydrophobic carbon increased by 13 percent when k' was decreased from 50 to 2. When only XAD-4 resin was employed as desalting step, transphilic carbon was rejected along with hydrophobic carbon. The RO/XAD-4 approach resulted in a 8 percent higher proportion of hydrophobic/transphilic carbon.

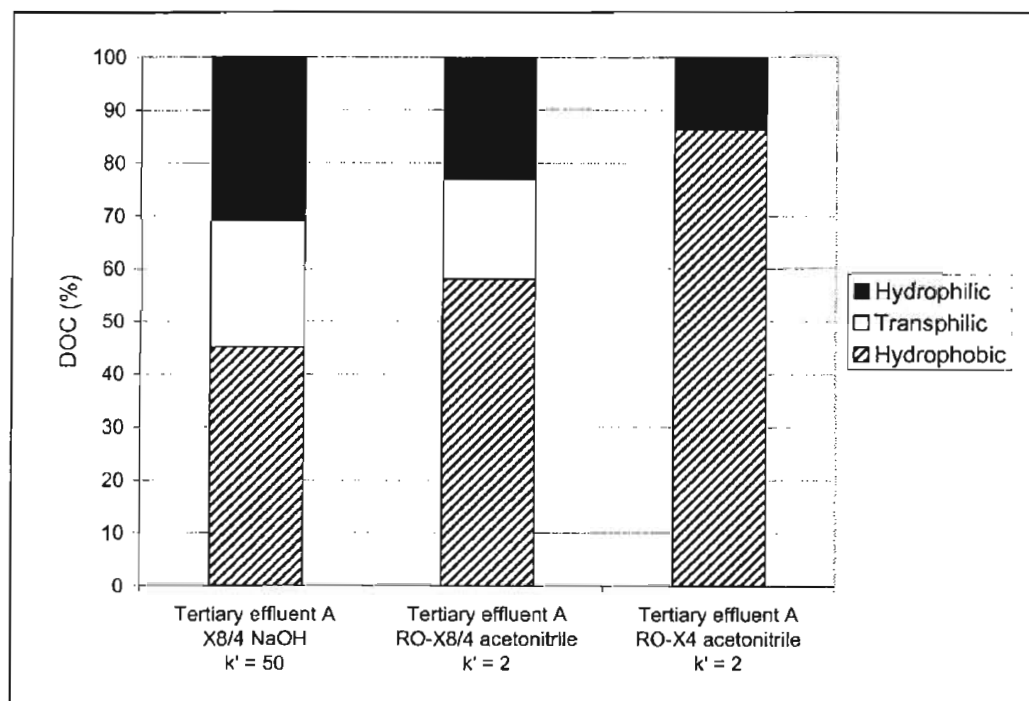


Figure 2.10 Proportion of hydrophobic/hydrophilic carbon after applying different capacity factors processing Mesa tertiary effluent A (10/10/2000)

Pre-concentration of Organics using Reverse Osmosis – Total recovery

The pre-concentration step using the laboratory-scale reverse osmosis unit was used to process Mesa tertiary effluent A, groundwater monitoring well samples and NF permeates A and C. The RO approach provided three fractions, a concentrate, a permeate, and a NaOH rinse. The latter contains organic carbon compounds desorbed from the membrane surface. Table 2.6 summarizes DOC and UVA data of samples concentrated in the RO unit. Only the concentrate was used for subsequent organic carbon characterization techniques. However, the total recovery stated in Table 2.6 in *italics* refers to organic carbon recovered in the concentrate and the NaOH

rinse. Total recoveries of organic carbon for Mesa tertiary effluent A and monitoring well NW-4 were 92 percent and 109 percent, respectively.

Table 2.6 UVA (1/m) and DOC (mg/L) after RO pre-concentration

Sample	Volume (L)	UVA (1/m)	DOC (mg/L)	DOC (mg)	Percent of total carbon
Mesa tertiary effluent A 10/10/00	100	5.43	4.95	495	
Concentrate	15	32.14	30	450	90.9
NaOH rinse	3	1.82	1.71	5.13	1.1
Permeate	85	0.03	0.08	6.8	1.4
<i>Total recovery*</i>					92
NW-4 12/18/00	180	2.59	1.35	243	
Concentrate	11.3	33.76	20	226	93
NaOH rinse	3	0.22	13	39	16.1
Permeate	168.7	n.d.	0.06	9.45	3.9
<i>Total recovery*</i>					109
NF A 10/11/00	200	0.41	0.36	72	
Concentrate	9.8	3.12	2.69	26.36	36.6
NaOH rinse	3	1.91	1.56	4.68	6.5
Permeate	190	0	0.17	32.3	44.9
<i>Total recovery*</i>					43
NF C 10/25/00	200	0.19	0.31	62	
Concentrate	9.8	3.11	2.81	28.1	45.3
NaOH rinse	3	2.13	1.8	5.4	8.7
Permeate	190	0.1	0.13	24.7	39.8
<i>Total recovery*</i>					54

* Total recovery refers to the percentage of organic carbon mass recovered in the concentrate and NaOH rinse.

Nanofiltration permeates A and C, which were also concentrated in the RO laboratory unit, revealed organic carbon recoveries of only 43 and 54 percent, respectively. Although, a high rejecting RO membrane was employed to concentrate organics, the relatively low recovery for NF permeates was expected. The majority of high molecular weight organics were already removed during NF treatment resulting in organics of low molecular weight. The three fractions of the RO pre-concentration step are presented in Figure 2.11 for Mesa tertiary effluent prior to and after SAT and for the NF permeates.

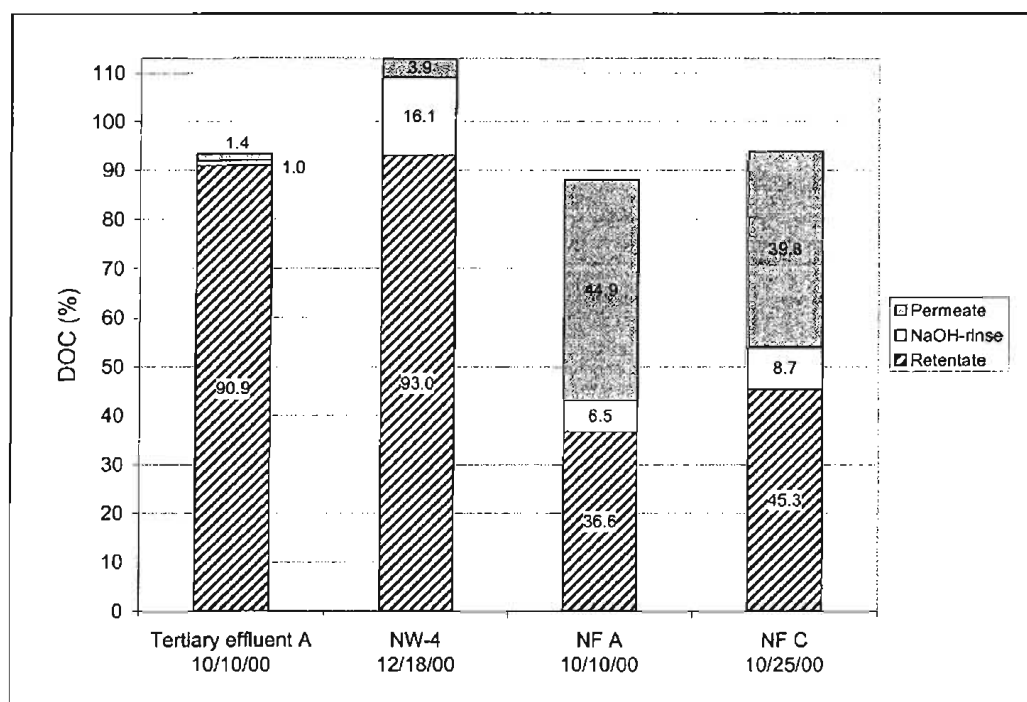


Figure 2.11 Distribution of total organic carbon during RO pre-concentration in percent

Calculation of recovery rates using fractionation techniques with acetonitrile backelution

The purpose of employing different fractionation techniques during this study was motivated by increasing the recovery of organic carbon using acetonitrile during backelution. Table 2.7 summarizes selected recoveries obtained for samples which were fractionated using a pre-concentrated sample (using RO) and isolated using XAD-8 and XAD-4 resins in series with acetonitrile backelution. Hydrophobic carbon from Mesa tertiary effluent was recovered by more than 90 percent. For the NF A permeate fraction 86.7 percent of hydrophobic carbon was recovered. The groundwater sample NW-4 exhibit a recovery of 70 percent, however, variations of DOC concentrations might have affected the recovery calculations significantly. Recovery rates observed for acetonitrile desorption were significantly higher as compared to NaOH desorption, what is consistent with rates reported in other studies (Croue et al., 2000; Drewes et al., 1999a).

The recovery for the XAD resin fractionation was calculated considering the mass of carbon adsorbed onto a resin related to the mass of carbon desorbed from the resin (equation 3).

$$\text{Recovery}_{\text{XAD}} = (\text{Carbon desorbed onto resin} / \text{Carbon adsorbed from resin}) * 100\% \quad \text{Equation 3}$$

Table 2.7 Selected recovery rates for the fractionation techniques employed during the study

Sample	Hydrophobic carbon (mg/L)	Mass of carbon adsorbed onto resin (mg)	Mass of carbon desorbed from resin (mg)	Recovery (%)
Mesa tertiary effluent A (RO-XAD-8)	17.3	51.9	47	90.6
NF A (RO-XAD-8)	1.23	24.1	20.9	86.7
NW-4 (RO-XAD-8)	18.4	83	57.7	69.5

Evaporation method to isolate organic matter from RO permeates

A rotoevaporation approach was developed and employed to concentrate samples with low DOC concentration, e.g. RO permeates, to provide sufficient carbon mass for subsequent analyses. A Buechi Rotavapor vacuum evaporator R-153, Brinkmann Switzerland with a flow rate of 2 L per hour was used. The rotor flask had a capacity of 10 L. The cooling water temperature was set at +3°C and the water bath at 32-35°C. Prior to the experiment the apparatus was cleaned with acetone and approximately 20 liters of d.i. water were evaporated to eliminate any contaminants potentially present in the flask. The TOC of the concentrate and the evaporated d.i. water were determined and showed no detectable contamination.

Exactly 50 liters of reverse osmosis permeate were rotoevaporated to 1 liter to achieve a concentration factor of 50. The evaporation process was performed in increments of 8 liters, which were added to the concentrate present in the flask. During the concentration step, TOC

and UV absorbance measurement were performed. The remaining sample volume of 1 liter was freeze-dried. The solid product was provided for subsequent ^{13}C -NMR spectroscopy.

Selection of Trace Organics

Any analytical protocol applied for trace organic analyses always represents a particular analytical window due to the extraction method applied and the instrument selected for detection. Therefore, a particular method is always limited to identification of specific groups of compounds. The analytical window selected in this study favours non-volatile compounds that can be esterified to increase their volatility. Representatives of this group are ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and alkylphenolpolyethoxycarboxylates (APEC). These particular compounds were chosen because they are the most abundant anthropogenic compounds detected in wastewater effluents (i.e., present in almost all wastewater effluents) and can account for a few percent of the DOC (Fox et al., in press). The selected target compounds represent wastewater indicators (WWI) and do not account for all trace organic compounds. However, they were intended to be used as indicator species - similar to how *E. coli* is used to indicate contaminated drinking waters. The solubility, biodegradability, and known effects for these target compounds are summarized in Table 2.8.

Table 2.8 Summary of solubility, biodegradability, and potential health effects of selected target compounds

Compound	Solubility	Biodegradability	Effects
EDTA	High	Low	None
NTA	Moderate	High	Carcinogenic
APECs	Moderate (varies)	Moderate (varies)	Estrogenic disruption

The analytical procedure employed might miss high MW compounds (400+ g/mol) with low volatility and no acid functional groups. Highly volatile compounds are lost during the evaporation step. Because very small quantities (~1 μL) of the sample were injected into the mass spectrometer, quantification is limited to compounds that are present in relatively high concentrations (i.e., in the $\mu\text{g/L}$ range rather than the ng/L range).

To more easily convey our results, compounds were quantified using their base ion in the mass spectrum and their approximate retention times. No effort was spend to identify every peak in the Total Ion Chromatogram (TIC). Furthermore, since specific m/z ratios are quantified, minimal effort has been put into reducing background sources of contamination that do not affect quantitation of the selected micropollutants (i.e., the quantification procedure acts like an internal filter). Table 2.9 lists the compounds quantified, their approximate retention times, and their respective m/z ratios. The minimum quantitation limit (MQL) is $0.1 \mu\text{g/L}$ and the lower limit of detection (LLD) is $0.01 \mu\text{g/L}$ for this analytical procedure.

Table 2.9 Summary of the trace organic compounds quantified, their approximate retention times and their mass-to-charge ratios

Compound	Approximate Retention Time (min)	m/z ratio
EDTA	36	230
NTA	23	230
AP1EC	29-35	235
NP1EC	31-40	249
NP2EC	35+	279
APnEC ($n \geq 2$)	32+	103/145

Analytical methods

Samples were analyzed for pH, temperature, conductivity and dissolved oxygen in the field. In the laboratory, all samples were filtered using $0.45 \mu\text{m}$ cellulose nitrate membrane filters and stored at 4°C pending further analyses.

Total Organic Carbon. Total and dissolved organic carbon were analyzed as non-purgeable dissolved organic carbon (NPDOC) by thermal combustion with infrared detection of CO_2 using a Shimadzu 5000 TOC-analyzer with an ASI-5000 autosampler (Standard Method 5310 B) (method detection limit (MQL) = 0.15 mg/L ; lower level of detection (LLD) = 0.10 mg/L). Performance of the TOC analyzer was monitored by including both a blank and a QA/QC

standard with each batch of eight samples analyzed. All standards and samples were acidified to pH 2 with 2 N HCl and sparged with ultrapure grade air for 6 minutes prior to analysis, in order to remove volatile compounds and inorganic carbon (CO₂).

UV₂₅₄ absorbance. UV-absorbance (UVA) was measured at a wavelength of 254 nm with a Hewlett Packard 8452A spectrophotometer (path length 5 cm).

Fluorescence Spectroscopy. Fluorescence spectroscopy is a spectrophotometric measurement involving two steps, excitation of molecules that fluoresce (fluorophores) at a UV wavelength (excitation wavelength) and subsequent measurement of their fluorescence at a (higher) emission wavelength. Fluorescence spectroscopy offers an additional tool for characterizing bulk, or isolated, DOC. A fluorescence spectrometer (Perkin-Elmer LS50B) was employed for excitation-emission matrix (EEM) fluorescence spectra. A uniform method of sample preparation was adopted for all three types of fluorescence analysis. Filtered water samples were diluted to 1 ppm of DOC with 0.01 N KCl and acidified to pH 3 with HCl. Samples with less than 1 ppm DOC (e.g., background groundwater) did not require dilution, but did require acidification; all fluorescence intensity values were normalized to 1 ppm. Fluorophores react with metals and can increase or decrease measured fluorescence. Therefore, all samples were diluted to a pH of 3 to minimize complexation of metals with DOC. Below pH 2, fluorescence efficiency decreases dramatically, independent of metal concentrations, due to structural changes in the DOC molecules. EEM profiles were conducted from 200 to 600 nm (5 nm increments) with a 10 nm slit width and a 290 nm-cutoff filter. Blank sample (0.01 N KCl at pH 3) fluorescence was subtracted from all spectra. No inner-filter correction was applied to the samples.

Cations. Cations were quantified using a Perkin-Elmer 3110 atomic absorption spectrometer operated in the flame mode. Samples were introduced into the analyzer to measure the concentration of an element for which the analyzer was adjusted and calibrated. Standard solutions are measured after 5 samples twice to check the accuracy, precision, and reproducibility of the analysis. Variations greater than 5 percent were not accepted.

Anions. Anions were analyzed using a Dionex DX 500 ion chromatograph installed with an AS12A analytical column and combined with an AS 40 autosampler.

Trace Organics. Filtered samples were shipped to Stanford University for trace organic analysis in ice-packed containers and stored at 4° C until analyzed. A sample preparation procedure which involved conversion of the acids into propyl esters was used for the analysis of highly polar anthropogenic organic compounds which served as wastewater indicators, such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and alkylphenolpolyethoxycarboxylates (APEC). A subsample of 25 mL was evaporated to dryness using a Speedvac Model SC210A evaporator (Savant, Farmingdale, NY). After a sequence of extraction steps, an organic phase was generated from which 1 µL of extract was injected into a Hewlett-Packard Model GC/EI-MS (5970 MSD) equipped with a 30 m DB-5 capillary column. All samples were spiked with EDTA-d12 except NW2 (2/15/00), NW3 (1/17/00), and OW2-90' (3/15/00). Quantification of EDTA was performed using internal standards, whereas other trace organic compounds (APEC) were semi-quantified by comparing the base ion with the m/z 240 ion of chrysene-d₁₂. The reported concentrations were based upon the assumption that the response factors for the internal standard and the analyte were the same. The mixture of APEC compounds was quantified using three ions at m/z ratios of 235, 249, and 279 (see also Table 2.9).

Disinfection by-products. Two trihalomethanes (THMs) that were of concern were chloroform (CHCl₃) and bromodichloromethane (CHBrCl₂) were selected as target compounds during membrane studies. THMs were measured using a Hewlett Packard 5890 Series 2 Gas Chromatograph.

LC-OCD analysis. Samples for LC-OCD analysis were shipped to the DOC-Laboratory of Dr. Huber in Karlsruhe, Germany in ice-packed containers. Chromatographic characterization was performed using a high-pressure liquid chromatography-system (LC-OCD) equipped with a conventional GAT PHD-500 UV-Vis detector in association with a Gräntzel thin film photochemical reactor combined with an IR-Ultramat 3 from Siemens. The method is described in Huber and Frimmel (1992).

Carbon-13 nuclear magnetic resonance spectroscopy. A Unity Plus 400 NMR spectrometer (Varian Instruments, Inc.) using proton-carbon cross-polarization was used to generate the ^{13}C -NMR spectra. The instrument contains a 9.4 Tesla Oxford magnet and operates at 100.56 MHz. The ^{13}C -NMR signal was Fourier transformed and the peak areas were electronically integrated by the software VNMR version 5.3, Varian Instruments, Inc. Between 20-50 mg of sample were loaded into the 4 mm silicon nitride MAS rotor and sealed with a Torlon end cap (Varian Instruments, Inc.). The packed rotor was set in the Varian CP-MAS probe and spun at 9000-Hz at the magic angle of 54° and operated at the conditions shown in Table 2.10.

Table 2.10 Instrumental set up for carbon-13 NMR analysis

^{13}C -NMR Examination	Parameter	^{13}C -NMR Examination	Parameter
Magnet	Superconducting magnet 9.4 T, 100.58 MHz	Spinning Rate	9000 Hz
Variable Amplitude Cross-Polarization Sequence	2250	Gain	60
Variable Amplitude Cross Polarization	arrayed	Spectrometer Frequency	100.56 MHz
Cross Polarization Power	on HMB ¹	Spectrum, sweep width	497 ppm
Dipolarization	4095	Pulse Delay	3 s
Decoupler frequency	400 MHz	Line broadening	150 Hz
Decoupler Power	40-50 kHz	Acquisition Time	0.2 s
Cross polarization contact time	3 ms	Probe Temperature	22 –25 °C

¹ Hexamethylbenzene

The instrument was calibrated with Suwannee River Fulvic Acid (SRFA) provided by the U.S. Geological Survey. Peak frequencies were calibrated using the methyl carbon of hexamethylbenzene as an external reference. A background spectrum was generated using an empty rotor and was subtracted from each sample spectrum. Peak areas of the ^{13}C -NMR spectra were calculated by electronic integration using a 7th-order polynomial fit.

Percentages of integrated shift ranges representing different functional groups can be compared to describe potential changes of chemical properties. Table 2.11 presents chemical shift areas of ^{13}C -NMR used in this study.

Table 2.11 Chemical shift areas of ^{13}C -NMR spectroscopy (Drewes et al., 1999)

Chemical shift	Group	Functions
0 – 62 ppm	Aliphatics	Unsubstituted saturated aliphatic carbon
62 – 90 ppm	Carbohydrates	Carbon single bonded with oxygen C-O groups
90 – 110 ppm	Anomerics	Carbon single bonded to two oxygens
110 – 140 ppm	Aromatic I	Protonated, alkyl-substituted aromatic carbon
140 – 160 ppm	Aromatic II	Aromatic carbon substituted with oxygen and nitrogen
160 – 190 ppm	Carboxylic	Carboxyl and ester groups
190 – 230 ppm	Ketonic	Carbonyl, amid, and ester groups

CHN – Analysis. CHN analysis was conducted using a Perkin-Elmer 2400 series II CHNS/O analyzer. The samples were well homogenized and encapsulated in tin cups. The weight of the cups was about 2 mg measured with a microbalance. After weighing the samples they were placed into an autosampler. The specimen was completely combusted at 1760 °C. The resulted gasses are chemically scrubbed of the halogen and sulfur in the CHN mode and separated in a GC column. A thermal conductivity detector (TCD) was used for detection. Prior to analysis of samples, 10-12 blanks and standard checks were run.

Timeframe

The different key tasks along with a schedule of the study are presented in Table 2.12.

Table 2.12 Schedule and list of key tasks of the study

Time	Tasks	Key tasks
August 2000	<ul style="list-style-type: none"> - Pre-studies to set-up the membrane test plant - Preparation for XAD-approach 	<ul style="list-style-type: none"> - Preparing the experimental set-up to compare a tertiary effluent feeding a SAT system with membrane treatment (BAT)
September 2000	<ul style="list-style-type: none"> - Sampling Mesa effluent Pre - Sampling Mesa monitoring well NW-2 - Run membrane test plant with Mesa effluent Pre 	<ul style="list-style-type: none"> - Optimize membrane pilot plant
October 2000	<ul style="list-style-type: none"> - Sampling Mesa effluent A - Sampling Mesa effluent B - Sampling Mesa effluent C - Start soil-column study using Mesa effluent A - XAD-laboratory work A - Run membrane test plant with Mesa effluent A, B, and C 	<ul style="list-style-type: none"> - Compare tertiary effluent A, B and C with BAT treated effluent - Investigate SAT of tertiary treated effluent
November 2000	<ul style="list-style-type: none"> - Trace organic analysis - XAD-laboratory work A, B 	<ul style="list-style-type: none"> - Compare tertiary effluent A, B and C with BAT treated effluent - Investigate SAT of tertiary treated effluent
December 2000	<ul style="list-style-type: none"> - Sampling Mesa monitoring well NW-4 - Start soil-column study using Mesa effluent C - XAD-laboratory work B, C - Trace organic analysis 	<ul style="list-style-type: none"> - Compare tertiary effluent A, B and C with BAT treated effluent - Investigate SAT of tertiary treated effluent
January 2001	<ul style="list-style-type: none"> - XAD-laboratory work C - ^{13}C-NMR spectroscopy - Trace organic analysis 	<ul style="list-style-type: none"> - Compare tertiary effluent A, B and C with BAT treated effluent - Investigate SAT of tertiary treated effluent
February 2001	<ul style="list-style-type: none"> - Preparing final report - ^{13}C-NMR spectroscopy - Elemental analysis 	<ul style="list-style-type: none"> - Preparing final report
March 2001	<ul style="list-style-type: none"> - ^{13}C-NMR spectroscopy - Preparing final report 	<ul style="list-style-type: none"> - Preparing final report

CHAPTER 3

REMOVAL OF BULK ORGANICS DURING LONG-TERM SAT AND NF/RO-MEMBRANE TREATMENT

To address the main objective of this study, this chapter will focus on removal processes of bulk organics and removal efficiencies during soil-aquifer treatment and advanced treatment using nanofiltration and reverse osmosis membranes.

