



TREATMENT OF TRACE ORGANIC COMPOUNDS BY MEMBRANE PROCESSES: AT THE LAKE ARROWHEAD WATER REUSE PILOT PLANT

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ABSTRACT

Organic and trace organic performance data for ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) at the Lake Arrowhead water reclamation pilot plant are analyzed to determine the treatment efficiency of these processes in an indirect potable reuse design. Four organic parameters were studied: dissolved organic carbon (DOC), ultra-violet absorbance at 254 nm (UV-254), SUVA and base neutral analysis (BNA).

UF and NF removed the larger compounds from the influent, but had no significant impact on the base neutral fraction with the exception of sterols. The RO process removed DOC and UV-absorbance compounds from the effluent to their respective detection limits. Base neutral compounds were significantly removed by RO, leaving at extremely low concentrations small molecular weight compounds, indicating indirect potable reuse is technically feasible. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Indirect potable reuse; micropollutants; nanofiltration, reverse osmosis; trace organics; ultrafiltration.

INTRODUCTION

Water Factory 21 (California, USA) was the first water reuse plant to have integrated membrane technology in its treatment chain. This choice was driven by the uncertainty associated with the water quality requirements prior to reuse and the high quality effluent and high process reliability thought to be guaranteed by this technology. Today, membrane technology is consistently considered for indirect potable reuse and industrial reuse applications.

The majority of the membranes used in water reuse are pressure-driven membrane processes which include reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF). RO membranes are used for their ability to remove dissolved salts and dissolved organic compounds. NF membranes are primarily used as a softening process and to remove organic compounds with molecular weight (MW) values greater than 200 Daltons. UF and MF membranes are effective for removing particulate contaminants including turbidity, total suspended solids (TSS) and microorganisms. The biggest advantage in using UF membranes over MF membranes resides in its ability to remove viruses. The approximate cut-off point of MF, UF and NF ranges from 100 000 D to 500 000 D, 2000 D to 100 000 D, and 200 D to 1000 D, respectively. For RO membranes, the cut-off point is generally less than 100 D.

A direct consequence of these different cut-off points is the difference in operating conditions and flux production for each membrane type. Hence, UF flux can be one order of magnitude greater than RO, with lower pressure requirements. Another factor which can impact membrane performances is the influent water quality. Particles, colloids and microorganisms which deposit on the membrane will generally cause membrane fouling. Therefore, membranes must be cleaned and washed at pre-defined conditions and the influent pretreated before exposure to the membrane. As a direct result of fouling, sophisticated treatment chains have been developed prior to RO membranes. Recently more efficient membranes have led to simpler designs using UF or MF membranes as RO pretreatment. In this configuration, UF or MF membranes are being considered directly after secondary clarification and before RO membranes.

To monitor the effluent water quality of membrane processes, non-specific parameters such as dissolved organic carbon (DOC), total suspended solids or turbidity are generally measured. These simple and cheap parameters are also required by certain regulations. Yet they are insufficient to perform a valid health risk evaluation of the effluent. Therefore more in depth analysis is required to evaluate the chemical risk of an effluent.

Presently, most health risk studies which have been performed for wastewater reuse were based on the presence of microorganisms or pathogens in the effluent (Tanaka *et al.*, 1993). Specific organic water quality parameters of health concern, such as pesticides are rarely monitored, yet they are known to be potentially harmful for public health. Among these chemicals are over 100 base neutral compounds which have been classified as target compounds by government organizations e.g. USEPA (Pointius, 1995). In addition to these compounds, other potentially harmful chemicals found in the water are identified as non-regulated "non-target compounds". The present study will focus on base neutral organic compounds, semi-volatile organic compounds extractable by dichloromethane (DCM) and analyzed by gas chromatography/mass spectroscopy (GC/MS) before and after membrane treatment.

