



# The control of *N*-nitrosodimethylamine, Halonitromethane, and Trihalomethane precursors by Nanofiltration

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## ABSTRACT

Nanofiltration (NF) is a promising technology for removing precursors of disinfection byproducts (DBPs) from source waters prior to oxidant addition in water treatment. The aims of this study were to investigate (i) the removal efficiencies of *N*-nitrosodimethylamine (NDMA), halonitromethane (HNM), and trihalomethane (THM) precursors by NF membranes from different source water types (i.e. surface water, wastewater impacted surface water, and municipal and industrial wastewater treatment effluents), (ii) the impact of membrane type, and (iii) the effects of background water components (i.e., pH, ionic strength, and  $\text{Ca}^{2+}$ ) on the removal of selected DBP precursors from different source waters. The results showed the overall precursor removal efficiencies were 57–83%, 48–87%, and 72–97% for NDMA, HNM, and THM precursors, respectively. The removal of NDMA precursors decreased with the increases in average molecular weight cut off and negative surface charge of NF membranes tested, while the removal of THM precursors was slightly affected. pH changes increased the removal of NDMA precursors, but pH did not affect the removal of THM and HNM precursors in municipal WWTP effluent. On the other hand, pH changes had little or no effect on DBP removal from industrial WWTP effluent. In addition, regardless of the membrane type or background water type/characteristics, ionic strength did not show any impact on DBP precursor removals. Lastly, an increase in  $\text{Ca}^{2+}$  concentration enhanced the removal of NDMA precursors while a slight decrease and no effect was observed for THM and HNM precursors, respectively, in municipal WWTP effluent.

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## 1. Introduction

Disinfection is a required process in drinking water treatment worldwide to eliminate pathogenic microorganisms. However, an unintended consequence is the formation of disinfection byproducts (DBPs) due to the reaction between precursors and oxidants. Owing to various health effects posed by DBPs, the US Environmental Protection Agency (USEPA) has been imposing increasingly stringent regulations for DBPs under the Disinfectants/DBP Rule (D/DBPR) (USEPA, 2006). The Stage 2 D/DBPR requires water utilities to comply with maximum contaminant levels for TTHM<sub>4</sub> (bromodichloromethane [BDCM], bromoform [ $\text{CHBr}_3$ ], chloroform [ $\text{CHCl}_3$ ], dibromochloromethane [DBCM]) and HAA<sub>5</sub> (dibromoacetic acid [DBAA], dichloroacetic acid [DCAA], monobromoacetic acid [MBAA], monochloroacetic acid [MCAA], trichloroacetic acid [TCAA]) at 80  $\mu\text{g/L}$  and 60  $\mu\text{g/L}$ , respectively, as a

locational running annual average in distribution systems. As a result, water utilities have in some cases switched to alternative disinfectants (e.g., chloramine, chlorine dioxide, and ozone) to reduce the formation of THMs and HAAs, which are the major DBPs of chlorination. Nevertheless, other unregulated DBPs such as *N*-nitrosodimethylamine (NDMA) and halonitromethanes (HNMs) have been observed during chloramination and ozonation-chlorination, respectively (Chen and Valentine, 2006; Krasner et al., 2006; Mitch et al., 2003; Nawrocki and Andrzejewski, 2011; Selbes et al., 2014, 2013; Song et al., 2010). NDMA is reported as a potential human carcinogen and has been detected mainly in distribution systems during chloramination of finished waters (Russell et al., 2012). Due to health concerns associated with NDMA, the California Department of Health Services set an NDMA action level of 10  $\text{ng/L}$  (CDPH, 2010). USEPA has been considering NDMA for regulation during the six year review of the D/DBPR. It has also been reported that HNMs are one of the most cytotoxic and genotoxic classes among the emerging DBPs, having orders of magnitude higher toxicity than the regulated THMs and HAAs (Plewa et al., 2004).