Performance of membrane pilot plant

The performance of the membrane pilot plant was evaluated by plotting variations in water mass transfer coefficient (K_w) against cumulative operating time. The K_w was determined by relating the water flux and the pressure difference as shown in equation 4. The water flux was determined by dividing permeate flux (Q_p) by total membrane surface area (A),

$$K_w = Q_p / A(\Delta P - \Delta \Pi) \quad \text{Equation 4}$$

where $\Delta \Pi$ is the average osmotic pressure gradient and ΔP is the average pressure gradient across the membrane. The mass transfer coefficient determined for the NF membranes over the course of all experiments is presented in Figure 3.1. The K_w for the reverse osmosis membrane TFC-HR is plotted in Figure 3.2. Data are presented for the lead and the second element of each membrane used per vessel.

Immediately after the startup of the NF-90 membrane (Pre), the K_w of the lead and second element showed a rapid decline. The same trend in mass transfer coefficient decline was observed for the startup of the TFC-S membrane in the lead element, which was likely due to membrane compaction. Following the rapid initial decline, the mass transfer coefficient of the NF-90 elements decreased gradually with time due to membrane fouling. No decrease of the water mass transfer coefficient was observed for the TFC-HR reverse osmosis membrane (Figure 3.2). However, the lead element constantly showed a slightly lower K_w , which most likely reflects fouling occurred within the vessel.

Experiment: Pre A B C

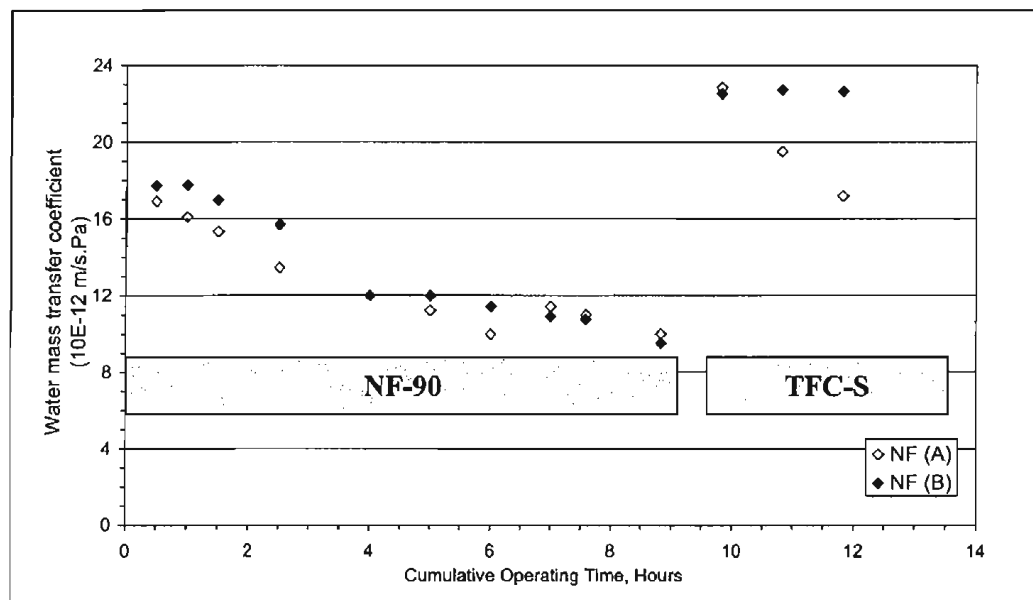


Figure 3.1 Water mass transfer coefficient K_w of NF membranes over cumulative operating time

Experiment: Pre A B C

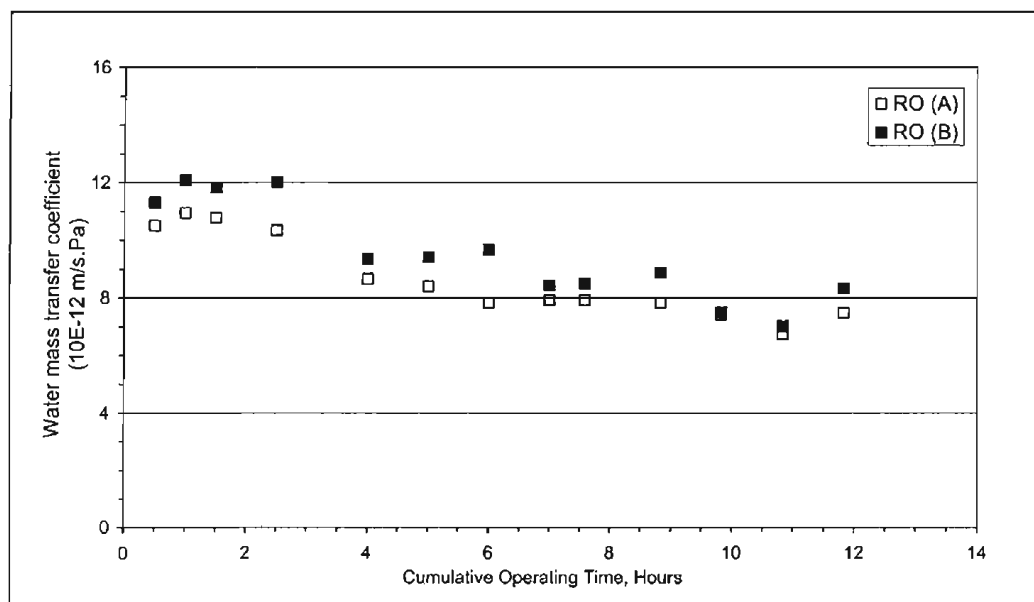


Figure 3.2 Water mass transfer coefficient K_w of RO membrane TFC-HR over cumulative operating time

During the series of all experiments, a feed pressure increase for the NF and RO was necessary in order to maintain a constant permeate flux. The feed and reject pressure measured during the test is presented in Figure 3.3. The feed pressure of the RO increased from initially 700 kPa to 1250 kPa during experiment C. The NF feed pressure was initially adjusted to 450 kPa for both NF membranes tested. During the three tests of the NF-90, the feed pressure increased from 450 to 750 kPa. The pressure drop during operation for both NF membranes was approximately 70 kPa. The RO membrane showed a differential pressure of approximately 50 kPa. With increasing time of operation the feed pressure of both vessels increased in order to maintain a constant flux.

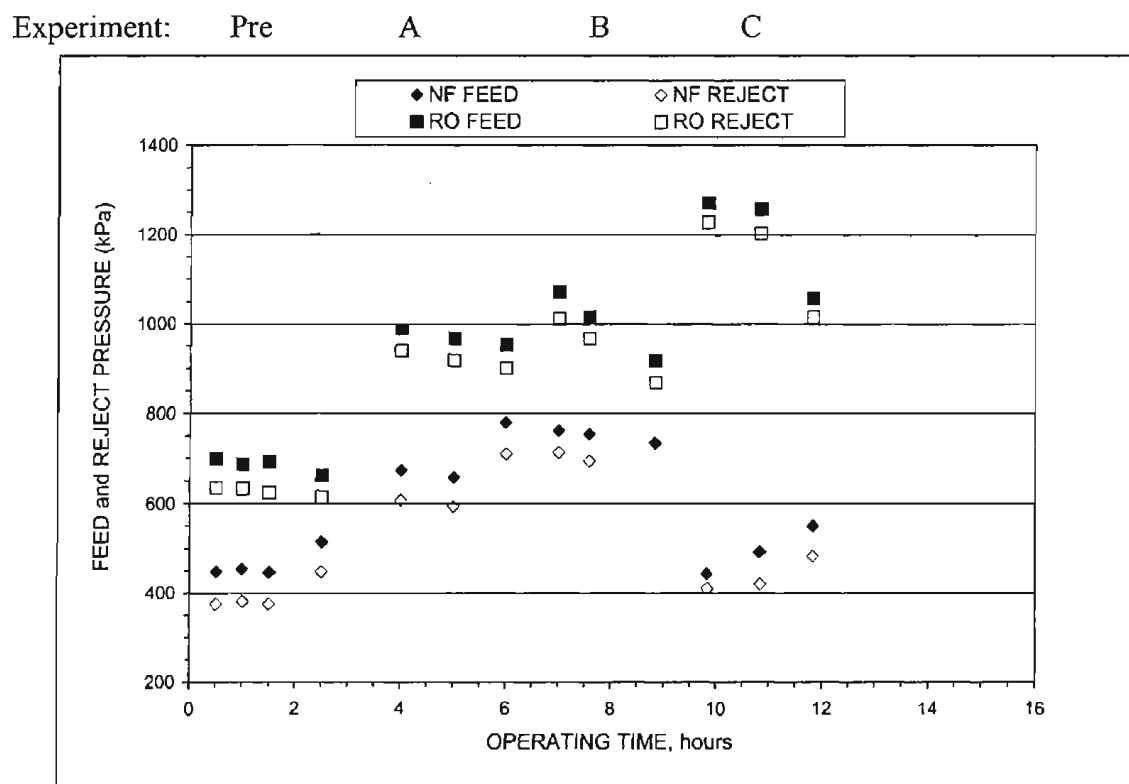


Figure 3.3 Feed and reject pressure in kPa for the NF and RO membranes during the course of all experiments (Pre, A, B, and C) (NF-90 was employed during tests Pre, A and B; TFC-S was used during test C).

The water flux of each element was determined considering the actual permeate flux and the specific membrane surface. The actual water flux is plotted over cumulative operating time in

Figure 3.4. The flux of the NF and RO lead elements varied slightly around 14 gallons per day and square foot representing a permeate flux as observed in full-scale facilities (AWWA, 1999).

Experiment: Pre

A

B

C

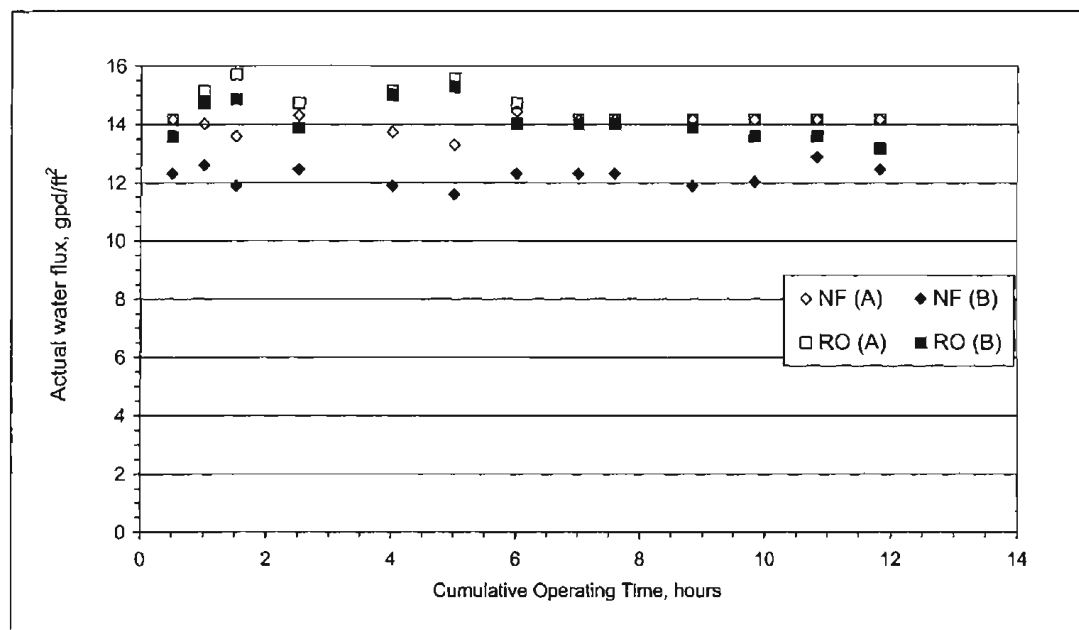


Figure 3.4 Actual water flux of all elements during membrane operation

Salt rejection during SAT and membrane treatment

In order to compare rejections of organics in both treatment systems, this subchapter provides data on salt rejections in SAT and advanced membrane systems.

Depending on redox conditions and soil properties of the recharge site, salts can be removed during SAT by ion exchange reactions, precipitation or reduction reactions. Cation and anion concentrations determined in Mesa tertiary effluent and groundwater monitoring wells located downgradient of the spreading basins are presented in Table 3.1. The standard deviation of anion and cation concentrations is small and indicates constant drinking water source composition and anthropogenic input within the service area during the course of the sampling. Monitoring well NW-2 is considered to represent final SAT product water quality. At the Mesa site, potassium was removed by approximately 55 percent during SAT, which might be

associated with the slight increase of calcium concentrations observed during SAT probably due to ion exchange reactions in the subsurface. Phosphate is sufficiently removed most likely due to iron-phosphate precipitation. Nitrate is partly removed to concentrations of approximately 15 mg/L NO_3^- due to denitrification reactions, which occurred under anoxic redox reactions present at this site (Fox et al., in press).

Ion concentrations determined are consistent with results from intensive sampling events previously conducted at this site (Fox et al., in press). In general, the majority of cations and anions were conservative during SAT resulting in a TDS rejection of only 10 percent. Especially, sodium, chloride and sulfate concentrations are elevated in reclaimed water due to anthropogenic activity and contribution from drinking water sources used in the service area. Since these ion concentrations remained the same during SAT and were higher than local groundwater concentrations, increasing salt concentrations are a potential concern in order to maintain a sustainable operation of a SAT facility.

Table 3.1 Cation and anion concentrations determined in Mesa tertiary effluent and groundwater monitoring wells in mg/L

Sample	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cl^-	Br^-	SO_4^{2-}	NO_3^-	PO_4^{3-}	TDS
Mesa tertiary effluent average and standard deviation*	46.6 ±4.6	28.8 ±1.8	14.2 ±0.9	210.4 ±16	317 ±6	n.d. ±0	177.6 ±24.1	19.2 ±4.6	6.0 ±1.6	1119 ±20.6
OW2-90' 3/15/00	59.5	28.4	8	178.9	297.6	0.12	174.1	14.5	1.19	1156
NW-2 9/6/00	58	30.4	6.6	203.7	368.5	0.11	141.4	15	0.72	1010
6U 4/11/00	47.1	26.3	5.3	182.9	236.3	n.d.	112.6	6.0	n.d.	989
SAT salt rejection ^Δ (%)	0	0	~55	0	0	0	~20	~22	~100	~10

* average out of three tertiary effluent composite samples (A, B and C)

^Δ rejection = $(1 - C_{\text{SAT-NW2}}/C_{\text{tertiary effluent}}) * 100 \%$

n.d. not detected

Nanofiltration membranes are designed for salt rejection and softening applications (AWWA, 1999). Therefore, it is not surprising that NF and RO membranes are very effective in rejecting salts. Cation and anion concentrations in Mesa tertiary effluent and corresponding

NF/RO permeates are reported in Table 3.2. No salt rejection was observed during MF treatment (data not shown).

Based on TDS concentrations analyzed, the salt rejections of all investigated membranes were above 92 percent. All membranes removed polyvalent anions and cations effectively with rejections greater than 97.5 percent, which is consistent with removal efficiencies reported by the manufacturers (see Table 2.1). With the exception of nitrate and sodium, all membranes showed a removal of monovalent ions of greater than 90 percent. With respect to salt rejection, the nanofiltration membrane TFC-S achieved the same performance as the TFC-HR reverse osmosis membrane. The results proved the efficient role of NF/RO membranes to act as salt barrier in indirect potable reuse systems. However, for subsurface injection projects, the permeate quality usually needs adjustment to the Langelier saturation index in order to avoid any dissolution of minerals after injection into the aquifer. This post-treatment can add minor amounts of additional ions to the permeates.

Table 3.2 Cation and anion concentrations in Mesa tertiary effluent prior to and after NF and RO treatment in mg/L

Sample	Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Cl ⁻	Br ⁻	SO ₄ ²⁻	NO ₃ ⁻	PO ₄ ³⁻	TDS
Mesa tertiary effluent average and standard deviation*	46.6 ±4.6	28.8 ±1.8	14.2 ±0.9	210.4 ±16	317 ±6	n.d. ±0	177.6 ±24.1	19.2 ±4.6	6.0 ±1.6	1119 ±20.6
NF-90 ⁺	0.5 ±0.28	0.65 ±0.21	1.4 ±0.42	23.75 ±7.42	24.85 ±7.62	n.d. ±0	1.77 ±0.62	4.38 ±2.09	0.08 ±0	85 ±20.6
NF-90 salt rejection ^Δ (%)	98.9	97.7	90.1	88.7	92.2	n.d.	99.0	77.2	98.7	92.4
NF TFC-S	0.3	0.3	0.9	12.8	14.47	n.d.	1.14	1.93	0.05	75
TFC-S salt rejection ^Δ (%)	99.4	99.0	93.7	93.9	95.4	n.d.	99.4	89.9	99.2	93
RO TFC-HR [°]	0.63 ±0.98	0.38 ±0.1	0.4 ±0.16	7.75 ±2.33	5.26 ±2.63	n.d. ±0	0.71 ±0.25	1.02 ±0.46	0.15 ±0.06	26.6 ±3.12
TFC-HR salt rejection ^Δ (%)	98.6	98.7	97.2	96.3	98.3	n.d.	99.6	94.7	97.5	97.6

* average out of three tertiary effluent composite samples (A, B and C)

⁺ average out of two tertiary effluent composite samples (A, B)

[°] average out of three RO permeate composite samples (A, B and C)

^Δ rejection = $(1 - C_{\text{permeate}}/C_{\text{feed}}) * 100 \%$

n.d. not detected

Fate of bulk organics during SAT

The average Mesa tertiary effluent DOC concentration of all three composite samples collected was 5.19 mg/L. The standard deviation of DOC for the three effluent samples was 0.41 mg/L indicating a very stable effluent quality. DOC concentrations and UV absorbance results of the tertiary effluent samples and groundwater monitoring wells are reported in Table 3.3. The specific UV absorbance (SUVA) for the tertiary effluent was 1.31 L/mg m. These results are consistent with findings reported by Fox et al. (in press) for Mesa tertiary effluent quality.

Table 3.3 DOC, UVA and SUVA data for Mesa tertiary effluent prior to and after soil-aquifer treatment

Sample location	DOC (mg/L)	UVA (1/m)	SUVA (L/mg m)
Mesa tertiary effluent (A, B, C) ⁺	5.19 ± 0.41	6.79 ± 0.34	1.31 ± 0.16
Soil column aerobic*	3.6	5.5	1.53
OW2-90' 3/15/00	1.31	2.44	1.86
NW-4 12/18/00	1.35	2.59	1.92
NW-2 9/6/00	0.95	2.06	2.17
6U 4/11/00	1.09	1.69	1.55
SAT DOC rejection ^Δ %	84	70	-

⁺ average out of three tertiary effluent composite samples (A, B and C)

* average based on soil column experiments with Mesa tertiary effluent A and C

^Δ rejection = $(1 - C_{\text{SAT-NW2}} / C_{\text{tertiary effluent}}) * 100 \%$

Subsequent SAT using Mesa tertiary effluents A and C simulated in an aerobic soil-column system with a detention time of 4 days decreased the DOC concentration on average by 30 percent to 3.6 mg/L. Drewes & Fox (2000) reported similar DOC removal efficiencies for short-term SAT at the Mesa site. Observations in the field at monitoring wells OW2-90', NW-4, and NW-2 downgradient of the spreading basins revealed a decrease of DOC concentration in reclaimed water by 80 percent resulting in DOC concentrations of 1.31 mg/L, 1.35 mg/L and 0.95 mg/L, respectively. The SUVA value increased from 1.31 in reclaimed water to 1.86 L/mg m at OW2-90' indicating a preferred removal of non-aromatic carbon during travel from the spreading basins to this well. No significant DOC removal occurred during travel from monitoring well NW-2, representing travel times of 12 – 18 months, to monitoring well 6 U,

representing travel times of more than 6 years. However, the SUVA value decreased to 1.55 L/mg m indicating transformation of organic carbon structures during long-term SAT resulting in a decrease of aromaticity in SAT product water.

Fluorescence. Fluorescence spectroscopy has been used for characterizing the structure of organic matter. An excitation-emission matrix (EEM) can be generated which allows distinguishing specific types of organic matter which emit fluorescence light. Fluorescence spectroscopy has been used to characterize organic matter in wastewater (Fox et al., in press), treated surface water (Croue et al., 2000), and detergent whiteners, present in treated wastewater (Poiger et al., 1999).

Three dimensional EEM plots for the three Mesa tertiary effluent samples are shown in Figure 3.5. The spectra are all normalized to 1 ppm DOC. For reference, the large diagonal band of high intensity represents first- and second-order light scattering where the excitation and emission wavelengths are equal (first-order) or two-fold greater (second-order). The y-axis represents the excitation wavelengths, and the x-axis represents the emission wavelengths. The Mesa tertiary effluent samples were quite similar and marked by three general fluorophore peaks (220/300 nm, 230/360 nm, and 280/360 nm), and a broad range of fluorescence response at excitation wavelengths longer than 300 nm. The intensity of the fluorophore peaks was similar for the tertiary effluent samples indicating a similar effluent quality. The three distinct peak locations were also observed in tertiary treated effluent samples from facilities in Arizona and Southern California (Fox et al., in press). Based on studies using single compounds, the peak location 230/360 nm seems to be caused by protein-like material, which is still present in tertiary treated effluent. Whereas, altered fulvic acids, such as the IHSS standard Suwannee River fulvic acid, show a specific maximum at peak location 210/440 nm. However, the peak maximum might shift slightly depending upon the composition and alteration of the fulvic acids examined.

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EEM plots of samples presenting SAT product water, such as OW2-90' and 6U, are presented in Figure 3.6. The SAT samples exhibited similar fluorescence peaks, although the intensity of fluorescence was significantly lower. Especially the peaks at 220/300 nm and 230/360 nm decreased and the prominent peak maximum of the entire spectrum shifted slightly to higher emission wavelengths. This finding is somewhat consistent with the observed decrease of non-aromatic carbon during initial SAT and might indicate to a character of the remaining organic carbon which is dominated by fulvic acid related material.