Few key water reuse studies have performed base neutral analysis. Among them are the Denver potable reuse study (US EPA, 1992) and the San Diego project (Western Consortium for Public Health, 1996). The Denver project did not detect the presence of micropollutants in its final effluent. However, acetaldehyde and formaldehyde were detected respectively at 7 µg/L and 13 µg/L after UF and before RO. The San Diego Project on the other hand detected a large number of micropollutants among which were purgeable and extractable compounds, such as disinfection by products. The key difference between both projects is that the San Diego project used large volume extractors, whereas the Denver project did not.

The purpose of this paper is to study the fate of organic micropollutants after membrane treatment at the Lake Arrowhead Water Reclamation Plant (Calif., USA); an indirect potable reuse project. Its objective was to guarantee the highest water quality effluent possible after the removal of most contaminants, nutrients, and microorganisms from the wastewater treatment plant effluent prior to disinfection (Madireddi *et al.*, 1997). The train process comprised of denitrification, coagulation/precipitation, sand filtration, ozonation, granulated activated carbon (GAC), UF/NF in parallel, RO and final ozonation (Figure 1). In this project, the GAC filter was designed to work as a biological activated carbon (BAC) filter and the membranes were used as the ultimate barrier in a multi-barrier system.

The paper will evaluate conventional organic parameters and both target and non-target base-neutral organic compounds, before and after the different membrane processes at the water reuse pilot plant, hence

highlighting trends and behaviors associated with the different membranes. The originality of this work resides in the use of integrated chromatographic analysis to assess the base neutral organic data and the assessment of the data through this method.

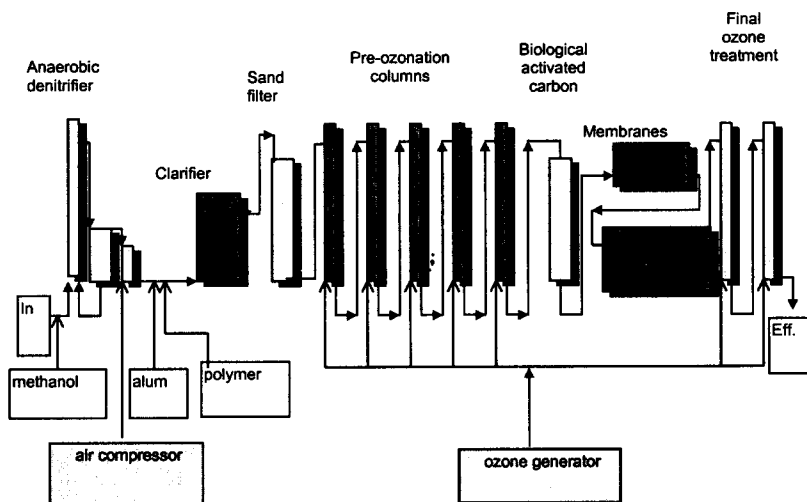


Figure 1. Flow chart of the Lake Arrowhead Water Reclamation Plant.

METHODS

Lake Arrowhead Wastewater Reuse Plant

The characteristics of the GAC down flow pressurized filter were 4 m high, 0.8 m in diameter. The GAC was loaded on April 12, 1994, with 1.2 m of Filtrasorb F-400 (Calgon Corp; Pittsburgh, PA.). The empty bed contact time of the GAC column was 15 minutes. The startup date of the GAC column is used as the reference point for time in this study. Non specific parameters were analyzed 90 days after GAC start up time when breakthrough of both DOC and UV-254 absorbance had occurred. The membranes used during this study are presented in Table 1. On December, 1994, the original set of membranes were replaced. At that time the GAC system was acting as a biological activated carbon (BAC) column.

Table 1. Membrane characteristics for the ultrafilter, nanofilter and reverse osmosis units used at the Lake Arrowhead Wastewater reuse pilot plant (Madireddi *et al*, 1997)

	Ultrafilter	Nanofilter	Reverse Osmosis
Model	G 10	DK 4040	SG/AG 4040
Diameter x Length (inchx inch)	4 x 40	4 x 40	4 x 40
Configuration	Spiral-Wound	Spiral-Wound	Spiral-Wound
Mol. Weight cutoff (Dalton)	2500	200	-
Operating pressure (psi)	75-200	150-250	100-400

General parameters

Turbidity, conductivity, DOC and UV-254 were analyzed in and out of each process according to the methods described by the APHA (1995). Turbidity and conductivity analysis were performed on site, immediately after sampling as physical parameters. DOC and UV-254 were performed as non-specific organic parameters. DOC measurements were made on a Dohrman DC-80 carbon analyzer. UV-254 nm absorption measurements were made on a 5652 Hewlett Packard diode array spectrophotometer.

