



Article Removal of Trihalomethane Precursors by Nanofiltration in Low-SUVA Drinking Water

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Abstract: Trihalomethanes (THMs) are prevalent disinfection by-products. High THM formation is usually associated with natural organic matter with high molecular weight and aromatic characteristics, which is efficiently removed by nanofiltration (NF). In the Sea of Galilee and the Israeli National Water Carrier (NWC), water shows high THM formation potential, although it mainly contains low molecular weight and hydrophilic organic matter with low aromaticity. In the present study, NF removal abilities were tested on treated NWC water using three different spiral wound membranes (NF90, NF270, and DL). Rejections and fluxes were tested as a function of pressure, water recovery, and membrane type. Feed and permeate dissolved organic carbon (DOC), UVA254, total THM formation (THMF), and total THM formation potential (THMFP), as well as alkalinity, conductivity, hardness, Ca²⁺, Mg²⁺, and Cl⁻ were measured to evaluate rejection and THM formation reduction. The results demonstrated that NF can efficiently remove natural organic matter (NOM) and reduce THM formation, even in this challenging type of water. At low water recovery, membranes showed average rejection of about 70–85% for THMFP and THM. Upon elevating recovery, average THM and THMFP rejection decreased to 55–70%, with THM content still well below regulation limits. Of the membranes tested, the higher permeability of NF270 appears to make it economically favorable for the applications tested in this work.

Keywords: nanofiltration; trihalomethanes (THMs); natural organic matter; disinfection by products; water treatment

1. Introduction

Chemical disinfection of drinking water is a common treatment against pathogens, but often generates disinfection by-products (DBPs) that may pose a health risk, such as trihalomethanes (THMs), haloacetonitriles, haloacetic acids, and other chemical compounds. The most common class of DBPs in chlorinated drinking water are THMs, which include chloroform (CHCl₃), bromodichloromethane (CHBrCl₂), dibromochloromethane (CHBr₂Cl), and bromoform (CHBr₃) [1,2]. THMs are suspected genotoxic and carcinogenic compounds [3] and their concentrations are regulated in many countries (often the only regulated DBPs). Current Israeli and European Union regulations [4] set a maximum concentration limit (MCL) for all four THMs together (TTHM) at 0.1 mg L⁻¹, while the United States set an MCL of 0.080 mg L⁻¹. THMs are formed in a complex set of reactions between the chlorine disinfectant and natural organic matter (NOM). In general, aromatic NOM with high molecular weight (e.g., humic acids) is considered more reactive towards THM formation [5,6]. Hence, an appealing approach to reduce THM formation is by removal of their organic precursors (which are usually easier to remove than small and stable molecules like THMs).

Nanofiltration (NF) membranes can be very effective in the removal of DBP precursors [7–9]. Previous studies have shown that due to NOM removal by NF, TTHM formation was reduced by

70–99% [10–15], at varying water recovery ratios. Most of these studies, however, were conducted on waters with relatively high dissolved organic carbon (DOC) concentrations and high specific ultra violet absorbance (SUVA; light absorbance at 254 nm, UVA₂₅₄, normalized to DOC content). Major contributors to high SUVA are aromatic NOM with high molecular weight (e.g., humic acids), which are also more reactive towards THM formation [5,6] and are more readily removed by NF. In fact, removal of THM precursors was often estimated in these studies based on SUVA reduction.

In this regard, Lake Kinneret (Sea of Galilee) is unique. It has a high NOM content (DOC 2–3 mg L⁻¹) but very low UVA₂₅₄ (i.e., SUVA values <1 L mg⁻¹ m⁻¹) [16,17]. Despite its low SUVA values and dominance by low molecular weight (LMW) NOM, the water in Lake Kinneret results in high THM formation upon chlorination. This is most likely due to its very high bromide content (~2 mg L⁻¹), which oxidizes by HOCl following chlorination to form HOBr that efficiently reacts with LMW NOM [2,18,19].