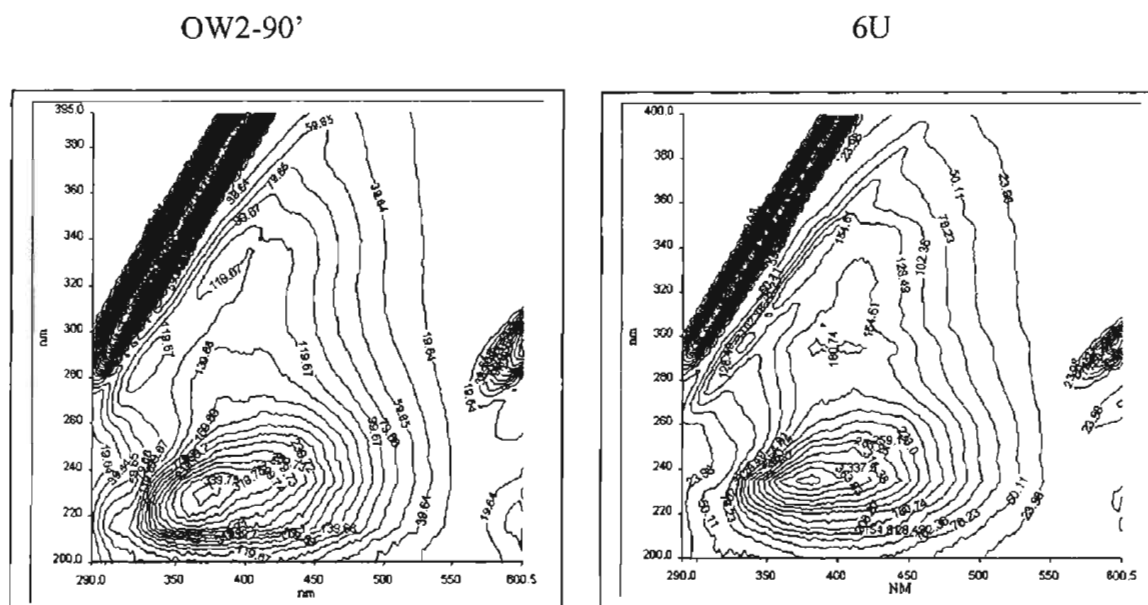


Figure 3.6 Excitation-emission spectra of monitoring well OW2-90' and 6U

Character of organic matter in SAT systems

Hydrophobicity/Hydrophilicity. The humic and non-humic character of organic matter was examined using two resin adsorption chromatography approaches, which differ in the capacity factor k' used during the adsorption step. In order to improve the recovery, reverse osmosis was employed to pre-concentrate organic carbon for samples characterized by low TOC concentration. Mesa tertiary effluents A and C were used to represent reclaimed water prior to SAT. SAT product water was characterized using groundwater samples from monitoring wells NW-2, NW-4 and 6U. The resin fractionation technique provides three operational defined

fractions, hydrophobic, transphilic and hydrophilic carbon. Results of the resin adsorption chromatography using tertiary effluent prior to and after SAT are summarized in Table 3.4. The fractionation results of Mesa reclaimed water prior to and after SAT are presented in Figure 3.7 and 3.8 for the two approaches employed. Tertiary effluents A and C and groundwater wells NW-2 and 6U were fractionated using the conventional XAD-8/-4 resin approach with k' of 50. For comparison, samples of Mesa tertiary effluent A and monitoring well NW-4 were fractionated after RO pre-concentration using XAD-8/4 resins and a k' of 2.

Table 3.4 Hydrophobic/hydrophilic carbon based on resin adsorption chromatography

Sample	Hydrophobic		Transphilic		Hydrophilic		Total	
	UVA	DOC	UVA	DOC	UVA	DOC	UVA	DOC
Mesa tertiary effluent A X8/4 NaOH, $k'=50$	1.01	2.23	2.02	1.53	2.01	1.19	7.16	4.95
Mesa tertiary effluent C X8/4 NaOH, $k'=50$	0.59	1.81	1.45	0.94	1.36	2.21	6.74	4.96
Monitoring well NW 2 X8/4 NaOH, $k'=50$	1.14	0.61	0.56	0.31	1.54	0.57	3.24	1.48
Monitoring well 6U X8/4 NaOH, $k'=50$	0.74	0.65	0.77	0.14	0.19	0.31	1.7	1.1
Mesa tertiary effluent A RO/X4, $k'=2$	36.41	25.88	N/A	N/A	2.89	4.12	32.14	30
Mesa tertiary effluent A RO/X8/4, $k'=2$	23.9	17.29	7.65	6.85	6.2	5.69	31.89	29.8
Monitoring well NW-4 RO/X8/4, $k'=2$	25.59	18.44	2.93	2.13	2.03	1.53	2.59	22.03

For Mesa tertiary effluents A and C, XAD-8/-4 resin fractionation ($k' = 50$) indicated that 24 to 45 percent of the total DOC was hydrophilic, 19 to 31 percent consisted of transphilic carbon, and 37 to 45 percent consisted of hydrophobic acids and neutrals. The relatively large variation of transphilic carbon in the effluent samples is not consistent with previous studies at this site (Drewes and Fox, 1999; Drewes et al., 1999), where only approximately 20 percent of organic carbon was classified as transphilic. Considering groundwater well 6U representing post-

SAT reclaimed water sample, hydrophilic and transphilic carbon tended to be preferably removed resulting in a more hydrophobic character of long-term SAT water (Figure 3.8).

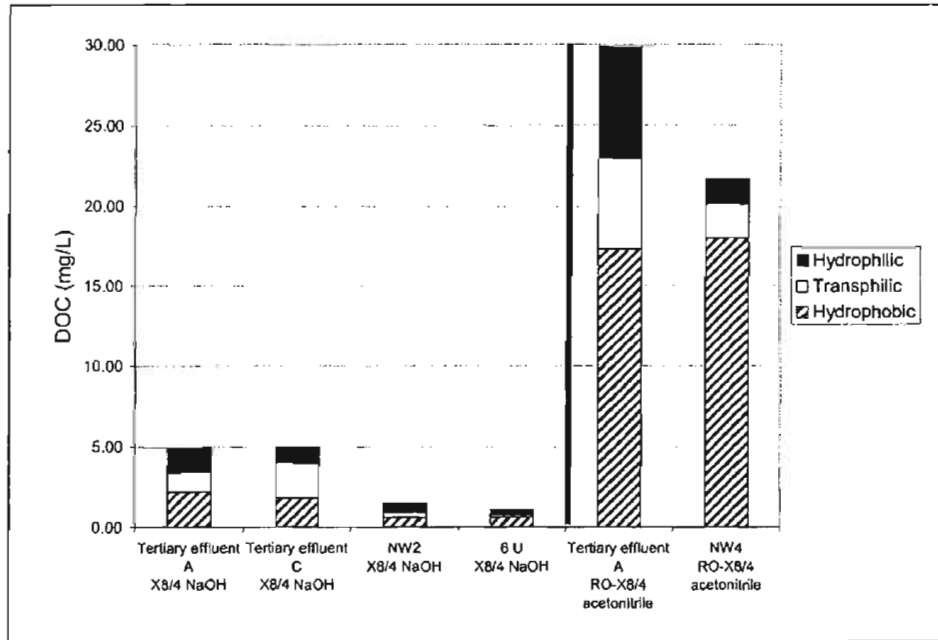


Figure 3.7 Resin fractionation results as DOC in mg/L for Mesa tertiary effluent prior to and after SAT

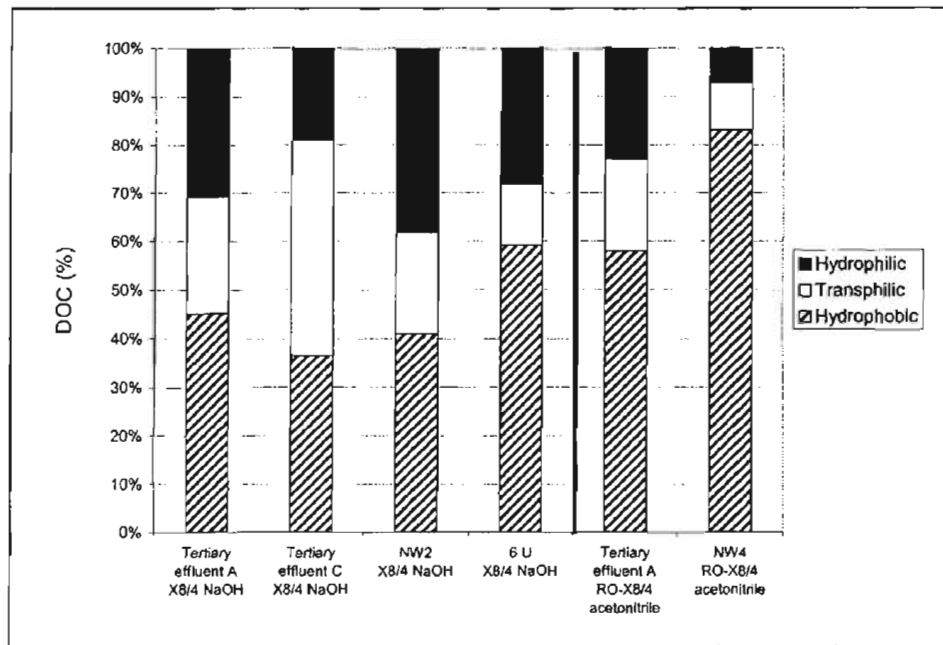


Figure 3.8 Resin fractionation results as percent of DOC for Mesa tertiary effluent prior to and after SAT

Monitoring well sample NW-2 downgradient of the spreading basins confirmed the substantial removal of transphilic and hydrophilic organic compounds by more than 70 percent and revealed a significant removal of hydrophobic carbon during SAT by more than 66 percent. The same trend of a preferred removal of transphilic and hydrophilic carbon was observed for samples fractionated using a k' of 2 (Figure 3.8). Hydrophobic carbon in reclaimed water increased from 58 percent to 82 percent in SAT product water (NW-4). A comparison of SAT product water (NW-2) with Mesa groundwater not affected by reclaimed water examined by Drewes & Fox (1999) revealed a similar distribution of organic carbon fractions with a smaller portion of hydrophobic carbon present in background water.

^{13}C -NMR spectroscopy. In addition to classify organic carbon into humic and non-humic, advanced carbon-13 nuclear magnetic resonance spectroscopy were applied to provide further insight into structural changes of organic matter during SAT. Since solid-state ^{13}C -NMR was employed, only XAD-8 (hydrophobic carbon) and XAD-4 (transphilic carbon) isolates were considered for this analysis. The International Humic Substances Society (IHSS) standard Suwannee River fulvic acid provided by the USGS was used as a reference standard for ^{13}C -NMR spectroscopy.

^{13}C -NMR spectra were obtained for XAD-8 and XAD-4 isolates of Mesa tertiary effluent and subsequent SAT samples collected at monitoring wells NW-4, NW-2, and 6U downgradient of the spreading basins. Figure 3.9 presents ^{13}C -NMR spectra of XAD-8 isolates (NaOH desorption) from Mesa tertiary effluent and groundwater wells NW-2 and 6U. The comparison indicated a generally similar distribution of four structural groups such as aliphatic carbon (0 – 62 ppm), carbohydrates (62 – 90 ppm), aromatic carbon (110 – 160 ppm), and carboxylic carbon (160 – 190 ppm). During SAT a slight change occurred for carbohydrates, and a difference in aromatic carbon was noticeable between Mesa reclaimed water and SAT product water.

Using acetonitrile during the desorption step of the resin fractionation resulted in a higher recovery of organic carbon due to the desorption of hydrophobic neutrals. Based on a comparison of Mesa tertiary effluent ^{13}C -NMR spectra, the additionally recovered carbon (hydrophobic neutrals) seems to cause a distinct carbohydrate peak at 70 ppm and a slightly stronger aromatic carbon peak at 125 ppm. During SAT, the carbon fraction causing the distinct peak at 70 ppm was removed in the isolate of monitoring well NW-4.

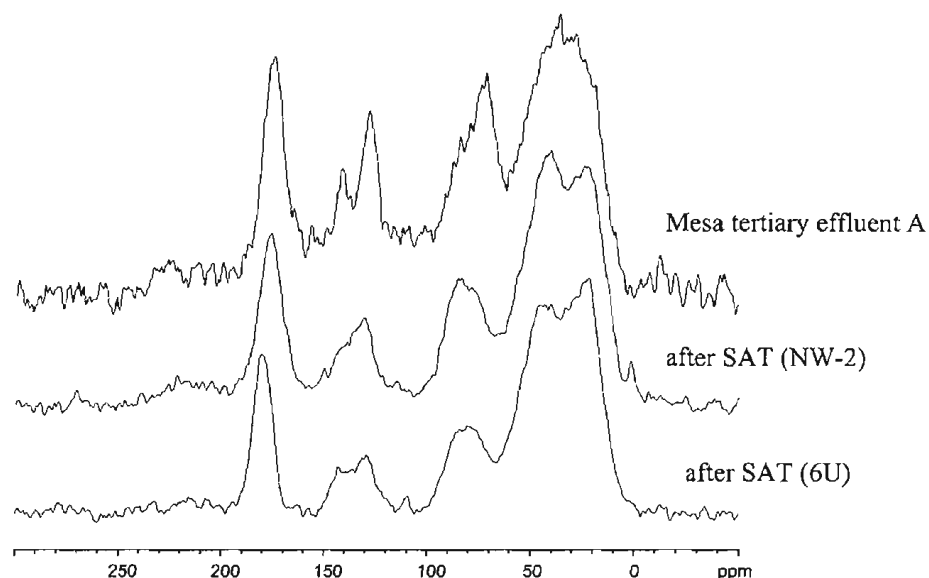


Figure 3.9 ^{13}C -NMR spectra for XAD-8 isolates (NaOH desorption) of Mesa tertiary effluent A (10/10/00) and monitoring wells NW-2 and 6U

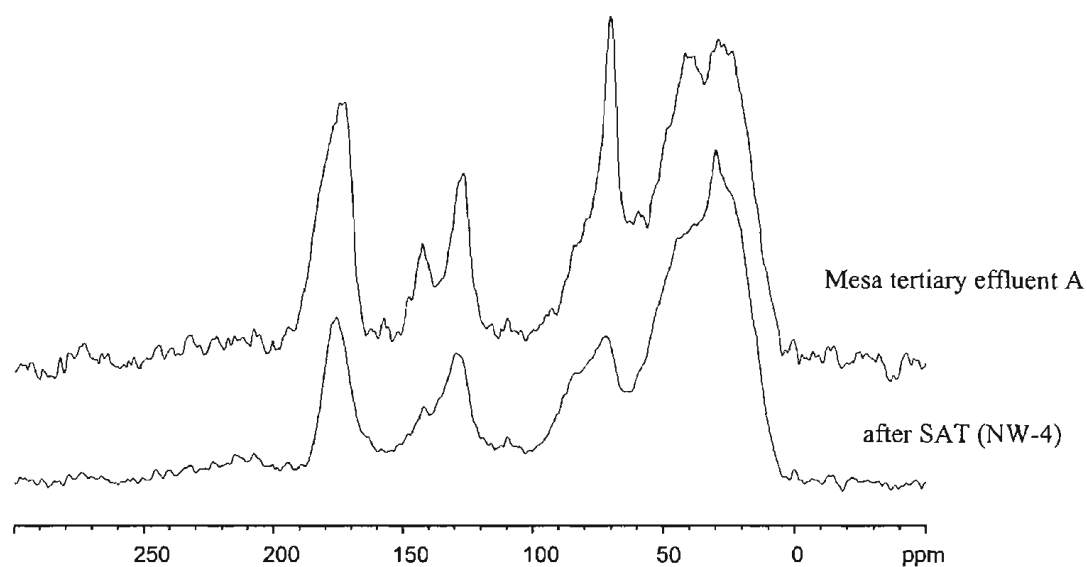


Figure 3.10 ^{13}C -NMR spectra for XAD-8 isolates (acetonitrile desorption) of Mesa tertiary effluent A (10/10/00) and monitoring well NW-4

Integration results of the different peak areas presented in Table 3.5 indicate that there were subtle shifts in the distribution of organic carbon functional groups during travel through

the subsurface. Data presented in Table 3.5 are differentiated according to the fractionation techniques applied, which differ in the solvent used for recovery (NaOH versus acetonitrile). Backelution using acetonitrile is capable to recover also neutrals along with acids from the resins whereas NaOH can only recover the acid fraction. Although, the character of recovered hydrophobic carbon differed, a similar trend in carbon transformation was obvious indicating that Mesa tertiary effluent hydrophobic and transphilic carbon became more aliphatic (chemical shift 0-62 ppm) and slightly less aromatic (chemical shift 110-160 ppm) as a consequence of SAT.

Table 3.5 Shift areas of ^{13}C -NMR spectra of XAD isolates from Mesa tertiary effluent prior to and after SAT

Sample	XAD-8 isolate							XAD-4 isolate						
	Chemical shift in ppm							Chemical shift in ppm						
	0-62	62-90	90-110	110-140	140-160	160-190	190-230	0-62	62-90	90-110	110-140	140-160	160-190	190-230
	proportion of total spectra (%)							proportion of total spectra (%)						
Tertiary effluent A (acetonitrile)	40.2	26.9	5.2	8.2	4.1	13.8	1.7	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Tertiary effluent A (acetonitrile)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	44	21.5	3.9	6.9	3.5	18.2	6
NW-4 (acetonitrile)	53.2	14.6	3.7	10.2	4.2	11.1	3.0	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Tertiary effluent A (NaOH)	42.2	18.1	4.3	15.8	6.3	11.3	2.0	46.1	20.5	3.5	7.2	3.5	17.2	2.0
Tertiary effluent C (NaOH)	43	18.1	5.0	11.7	5.3	14.4	2.4	N/A	N/A	N/A	N/A	N/A	N/A	N/A
NW-2 (NaOH)	56.8	12.9	2.2	6.3	2.8	14.6	4.5	NA	NA	NA	NA	NA	NA	NA
6U (NaOH)	63.6	12.6	1.4	5.4	1.8	12.9	2.4	52.1	20.6	5.7	3.7	0.19	16.7	0.9
city well #7* (NaOH)	61.5	14.7	3.2	4.2	0.5	14.2	1.6	N/A	N/A	N/A	N/A	N/A	N/A	N/A

NA - not available

* adopted from Drewes et al., 1999

The changes in aliphaticity and aromaticity of reclaimed water during SAT are summarized in Table 3.6. Aliphaticity is defined as the sum of aliphatic carbon and carbohydrates related to the total spectrum according to equation 5, whereas aromaticity reflects the proportion of aromatic carbon (chemical shift of 110 to 160 ppm) as expressed in equation 6.

$$\text{Aliphaticity} = \frac{\text{Peak area}_{\text{Chemical shift } 0 - 90 \text{ ppm}}}{\text{Peak area}_{\text{chemical shift } 0 - 230 \text{ ppm}}} \quad \text{Equation 5}$$

$$\text{Aromaticity} = \frac{\text{Peak area}_{\text{Chemical shift } 110 - 160 \text{ ppm}}}{\text{Peak area}_{\text{chemical shift } 0 - 230 \text{ ppm}}} \quad \text{Equation 6}$$

Table 3.6 Aliphaticity and aromaticity of hydrophobic and transphilic carbon isolated from Mesa tertiary effluent prior to and after SAT

Sample	XAD-8 (hydrophobic carbon)		XAD-4 (transphilic carbon)	
	Aliphaticity (%)	Aromaticity (%)	Aliphaticity (%)	Aromaticity (%)
Tertiary effluent A (acetonitrile)	67.1	12.3	N/A	N/A
Tertiary effluent A (acetonitrile)	NA	N/A	65.5	10.4
NW-4 (acetonitrile)	67.8	14.4	N/A	N/A
Tertiary effluent A (NaOH)	60.3	22.1	66.6	10.7
Tertiary effluent C (NaOH)	61.1	17	N/A	N/A
NW-2 (NaOH)	69.7	9.1	N/A	N/A
6U (NaOH)	76.2	7.2	72.7	3.9
city well #7* (NaOH)	76.2	4.7	N/A	N/A

N/A – not available

* adopted from Drewes et al., 1999

From the ^{13}C -NMR data, it is apparent that the hydrophilic acids are less aromatic than hydrophobic acids and have a greater percentage of carboxylic and heteroaliphatic carbons (carbohydrates). This is supported by UV absorbance values and by findings reported by Aiken et al. (1992) and Drewes et al. (1999).

Considering isolates, which were obtained by using NaOH as solvent to recover hydrophobic and transphilic acid, a similar trend of organic carbon transformation was observed. During long-term SAT, aromatic carbon of hydrophobic acids, ranging from 17 to 22.1 percent

in the Mesa tertiary effluent isolates, decreased to 9.1 percent at monitoring well NW-2 and to 7.2 percent at monitoring well 6U, respectively. Aromatic carbon of transphilic acids (XAD-4 isolates) decreased from 10.7 percent in Mesa tertiary effluent to 3.9 percent at monitoring well 6U. That is, residual hydrophobic and transphilic acids lose some of their aromatic character during long-term SAT. After long-term SAT, residual organics strongly resembled the original character of local source waters (city well #7) at least in terms of aromaticity (4.7%), and aliphaticity (76.2 %) among the hydrophobic acids isolated.

For isolates, which were obtained by using acetonitrile as solvent and which represents both hydrophobic and transphilic acids and neutrals, an increase of aliphatic carbon as a consequence of SAT was also observed, which went along with a relative decrease of carbohydrates (Table 3.5). In contrast, a declining aromaticity during SAT was not obvious. However, only one groundwater sample (NW-4) was considered in this comparison.

Elemental analysis. Elemental analysis was used to further examine the elemental composition of hydrophobic and transphilic acids and their potential change during SAT. The analysis provided the percentage of carbon, hydrogen and nitrogen among all elements. For the hydrophobic carbon fraction isolated from Mesa tertiary effluent A (10/10/00) prior to and after SAT (NW-4, NW-2, and 6U) the results of the elemental analysis are summarized in Table 3.7. The table also includes the ratios of hydrogen to carbon and nitrogen to carbon.

Table 3.7 Elemental analysis of hydrophobic carbon isolated from Mesa tertiary effluent prior to and after NF treatment

Sample	XAD-8 (hydrophobic carbon)			Ratios	
	C (%)	H (%)	N (%)	H/C	N/C
Tertiary effluent A (acetonitrile)	42.4	5.5	4.7	0.13	0.11
NW-4	45.2	5.4	2.2	0.12	0.05
NW-2	42.1	4.9	1.2	0.12	0.03
6U	42.5	5.3	0.9	0.12	0.02

Considering SAT product water isolates, the H/C of 0.12 and N/C ratios (ranging from 0.02 to 0.05) of these isolates resembled river water NOM isolate samples, ranging from 0.11 to 0.12 and 0.02 to 0.04, respectively (Croue et al., 2000). In contrast, the effluent organic matter isolate prior to SAT showed a N/C ratio of 0.11, indicating relatively more nitrogen in the reclaimed water XAD-8 isolate sample. High N/C ratios might be caused by proteins from microbiological activity. However, the change in the N/C ratio confirmed the structural change of organic matter during SAT toward natural organic matter postulated based on ^{13}C -NMR spectroscopic results.

Size exclusion chromatography. Additionally, high pressure liquid chromatography with online DOC and UV detection (LC-OCD) was applied using samples from Mesa tertiary effluents A, B, and C and groundwater monitoring wells OW2-09', NW-2 and 6U. This analytical technique uses bulk water samples and allows to differentiate organic carbon by integrating the chromatograms into five different fractions: (1) humics (HS), (2) humic substances (HS) hydrolysates, (3) low molecular mass acids, (4) low molecular mass neutrals and amphiphilics, and (5) polysaccharides. Integration of the chromatograms, allows quantification of the five different fractions (Huber & Frimmel, 1992). The advantage using this technique is that it not only provides a continuous chromatographic distribution of organic matter but also characterizes polysaccharides and low molecular acids and neutrals, which cannot be captured quantitatively by adsorption onto XAD-8 and XAD-4 resins.

Similar average DOC concentrations and low standard deviations measured in the Mesa tertiary effluent samples indicated already that treatment at the Mesa Northwest plant provides a very stable water quality. The LC-OCD chromatograms of the three Mesa tertiary effluents (A, B, and C) confirmed a similar organic carbon composition (Figure 3.11). Microfiltration does not significantly change the organic carbon distribution of the tertiary treated effluent. The chromatograms of Mesa tertiary effluent based on UV detection are presented in Figure 3.12. The UV signal is consistent with the organic carbon signal for compounds related to humic substances, such as humics, HS hydrolysates and low molecular weight acids. Polysaccharides are not UV active. The peak at 88 min in the organic carbon chromatogram is a contaminant, which also appeared in the blank (chromatogram of blank not shown).