Measurements were made on grab samples collected before and after each process and stored before analysis in amber vials with Teflon lined caps, without head space. SUVA values were calculated by dividing the UV-254 absorbance value reported in cm^{-1} , by the corresponding DOC value and multiplying by 100.

Base neutral analysis

In addition to non-specific organic analysis, base neutral analysis (BNA) was performed to understand the impact of each process on the potentially hazardous trace organic fraction.

Analytical protocol. Large sample volumes were extracted with DCM less than 2 hours after sampling with a continuous liquid liquid extractor (CLLE) (Baker *et al.*, 1987). The average volume sample was of 40 L with the exception of the April 8th sample, for which 130 L and 360 L were sampled, respectively after UF and RO unit. The pH of the sample was brought down to 3 with the addition of concentrated phosphoric acid. Sodium sulfate was added to the sample at a concentration of 50 ppm. The extraction rate was adjusted to 3 L/hr with a 10 to 1 ratio between the water and the solvent. The overall estimated average extraction efficiency was 45% (Levine, 1999)

After extraction, the samples were dried on a sodium sulfate column, concentrated to 1 ml by Kuderna Danish evaporation, and analyzed on a Finigan-4000 automated GC/MS analyzer. The GC column used was a DB-5MS, 30 m x 0.25 mm. The temperature program was 4 min at 30°C, 6°C/min to 300°C and 30 min hold. For analytical purposes, six internal standards (IS) were injected in the sample prior to GC/MS analysis at 40 $\mu\text{g/L}$. MS analysis was performed for both target and non-target compounds. Non-target compounds were tentatively identified based on an MS library search and mass spectra evaluation, while target compounds were confirmed and quantified.

BNA interpretation. The original chromatograms obtained after GC/MS analysis were normalized on the average GC/MS scan index numbers of the six IS injected prior to analysis. Data analysis was performed by integrated chromatographic analysis (ICA) comparing influents and effluents of a same process for the same sampling date Levine (1999). In this paper, ICA was used to quantify base neutral organic changes occurring in the water matrix before and after membranes. Finally, lists of tentatively identified compounds were built, highlighting the change in the chemical composition of the base neutral fraction.

RESULTS

General parameters

Conductivity and turbidity data are presented in Figures 2a and 2b. The data show that after BAC filtration, turbidity data varies between 0.5 and 1.5 NTU. Turbidity after UF/NF dropped to an average turbidity value of 0.2 NTU. After RO, turbidity values are slightly less than after UF/NF, even though the ranges tend to be very similar. Conductivity values were consistently less than 500 $\mu\Omega$. The average conductivity values after BAC, UF/NF and RO were 450, 310 and 75 $\mu\Omega$ for each respective process.

Figures 2c, 2d and 2e show temporal data after BAC filtration, UF/NF and RO for DOC, UV-254 and SUVA. Having reached "steady state" after 90 days, the BAC filter effluent remained fairly constant for DOC and UV absorbance respectively: $8.2 \pm 1.3 \text{ mg/L}$ and 0.07 ± 0.02 . The UF/NF processes significantly decreased the level of both DOC and UV absorbance. DOC dropped by 75% from an average concentration of 8.2 mg/L to $2.2 \pm 0.7 \text{ mg/L}$, and UV-254 absorbance dropped by approximately 70% from an average of 0.07 cm^{-1} to $0.025 \pm 0.01 \text{ cm}^{-1}$. SUVA values were slightly higher after UF/NF than after BAC filtration, which suggests that aromatic and unsaturated compounds were not as readily removed by the first stage membrane treatment in comparison to DOC.