Information regarding the efficiency of NF for removal of NOM with low SUVA and low MW (as in Lake Kinneret) is limited, but the notion is that hydrophilic LMW NOM is harder to remove [7,9,20,21]. Only very few studies [21,22] have examined reductions in THM formation following NF in water with very low SUVA values (<1 L mg⁻¹ m⁻¹). These studies, conducted in dead-end settings, reported a high reduction in THM formation but very different DOC removal efficiencies.

Lake Kinneret is a major freshwater body in Israel, and the water source for its National Water Carrier (NWC). About 80% of the THM precursors in Lake Kinneret (and in the NWC) are estimated to be hydrophilic LMW organic substances [16,23]. The total THM formation potential (TTHMFP) values in the lake water and in the NWC are around 240 and 160 μ g L⁻¹, respectively, with higher values in summer (unpublished data, Israel National Water Company). A previous study in Lake Kinneret showed that TTHMFP constitutes over 50% of the total organic halogen formation potential (TOXFP), suggesting that THMs are a major DBP group in this water [19]. Furthermore, the high bromide content in Lake Kinneret results in a shift toward brominated DBPs, with brominated THMs accounting for >90% of TTHM [23]. This phenomenon also results in higher overall mass-based concentrations since the molecular weights of brominated THMs are significantly higher.

According to the Israel National Water Company, current TTHM values in the NWC system vary between 20 and 65 μ g L⁻¹. However, in some cities this value may reach 80 μ g L⁻¹ and in certain events even more. These levels are getting close to Israel's MCL, and current changes in its water distribution systems (e.g., enhanced water retention times and additional chlorination at city entry points) may lead in certain places to an increase in THM concentration, even above the allowed limit.

To summarize, although Lake Kinneret and Israeli NWC water contain NOM that is mainly of LMW and hydrophilic in nature, it has a high potential to generate THMs as DBPs. NF may help addressing this problem by removal of THM precursors, but the efficiency of this process to remove LMW and hydrophilic NOM is not fully clear yet.

The present study focuses on this issue, examining NF ability to remove LMW and hydrophilic NOM (as in the Israeli NWC), and to reduce THM formation. Permeate quality, considering both organic and inorganic parameters, was investigated as function of water recovery and applied pressure for three different NF membranes.

2. Materials and Methods

Experiments were performed with three spiral wound NF membranes: DL, NF270, and NF90, measuring 6.4 cm in diameter and 101.6 cm long. Detailed specifications of these membranes are provided in Table S1.

2.1. Experimental

Feed water for filtration experiments was collected at the outlet of the central treatment plant of the National Water Carrier (NWC) at the Eshkol site before final chlorination. Water samples were collected in clean 20 L plastic containers and kept refrigerated at 4 °C for no more than 3 days until experiments. Sampling and filtration experiments were conducted between October 2011 and June 2012. First approximation of the size distribution of the NOM in this water was obtained by dead-end filtration via three flat membranes with molecular weight cut-offs of about 5000, 1000, and 500 Da (GE-SEPA-CF-PT, GE-SEPA-CF-GH, and NF270, respectively). DOC, UVA₂₅₄, and TTHMF values were measured in both the feed and permeate of each membrane.

Water treatment experiments were done using spiral wound membranes. A scheme of the experimental system is given in Figure 1. The feed water tank was kept at 25 ± 5 °C by a heat exchange system. Before starting the experiments, feed pH was adjusted to 6.5 using HCl (1N) and a sample was taken for chemical analysis. In each experiment two parameters were kept constant: feed pressure and concentrate flow rate. Desired feed pressure and constant concentrate flow were obtained by adjusting the feed flow to the membrane (using a by-pass) and pressure, with all flows circulating back to the feed tank. After the operation, conditions were set and when a steady state was reached, the experiments were initiated. During experiments, permeate samples (0.5 L each) were collected; feed and concentrate pressures as well as permeate flow rate were recorded. In experiments testing membranes performance as function of pressure, the feed pressure was varied between 3, 5, and 10 bar. When the effect of water recovery was tested, feed pressure was constant at 3 or 5 bar, but instead of circulating permeate to the feed tank it was collected continuously until reaching the desired water recovery. The permeate sample was then chemically analyzed. Water recoveries alternated between 0%, 20%, 50%, 70%, and 85%.