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One of the approaches to control the formation of DBPs during water treatment is to eliminate their precursors before oxidant addition. Various treatment techniques including enhanced coagulation, powdered and granular activated carbon adsorption, ion exchange, nanofiltration (NF) and reverse osmosis have been studied for this purpose (Beita-Sandí et al., 2016; Boyer and Singer, 2005; Gan et al., 2013; Krauss et al., 2010; Miyashita et al., 2009; Schmidt and Brauch, 2008; Snyder et al., 2007; Uyak et al., 2007). Although the removal efficiency of NDMA precursors (e.g. DMA, MEA, DEA, DPA, DMS, ranitidine, DMAE, DMAP, Michler's ketone, DMHA, and gramine) by NF membranes has been evaluated for selected model precursors (Krauss et al., 2010; Miyashita et al., 2009; Schmidt and Brauch, 2008), there is very limited information about their NF removal from natural source waters with different water characteristics (Snyder et al., 2007; Woods et al., 2016). Natural organic matter (NOM) is known as one of the main precursor of THMs, which is generally associated with higher molecular weight organic molecules as opposed to NDMA precursors (Gerecke and Sedlak, 2003; Krasner et al., 2013; Mitch and Sedlak, 2004), which are mostly related to small molecular weight compounds (Gerecke and Sedlak, 2003; Krasner et al., 2009; Mitch and Sedlak, 2004; Pehlivanoglu-Mantas and Sedlak, 2008; Selbes et al., 2013). Several studies have examined the removal of NOM from laboratory simulated and natural waters by NF (Braghetta et al., 1997; Cho et al., 1999; Hong and Elimelech, 1997; Schafer et al., 1998). These studies have shown that the change in solution characteristics had an impact on size and structure of molecules as well as the conformation of the membrane surface (Ghosh and Schnitzer, 1980). Even though several studies have examined the removal of THM precursors by NF due to regulatory concerns, there is a lack of information regarding the removal of unregulated DBP precursors (e.g., NDMA, HNMs) by NF membranes.

The objective of this study was to examine the removal of selected unregulated (i.e., NDMA and HNMs) and regulated THM precursors by NF membranes under varying background water chemistry conditions. The removal of these precursors from two municipal wastewater treatment plant effluents, one industrial wastewater effluent, one wastewater impacted surface water, and one non-impacted surface source were evaluated. Experiments were conducted at different pH (6–9), ionic strength (0.005–0.05 M),  $\text{Ca}^{2+}$  concentration (6–60 mg/L), and with different NF membranes to assess the effectiveness of NF filtration on DBP precursor control. To the best of our knowledge, this is the first study in literature providing a side-by-side comparison of NDMA, HNM, and THM precursor removals under various water chemistry conditions. The results provide insights about the control of emerging and regulated DBP precursors using NF membranes.

## 2. Materials and methods

### 2.1. Filtration experiments

Three commercially available flat sheet polyamide thin film composite NF membranes, TS80, ESNA 1-LF2 and NF270 (TriSep Corp., Hydranautics, and FilmTec Corp., respectively) were tested (Table 1). In each experiment, membranes were initially cleaned following a procedure described elsewhere (Ersan et al., 2015) to prevent the leaching of NDMA precursors from membranes. In brief, membranes were flushed with ~5 L of 1 mg/L chlorine solution. Afterwards, the feed tank solution was replaced with distilled and de-ionized (DDI) water and membranes were flushed until no residual chlorine remained in the permeate side. All experiments were carried out at  $25 \pm 1$  °C and at a pressure of 34.5 bar (500 psi) using a cross-flow filtration cell (Fig. S1). The effective area of the

membrane cell was 140 cm<sup>2</sup>. Treated water samples were collected in 500 mL amber glass bottles from the permeate side of the membrane and tested for desired analytes.

The removal efficiency,  $R$  (%) was calculated as

$$R = \left(1 - \frac{C_p}{C_f}\right) * 100 \quad (1)$$

where  $C_p$  is the concentration in the permeate and  $C_f$  is the concentration in the feed.

During filtration experiments, flux data were also obtained and normalized according to Equation (2) to account for flux changes with changing background water characteristics and coupon to coupon variability.

$$J_N = \left(\frac{J_f}{J_{cw}}\right) \quad (2)$$

Here  $J_N$  is the normalized flux,  $J_f$  is the final flux at the end of the experiment, and  $J_{cw}$  is the clean-water flux, measured using DDI water.

### 2.2. Experimental design

In this study three sets of experiments were systematically conducted to evaluate the effect of different variables on the removal of DBP precursors. The first experimental set was to determine the effect of source water type on NDMA, HNM and THM precursor removal using one membrane (TS80). There were five different source waters (Table 2): a non-impacted surface water (SW) that serves as a source for a drinking water treatment plant, a wastewater impacted surface water (ISW), treated effluents of two municipal wastewater treatment plants (WWTP-1, WWTP-2), and an industrial (textile dyeing/finishing) wastewater treatment plant (IWWTP) effluent. Water samples were immediately filtered with pre-washed 0.2 µm cartridge filters (Whatman™ Polycap™ TC) upon arrival at the laboratory to eliminate biological activity and were stored for no longer than 10 days at 4 °C in the dark.