After RO, DOC and UV-254 absorbance dropped respectively to 0.4 mg/L and close to below the detection limit of the method. However, for those points which UV-absorbance was positive, the SUVA values were less than 1, indicating that the RO membrane preferentially removed from the water the aromatic and

unsaturated compounds from the organic fraction. DOC data after RO tend to increase with time, which can be an indication of a slight loss of efficiency with time.

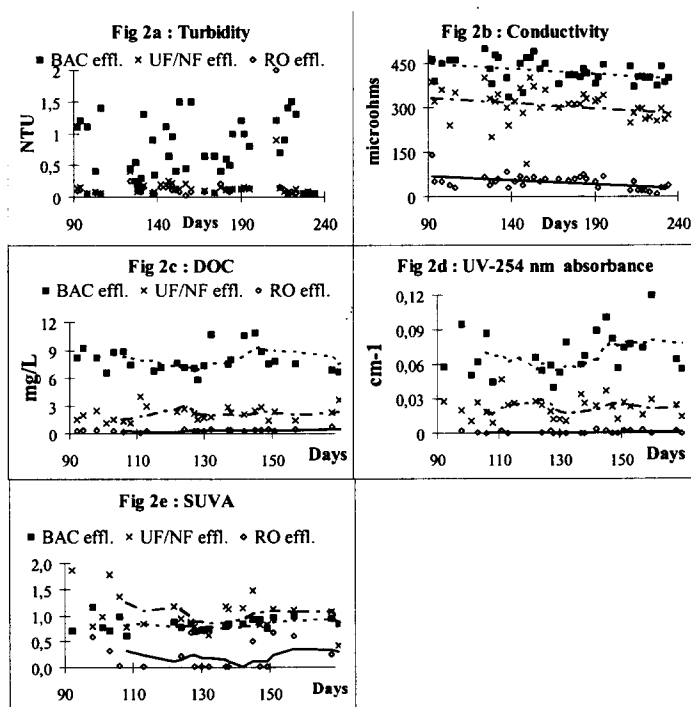


Figure 2. Turbidity, Conductivity, DOC, UV, and SUVA data as function of days after BAC start up at the Lake Arrowhead Water Reclamation Plant after BAC, UF/NF and RO treatment.

Base Neutral Compounds

Examples of computer reconstructed chromatograms are presented in Figure 3. A direct comparison of 17 chromatograms indicates similarities before and after UF and before and after NF. However, some of the later eluting compounds were never detected after UF or NF. For example, peak 1 and 2 were systematically absent after NF and UF. These peaks were respectively identified as standard coprostanols, which have been used as indicators of sewage contamination (Venkatesan *et al.*, 1990). The RO membrane removed significant amounts of base neutral compounds including most of the later eluting higher molecular weight compounds.

Mass spectral analysis of the different chromatograms confirmed the similarities before and after UF or NF. Target compounds such as nitrobenzene, fluorene, pyrene, acenaphthene were detected at trace levels. The measured concentration for any one of these compounds was systematically less than 0.01 ppm. The majority of the non-target compounds tentatively identified by MS were aldehydes, ketones, acids and alcohols. After RO, MS analysis indicated the presence of nitrobenzene and benzoic acid at trace levels of disinfection by-products such as bromodichloromethane, and other non-target compounds such as aldehydes (octanal, nonanal, decanal), octane derivative compounds, acids (hexanoic, decanoic) and alcohols.