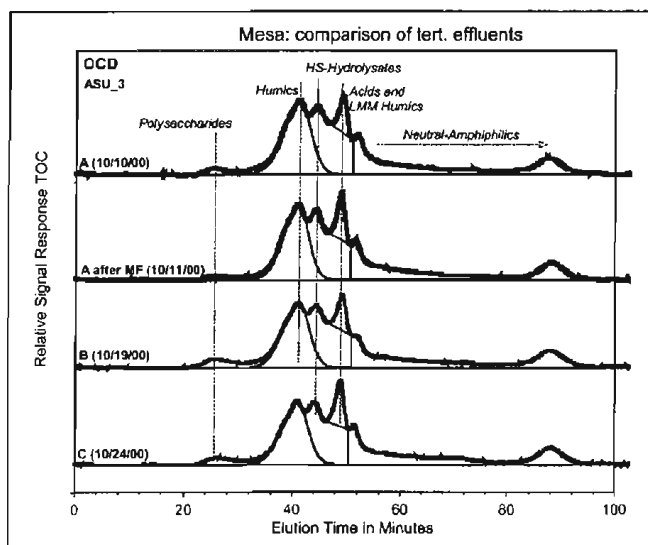


Figure 3.11 LC-OCD chromatograms of Mesa tertiary effluents (A, B, and C, including tertiary effluent A after microfiltration).

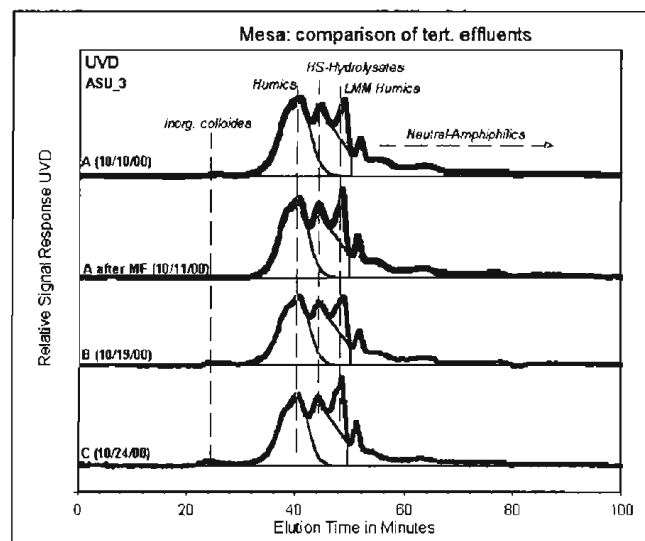


Figure 3.12 LC-UVA chromatograms of Mesa tertiary effluents (A, B, and C, including tertiary effluent A after microfiltration)

Integration of the chromatograms allows quantifying the different organic carbon fractions. Concentrations of these fractions are reported in Table 3.8 and 3.9. Humics, HS hydrolysates, and low molecular neutrals account for more than 97 percent of the chromatographable organic carbon in Mesa tertiary effluents. The hydrophobic carbon (HOC), which is not chromatographable using LC-OCD analysis, varied between 10 and 16.7 percent of the total organic carbon concentration in the three Mesa tertiary effluents. It is noted that the term “hydrophobic carbon” in the context of LC-OCD analysis is an operational definition and refers to lipid derived organic carbon (Huber & Frimmel, 1992). The term “hydrophobic carbon” referred to XAD-8 resin fractionation, and based on the operational definition of humic substances should represent the sum of humics, HS-hydrolysates and low molecular weight acids of the LC-OCD analysis, which account for 64 percent of organic carbon in Mesa tertiary effluent. Low molecular weight neutrals, substantially contributing to hydrophilic carbon (referred to XAD-8 resin fractionation), account for approximately 32 percent of organic carbon. Based on the LC-UVA analysis, approximately 70 percent of the UV absorbance in Mesa tertiary effluent is associated with humics and humic substances hydrolysates.

Table 3.8 Organic carbon fractions in Mesa tertiary effluents based on LC-OCD analysis

Sample	Date	DOC mg/L	Poly- Saccharides mg/L	Humics mg/L	HS- hydrolysates mg/L	LMM acids mg/L*	LMM neutrals mg/L*	Sum CHOC mg/L [∇]	HOC mg/L ⁺
Tertiary effluent A	10/10/00	4.95	0.16 (3.9%)	1.63 (39.5%)	1.11 (26.9 %)	0.007 (0.2%)	1.22 (29.6 %)	4.13	0.83
Tertiary effluent B	10/19/00	4.58	0.28 (6.9%)	1.45 (36.6%)	1.04 (26.6 %)	0 (0 %)	1.3 (31.9 %)	4.07	0.52
Tertiary effluent C	10/24/00	4.31	0.18 (4.6 %)	1.4 (36.1%)	0.99 (25.5 %)	0.028 (0.7%)	1.28 (33 %)	3.88	0.43

*: CHOC = chromatographable organic carbon

∇: HOC = "hydrophobic" organic carbon

+: LMM = low molecular weight

Table 3.9 Organic carbon fractions in Mesa tertiary effluents based on LC-UVA analysis

Sample	Date	UVA 1/m	Inorganic colloides 1/m	Humics 1/m	HS- hydrolysates 1/m	LMM humics 1/m	LMM neutrals 1/m
Tertiary effluent A	10/10/00	7.61	0.13 (1.8 %)	3.48 (45.7%)	1.89 (24.8 %)	n.d.	2.12 (27.8 %)
Tertiary effluent B	10/19/00	6.5	0.17 (2.6 %)	3.12 (47.9%)	1.72 (26.5 %)	0.02 (0.4 %)	1.47 (22.6 %)
Tertiary effluent C	10/24/00	7.13	0.17 (2.3 %)	3.23 (45.3%)	1.89 (26.6 %)	n.d.	1.84 (25.8 %)

n.d. – not detectable

By using single compounds with different molecular weight, the elution time of the size exclusion chromatogram can be calibrated to specific molecular weights. This allows determining an average molecular weight M_n in g/mol for a specific sample. Huber & Frimmel (1992) used this measure along with the specific UV absorbance to develop a humic substances diagram. This diagram allows assessing the character of organic matter within a humification pathway. Based on their average molecular weight and specific UV absorbance, the Mesa tertiary effluent samples represent aquagenic fulvic acids similar to natural organic matter found in surface water samples in Middle Europe, which can be classified as relatively young considering the genesis of humic substances (Figure 3.13).

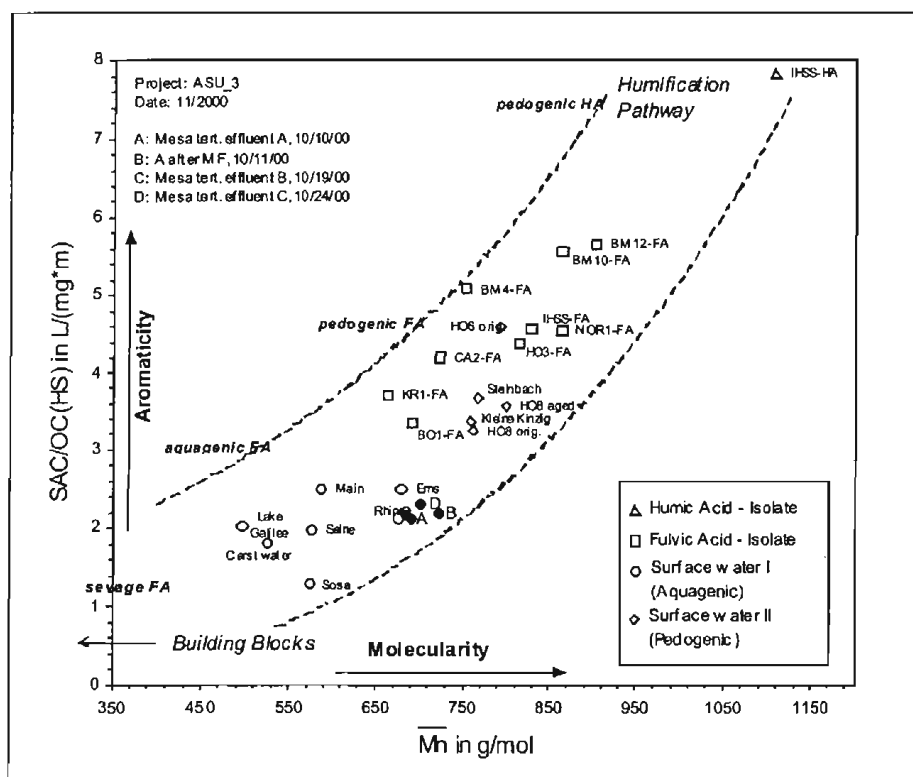


Figure 3.13 Humic substance diagram (provided by DOC Laboratory Dr. Huber, Germany)

LC-OCD analysis results for Mesa tertiary effluent and SAT product water are summarized in Table 3.10. Humic substances along with HS-hydrolysates are substantially removed by 77 percent and 83 percent, respectively, within the first 12 months of SAT. During longer retention times, a steady slight decrease of humic substances concentration is obvious. Polysaccharides are removed by 78 percent during travel to monitoring well NW-2, however, a small concentration of polysaccharides remains. Low molecular weight acid concentration, contributing to 36 percent of organic carbon in Mesa tertiary effluent, decreased by 85 percent in monitoring well NW-2. The remaining low molecular weight neutrals seem to be refractory since the concentration did not change during additional SAT to monitoring well 6U.

Table 3.10 Organic carbon characteristics of Mesa reclaimed water prior to and after SAT

Method		Mesa tertiary effluent*	OW2-90'	NW-2	6U	City well #7 ⁺
Bulk water	DOC (mg/L)	5.19	1.31	0.95	1.09	0.5
	UVA (1/m)	6.79	2.44	2.06	1.69	0.5
	SUVA (L/mg m)	1.31	1.86	2.17	1.55	1.0
LC-OCD (mg/L)	Total DOC	4.61	1.42	1.02	0.87	0.57
	Hydrophobic carbon (HOC)	0.59	0.21	0.23	0.15	0.17
	Chromato-graphable DOC	4.03	1.22	0.78	0.73	0.395
	polysaccharides	0.21	0.047	0.047	0.006	0.066
	low molecular weight neutrals	1.42	0.32	0.22	0.225	0.155
	low molecular weight humics	0.012	0	0	0	0
	HS-hydrolysates	1.05	0.27	0.175	0.2	0.06
	humics (HS)	1.49	0.59	0.344	0.293	0.114
LC-UVA (1/m)	Total UVA	7.08	2.83	1.59	1.35	0.47
	inorganic colloides	0.16	n.d.	0.04	n.d.	0.02
	low molecular weight neutrals	1.81	0.82	0.44	0.39	0.19
	HS-hydrolysates	1.83	0.54	0.39	0.3	0.09
	humics (HS)	3.28	1.41	0.7	0.62	0.15

* average out of three Mesa tertiary effluents (A, B, and C)

+: representing local background water quality; adopted from Drewes et al., 1999

n.d. not detectable

The final SAT product water was dominated by humic substances (44%), HS-hydrolysates (22%) and low molecular mass neutrals (28%). The comparison of final SAT product water with the DOC distribution of local background water not affected by reclaimed water indicates a similar distribution of different structural groups and molecular weight ranges. These findings imply that the majority of wastewater organics present in final SAT product water is natural organic material that was present in the original water supply or generated during wastewater treatment. Therefore, it seems to be reasonable to conclude that the potential health

risk associated with the bulk of organics present in SAT product water is comparable to natural organic matter present in drinking water sources.

Removal of bulk organics during advanced membrane treatment

The efficiency of organics rejection during advanced membrane treatment was studied using two nanofiltration membranes (NF-90, DOW/Filmtec and TFC-S, Koch) and one reverse osmosis membrane (TFC-HR, Koch). Mesa tertiary effluent after microfiltration served as feedwater for the performance tests. As expected, the NF and RO membranes showed a very efficient TOC rejection of more than 94 percent. Bulk organics removal data and calculated rejections for NF and RO treatment of Mesa tertiary effluent are reported in Table 3.11. The investigated NF-90 membrane showed a bulk organics rejection of approximately 93 percent. The NF membrane TFC-S revealed a rejection for organics of 91.3 percent. For the reverse osmosis membrane TFC-HR, the rejection of organics varied between 94.4 and 96.4 percent. Although, the NF-90 showed a less efficient salt rejection as compared to the RO membrane (Table 3.2), the efficiencies to reject organics were similar (Table 3.11) by requiring 300 kPa less feed pressure as compared to the TFC-HR. The removal of UV-absorbance during NF and RO membrane treatment confirmed the observed TOC rejections.

Table 3.11 TOC and UV absorbance data for Mesa tertiary effluent and NF/RO permeates

Sample location	TOC (mg/L)	UVA (1/m)	Rejection ^Δ (%)
Tertiary effluent A	4.95	7.16	
after MF	4.55	7.26	0
after NF (NF-90)	0.36	0.41	92
after RO (TFC-HR)	0.28	0.19	94
Tertiary effluent B	5.66	6.48	
after NF (NF-90)	0.31	0.22	94.5
after RO (TFC-HR)	0.23	0.35	95.9
Tertiary effluent C	4.96	6.74	
after NF (TFC-S)	0.43	0.19	91.3
after RO (TFC-HR) 2A	0.18	0.14	96.4
after RO (TFC-HR) 2B	0.28	0.08	94.4

$$^{\Delta} \text{ rejection} = (1 - C_{\text{permeate}}/C_{\text{feed}}) * 100 \%$$

Nanofiltration and reverse osmosis are characterized as diffusion-controlled membrane processes where water is forced through the membrane by a pressure differential, and dissolved salts pass through the membrane because of a concentration differential. Operational parameters, such as membrane characteristics, feed concentration, recovery, and feed pressure, are determining factors how effective constituents are rejected during NF and RO treatment. In addition, the chemical-physical properties of constituents can affect interactions with the membrane surface as well. According to equation 7, the permeate concentration C_p depends on the solute mass transfer coefficient K_s , the membrane surface A , the concentration differential ΔC , and the permeate flow Q_p .

$$C_p = K_s * A * \Delta C / Q_p \qquad \text{Equation 7}$$

During the pilot-scale membrane experiments the permeate flow Q_p was kept constant. The membrane surface and the mass transfer coefficient did also not change during each test. Therefore, the permeate concentration C_p is directly proportional to the concentration differential. Since the pilot-scale unit was operated in a recycle mode in order to achieve a recovery of 85 percent, the concentration differential between membrane surface concentration and permeate increased during the experiment. In order to illustrate the effect of increasing feed concentrations on permeate quality, permeate conductivity and TOC concentration were plotted versus feed water conductivity and TOC for both types of membranes (Figure 3.14 and Figure 3.15). Conductivity in the NF permeates, representing total dissolved solids, correlated well with feed water conductivity. High feed TDS concentrations led to an increase of permeate conductivity. In contrast, TOC did not show any positive correlation between feed and permeate concentration. However, TOC of reclaimed water is a surrogate parameter, which represents a variety of different organic compounds and properties, and might be therefore not suitable to examine a diffusion controlled mass transfer of organics. The issue of mass transfer of specific fractions of the TOC will be discussed later in the report.

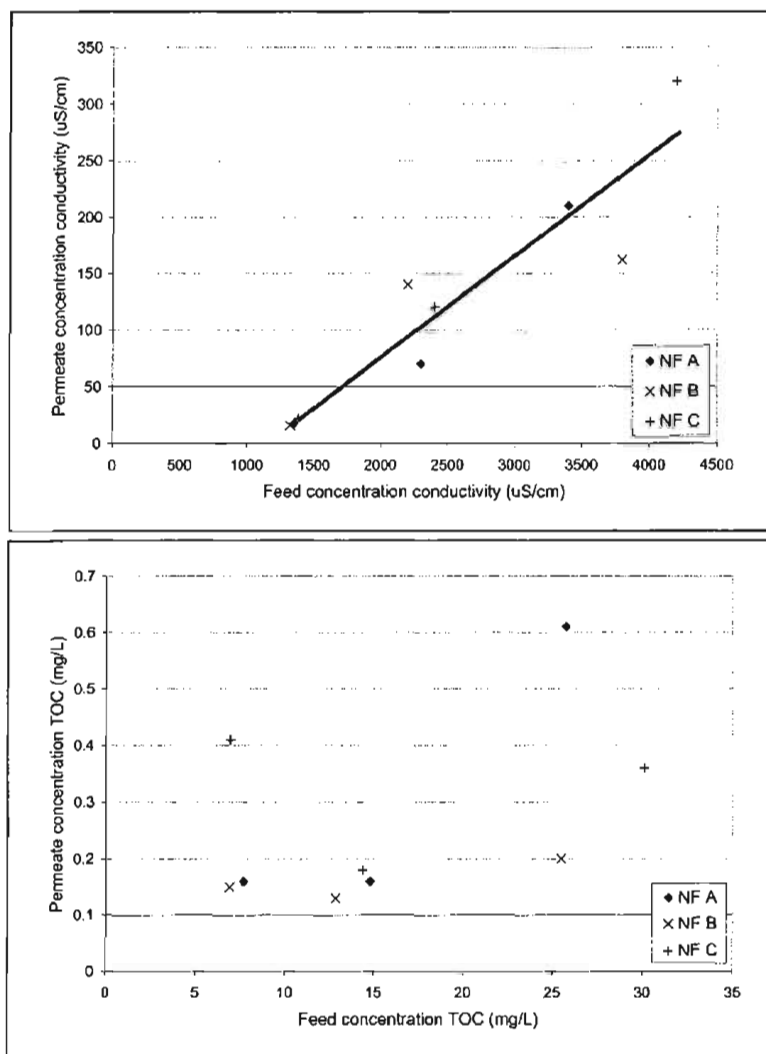


Figure 3.14 Conductivity and TOC concentrations in feed and permeate during NF treatment

For the RO membrane, feed water conductivity also correlated positively with permeate conductivity (Figure 3.15). Data presented in Figure 3.15 are gathered from all experiments (Pre, A, B, C), however, the permeate quality during the initial experiment (Pre) showed elevated conductivity (white and black square). Permeate quality data of test Pre were not considered during correlation calculations. For total organic carbon no correlation was observed between increasing feed concentration and permeate concentration.

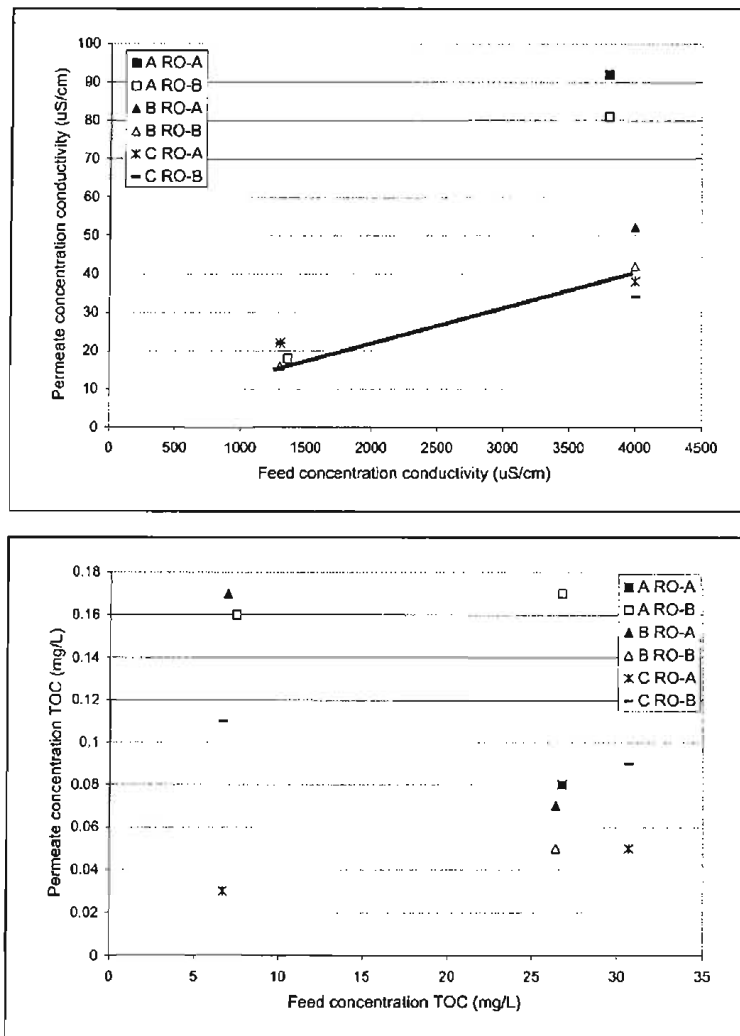


Figure 3.15 Conductivity and TOC concentrations in feed and permeate during RO treatment

Fluorescence. Since fluorescence can be caused by organic matter and by specific wastewater indicators, such as detergent whiteners (Poiger et al., 1999), fluorescence spectroscopy has been used for characterizing the structure of organic matter in membrane permeates. It is expected that the majority of fluorescence intensity is associated with fulvic and humic acids. Three-dimensional EEM plots for each Mesa tertiary effluent sample along with the NF and RO permeates are shown in Figure 3.16 to 3.18. The fluorescence spectra of permeates

were not normalized since TOC concentration was less than 1 ppm. For comparison, the fluorescence spectrum of d.i. water is plotted in Figure 3.19.