Figure 1. Schematic diagram of nanofiltration (NF) spiral wound system.

After each experiment the system was cleaned by washing the membrane, for about 15 min, with distilled water at high pressure and high concentrate flow without circulation to the feed tank. Then, distilled water was circulated in the system (at a high pressure and concentrate flow) for an additional 30 min.

2.2. Analytical

For each experiment feed water and permeates were tested for TTHM, TTHMFP, DOC, UVA₂₅₄, UVA₄₀₅ (light absorbance at 405 nm), hardness, alkalinity, calcium, magnesium, and chloride concentrations.

Alkalinity, hardness, [Ca²⁺], and [Cl⁻] were measured following standard methods 2320, 2340, 3500 B, and 4500 B, respectively [24]. DOC was measured following standard method 5310 B using a multi N/C TOC analyzer (Analytik Jena, Jena, Germany). Conductivity and pH were measured using commercial meters (con510 EUTECH Instruments and 510 pH Cyberscan, respectively). Absorbance at 405 and 254 nm was measured as surrogate for suspended solids and organic matter concentrations,

respectively. The measurements were conducted using Genesys 10 UV spectrophotometer (Thermo Electron Corporation, Waltham, MA, USA) with a 10-cm-long quartz cell.

THM formation (THMF) and THM formation potential (THMFP) values were measured following chlorination with commercial bleach (NaOCl). The hypochlorite content of the latter was measured (as Cl₂) by redox titration with sodium thiosulphate (standard method 2580 B). After chlorination, pH was adjusted to 7.0 (to eliminate variation in THM formation due to pH variations). Chlorine concentration was confirmed using a colorimetric test with *N*,*N*-diethyl-*p*-phenylenediamine reagent (DPD) kit at 540 nm according to standard method 4500 G [24].

Two chlorination procedures were performed (in duplicates) for each sample:

TTHMF was measured by a simulated distribution system (SDS) test in which 150 mL sample was chlorinated with a dose of 2 mg L^{-1} as Cl_2 (similar to the chlorination dose used in the Israeli water distribution system). The sample was then split into two sealed 60-mL flasks (with no headspace) that were kept in the dark at 20 °C for 48 h.

For total THM formation potential (TTHMFP) 150 mL sample was chlorinated with a high dose of 20 mg L^{-1} as Cl₂. Chlorinated sample was then split and stored for a week under the same conditions as in the SDS test described above. At the end of incubation 20 mL from each replicate were neutralized by Na₂SO₃, transferred to a sealed vail (without headspace) and kept refrigerated till THM analysis. Then, 40 mL of the remaining sample served for residual chlorine measurement using a colorimetric test with a DPD kit.

THM analysis was done following liquid–liquid extraction using 10 mL of a water sample and 1 mL of isooctane with the addition of internal standard (1,2-dibromopropane). After 2 min of mixing, samples were placed to rest for 4 min to enable phase separation. About 1 mL of the organic phase was then extracted (using a Pasteur pipette) and analyzed using gas chromatography (GC). The extractions of THMFP samples were further diluted into a 1:5 ratio with clean isooctane to avoid saturation of the GC detector (see below).

THM concentrations in the extracted isooctane samples were determined by gas-chromatography (Varian CP 3800, Walnut Creek, CA, USA) equipped with electron capture detector and DB-5 column (30-meters-long, with a 0.32- μ m inner diameter and 0.25- μ m film thickness). Helium (99.999%) was used as a carrier gas with flow rate of 2 mL/min. The volume of sample injected was 2 μ L. The injector temperature was 150 °C and the detector temperature was 300 °C. The initial column temperature was 40 °C and it was elevated gradually up to 70 °C at a rate of 6 °C min⁻¹. THM concentrations were calculated based on external calibration curves generated with solutions of analytical standards of the four THMs (>99% purity from Sigma-Aldrich, Rehovot, Israel) in distilled water (Millipore, Billerica, MA, USA; 18.2 MΩ), which were extracted and analyzed in the method described above. To reduce analytical noise, peak area of each THM was normalized to that of internal standard.