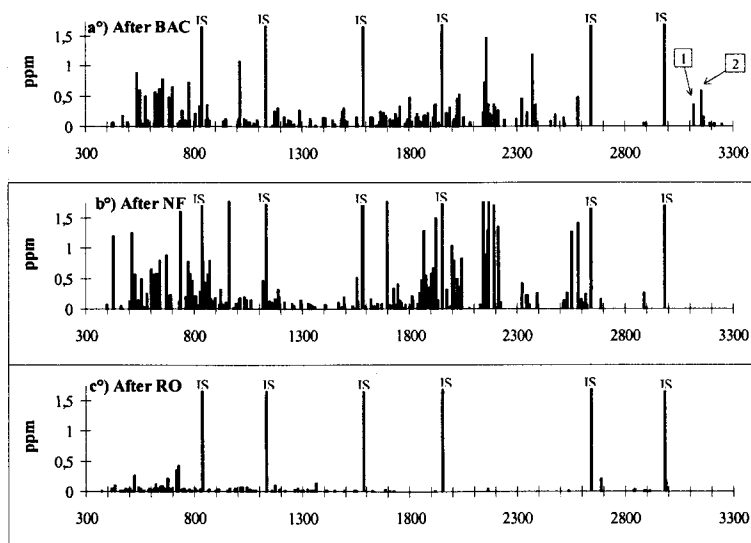


Figure 3. Computer reconstructed GC/MS profiles of the Lake Arrowhead pilot plant on 02/03/95 after (a) BAC and (b) NF, and after c) RO, on 04/08/95 (IS : Internal standard).

DISCUSSION

General data

The background information provided by non-specific parameters were consistent with the literature (Table 2). DOC and UV-254 data values decreased after UF/NF treatment and after RO. The decrease in turbidity from 1 NTU to 0.2 NTU was comparable to that undergone by DOC. The UF/NF membranes were therefore able to remove the high molecular weight DOC fraction (greater than 1000 daltons) from the influent. The removal by the RO unit of the remaining DOC (i.e. the low molecular weight DOC fraction, less than 1000 daltons) had no significant effect on the turbidity. Hence, turbidity removal by UF/NF could be in this case used as a first approximation of the removal of the high molecular weight DOC fraction.

Table 2. Summary table of existing water reuse membrane applications

Location/ State	MF		MF/UF	UF		RO (after MF)	
	Livermore, USA	Belgium	Georgia, USA	Denver, USA	France	San Diego USA	Belgium
Turbidity-NTU	0.09		0.06	0.2	< 0.1		
% removal			75				
UV254 -cm ⁻¹		0.261	0.105		0.063		0
% removal		8			93		
TOC mg/L	7.8	14		0.7	2.4	10	<5
% removal		20			82	99	
References	Geselbracht, 1996	Van Houtte <i>et al.</i> , 1998	Levesque <i>et al.</i> , 1998	USEPA, 1992	Glucina <i>et al.</i> 1997	Gagliardo, 1998	Van Houtte <i>et al.</i> , 1998

SUVA values after UF/NF were slightly greater than the BAC effluent. However, the large distribution of DOC values after BAC filtration makes it difficult to account for any true differences of SUVA before and

after UF/NF. Hence, aromatic and unsaturated compounds measured by UV-254 would be associated with both high and low molecular weight DOC fractions. After RO, SUVA values decreased indicating that the aromatic and unsaturated compounds were preferentially removed from the influent, when compared to the remaining DOC. This selective process could be the result of the membrane's structure, the compounds behavior or both.

Base neutral compounds

Chi-square statistics were used to compare chromatograms. This method, already used at the Lake Arrowhead water reuse project, compares chromatograms on the basis of peak eluting time and peak height (Levine, 1999). Table 3 summarizes the different tests performed before and after membrane treatment.

Table 3. Chi-square statistics summary table
(*: no ozonation prior to BAC, x5: number of chromatograms analyzed)

Test number	1		2		3	4	
Sampling period	Aug - Feb		Jan. 13		Feb.3	Aug. 8	April 8
Comparison	BAC (x5)	BAC*-UF*	BAC-UF	BAC*-BAC	BAC-NF	BAC-RO	UF-RO
Calculated Value	167,58	14,56	20,27	21,1	32,50	28,2	157,12
Degree of Freedom	140	35	35	35	35	35	35
Theoretical Value	186,5	47.77	47.77	47.77	47.77	47.77	47.77
Conclusion	not different	not different	not different	not different	not different	different	Different

Test 1 compared the base neutral chi-square distribution after BAC filtration for five computer reconstructed chromatograms sampled over a 7 month period. No significant differences between the chromatograms were found, however, this does not mean that the BAC chromatograms were identical, but that the changes between the chromatograms were not significant.