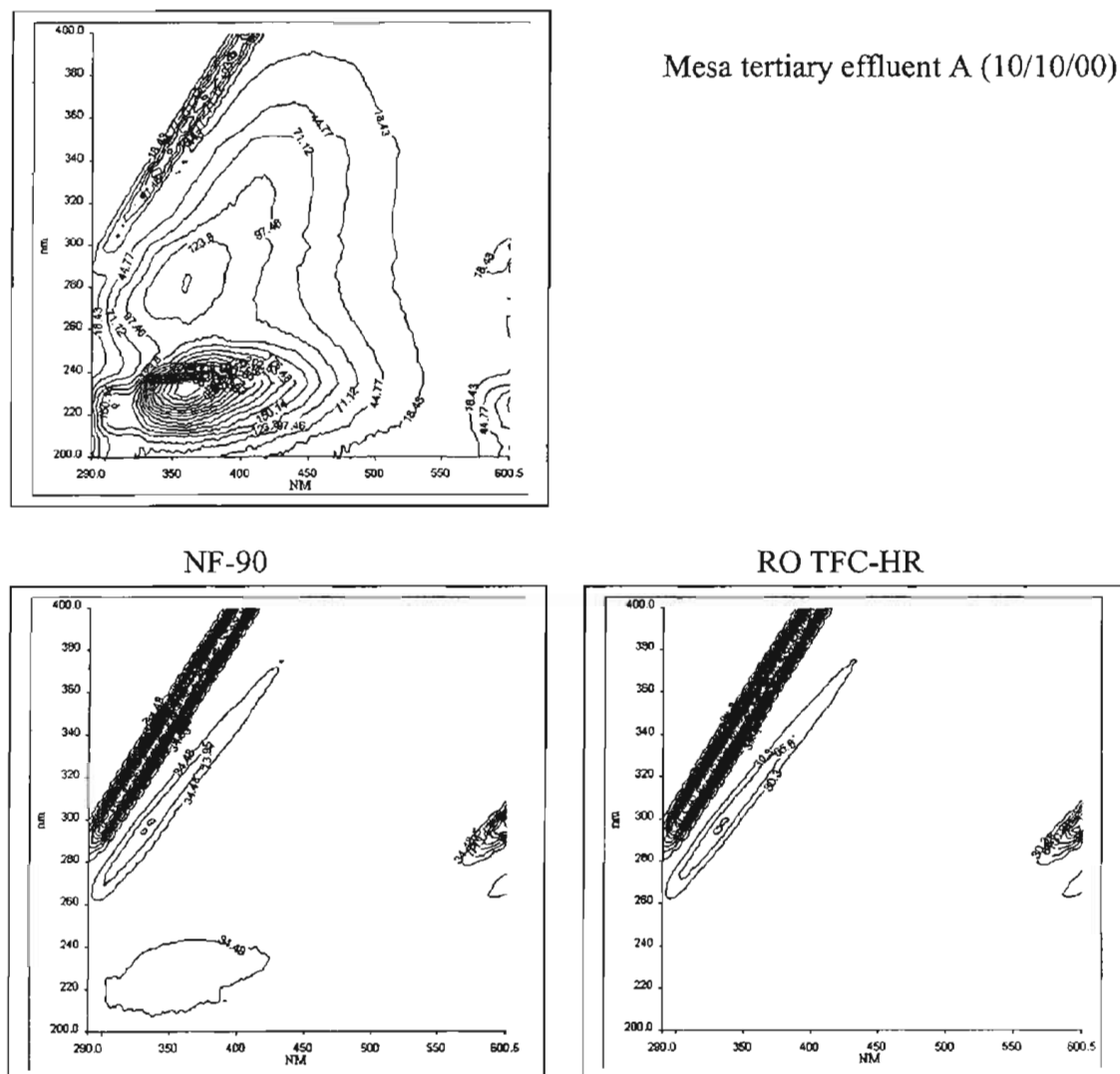


Figure 3.16 Excitation-emission spectra of Mesa tertiary effluent A prior to and after NF and RO treatment

All three distinct fluorophore peaks observed in Mesa tertiary effluent (220/300 nm, 230/360 nm, and 280/360 nm) were not present in RO permeates. A remaining signal representing peak location 290/340 nm was present in all RO permeate samples. However, this peak was also observed in a fluorescence spectrum of d.i. water (Figure 3.19). Therefore, based on fluorescence spectroscopy there is no evidence of the presence of wastewater indicators in RO

product water. It can also be stated that low molecular weight carbon contributing to the RO permeate TOC does not contain fluorophores.

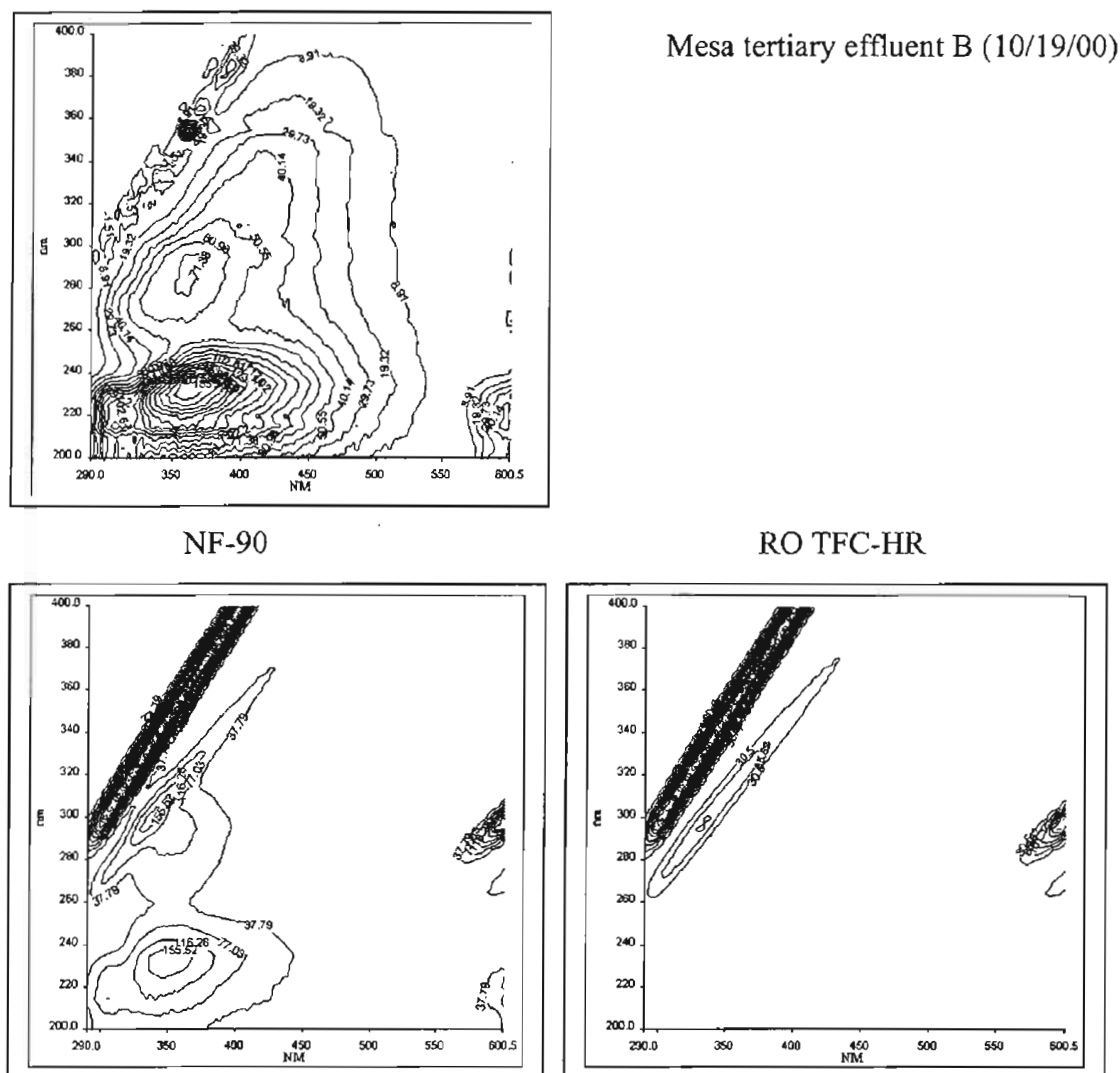
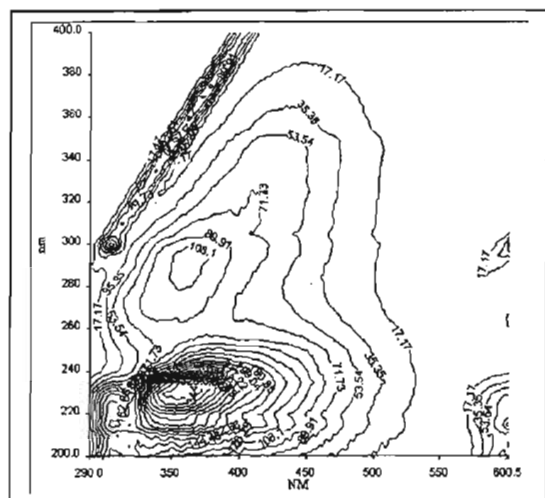


Figure 3.17 Excitation-emission spectra of Mesa tertiary effluent B prior to and after NF and RO treatment

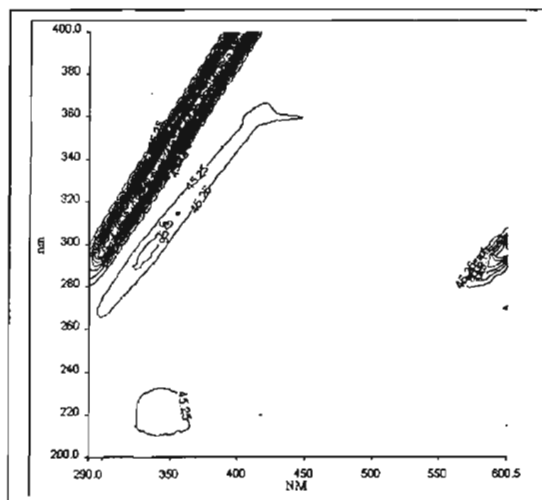
The nanofiltration membranes NF-90 and TFC-S were also very effective in rejecting fluorophores. With respect to intensity, the fluorescence spectra of NF permeates were dominated by peak location 290/340 nm which was also present in RO permeate samples and d.i. water. However, some fluorescence intensity of peak location 230/360 nm remained after NF treatment which dominated fluorescence spectra of the tertiary effluent samples. The intensity of

this peak in the NF permeates was significantly reduced. Since the NF membranes are slightly looser as compared to the RO TFC-HR, an explanation for this observation might be that humic substances related material is rejected less efficiently and only small amounts of this chemical entity can cause significant fluorescence signals.



Mesa tertiary effluent C (10/25/00)

NF TFC-S



RO TFC-HR

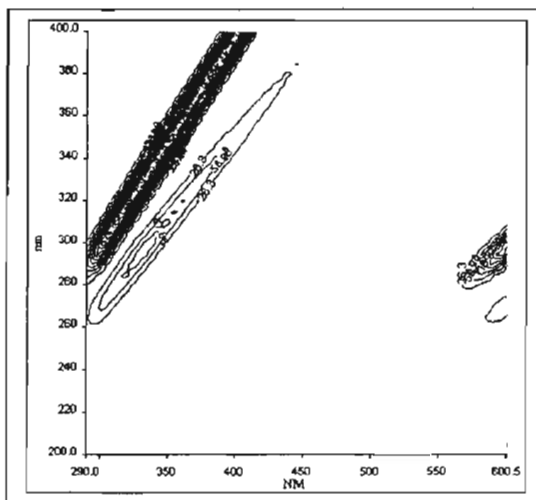


Figure 3.18 Excitation-emission spectra of Mesa tertiary effluent C prior to and after NF and RO treatment

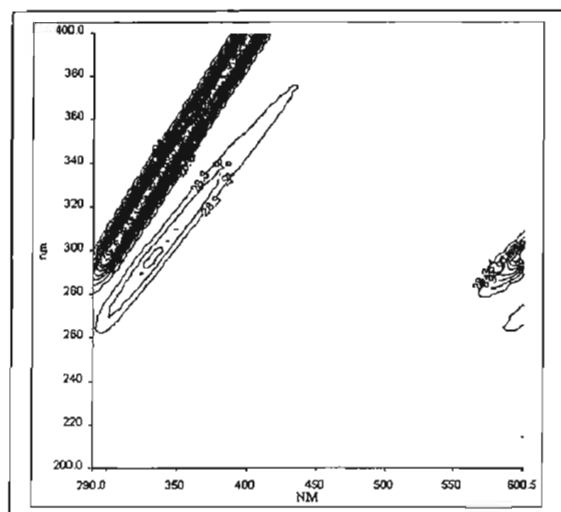


Figure 3.19 Excitation-emission spectra of d.i. water

Character of organic matter in permeates after advanced membrane treatment

Size exclusion chromatography. In order to investigate the impact of membrane treatment on the character of the remaining TOC in membrane product water, size exclusion chromatography with online DOC and UV absorbance detection was employed using NF and RO permeate samples. Figure 3.20 and 3.21 present DOC chromatograms of Mesa reclaimed water after NF and RO treatment. Figure 3.22 and 3.23 present UV absorbance chromatograms of Mesa reclaimed water after NF and RO treatment. Figures 3.21 and 3.23 present chromatograms of the reverse osmosis permeate quality of each single element (2A and 2B). Due to the molecular cut-off of 200 and 100 Dalton for the NF and RO membranes, respectively, high molecular weight carbon, such as humics, was entirely rejected by both membranes. Humic substances hydrolysates, - the building blocks of humics -, were also efficiently removed during advanced membrane treatment. However, the remaining organics in these permeates still present a range of different constituents representing molecular weights of less than 500 Dalton. This range of organic compounds is comprised of remaining HS-hydrolysates, polysaccharides, and low molecular weight acids and neutrals. Low molecular weight acids and neutrals seem to contribute to the majority of organic carbon in NF and RO permeates.

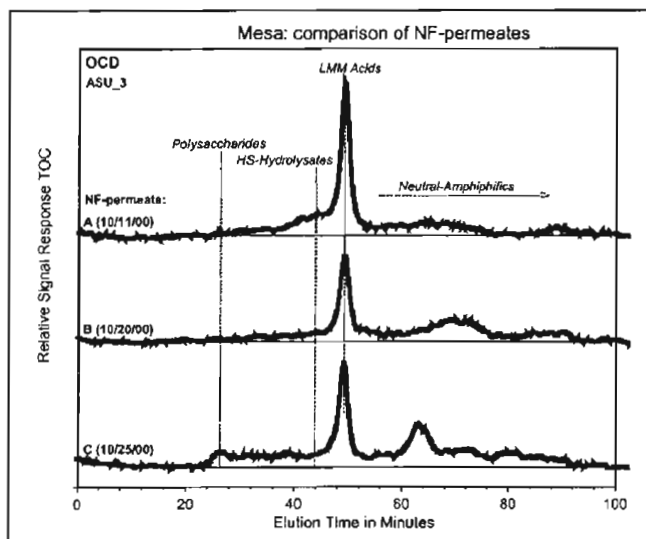


Figure 3.20 LC-OCD chromatograms of Mesa tertiary effluents (A, B, and C) after NF

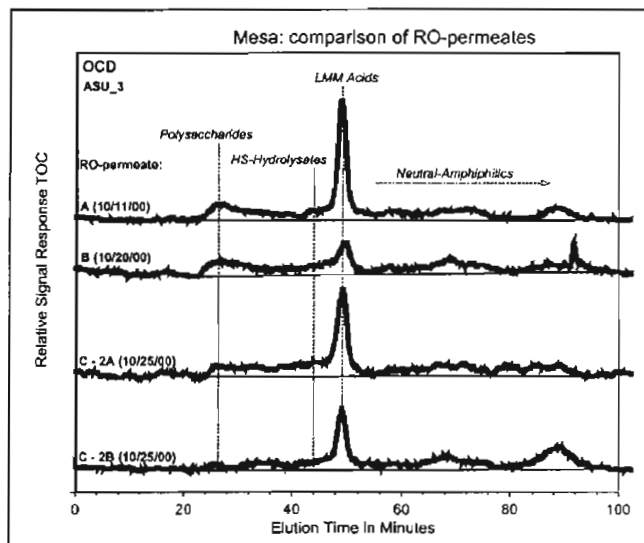


Figure 3.21 LC-OCD chromatograms of Mesa tertiary effluents (A, B, C-2A, and C-2B) after RO treatment

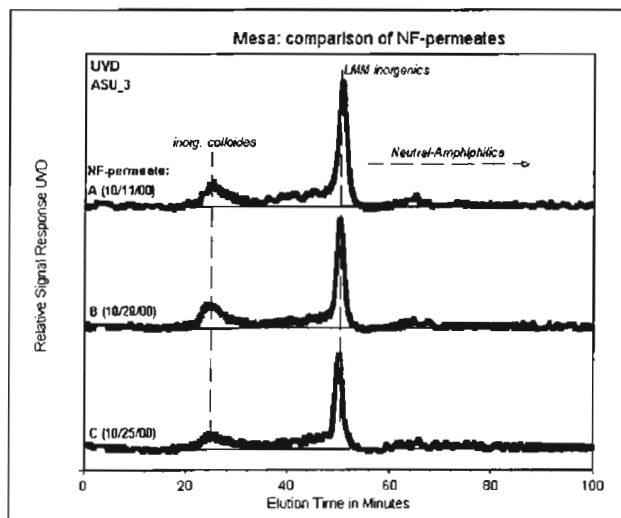


Figure 3.22 LC-UVA chromatograms of Mesa tertiary effluents (A, B, and C) after NF

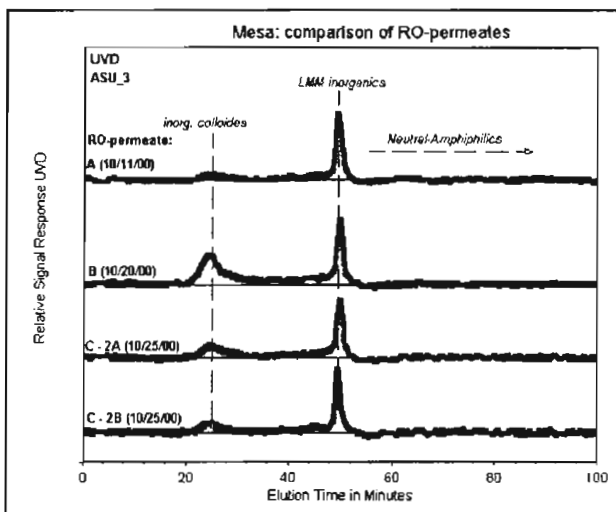


Figure 3.23 LC-UVA chromatograms of Mesa tertiary effluents (A, B, C-2A, and C-2B) after RO treatment

By integrating the chromatograms specific fractions of organic carbon and UV absorbance can be quantified. Table 3.12 summarizes the organic carbon concentrations and UV absorbance of each group in the NF and RO permeates. Average data for experiments using the

NF-90 and the reverse osmosis membrane TFC-HR were considered in the table. The contribution of each group relative to the remaining TOC concentration in NF and RO permeates is summarized in Table 3.13.

Table 3.12 Organic carbon characteristics of Mesa reclaimed water prior to and after NF and RO treatment

Method		Mesa tertiary effluent*	NF-90 ⁺	NF TFC-S	RO TFC-HR [#]
Bulk water	DOC (mg/L)	5.19	0.34	0.43	0.26
	UVA (1/m)	6.79	0.31	0.19	0.19
	SUVA (L/mg m)	1.31	0.91	0.44	0.73
LC-OCD (mg/L)	Total DOC	4.61	0.34	0.43	0.24
	Hydrophobic carbon (HOC)	0.59	0.12	0.1	0.08
	Chromatographable DOC	4.03	0.22	0.33	0.16
	polysaccharides	0.21	0.02	0.043	0.03
	low molecular weight neutrals	1.42	0.09	0.184	0.07
	low molecular weight humics	0.012	0.06	0.053	0.03
	HS-hydrolysates	1.05	0.05	0.052	0.02
	humics (HS)	1.49	n.d.	n.d.	n.d.
LC-UVA (1/m)	Total UVA	7.08	0.24	0.14	0.16
	inorganic colloides	0.16	0.07	0.03	0.05
	low molecular weight neutrals	1.81	n.d.	n.d.	n.d.
	HS-hydrolysates	1.83	n.d.	n.d.	n.d.
	humics (HS)	3.28	n.d.	n.d.	n.d.

* average out of three Mesa tertiary effluent composites (A, B, and C)

+ : average out of two NF-90 permeate composites (A, B)

: average out of three RO permeate composites (A, B, and C)

n.d. not detectable

Based on the LC-OCD analysis, more than 50 percent of the remaining TOC in NF permeates consists of low molecular weight acids and neutrals, which derive 30 to 40 percent of the remaining TOC in RO permeates. The concentration of low molecular weight neutrals in permeates investigated varied between 0.07 and 0.184 mg/L. SAT product water, represented by monitoring well NW-2, revealed a similar concentration of neutrals of 0.22 mg/L (Table 3.10). Specific anthropogenic organic micropollutants can still be present in the low molecular weight neutral fraction beside neutral compounds occurring naturally (Reinhard et al., 1986). Mesa groundwater well #7, not affected by reclaimed water, showed a low molecular weight neutral concentration of 0.16 mg/L. The occurrence of low molecular weight acids in permeates might be due to high shear forces, which occur during operation at the membrane surface, which could detach low molecular weight acids from associated humics. However, further research is necessary to examine this effect.

Table 3.13 Proportion of HS-hydrolysates, low molecular weight acids and neutrals, and polysaccharides in percent of total organic carbon concentration of NF and RO permeates (feedwater: Mesa tertiary effluent after microfiltration)

Treatment	HS-hydrolysates	LMM acids	LMM neutrals	Polysaccharides
	% of total organic carbon			
A: NF-90	17	22.3	18.8	5.4
B: NF-90	11	14.6	37.6	5.5
C: NF TFC-S	12.1	12.3	42.7	10.0
A: RO TFC-HR	8.8	18.2	23.5	12.8
B: RO TFC-HR	10	7.4	28.2	15.1
C-2A: RO TFC-HR	12.4	14.7	22.3	10.5
C-2B: RO TFC-HR	9.4	15.5	47.3	9.3

Since performance of each single membrane element can differ, it is important to investigate how different TOC fractions are rejected. Concentrations of low molecular weight acids and neutrals concentration of all NF and RO experiments were plotted versus permeate TOC concentration in Figure 3.24 and Figure 3.25. Although data considered are preliminary, positive correlations between permeate TOC concentration and low molecular weight acids and neutrals were observed.

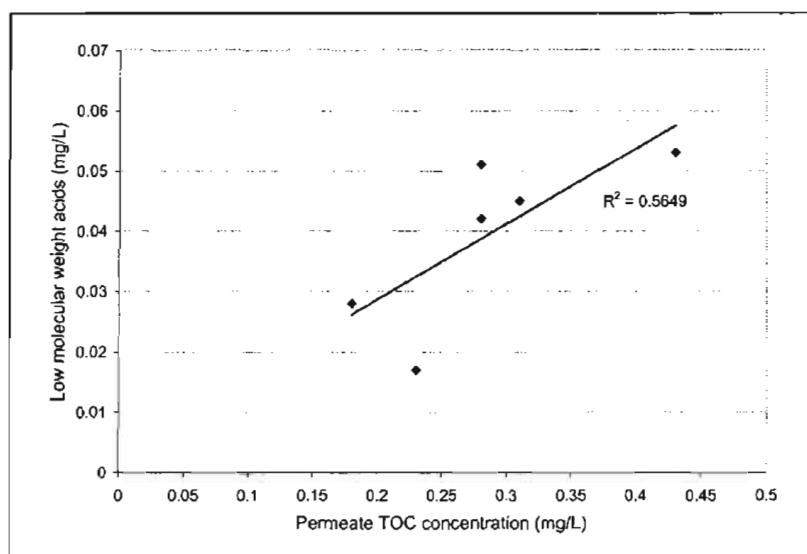


Figure 3.24 Low molecular weight acids concentration versus TOC permeate concentration

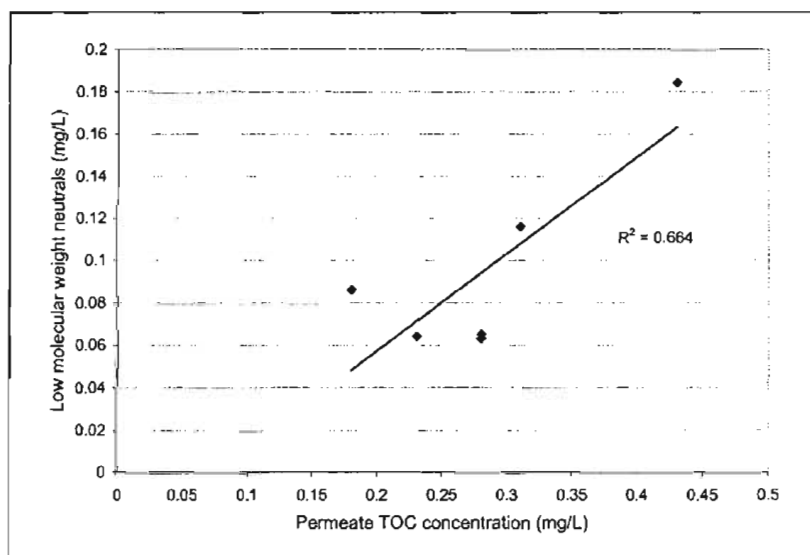


Figure 3.25 Low molecular weight neutrals concentration versus TOC permeate concentration

Lower rejections resulting in higher TOC permeate concentrations preferably tend to lead to an increased permeate concentration of low molecular organic neutrals. During experiment C, each element of the RO TFC-HR membrane was examined by LC-OCD analysis and element C-2B showed slightly higher neutral concentrations (Table 3.13). This trend of relatively higher proportions of organic neutrals in permeates was also determined for the TFC-S nanofiltration membrane, which showed a slightly higher permeate TOC concentration as compared to the NF-

90. This finding underlines the important role of low molecular weight neutrals both with respect to concentration and character of the final product water of advanced membrane treatments.