3. Results and Discussion

3.1. NWC Water Characterization

Chemical analysis of sampled NWC water (Table S2) indicates that the NOM in this water has a very low SUVA value (<1 L mg⁻¹ m⁻¹) and yet is highly reactive toward THM formation (average TTHMF and TTHMFP of 60–90 and 125–163 μ g L⁻¹, respectively). These parameters also show clear seasonal variability, with higher values in spring/summer, when alga blooms are common. Initial DOC rejection measurements in a dead-end filtration setting suggest that most of the NOM in the NWC water is smaller than 500 Da, whereas only ~2% of it is >5000 Da. These results are in agreement with previous studies on NOM size distribution in Lake Kinneret and in NWC water conducted over 20 years ago [25]. Unfortunately, more recent data regarding NOM analysis in these waters is not available.

3.2. Membrane Rejection of NOM and Resulting TTHM Reduction as a Function of Applied Pressure (Recovery Ratio Approaching 0)

Table 1 summarizes the rejection/reduction (R) in all tested organic parameters following filtration via the three selected spiral wound membranes under different feed pressures (3, 5, and 10 bar). Concentrations data in feed and permeates of these experiments are shown in Table S3. For all three membranes there was a high decrease in tested organic parameters following filtration, indicating high NOM removal and resulting high reduction in TTHM formation. Observed reductions in all four organic parameters are in the range of previously reported values [5,10,12,14,22,26], despite the differences in the organic matter characteristics. Overall, no strong pressure dependency was observed for any of these measured parameters. Statistically significant (*t*-test, $\alpha < 0.05$) positive pressure dependency was observed only between 3 and 5 bar for UVA₂₅₄ (following filtration via DL and NF270) and for TTHMF reduction (with NF90 membrane). Further increase in pressure (from 5 to 10 bar) did not result in significant changes in the last two parameters. The observed lack of clear pressure dependency is surprising [27], but in agreement with a previous study conducted on water containing LMW and hydrophilic NOM [21], and is possibly due to concentration polarization affect.

Table 1. Average rejection (R) in dissolved organic carbon (DOC) and 254 nm absorbance (UVA₂₅₄) and resulting reductions in total trihalomethane (THM) formation (TTHMF) and total THM formation potential (TTHMFP), as a function of membrane type and feed pressure.

		Average Rejection/Reduction			
Net Driving Pressure (NDP)	Membrane	mbrane (Relative to Feed) (%)			
		DOC	UVA ₂₅₄	TTHMF	TTHMFP
	NF270	86 ± 3	94 ± 1	79 ± 12	85 ± 3
3	NF90	80 ± 4	92 ± 4	83 ± 3	85 ± 5
	DL	78 ± 7	70 ± 6	64 ± 10	76 ± 3
	NF270	89 ± 3	96 ± 1	82 ± 6	83 ± 5
5	NF90	82 ± 6	94 ± 4	89 ± 1	89 ± 1
	DL	79 ± 5	87 ± 7	69 ± 3	72 ± 10
	NF270	88 ± 2	96 ± 2	80 ± 7	86 ± 3
10	NF90	83 ± 7	95 ± 3	91 ± 1	88 ± 4
	DL	78 ± 3	93 ± 7	69 ± 2	78 ± 4

For all three membranes, the average reduction of UVA₂₅₄ was higher than that of DOC, indicating a preferred rejection of high MW aromatic/hydrophobic organic compounds [5,10,21,22]. Reduction in THM formation showed a slightly better correlation with DOC removal than with UVA₂₅₄ reduction, further supporting the assumption that the main THM precursors in NWC are forms of LMW NOM with low UVA₂₅₄.