The second experimental set was to evaluate the effect of membrane type on the removal of NDMA and THM precursors. Table S1 shows the experimental matrix. One water source (municipal WWTP effluent) was used and three membranes were evaluated: TS80, NF270, and ESNA.

The third experimental set was to evaluate the effects of pH, ionic strength, and  $\text{Ca}^{2+}$  concentration on DBP precursor removal. One membrane type was used along with two source waters: municipal and industrial WWTP effluents. Using factorial design, eight different experiments were performed per water type. Tables S2 and S3 show the experimental matrices (one for each water type). Feed solutions were adjusted to the target pH values by addition of HCl or NaOH.  $\text{Ca}^{2+}$  and ionic strengths of the feed solutions were adjusted sequentially to keep the target ionic strength concentrations the same for the waters under analogous experimental conditions. While the target  $\text{Ca}^{2+}$  levels were adjusted with  $\text{CaCl}_2$  addition, the ionic strengths of the samples were adjusted by addition of NaCl, and the concentration was expressed in molar units as NaCl (Fisher Scientific, Pittsburgh, PA).

### 2.3. NDMA, HNM, and THM formation potential tests

DBP formation potential (FP) tests were conducted under excess amount of oxidant to ensure the highest formation of DBPs. Chloramination, ozonation followed by chlorination, and chlorination were used to determine NDMA, HNM and THM precursors, respectively. For NDMA formation potential (FP) tests, a chloramine

**Table 1**  
Membrane characteristics.

| Designation  | ESNA 1-LF2            | TS80                           | NF270                        |
|--|-----------------------|--------------------------------|------------------------------|
| Manufacturer   | Hydranautics          | Trisep                         | Dow filmtech                 |
| Active layer composition <sup>a</sup>  | Polyamide             | Polyamide                      | Polyamide                    |
| MWCO (Dalton) <sup>a</sup>   | 200                   | 150                            | 200–400                      |
| NaCl rejection (%) <sup>a</sup>  | 80                    | 80–90                          | 99                           |
| pH range (25 °C) <sup>a</sup>  | 2–10                  | 2–11                           | 2–11                         |
| Typical flux (L m <sup>2</sup> hr <sup>−1</sup> psi <sup>−1</sup> ) <sup>a</sup> | 21/75                 | 34/110                         | 72–98/130                    |
| Surface charge (at pH:7)   | Negative <sup>a</sup> | Slightly negative <sup>a</sup> | Highly negative <sup>b</sup> |

<sup>a</sup> Specified by the manufacturer.

<sup>b</sup> Information obtained from the literature (Li and Elimelech, 2004).

**Table 2**  
Water characteristics of source waters.

| Parameter                           | SW                 | ISW                | WWTP-1               | WWTP-2             | IWWTP                |
|-------------------------------------|--------------------|--------------------|----------------------|--------------------|----------------------|
| UV <sub>254nm</sub>                 | 0.06               | 0.30               | 0.13                 | 0.11               | 0.24                 |
| DOC (mg/L)                          | 2.2                | 6.5                | 5.3                  | 4.5                | 26                   |
| SUVA <sub>254</sub> (L/mg/m)        | 2.63               | 4.55               | 2.45                 | 2.4                | 0.91                 |
| DON (mg/L)                          | 0.6                | 0.6                | 4.9                  | 9.7                | 0.6                  |
| NH <sub>4</sub> <sup>+</sup> (mg/L) | 0.025              | 0.075              | 4                    | 0.025              | 2                    |
| Ca <sup>2+</sup> (mg/L)             | 5                  | 4                  | 5                    | 20                 | 2                    |
| pH                                  | 7.7                | 7.2                | 7.6                  | 7.4                | 8                    |
| Ionic Strength (Molar as NaCl)      | $8 \times 10^{-4}$ | $9 \times 10^{-4}$ | $3.1 \times 10^{-3}$ | $1 \times 10^{-2}$ | $4.8 \times 10^{-3}$ |
| NDMAFP (ng/L)                       | 112                | 148                | 1078                 | 629                | 193                  |
| HNMFP (μg/L)                        | 7                  | 14                 | 27                   | 46                 | 16                   |
| THMFP (μg/L)                        | 230                | 578                | 244                  | 351                | 1092                 |

**SW:** Surface Water; **ISW:** Impacted Surface Water; **WWTP-1:** Municipal Wastewater Treatment Plant-1; **WWTP-2:** Municipal Wastewater Treatment Plant-2; **IWWTP:** Industrial Wastewater Treatment Plant.

stock solution (2500 mg/L as Cl<sub>2</sub>) was prepared by titrating ammonium sulfate stock solution (5000 mg/L) with sodium hypochlorite solution (5000 mg/L) at a Cl<sub>2</sub>:N mass ratio of 4:1 at pH 7.8. NDMA FP tests were performed by treating permeate samples with 100 mg/L chloramine as Cl<sub>2</sub> at pH 7.8 in the presence of 20 mM phosphate buffer for 5 days of contact time.