Hydrophobicity/Hydrophilicity. Based on size exclusion chromatography results, nanofiltration permeates still exhibit a humic substances related character. To further investigate the presence of humic related compounds in NF permeates, reverse osmosis was employed to concentrate the NF permeate TOC in order to provide sufficient mass for subsequent ^{13}C -NMR spectroscopy. Two nanofiltration permeates (A, C) were used for RO/XAD resin fractionation. The isolates of the XAD-8 and XAD-4 resins were backeluted using acetonitrile. A volume of 200 Liter of each NF permeate was passed through the RO laboratory unit reducing the sample volume by factor 20. Mesa tertiary effluent A was treated the same way as the NF permeate samples. Table 3.14 summarizes the classification results into hydrophobic, transphilic and hydrophilic carbon.

Table 3.14 Hydrophobic/hydrophilic carbon based on resin adsorption chromatography

Sample	Hydrophobic		Transphilic		Hydrophilic		Total	
	UVA 1/m	DOC mg/L	UVA 1/m	DOC mg/L	UVA 1/m	DOC mg/L	UVA 1/m	DOC mg/L
Mesa tertiary effluent A $k'=2$	36.41	25.88	N/A	N/A	2.89	4.12	32.14	30
NF permeate A $k'=2$	0.51	1.19	1.3	0.5	1.53	1	3.12	2.69
NF permeate C $k'=2$	0.62	1.27	1.12	0.61	1.73	0.93	3.47	2.81

It is important to note that the RO concentration step can only concentrate organics which are retained by the RO membrane. Using permeate samples treated already by NF, therefore only allows to concentrate larger molecular weight organics during RO treatment. Actually, this is supposed to be the target class of constituents where humic substances related compounds can be expected. The recoveries of organics for permeate samples NF A and NF C using the laboratory RO unit were 36.6 and 45.3 percent, respectively (Table 2.6). Resin fractionation results of the two NF permeates and Mesa tertiary effluent A are presented in Figure 3.26 and Figure 3.27.

Based on the XAD-8/-4 resin fractionation, approximately 45 percent of organic carbon can be classified as hydrophobic acids and neutrals (operational definition for humic substances). Considering the TOC of the NF permeate samples and the recovery achieved during the RO concentration step, hydrophobic acids and neutrals would account for approximately 0.08 mg/L organic carbon. Based on the LC-OCD analysis, the sum of HS-hydrolysates and low molecular weight acids in NF permeates accounted for 0.1 mg/L carbon (Table 3.12).

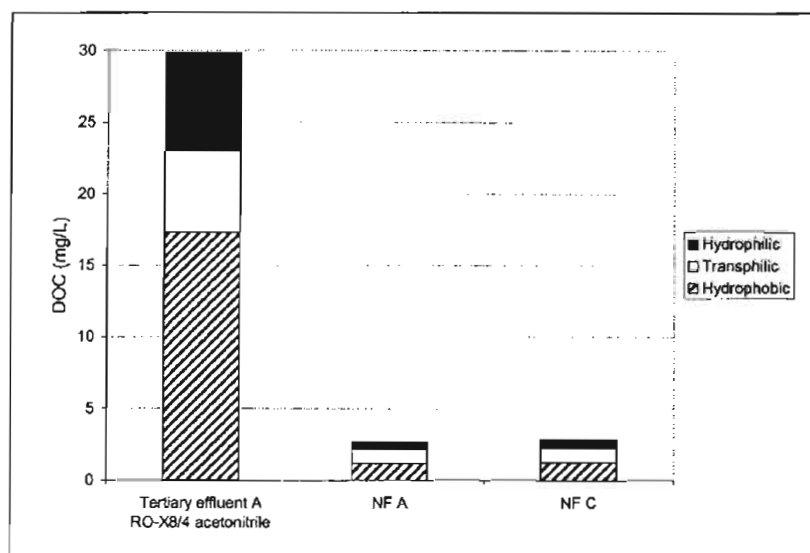


Figure 3.26 Resin fractionation results as DOC in mg/L for Mesa tertiary effluent A prior to and after NF treatment

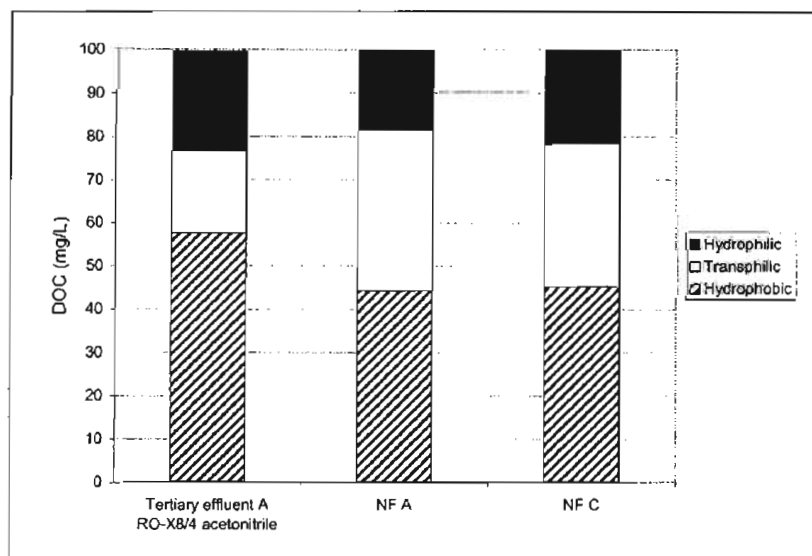


Figure 3.27 Resin fractionation results as DOC in mg/L for Mesa tertiary effluent A prior to and after NF treatment

^{13}C -NMR spectroscopy. In order to examine the structural relationship of hydrophobic acids and neutrals isolated from NF permeates, ^{13}C NMR spectroscopy was employed. The XAD-8 isolates of both NF permeates were combined to provide enough mass. ^{13}C -NMR spectra were obtained from the combined NF and the Mesa tertiary effluent A XAD-8 isolates. Spectra are presented in Figure 3.28. The chemical shift areas of ^{13}C -NMR spectra for both isolates are reported in Table 3.16.

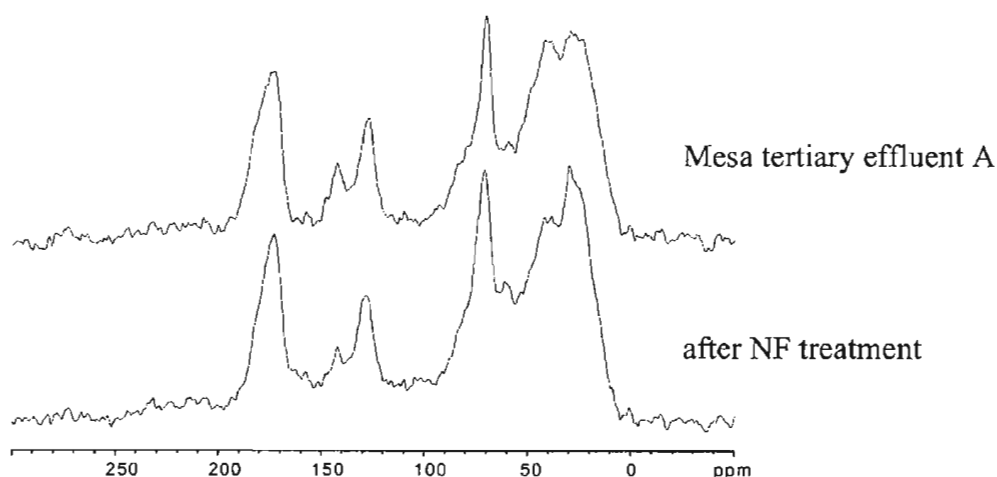


Figure 3.28 ^{13}C -NMR spectra of hydrophobic acids and neutrals isolated from Mesa tertiary effluent A (10/10/00) prior to and after NF treatment (acetonitrile was used for desorption of hydrophobic acids and neutrals)

Both ^{13}C -NMR spectra exhibit similar peaks indicating that the structure of organic carbon did not change during treatment. Considering the shift areas reported in Table 3.15 only slight changes occurred for aliphatic carbon and carbohydrates whereas aromatic and carboxylic carbon remained unaltered.

Table 3.15 Shift areas of ^{13}C -NMR spectra of XAD isolates from Mesa tertiary effluent A prior to and after NF treatment

Sample	XAD-8 isolate						
	Chemical shift in ppm						
	0-62	62-90	90-110	110-140	140-160	160-190	190-230
	proportion of total spectra (%)						
Tertiary effluent A (acetonitrile)	40.2	26.9	5.2	8.2	4.1	13.8	1.7
NF A (acetonitrile)	45.4	20.2	3.5	9.8	4.3	14.8	2.0

Elemental analysis. The combined XAD-8 isolate of NF permeates A and C was used for elemental analysis along with the XAD-8 isolate of Mesa tertiary effluent A. Results of the elemental analysis are stated in Table 3.16. The N/C ratio did not indicate any structural changes of hydrophobic acids and neutrals of NF permeate, which is consistent with the ^{13}C -NMR results.

Table 3.16 Elemental analysis of hydrophobic carbon isolated from Mesa tertiary effluent prior to and after NF treatment

Sample	XAD-8 (hydrophobic carbon)			Ratios	
	C (%)	H (%)	N (%)	H/C	N/C
Tertiary effluent A (acetonitrile)	42.4	5.5	4.7	0.13	0.11
NF A (acetonitrile)	35.4	4.4	3.8	0.12	0.11

Rotary Evaporation for RO permeates. Organic carbon in RO permeates is not only characterized by low TOC concentrations but also by low molecular weight. Thus, fractionation techniques for organic matter applied for Mesa tertiary effluent, groundwater, and NF permeate samples are not capable to concentrate organics from RO permeates. Therefore, vacuum evaporation was employed in order to concentrate organic carbon mass from two RO permeates (A and C) for subsequent spectroscopic analysis. The initial sample properties and conditions after rotor-evaporation are stated in Table 3.17. A volume of 50 Liter was processed of each RO

permeate and reduced to 1.42 and 1.5 L, respectively. This reduction corresponds to concentration factors C_f of 35.2 percent for RO permeate A and 33.3 percent for RO permeate C, respectively. Based on mass balance calculations for each RO permeate TOC recovery of the evaporation step was calculated to vary between 50.5 and 76 percent. Since RO permeate is comprised by mainly low molecular weight compounds, constituents such volatile organics are lost during the evaporation procedure.

Table 3.17 Properties of RO permeate samples used for vacuum evaporation

	Initial conditions		Conditions after evaporation						
	DOC (mg/L)	Volume (L)	Volume (L)	C_f^*	DOC expected (mg/L)	DOC expected (mg)	DOC measured (mg/L)	DOC measured (mg)	R^+ (%)
RO permeate A 10/10/00	0.28	50	1.42	35.2	9.86	14	4.96	7.04	50.3
RO permeate C 10/25/00	0.18	50	1.5	33.3	6.0	9	4.56	6.84	76

* C_f represents the concentration factor, calculated as ratio between initial volume and final volume after evaporation

⁺ R = recovery, considering ratio between mass measured in the final concentrate and initial mass in percent

The concentrate of the RO permeates after vacuum evaporation was freeze-dried and analyzed by subsequent solid-state ^{13}C -NMR spectroscopy. The total mass of carbon generated during this procedure represents a critical mass to successfully generate a NMR spectrum. This was not anticipated when the isolation protocol of this study was designed. Since remaining salts in the RO permeate were also concentrated during the evaporation procedure, remaining salts caused interference during the NMR resulting in a poor signal to noise ratio of the generated isolate. The ^{13}C -NMR spectrum of the RO permeate A concentrate is presented in Figure 3.29. It

is obvious, that there is no significant difference between peaks representing aliphatic carbon (chemical shift 0 to 62 ppm) and carbohydrates (chemical shift 62 – 90 ppm). Only carboxylic carbon caused a significant NMR signal. Although, this technique was previously successfully applied to a concentrate generated from a RO permeate of a full-scale water reclamation facility, the characterization approach for RO permeates in this study failed. Future work will consider larger sample volumes and an additional desalting step to generate sufficient mass for subsequent spectroscopic analysis.

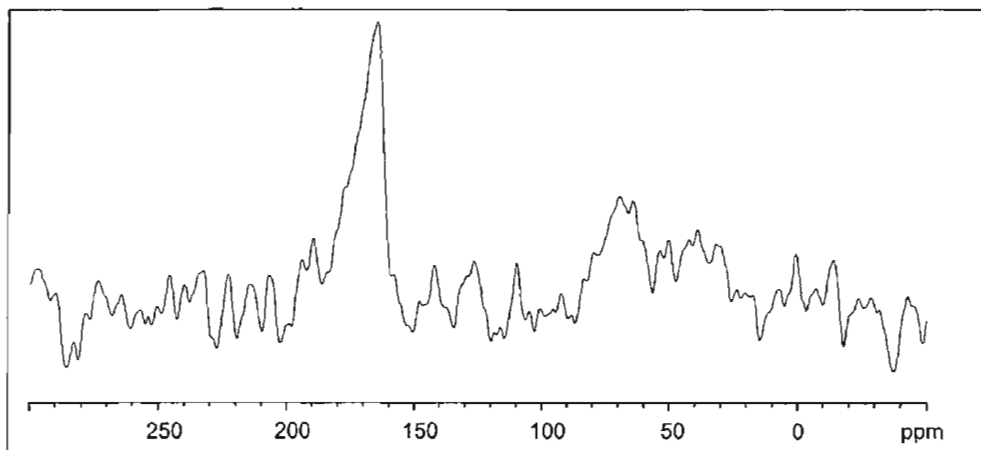


Figure 3.29 ^{13}C -NMR spectra of organic carbon isolated from Mesa tertiary effluent A (10/10/00) after RO treatment und vacuum evaporation

CHAPTER 4

REMOVAL OF TRACE ORGANICS DURING LONG-TERM SAT AND DURING NF/RO-MEMBRANE TREATMENT

A two-pronged approach was used to address the fate of trace organics during soil-aquifer treatment and advanced membrane treatment using nanofiltration and reverse osmosis. A general screening using gas chromatograph/mass spectrometer (GC/MS) analysis was employed to address unidentified trace organics present in reclaimed water. In addition, a couple of target compounds were selected, which represent wastewater indicators, and their behavior was studied during various treatments. Representatives of this group are ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), and alkylphenolpolyethoxycarboxylates (APEC). These particular compounds were chosen because they are the most abundant anthropogenic compounds detected in wastewater effluents and can account for a few percent of the DOC (Fox et al., in press). Previous studies conducted at full-scale facilities reported that disinfection by-products are only partly rejected by reverse osmosis membranes (Vernon et al., 2000; Levine et al., 2000a). Since Mesa tertiary treated effluent is disinfected using chlorination prior to discharge, chloroform and bromodichloromethane were also analyzed in Mesa tertiary effluent and membrane permeates.

Removal of selected target compounds during soil-aquifer treatment

EDTA, NTA, and Total APECs. Selected target compounds were analyzed in Mesa tertiary effluent samples and groundwater monitoring well samples located downgradient of the spreading basins. The groundwater samples represent SAT product water after travel times varying between 6 to 12 months and 6 to 8 years based on groundwater modeling data. Concentrations determined are reported in Table 4.1. Total APECs and EDTA were detected in Mesa tertiary effluent in average concentrations of 18.6 and 19.6 µg/L, respectively. NTA was quantified by 0.4 µg/L in the effluent samples on average. The concentrations of the selected target compounds determined are consistent with concentrations observed during previous studies at the Mesa site (Fox et al., in press).

During soil-aquifer treatment, NTA was completely removed and not detected in any monitoring well downgradient of the recharge basins. After travel of 6 to 12 months to monitoring well OW2-90', EDTA and total APECs were reduced to average concentrations of 3.8 and 0.1 µg/L, respectively. During additional SAT from monitoring well OW2-90' to wells further downgradient (NW-2, 6U), the concentrations of EDTA and the remaining concentrations of total APECs remained constant. Considering the final SAT-product water quality represented by OW2-90', EDTA, NTA and total APECs were rejected during SAT by 81, 100, and 99.5 percent, respectively. Removal efficiencies for these target compounds are consistent with findings reported in previous studies (Fox et al., in press). Final concentrations of EDTA in SAT product water are similar to concentrations found in groundwater and surface waters reported by Kari & Giger (1995) and Witschel et al. (1997).

Table 4.1 Concentration (and standard deviation) of selected trace organics in µg/L in Mesa tertiary effluent prior to and after SAT

	Mesa tertiary effluent n = 3	OW2-90' n = 2	NW-2 n = 8	6U n = 3	Rejection ^Δ (%)
EDTA (µg/L)	19.6 ± 13.7	3.8 ± 3.1	2.53 ± 3.5	3.8 ± 3.5	81
NTA (µg/L)	0.4 ± 0.1	n.d.	n.d.	n.d.	100
Total APEC (µg/L)	18.6 ± 6.1	0.1 ± 0.2	0.2 ± 0.2	0.1 ± 0.1	99.5

^Δ rejection = $(1 - C_{\text{SAT-OW2}}/C_{\text{tertiary effluent}}) * 100 \%$

n.d. – not detected

n = number of samples

Removal of selected target compounds during advanced membrane treatment

EDTA, NTA, and Total APECs. The behavior of organic target compounds was studied during NF and RO treatment when Mesa tertiary effluent was used as feed water. The concentrations of selected wastewater indicators are listed in Table 4.2. Microfiltration was found to be ineffective for removing trace organics. EDTA, NTA, and APECs were not detected in NF and RO permeates. Based on the average wastewater indicator concentrations in the RO and NF permeates, there does not appear to be any significant difference in membrane efficiencies. Fujita et al. (1996) detected EDTA and APEC compounds in product water after RO

treatment at the Water Factory 21 (Orange County Water District, California) and determined concentrations of 4.3 µg/L, and 0.5 µg/L, respectively. During the time of this study, the facility used a cellulose acetate RO membrane for full-scale operation, which tends to be less efficient regarding rejection of organic micropollutants as compared to PA membranes. Reinhard et al. (1986) performed a comparison study of PA and CA membranes at Water Factory 21. Results reported showed higher rejections for trace organics after PA membrane treatment as compared to CA membranes using the same feedwater for both systems.

Table 4.2 Concentration of selected trace organics in µg/L in Mesa tertiary effluent, corresponding NF and RO permeates

	Mesa tertiary effluent n = 3	Microfiltration n = 1	NF NF-90 n = 2	RO TFC-HR n = 3	Rejection ^Δ (%)
EDTA (µg/L)	19.6 ± 13.7*	5.6	n.d.	n.d.	100
NTA (µg/L)	0.4 ± 0.1	0.4	n.d.	n.d.	100
Total APEC (µg/L)	18.6 ± 6.1	23.4	n.d.	n.d.	100

^Δ rejection = $(1 - C_{\text{permeate}}/C_{\text{feed}}) * 100 \%$

n.d. not detected

n = number of samples

* standard deviation

Disinfection by-products. Two trihalomethanes were selected for membrane studies, chloroform and bromodichloromethane. Concentrations of THMs in Mesa tertiary effluent and NF and RO permeates are reported in Table 4.3. Rejection of chloroform during NF treatment varied between 75 and 92.3 percent. RO treatment was slightly more efficient for chloroform removal and rejections varied between 84.5 and 95.3 percent. Residual concentrations of chloroform in the NF and RO permeates was well below 7 µg/L. Bromodichloromethane was less efficiently removed during NF and RO treatment. Rejection of bromodichloromethane varied during NF treatment between 0 and 37.5 percent. RO treatment led to a bromodichloromethane rejection which varied between 13.2 and 44.4 percent. Remaining concentrations of bromodichloromethane after NF and RO treatment varied between 7.5 and 17 µg/L. The observed partial removal of disinfection by-products during membrane treatment is consistent with findings reported in other studies (Levine et al., 2000a; Vernon et al., 2001). Full-

scale treatment studies performed by Vernon et al. (2000) at the Scottsdale Water Campus, Arizona, revealed rejections of chloroform and bromodichloromethane which varied between 18 and 65 percent during RO treatment (type of membrane: TFC-HR Magnum). Remaining concentrations reported were similar to concentrations found in this study for the two THMs investigated.

Table 4.3 Rejection of selected disinfection by-products during advanced membrane treatment

Sample	Chloroform (µg/L)	Rejection ^Δ (%)	Bromodichloro- methane (µg/L)	Rejection ^Δ (%)
Tertiary effluent A 10/10/00	26.4		15.2	
after NF A	6.6	75	17.1	0
after RO A	4.1	84.5	13.2	13.2
Tertiary effluent B 10/19/00	22.2		12.8	
after NF B	1.7	92.3	8.0	37.5
after RO B	1.7	92.3	8.5	33.6
Tertiary effluent C 10/25/00	31.8		16.9	
after NF C	5.4	83	15.3	9.5
after RO C – 2A	2.7	91.5	10.3	39
after RO C – 2B	1.5	95.3	7.5	44.4

$$^{\Delta} \text{ rejection} = (1 - C_{\text{permeate}}/C_{\text{feed}}) * 100 \%$$

GC-MS screening of SAT product water

The selection of target compounds to study the removal efficiency of trace organics during treatment processes is limited because only a small analytical window is usually examined. In this study, the analytical window selected favors relatively small (MW < 500) non-

volative compounds that can be esterified to increase their volatility. When studying the fate and transport of trace organic compounds, the use of target compounds to represent trace organics is justified. By examining the entire ion chromatograms obtained by GC/MS, removals of non-target compounds (i.e., other trace organic compounds) can be seen. Other researchers have chosen another analytical window (base-neutral analysis) that captures non-polar, semi-volatile compounds that partition into methylene chloride using USEPA Method 625 (Madireddi, et al., 1997; Levine et al., 2000a). By increasing the sample volume used during extraction, Levine et al. (2000b) improved the sensitivity of this method and successfully applied the analysis to several facilities using advanced membrane treatment.

Mesa tertiary effluent samples, SAT samples and NF and RO permeates were extracted from water into methylene chloride for derivitization followed by GC/MS analysis. A Total Ion Chromatogram (TIC) was generated for each sample; a blank TIC is presented in Figure 4.1. It is apparent from this chromatogram that most compounds (within our analytical window) have elution times between 25 and 45 minutes. For semi-quantitation purposes, target compounds (i.e., EDTA, NTA, and APECs) were represented by their base ions (mass-to-charge ratios (m/z) = 230, 203, 145, 235, 249, 279); for the blank sample, these ions are presented in Figure 4.2. Figure 4.3 focuses on the target compounds (m/z = 230, 103, 145, 235, 249, 279) in the region of interest (i.e., between 25 and 45 minutes). The distinct peaks present in Figure 4.3 result from impurities in the reagents used during the extraction and esterification procedures; the peak at 34 minutes represents the internal standard.