In test number 2 two sets of experimental conditions were compared (1) without ozone before the BAC filter and (2) with ozone before BAC. Chi-square statistics showed no significant differences between both conditions before and after UF effluent. The lack of differences with and without ozone can be explained by the nature of the BAC filter, which behaved similarly to a buffer.

Test 2 also indicated the absence of differences before and after UF. This result is consistent with the fact that the cut off point of the UF membrane is greater than the base neutral compounds (less than 500 D). On the other hand, some of the later eluting compounds were unexpectedly removed (e.g. sterols), which is inconsistent with the above result. However, this phenomenon could be explained either by sorption mechanisms with the membrane or by possible cake layer formation on the membrane surface.

Test number 3 indicated insufficient evidence to differentiate between chromatograms obtained before and after NF. This result is inconsistent with respect to the NF membrane cut off point unless base neutral compounds are less than 200D. In summary, UF and NF do not statistically impact the peak distribution associated to base neutral chromatographic data. Hence, base neutral organic compounds are poorly separated by the tested UF and NF membranes. From a management point of view, the additional cost associated to NF is not counterbalanced by enhanced water quality. Therefore, the choice of UF over NF as a pretreatment to RO is preferred.

Finally, test number 4 shows that after RO the peak distribution changes enough for the statistical test to accept the null hypothesis being that chromatograms are different. However, chi-square statistics does not explain the differences.

Table 4 indicates the estimated base neutral concentration for the earlier eluting compounds (before scan index number 1583) and the later eluting compounds (after scan index number 1583). With pre-ozonation, the concentration of the earlier eluting compounds was greater after BAC and UF. This observation is consistent with the shift in mass presented by Levine (1999) after ozonation from the higher molecular weight base neutral compounds to the lower molecular weight base neutral compounds. After UF and NF,

the data show a slight change in concentration of base neutral compounds. Finally after RO, the total estimated base neutral concentration decreased from 30 to 40 ppm, to 4 ppm. The later eluting compounds were almost totally removed while the remaining base neutral compounds were mainly low molecular weight high volatility base neutral compounds, such as disinfection by-products.

Table 4. Total base neutral concentration for two chromatographic fractions based on estimated scan index numbers (L_{mw}) 300-1583 and (H_{mw}) 1585-2980: The Lake Arrowhead water reuse plant as a function of process and time (*: no ozone applied prior to BAC)

Sampling Dates	BAC		UF		NF		RO	
	L_{mw}	H_{mw}	L_{mw}	H_{mw}	L_{mw}	H_{mw}	L_{mw}	H_{mw}
27-Aug	26,9	21,1					37,7	2,3
25-Nov	55,8	58,0			31,0	49,8		
13-Jan*	16,8	30,6	25,1	31,8				
13-Jan	32,9	27,9	39,1	36,6				
08-April			33,6	25,8			4,4	0,5

The above data show the complementary role played by UF/NF and RO processes. The first stage removing from the influent all the larger compounds and the RO unit removing the smaller compounds, such as base neutral organics and salts. Hence, in view of the data presented in the paper and those presented by Madireddi *et al.* (1997) concerning inorganic and microbial contaminants, the final effluent produced at the Lake Arrowhead water reclamation plant can be considered as environmentally safe to be reclaimed to a storage like Lake Papoose for a one-year retention before reentering Lake Arrowhead, which is used as a water supply.

CONCLUSIONS

The monitoring strategy developed in this paper provides an in-depth understanding of the fate of organics before and after membrane treatment, in an indirect potable water reuse project. Some of the key conclusions drawn from this work concern the plant design and operations: (1) the studied NF membrane did not present any key advantages over UF; (2) the RO membrane removed most of the base neutral compounds from the effluent; (3) disinfection by-products were the most persistent compounds and the most difficult to treat; (4) pre-ozonation increased the base neutral content in the BAC and UF effluent.

In addition this work provides a new perspective to organic analysis combining both non-specific parameters and base neutral analysis. The combination of DOC, UV and turbidity provided useful background information on the total organic content of the water. This information can be used to monitor water quality along the treatment chain. Finally, to complete this vision, an analysis of polar compounds and toxicity testing of extract are recommended.

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