NOM reactivity toward THM formation (i.e., THM formation yield per dissolved organic carbon) may change upon filtration. Although SUVA is most often used as proxy for such water reactivity, in cases where THM formation is mainly caused by non-aromatic light NOM (as in Lake Kinneret water), a more direct parameter describing such reactivity is TTHMF normalized to DOC [22]. Table 2 displays changes in average SUVA and TTHMF/DOC upon filtration for all three membranes as a function of pressure. The feed average SUVA ($0.6-0.9 \text{ Lmg}^{-1} \text{ m}^{-1}$) and TTHMF/DOC (23–39 µg mg⁻¹) values were higher in spring/summer when membranes NF 70 and NF90 were tested, suggesting that during times of alga bloom the NOM in this water is slightly more aromatic in nature and is more reactive toward THM formation. Following filtration, SUVA values decreased (to about $0.3 \text{ Lmg}^{-1} \text{ m}^{-1}$, expected for the DL membrane at 3 bar), in line with greater rejection of UVA₂₅₄ relative to DOC by NF membranes. Average SUVA reduction shows no clear pressure dependency between 3 and 10 bar but does depend on membrane type, following the order: NF90 > NF270 > DL.

NDP	Membrane	SUVA (L mg ^{-1} m ^{-1})	TTHMF/DOC (μg/mg)	Δ (TTHMFP – TTHMF) (µg L ⁻¹)
Feed	NF270	0.9 ± 0.1	39 ± 5	54 ± 17
	NF90	0.8 ± 0.1	25 ± 4	72 ± 20
	DL	0.6 ± 0.05	23 ± 5	96 ± 31
3	NF270	0.4 ± 0.2	66 ± 32	7 ± 4
	NF90	0.3 ± 0.1	23 ± 4	9 ± 7
	DL	0.8 ± 0.3	36 ± 9	14 ± 10
	NF270	0.3 ± 0.2	69 ± 22	8 ± 2
5	NF90	0.3 ± 0.2	18 ± 9	7 ± 2
	DL	0.4 ± 0.1	34 ± 6	25 ± 28
10	NF270	0.3 ± 0.1	67 ± 15	3 ± 5
	NF90	0.1 ± 0.1	17 ± 11	14 ± 7
	DL	0.2 ± 0.2	32 ± 2	14 ± 12

Table 2. Average values of specific UV₂₅₄ absorbance (SUVA), TTHMF/DOC, and Δ (TTHMFP – TTHMF) measurements for NF270, NF90, and DL as a function of feed pressure.

For NF270 and DL, average TTHMF/DOC values seem to be higher in permeates than in the feed by 70% and 50%, respectively. This is a result of lower reduction in TTHMF than in NOM rejection, suggesting that the LMW NOM that does pass these membranes is very reactive toward THM formation. The opposite trend is observed for NF90 (i.e., lower permeate reactivity to THMF), which may be attributed to the higher density of this membrane and its potential to better reject the small MW and very reactive NOM. No clear pressure trend was observed for this parameter either. Similar results were obtained by de la Rubia et al. (2008) who reported increased THM reactivity in permeates from the NF270 membrane (Molecular weight cut off, MWCO, ~500 (Da)) but not from the NF90 membrane (MWCO ~200 (Da)), also in water with LMW NOM and low SUVA [22]. Likewise, Amy et al. (1990) reported that NOM with MW <1000 Da was the major THM precursor in their experiments [20]. All these findings indicate that LMW NOM may also be very reactive toward THM formation.

The difference between TTHMFP and TTHMF values, Δ (TTHMFP – TTHMF), represents THM formation via reactions with less reactive NOM. The decrease in Δ (TTHMFP – TTHMF) following filtration (Table 2) suggests that all three membranes reject less efficiently NOM that generates THM with fast kinetics (relative to the rejection of the less reactive NOM).