The total ion chromatogram and the chromatogram representing specific m/z ratios for Mesa tertiary effluent A (10/10/00) is presented in Figures 4.4 to 4.6. The majority of fragments occurred between 25 and 45 min elution time as observed in the blank sample. Due to this fact, the following chromatograms are only plotted for this specific time window. Specific chromatograms of Mesa tertiary effluents A, B, and C are presented in Figures 4.7 to 4.9. All effluent chromatograms are abundant in peaks between 31 and 39 minutes representing a similar pattern of all three chromatograms. However, variations in the discharge of micropollutants can cause variations as seen in the chromatogram of Mesa tertiary effluent C (Figure 4.9), which tends to exhibit less intense peaks.

Three groundwater well samples were selected for GC/MS screening representing SAT product water after different retention times. The GC/MS chromatograms of OW2-90', NW-2, and 6U are presented in Figures 4.11 to 4.13 allowing a comparison to Mesa tertiary effluent A presented in Figure 4.10. Based on the GC/MS chromatogram of monitoring well OW2-90', the initial phase of SAT obviously provides not only a significant removal of target compounds but also a substantial removal of unidentified trace organics. There does not appear to be any significant differences between the chromatograms provided for OW2-90', NW-2, and 6U (Figures 4.11 to 4.13), and the major peaks found in these chromatograms are also present in the blank (Figure 4.3). The distinct peak at 36 min, which varied between the samples, represents EDTA. The minor peaks in Figure 4.13 are background effects. Two additional monitoring well samples representing SAT product water were examined. The GC/MS chromatograms of NW-3 and NW-4 are presented in Figure 4.15 and 4.16. They confirm the absence of non-target compounds in SAT product water with the exception of EDTA.

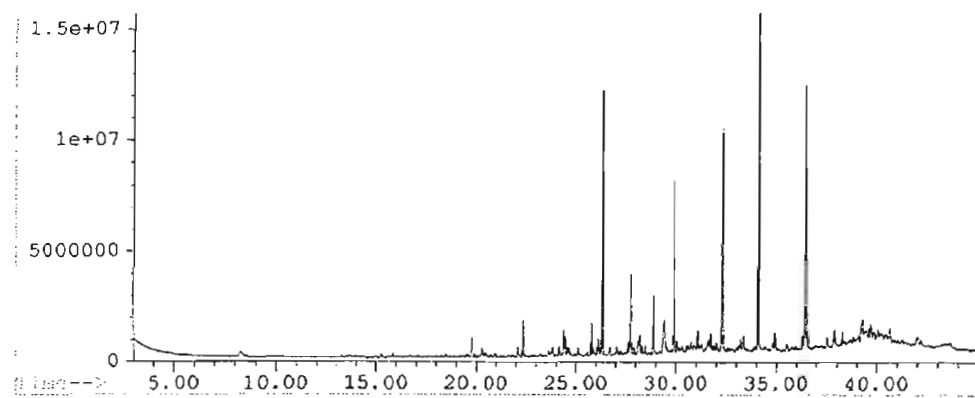


Figure 4.1 TIC of blank.

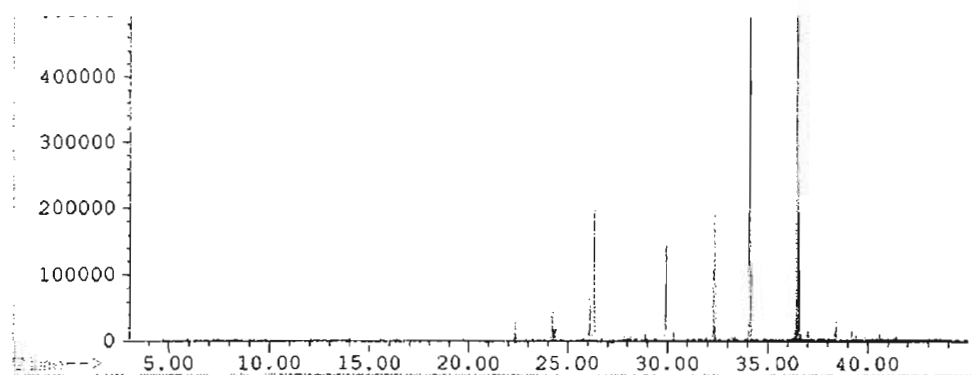


Figure 4.2 Blank ions ($m/z = 230, 103, 145, 235, 249, 279$).

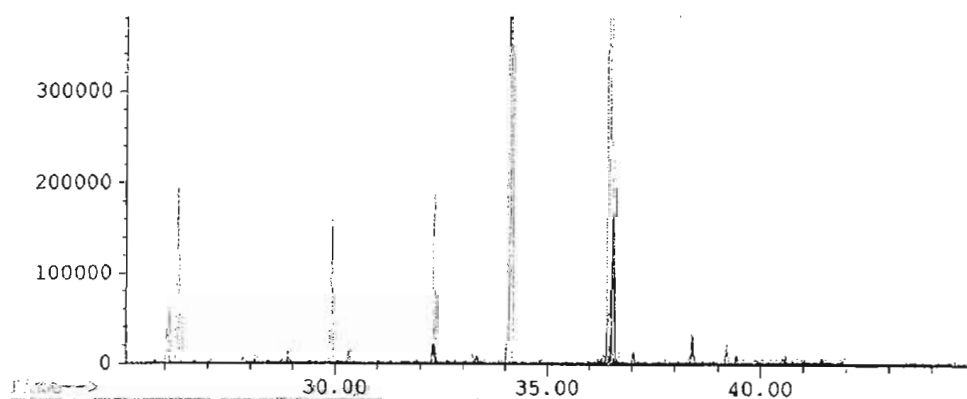


Figure 4.3 Blank ions ($m/z = 230, 103, 145, 235, 249, 279$).

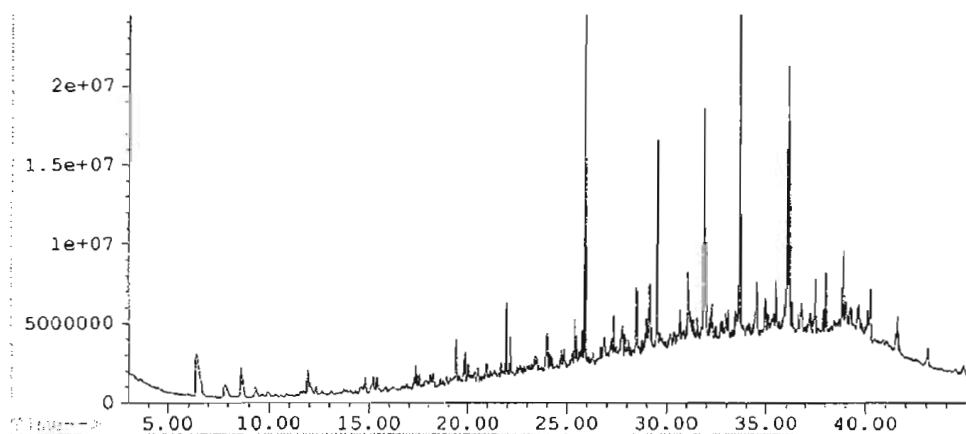


Figure 4.4 TIC of Tertiary Effluent A (10/11/00)

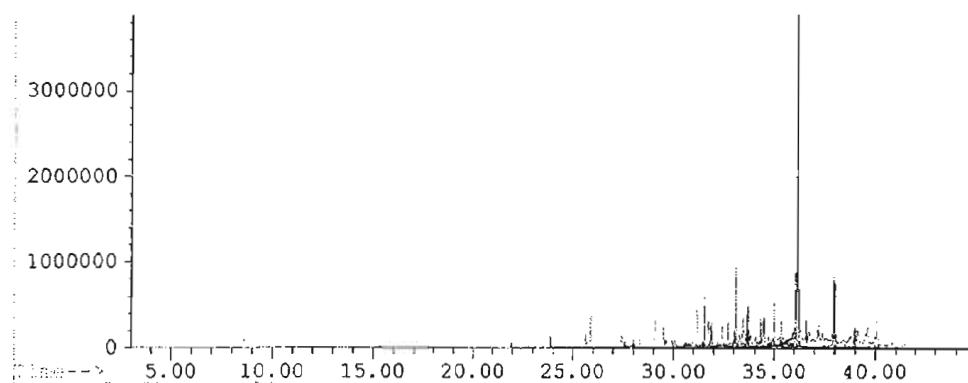


Figure 4.5 Tertiary Effluent A (10/11/00) ions (m/z = 230, 103, 145, 235, 249, 279)

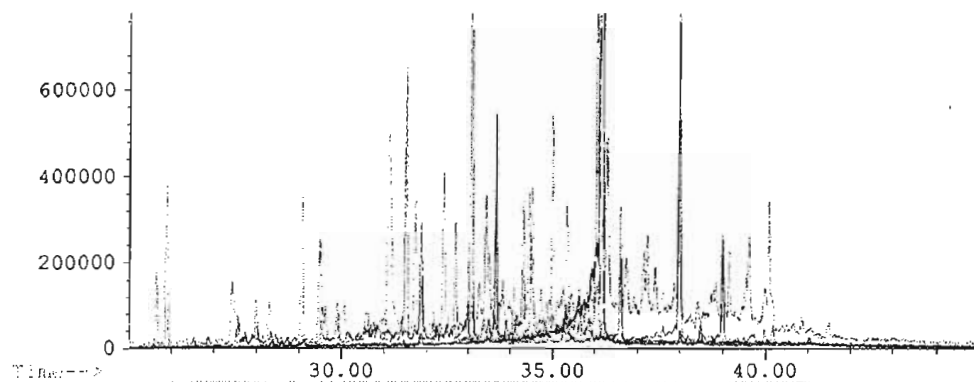


Figure 4.6 Tertiary Effluent A (10/11/00) ions (m/z = 230, 103, 145, 235, 249, 279)

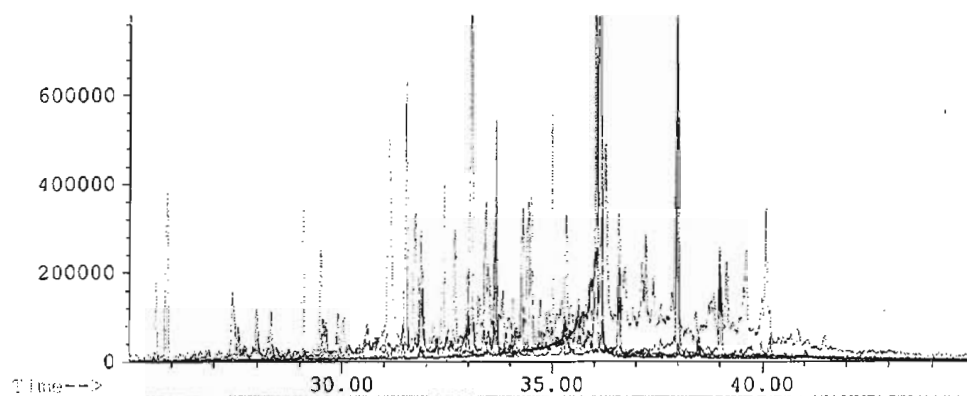


Figure 4.7 Tertiary Effluent A (10/11/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

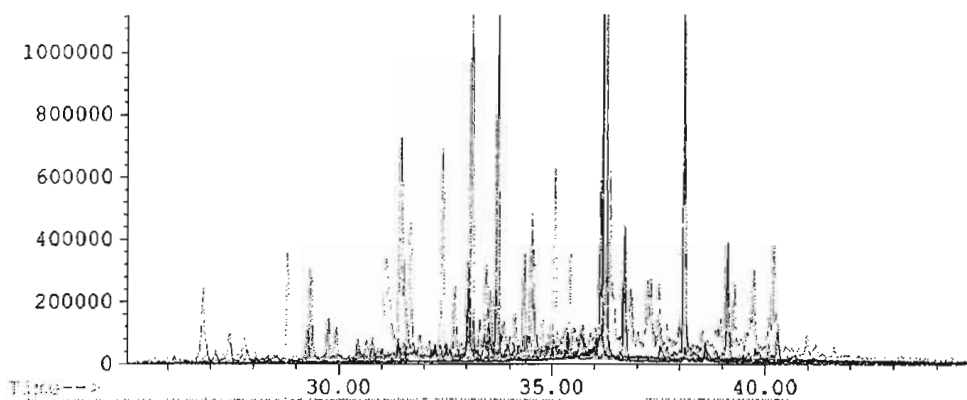


Figure 4.8 Tertiary Effluent B (10/20/00) ions ($m/z = 230, 103, 145, 235, 249, 279$).

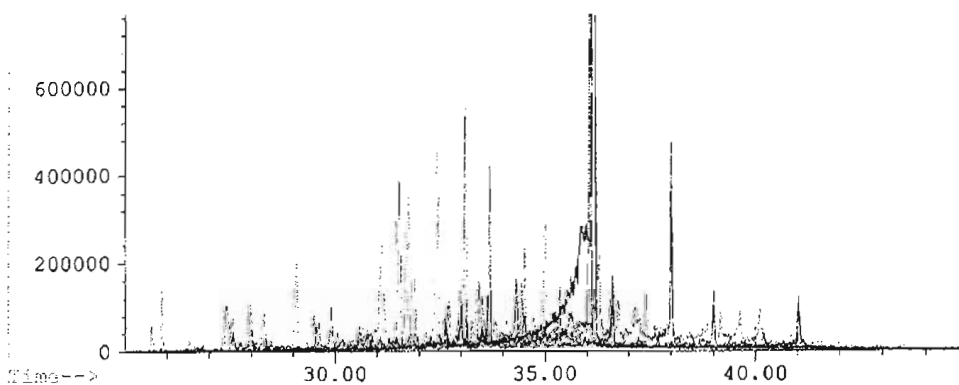


Figure 4.9 Tertiary Effluent C (10/24/00) ions ($m/z = 230, 103, 145, 235, 249, 279$).

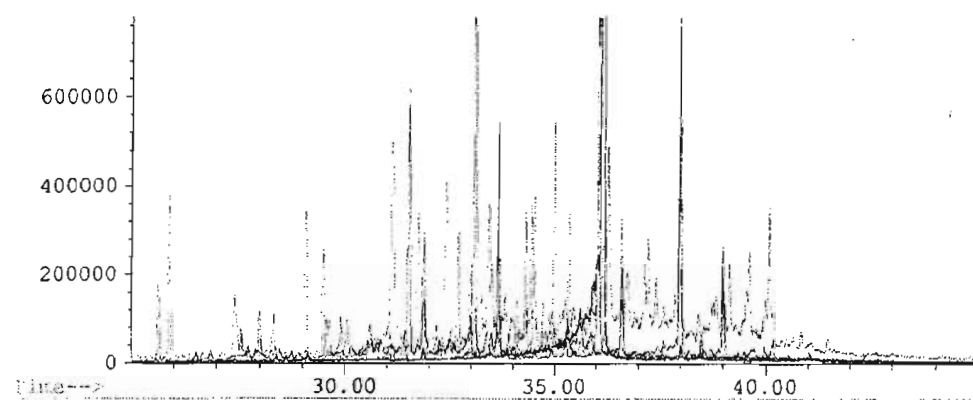


Figure 4.10 Tertiary Effluent A (10/11/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

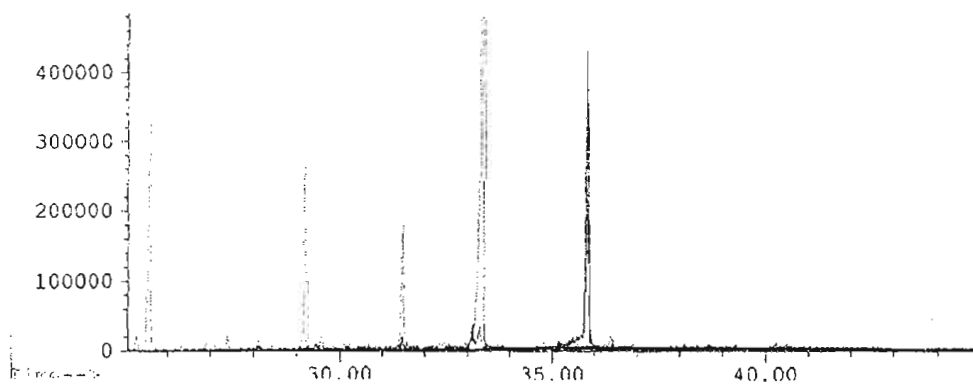


Figure 4.11 OW2 90' (3/15/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

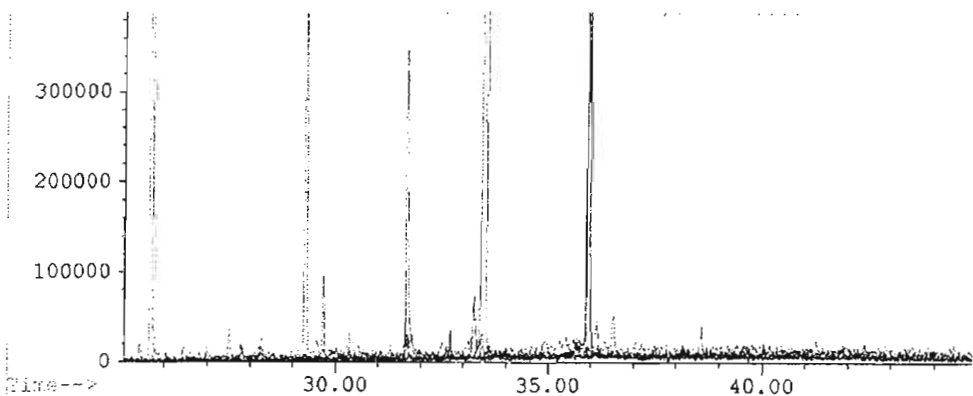


Figure 4.12 NW2 (2/15/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

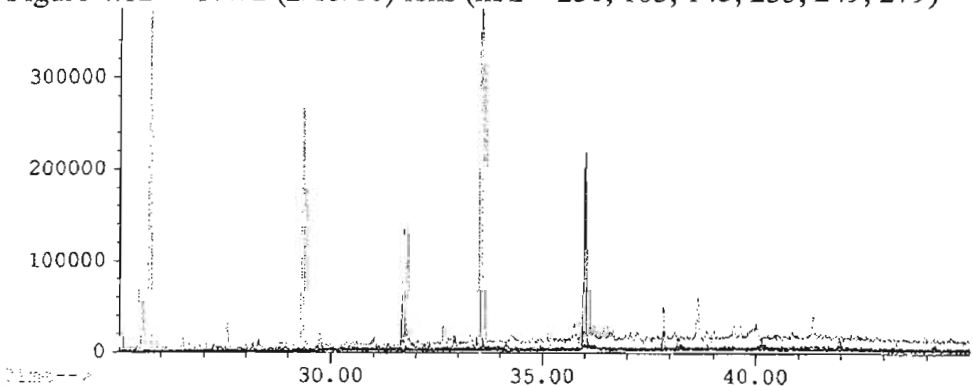


Figure 4.13 6U (10/19/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

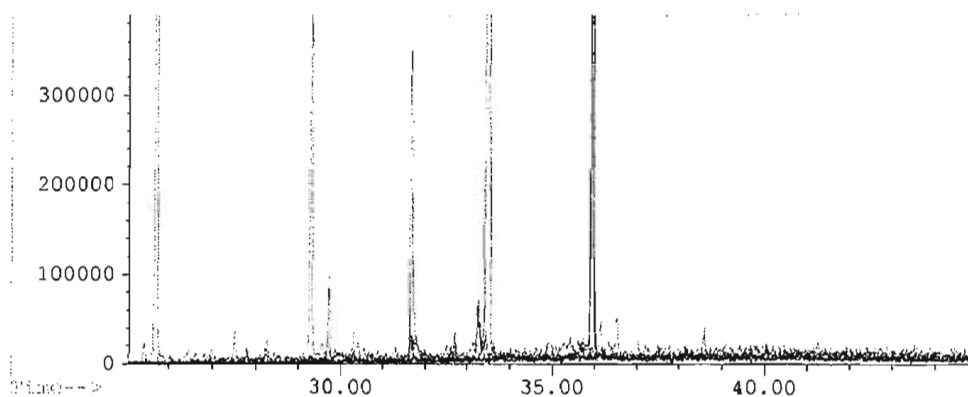


Figure 4.14 NW-2 (2/15/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

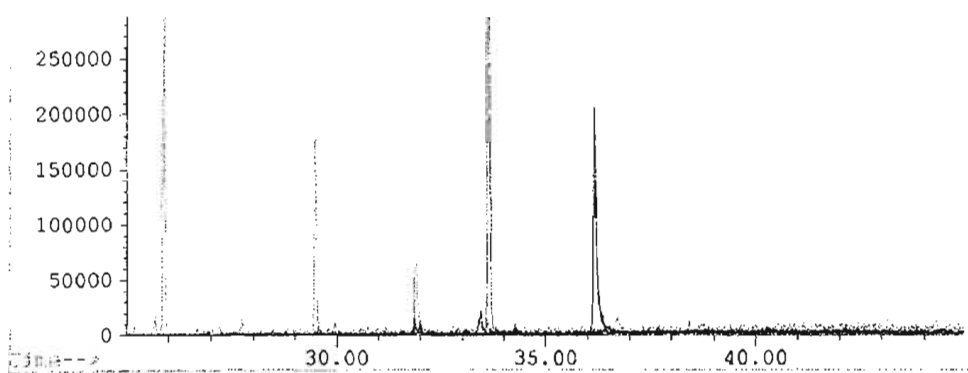


Figure 4.15 NW-3 (1/17/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

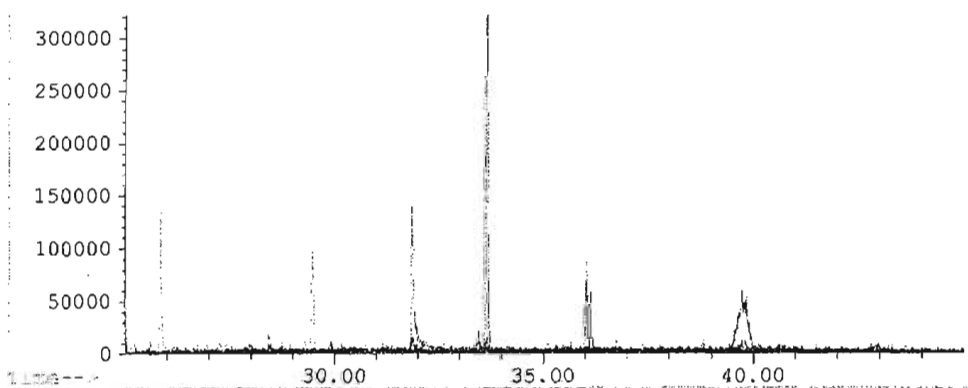


Figure 4.16 NW-4 (12/18/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

GC-MS screening of NF and RO product water

Removal of non-target compounds was studied during NF and RO treatment. Samples for GC/MS screening were provided by using composites of the feed water (Mesa tertiary effluent after microfiltration) and the permeates from each experiment conducted (A, B, and C). As an additional surrogate standard, deuterated EDTA-d12 was used during the extraction procedure of the permeates, which caused a strong peak at 36 minutes. The GC/MS chromatograms are presented in Figures 4.17 to 4.19 for experiment A, in Figures 4.20 to 4.22 for experiment B, and in Figure 4.23 to 4.25 for experiment C, respectively.

Detailed examination of chromatograms obtained from NF permeate and RO permeate extracts indicate that most compounds are removed to below the detection limit of the analytical method applied (reporting limit 0.1 µg/L). There are no significant differences between any of these chromatograms; the major peaks present are also present in the blank (Figure 4.3). The minor peaks in these chromatograms are due to background effects and column bleed (e.g., Figure 4.19 between 38 and 39 minutes). Significant losses of EDTA-d12 (peak located at 36 minutes) were noted in two of the NF permeates (Figures 4.22 and 4.25); it is unknown where these losses occurred, however, using an alternate technique (detection limit 10 µg/L), EDTA concentrations were still below detection limits (data not shown).

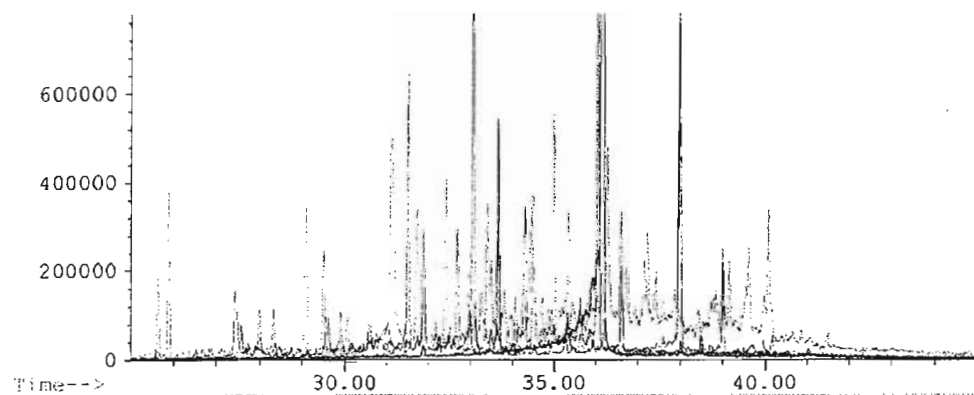


Figure 4.17 Tertiary Effluent A (10/11/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

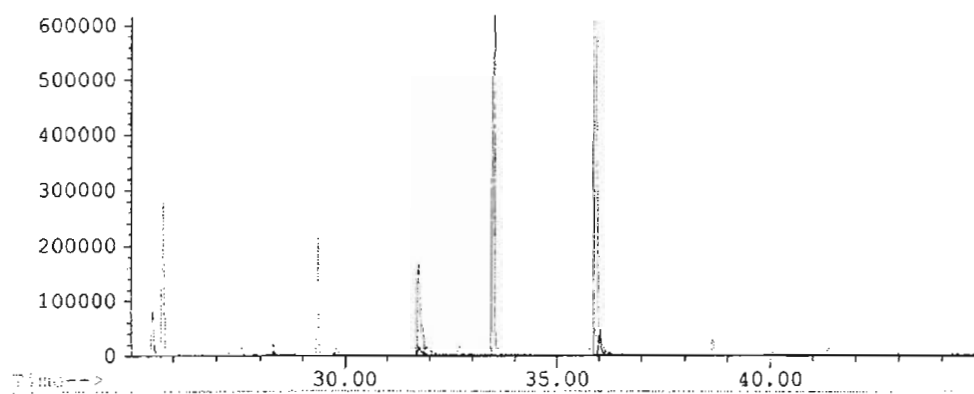


Figure 4.18 RO permeate A (10/11/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

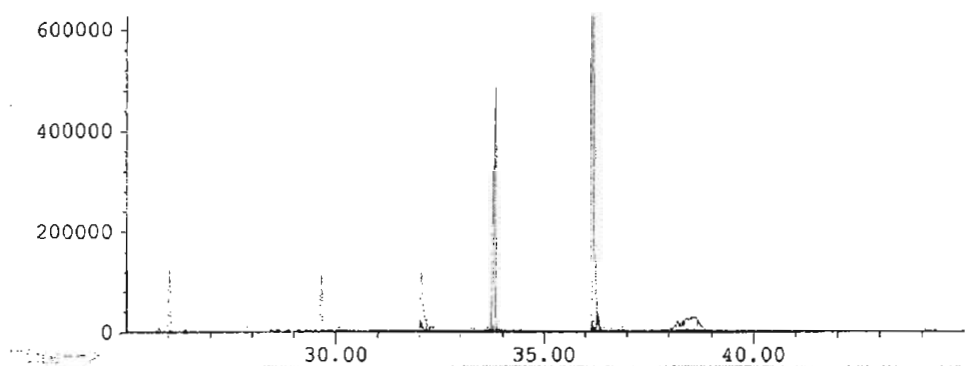


Figure 4.19 NF Permeate A (10/11/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

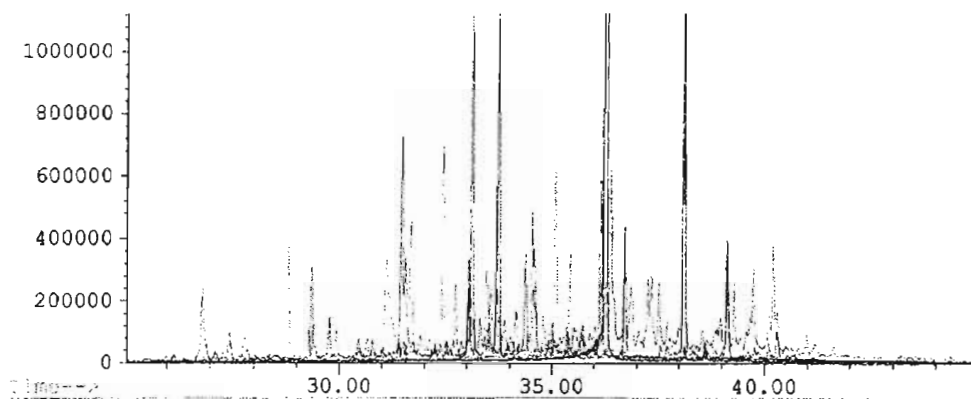


Figure 4.20 Tertiary Effluent B (10/20/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

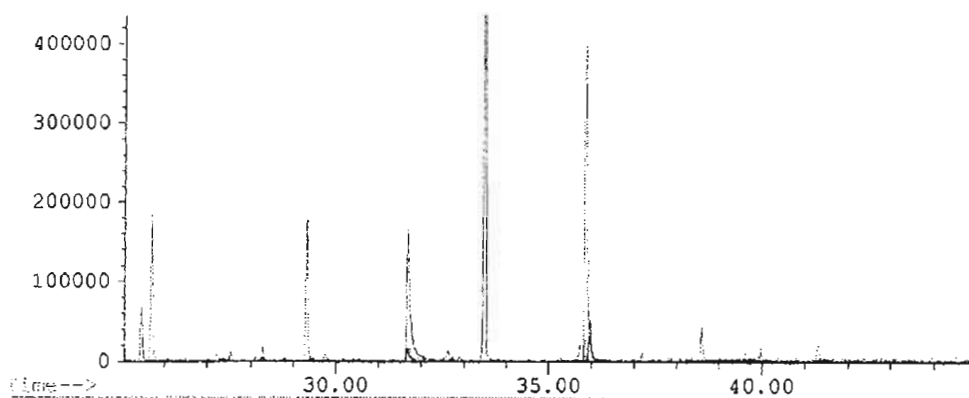


Figure 4.21 RO permeate B (10/20/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

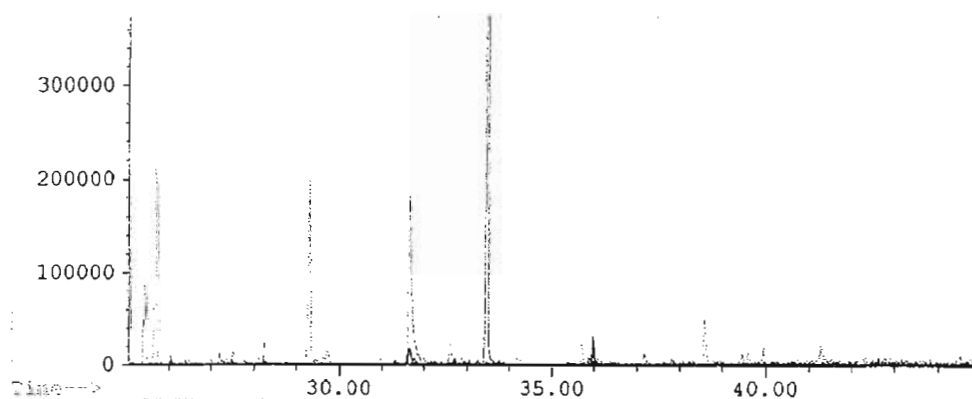


Figure 4.22 NF permeate B (10/20/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

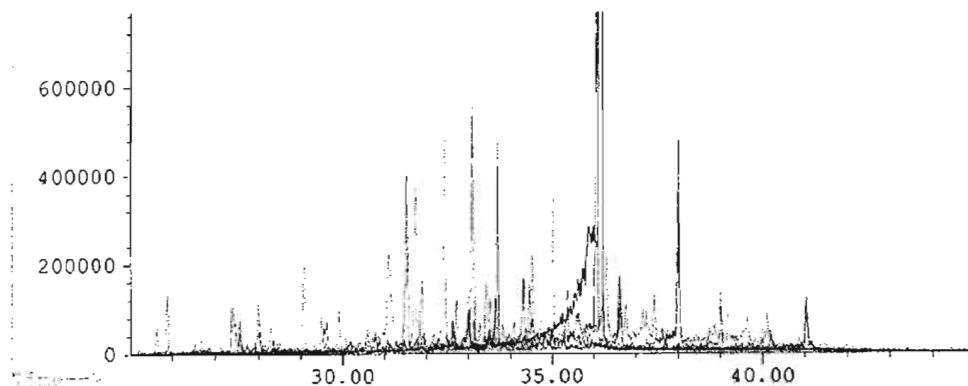


Figure 4.23 Tertiary Effluent C (10/24/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

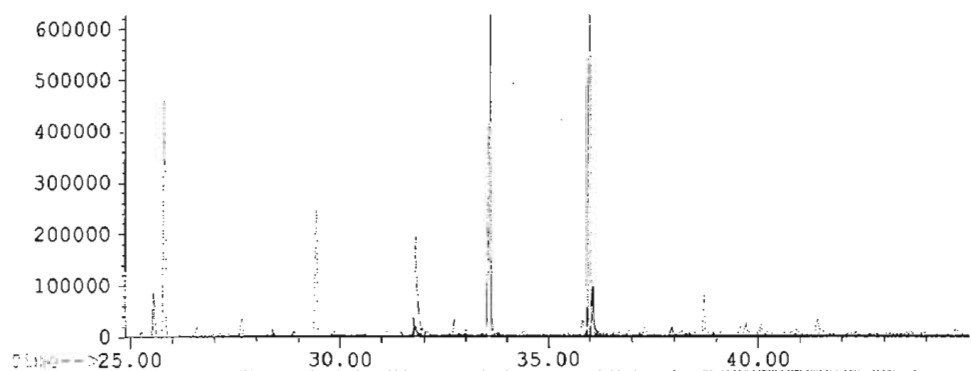


Figure 4.24 RO permeate C (10/24/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

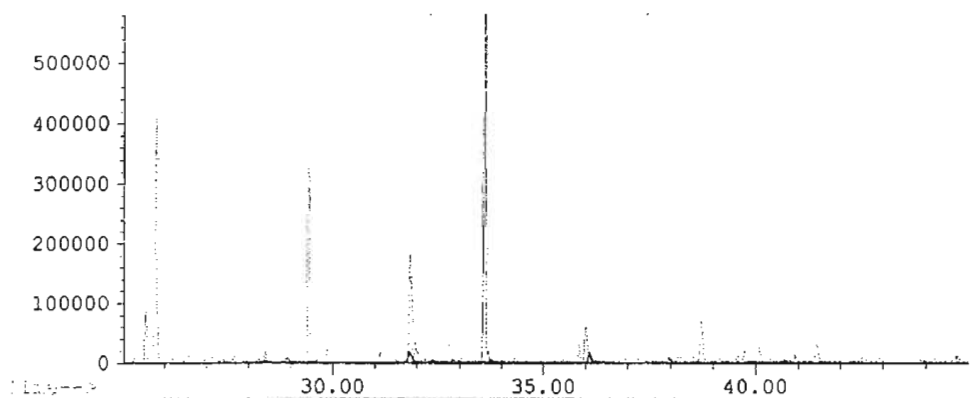


Figure 4.25 NF permeate C (10/24/00) ions ($m/z = 230, 103, 145, 235, 249, 279$)

Results of the GC/MS screening has proven that both systems, SAT and advanced membrane treatment, can function as substantial barriers to remove non-target and target compounds originating from wastewater. This finding is consistent with studies reported from field sites employing SAT (Fox et al., in press) and advanced membrane treatment (Fujita et al., 1996; Levine et al., 2000a, Levine et al., 2000b; Salveson et al., 2000) leading to indirect potable reuse. Based on the fundamental differences of removal principles which function as the main barrier for trace organics in SAT and advanced membrane treatment systems, the final products of both systems still exhibit remaining concentrations of trace organic compounds which are either refractory to biodegradation or polar and low in molecular weight. Low molecular weight neutral concentrations varied between 70 and 184 $\mu\text{g/L}$ in membrane permeates and between 150 and 230 $\mu\text{g/L}$ in SAT product water based on size exclusion chromatography (see Chapter 3). None of the selected target compounds examined during this study was detected in SAT or NF/RO product water in concentrations of concern and therefore did not contribute to the low molecular weight neutral concentration. EDTA survived SAT at low concentrations between 2 to 4 $\mu\text{g/L}$, whereas it was completely rejected during membrane treatment. Disinfection by-products were completely removed during SAT (Singer et al., 1993), whereas THMs were only partly rejected in NF and RO treatment resulting in remaining concentrations of 4 to 25 $\mu\text{g/L}$. Studies performed by Drewes et al. (submitted) showed that highly polar organic iodine compounds, originating from contrast media used during X-ray examination, survive soil-aquifer treatment at remaining concentrations of 12 $\mu\text{g/L}$ and are completely rejected by RO treatment. This list could be continued, however, the examples illustrate that the final product of SAT and membrane treatment shares the same concern regarding the fate of polar and refractory micropollutants associated with a health concern, which might survive both treatments.

CHAPTER 5

CONCLUSIONS

The scope of this study was directed to compare organics removal efficiencies between long-term SAT (travel times > 6 months) and advanced membrane treatment (MF followed by either NF or RO) leading to indirect potable reuse. Reclaimed water from the Mesa Northwest Water Reclamation Plant, Arizona, was used as feedwater for both treatment systems. Fundamental differences exist regarding how organic constituents are rejected in both systems. Whereas soil-aquifer treatment takes advantage of adsorption and biodegradation processes which occur under unsaturated and saturated flow conditions and usually represents detention times of several month prior to abstraction, membrane treatment such as RO is designed to remove high molecular weight carbon instantaneously due to physical separation. Therefore, quality issues for residual organic compounds present in reclaimed water prior to surface spreading originate from their resistance to both sorption and biodegradation during wastewater treatment and subsequent soil-aquifer treatment which can lead to their presence in SAT product water. Quality issues for residual organic compounds present in reclaimed water after NF/RO treatment are associated with polar, low molecular constituents not rejected during membrane treatment, which might survive travel through the aquifer after subsurface injection. The study sought to apply state-of-the-art techniques to characterize the remaining organic carbon in final SAT product water and compare its character to background water and membrane permeate quality.

Lessons learned from this study are that long-term SAT can lead to a substantial removal of effluent organic matter to product water concentrations of less than 1.3 mg/L TOC. The final SAT product water quality was examined using size exclusion chromatography and XAD-resin fractionation with subsequent ^{13}C -NMR spectroscopy. Based on these analyses, reclaimed water is comprised of approximately 65 percent humic substances and humic substances hydrolysates. Approximately 30 percent of reclaimed water DOC is characterized by low molecular weight neutrals. Figure 5.1 summarizes the size exclusion chromatography results obtained for both treatment systems. Low molecular weight neutrals were removed by 77 percent during the initial phase of SAT. After six months of travel in the subsurface, humics were removed by 60 percent.

During SAT, humics were also transformed and structure and composition of XAD-8 and XAD-4 isolates from organic matter in SAT product water and groundwater not affected by reclaimed water were similar and representative of natural organic matter. The alteration of humic substances was exhibited by a decrease of aromatic carbon, an increase of aliphatic carbon, and a decrease of the C/N ratio of hydrophobic acids isolated. Studies performed by Fox et al. (in press) revealed that the DBP formation potential in SAT product water was similar to drinking water based on surface water supply. The total organic carbon concentration of humics in SAT product water was slightly higher as compared to local background groundwater and the character of hydrophobic acids were slightly more aromatic. The potential health risk associated with the bulk of organics present in SAT product water seems to be comparable to natural organic matter present in drinking water.

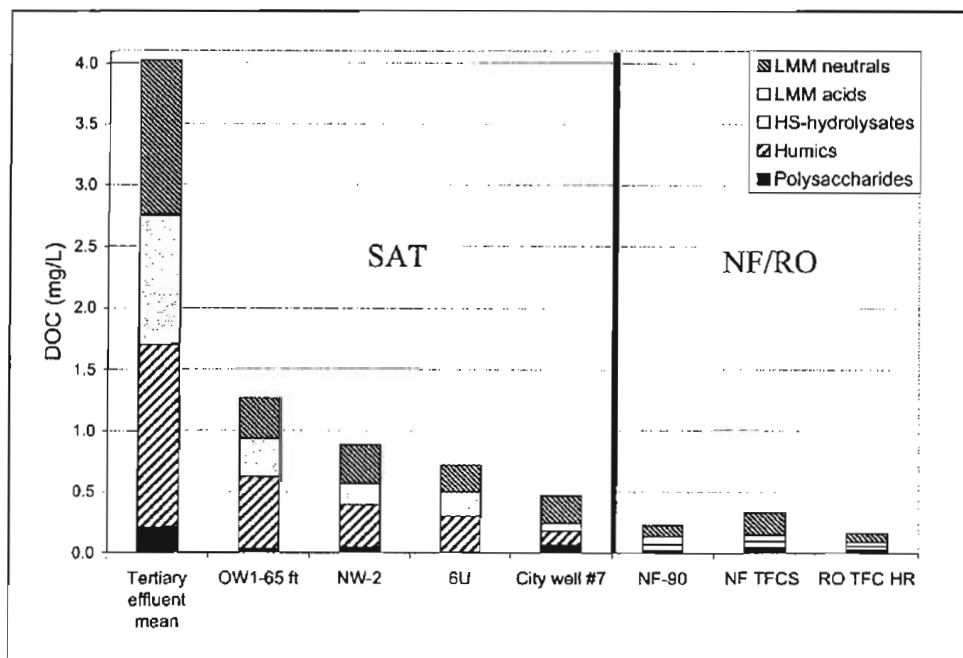


Figure 5.1 Chromatographic fractionation of Mesa tertiary effluent feedwater, SAT product water, and NF and RO permeates

(City well #7 represents local background groundwater not affected by reclaimed water)

Depending on the type of operation and the type of membrane, NF and RO membranes can efficiently reject high-molecular weight organic matter resulting in average permeate TOC concentrations of 0.37 and 0.25 mg/L, respectively. However, where complex solutions such as

reclaimed water are used as membrane feedwater, size exclusion chromatography results revealed that the molecular weight cut-off (MWCO) reported by membrane manufacturers only provides an estimate of physical separation rather than describes a clear threshold. For NF and RO permeates it appeared that the remaining TOC represents a range of different molecular weight constituents of less than 500 Dalton. The majority of organic compounds in NF and RO permeates is comprised of humic hydrolysates, polysaccharides, and low molecular weight acids and neutrals quantified by size exclusion chromatography (Figure 5.1). The presence of humic related organic matter in NF permeates was confirmed by XAD-resin fractionation. Based on ^{13}C -NMR spectroscopy and elemental analysis, no significant structural changes were observed for humics present in NF permeates and the C/N ratio did not change as compared to reclaimed water. However, the unaltered humics represent only 20 percent of the NF permeate TOC. More than 50 percent of the remaining TOC in NF permeates and 30 to 40 percent of the remaining TOC in RO permeates consisted of low molecular weight acids and neutrals.

Selected organic target compounds (EDTA, NTA, and total APECs) are efficiently removed as a function of travel time by 81, 100, and 99.5 percent, respectively, to very low concentrations or below detection limits. Observed concentrations of EDTA and APECs in SAT product water are also reported for drinking water sources (Kari & Giger, 1995; Witschel et al., 1997). Disinfection by-products were not studied in SAT product water, however, studies conducted by Singer et al. (1993) revealed a complete removal of trihalomethanes during aquifer storage. Based on GC/MS screening, unidentified organics were substantially removed during SAT and the major peaks found in chromatograms of SAT product water were also present in the blank. The target compounds EDTA, NTA and total APECs were completely rejected by NF and RO treatment. Two trihalomethanes were studied and rejection of chloroform and bromodichloromethane during NF and RO treatment varied between 84.5 and 95.3 percent and 18 and 65 percent, respectively. Detailed examination of GC/MS chromatograms obtained from NF and RO permeate extracts indicate that non-target compounds are removed to below the detection limit of the analytical method applied. There was no significant difference between any of the permeate chromatograms and the major peaks observed were also present in the blank. Based on size exclusion chromatography, the remaining low molecular weight neutral concentrations varied between 70 and 184 $\mu\text{g/L}$ in membrane permeates and between 150 and

230 µg/L in SAT product water. Mesa background groundwater not affected by reclaimed water showed a low molecular weight neutral concentration of 160 µg/L. None of the target and non-target compounds examined during this study was detected in SAT or NF/RO product water contributed to the low molecular weight neutral fraction. Therefore, the majority of low molecular weight neutrals present in SAT and membrane product water are probably similar to naturally occurring compounds and the potential health risks associated with this class of compounds might be similar.

Results of this study revealed that both treatment alternatives currently practiced for indirect potable reuse can provide high quality water and are able to provide a reliable barrier for trace organics present in reclaimed water. Findings of this study underline that the final product of SAT and membrane treatment shares the same concern regarding the presence of polar and refractory micropollutants. Future research should be directed to the fate of these compounds in indirect potable reuse systems and potential human health effects associated with emerging compounds of concern.

CHAPTER 6

BUDGET

The budget of the study is summarized in Table 6.1. Budget categories are presenting funds received by a grant from the NATIONAL CENTERS for WATER TREATMENT TECHNOLOGIES (Award No. 699-799-005) and matching by Arizona State University.

Table 6.1 Budget of the study

<i>Category</i>	<i>Centers (XCJ 6245)</i>	<i>Matching (XCT 9269)</i>
Salaries		
PI (1 month)		\$ 4,893.34
Co-PI (1 month)		\$ 4,889.00
Graduate Student (50%)		\$ 7,834.00
Equipment		
Computer and printer Shimadzu (TOC upgrade)	\$ 2,843.46	\$ 1,436.17
Materials & Supplies		
weatherstrip, rubber springs, foam packers		\$ 107.07
Travel		
to and from Yuma (lodging & transportation)		\$ 1,558.47
Other		
Stanford University (analytical services-DOC characterization)	\$ 1,850.00	
DOC Labor (analytical services-organic analysis with LC- OCD)	\$ 715.00	\$ 585.00
Service		
Bureau of Reclamation (use of Yuma Facility)	\$ 2,875.00	
Total Expenditures	\$ 8,283.46	\$ 21,303.05
Total Direct	\$ 8,287.00	\$ 23,273.00
Indirect Cost 26%	\$ 1,713.00	\$ 3,879.00
Total Cost	\$ 10,000.00	\$ 27,152.00

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