It is worth noting that permeate TTHM and TTHMFP concentrations in each of the applied pressures were about the same and independent of initial feed concentration. This independency suggests that with respect to THM, the membrane end-product is unaffected by the wide variability in feed NWC water quality.

3.3. Membrane Rejection of NOM and Resulting THM Reduction, as a Function of Recovery (at Constant Pressure)

The performance of the three mentioned membranes was also tested under five different recoveries (0%, 20%, 50%, 70%, and 85%). The effect of recovery on membrane rejections was tested at a feed pressure of 5 bar for NF90 and NF270 and 3 bar for DL, after a steady state was reached. Figure 2 and Table S4 summarize the observed rejections and concentrations, respectively.

The overall trend for NF90 and NF270 was a decrease in permeate quality with increasing recovery, especially at high recoveries (with NF270 showing slightly higher sensitivity to recovery changes). DL membrane performance was not dependent on recovery, but its rejections/reductions were lower than for the other two membranes in all tested recovery range. Furthermore, recovery dependency of DL was tested only up to 70% recovery. Overall, TTHMF and TTHMFP reductions are more affected by recovery increase than NOM removal. The lack of dependency at recoveries below 70% can be due to the low salinity and organic matter content of treated NWC water, making concentration effect become significant only at high recoveries.

It is important to note that even at high recoveries, end quality product was well below permitted TTHM concentration in drinking water. For TTHMF and TTHMFP, concentrations were respectively lower than 30 μ g L⁻¹ and 50 μ g L⁻¹ for NF90, and lower than 56 μ g L⁻¹ and 88 μ g L⁻¹ for NF270, respectively.

As in the pressure dependency experiments, in all tested recoveries reduction in UVA_{254} were higher than reduction in DOC for NF90 and NF270, and the opposite was observed for DL. In all cases, DOC continued to show better correlation to TTHMF and TTHMFP formation than UVA_{254} .



Figure 2. Average reductions in (**a**) DOC, (**b**) UVA₂₅₄, (**c**) TTHMF, and (**d**) TTHMFP for the NF270 (solid blue bars), NF90 (stripped orange bars), and DL (dotted gray bars) membranes as a function of recoveries.

TTHMF/DOC ratios indicate that upon filtration, under all tested pressures and water recoveries, only NF90 resulted in a reduction in NOM reactivity toward THM formation (Table 3). SUVA values showed less clear picture. For all three membranes, average values of SUVA and the TTHMF/DOC ratio show no clear dependency on water recovery over the tested range.

As observed in the previous set of experiments, Δ (TTHMFP – TTHMF) decreases upon filtration for all three membranes, with no clear dependency also on recovery (Table 3).

In summary, regarding removal of organic matter-related parameters (i.e., DOC, UVA₂₅₄, and THM formation) NF90 demonstrated the highest TTHMF and TTHMFP reductions, even at desired high recoveries (\geq 85%). Furthermore, it is the only membrane that showed reduction of NOM reactivity toward THM formation in permeates.

Table 3. Average values of SUVA, TTHMF/DOC, and Δ (TTHMFP – TTHMF) measurements for NF270, NF90, and DL as a function of recovery.

Recovery (%)	Membrane	SUVA ($L mg^{-1} m^{-1}$)	TTHMF/DOC (µg mg ⁻¹)	Δ (TTHMFP – TTHMF) (µg L ⁻¹)
	NF270	0.8 ± 0.2	35 ± 11	93 ± 42
Feed	NF90	0.9 ± 0.03	27 ± 3	70 ± 15
	DL	0.7 ± 0.04	21 ± 4	51 ± 12
	NF270	0.3 ± 0.2	69 ± 22	8 ± 2
0	NF90	0.3 ± 0.2	18 ± 9	7 ± 2
	DL	0.8 ± 0.3	36 ± 9	14 ± 10
	NF270	0.3 ± 0.1	50 ± 17	3 ± 3
20	NF90	0.2 ± 0.1	28 ± 9	4 ± 4
	DL	1.0 ± 0.1	56 ± 5	0.4 ± 0.3

Recovery (%)	Membrane	SUVA (L mg ^{-1} m ^{-1})	TTHMF/DOC $(\mu g m g^{-1})$	Δ (TTHMFP – TTHMF) (µg L ⁻¹)
50	NF270	0.3 ± 0.09	50 ± 15	11 ± 10
	NF90	0.4 ± 0.1	31 ± 11	12 ± 5
	DL	1.0 ± 0.3	45 ± 3	13 ± 9
70	NF270	0.3 ± 0.03	38 ± 6	5 ± 6
	NF90	0.5 ± 0.1	25 ± 5	10 ± 1
	DL	1.0 ± 0.7	44 ± 26	7 ± 7
85	NF270	0.5 ± 0.2	62 ± 17	16 ± 14
	NF90	0.3 ± 0.1	20 ± 3	24 ± 2

Table 3. Cont.

3.4. Membrane Rejection of Selected Inorganic Parameters

As expected, for all tested membranes rejection of the monovalent ion Cl⁻ was lower than of the divalent ions Ca²⁺ and Mg²⁺, and the average reduction in conductivity (affected by all ions) was indeed in between them. The effects of pressure and water recovery on the removal of each of these inorganic parameters are presented in detail in Tables S5 and S6, respectively. Overall, for inorganic ions, NF90 presented the highest rejections at all pressure and recoveries conditions, while DL had the lowest rejections. For all membranes, rejections of the inorganic ions did not show a strong dependency on water recovery (Table S6). The clearest trend was observed for NF270, which showed lower rejections with increasing recoveries. Deterioration of permeate quality for this membrane was observed at high water recoveries, as in the organic parameters. As mentioned above, DL performance was tested only up to recovery of 70% and hence its independency on water recovery should be considered with caution.

The presently observed lack of recovery dependency for DL and NF90 (in almost all parameters) is in agreement with a study by Gorenflo et al. (2002), who worked with the DOW's NF200 membrane [12].

It is worth noting that while NF270 and DL membranes depicted no flux decline upon elevating recovery, in NF90 a flux decline of about 25% occurred at high recovery (85%), suggesting that the later membrane is less favorable economically. The lack of flux dependency on water recovery for DL and NF270 is probably because feed NWC water has already undergone complete treatment at the Eshkol site, which resulted low-medium DOC content and low SUVA (Table S1). For NF90, however, the high inorganic rejections at high recoveries lead to the development of sufficient osmotic pressure in the brine that reduced the flux.

Furthermore, the high ion removal by NF90 leads to a high reduction in water hardness (Ca²⁺ and Mg²⁺) and alkalinity, which are needed in order to reduce water aggressiveness toward the distribution system. However, thanks to its high permeate quality this problem can be solved by treating only part of the NWC water by NF and then combining the treated and untreated water streams, such that end concentrations of alkalinity, hardness, and TTHM will be within regulatory requirements. For example, even for the highest TTHF and TTHMFP values we observed in summer (110 and 188 μ g L⁻¹, respectively), filtering only 30% of the water via NF90 and then mixing it with the 70% untreated water will reduce TTHMF and TTHMFP values to 87 and 149 μ g L⁻¹, respectively, and result in an alkalinity value of about 82 mg L⁻¹ as CaCO₃, and a Ca²⁺ concentration of 36 mg L⁻¹. To achieve positive CaCO₃ precipitation potential (CCPP) at such conditions (assuming total dissolved solids of 700 mg L⁻¹), pH should be maintained above 8.1. Such pH is not problematic in any way from a water quality perspective. The only consequence of the reduction in calcium and alkalinity values is that the NaOH dosage at the outlet of the water treatment plant would be slightly reduced (due to the lower buffering capacity of the treated water a less strong base is required to attain a pH of 8.1).

3.5. Membrane Performance Rejection—A Synthetic Solution

Due to technical limitations, feed water from NWC had to be taken at different seasons; DL was tested in fall/winter while NF90 and NF270 were tested in spring/summer when alga activity at the NWC was higher. To eliminate the option that observed differences in membranes performance are due to differences in feed characterizations, the membranes' NOM rejection and TTHMF, TTHMFP reductions were tested also with a synthetic solution as feed. The synthetic solution contained sonicated humic acid (technical grade from Aldrich, 1.6 mg L⁻¹) as DOC. The experiments were conducted at 5 bar pressure and 20% recovery, twice for each membrane. The overall order of the membranes' ability to reject organic matter (i.e., reduction in UVA₂₅₄ and in DOC) was similar when synthetic solution and NWC water were used as feed: NF90 > NF270 > DL. Regarding THM formation, NF90 performed better than DL and NF270, as with NWC, but the latter two yielded similar reductions (Table S7). Relative to the NWC water, absolute THM reduction values for the synthetic solution were similar for NF270 and NF90 and much higher for DL (by 7–30%). This increase in DL rejections could be a result of large difference in the nature of organic matter in the feed; the NOM in NWC water in fall (when original DL experiments were done) possibly had a much lower MW than the sonicated humic acid used in the synthetic solution.

4. Conclusions

The objective of the present study was to evaluate the ability of the NF membrane to remove THM precursors from water containing NOM of low MW and low SUVA, such as the NWC water, thus improving water quality. All three membranes tested showed high removal ability for NOM and resulted in high TTHMF and TTHMFP reductions, especially for NF90 and NF270, with negligible dependency on pressure (up to 10 bar) and inverse dependency on water recovery. At very low water recovery, NF90 and NF270 yielded a >83% average reduction in TTHMF and TTHMFP, which decreased to an about 60–70% reduction when elevating water recovery to 85%. DL results were a bit lower, with average reductions of 70–75% at low water recoveries and <60% at 70% water recovery (maximal recovery tested for this membrane). Despite this decrease in rejections, resulting permeate water quality for all membranes and under all tested conditions remained good, with TTHM concentrations well below Israel's MCL regulation values.

All membranes resulted in reduction in Δ (TTHMFP – TTHMF) between feed and permeate, indicating that these NF membranes preferably reject NOM with slower kinetics toward THMF. Thus, NF at specific sites may provide a solution to reduce THM formation following a second chlorination.

Beyond the performance of the membranes with respect to THM removal, additional parameters should also be considered. For example, the relatively high rejection of NF90 towards divalent and certain monovalent (e.g., HCO_3^{-}) ions may lead to low Ca^{2+} and alkalinity values, requiring a higher pH to be maintained in the water to prevent aggressiveness toward the distribution system. The same phenomenon may also lead to chemical fouling and reduction in water flux at high water recoveries over time. These problems can be partially addressed by treating only a fraction of the water stream and then mixing the two streams.

Out of the membranes tested, a strong advantage of NF270 was its high permeability, enabling a higher flux at a given pressure. Thus, despite better rejections shown by NF90, the higher permeability of NF270 appears to make it an economically favorable membrane for the applications tested in this work. However, more experiments are needed to examine membrane abilities in different seasons (change in NOM), to determine flux decline due to fouling under constant operation conditions over a long period of time, and to determine rejection changes due to recovery stabilization time.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/10/10/1370/ s1, Table S1: Membrane specification. Table S2: Characteristics of NWC water (after the central filtration plant at Eshkol site, where our water samples were taken). Table S3: Measurements of DOC, UVA₂₅₄, TTHMF and TTHMFP in feed and permeates, as a function of membrane type and feed pressure. Table S4: Measurements of DOC, UVA₂₅₄, TTHMF and TTHMFP in feed and permeates, as a function of membrane type and water recovery. rejection in NF90, NF 270 and DL. **Author Contributions:** All three authors took active role in carrying the experimental work, analyzing the data and preparing this manuscript.

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