For HNM FP tests, ozone was generated with a bench scale ozone generator (Model GTC-1B, Griffin Technics, NJ) fed with ultra-high purity oxygen gas and bubbled with fine diffusers for 50 min to obtain a stock solution at 25–30 mg O<sub>3</sub>/L. The concentration of ozone stock solution was measured with a Hach DR/890 colorimeter. Ozone stock solutions were introduced to the water samples at an O<sub>3</sub>: DOC mass ratio of 1:1 at pH 7.8 in the presence of 20 mM phosphate buffer for 5 min. Chlorine stock solutions (6250 mg/L as Cl<sub>2</sub>) were prepared by diluting sodium hypochlorite stock (5% available free chlorine), and was spiked into the ozonated samples with a target dose of 50 mg Cl<sub>2</sub>/L for 24 h.

For THM FP tests, samples were treated with only chlorine (50 mg/L) at pH 7.8 for five days. Formation potential tests were conducted for each sample with two measurements. The bars in the data plots represent the mean values, and the error bars show the data range.

#### 2.4. Statistical analysis

To optimize the time required for experiments and to decrease the storage time for water samples, the experiments were conducted using an unreplicated 2<sup>3</sup> factorial treatment structure with the factors: Ca<sup>2+</sup> (6 or 60 mg/L), pH (6 or 9) and ionic strength (0.005 M or 0.05 M). The selections of the levels for the factors were made based on characteristics of typical surface and wastewater impacted water sources. Because the experiments were unreplicated, there were no degrees of freedom for estimating experimental error. To obtain a surrogate estimation of the experimental error, the mean squares for two- and three-factor interactions were

combined. This approach provides a conservative procedure in that p-values computed using this approach can be larger than the true p-value and may reject the null hypothesis less often than it should be rejected (Oehlert, 2003). If the null hypothesis is rejected, there is an indication of a significant effect due to the factor. Statistical analysis was performed using SAS 9.3 software.

#### 2.5. Analytical methods

All analytical methods are described in the supporting information section (S1) and summarized in Table S4. They were also reported in our previous publications (Beita-Sandí et al., 2016; Gan et al., 2013; Selbes et al., 2013; Uzun et al., 2015).

### 3. Results and discussion

#### 3.1. Characteristics of water sources

In the examined waters, DOC, SUVA<sub>254</sub> and ionic strength ranged between 2.2 and 26 mg/L, 0.9–4.6 L/mg.m, and  $8 \times 10^{-4}$ – $1 \times 10^{-2}$  M (as NaCl), respectively. The two municipal wastewater effluents had distinctly higher DON and ionic strength levels as compared to other waters. pH values of all the waters were between 7.2 and 8.0. The DBP FPs of the samples ranged from 112 to 1078 ng/L for NDMA, 7 to 46 μg/L for HNM, and 230 to 1092 μg/L for THM (Table 2). In general, municipal wastewater effluents had higher NDMA and HNM formation potentials as compared to non-impacted and impacted surface water sources. This may be attributed to the abundance of reactive NDMA and HNM precursors in wastewater sources. THM FP values varied and it was highest in the industrial effluent. In general, THM levels correlated well with the DOC concentrations (~90%).

While municipal WWTP-1 effluent samples were collected at three different times (Tables 2–4), industrial WWTP effluent samples were collected twice for different sets of experiments

**Table 3**

Water characteristics for pH and ionic strength experiments using different NF membranes.

| Parameter                       | WWTP-1                |
|---------------------------------|-----------------------|
| UV <sub>254nm</sub>             | 0.0966                |
| DOC (mg/L)                      | 4.7                   |
| SUVA <sub>254</sub> (L/mg/m)    | 2.1                   |
| DON (mg/L)                      | 3.4                   |
| Ca <sup>2+</sup> (mg/L)         | 12                    |
| *pH                             | 7.2 (6*–9*)           |
| *Ionic Strength (Molar as NaCl) | 0.0032 (0.005*–0.05*) |
| NDMA FP (ng/L)                  | 544                   |
| HNM FP (μg/L)                   | ND                    |
| THM FP (μg/L)                   | 308                   |

\*Values were adjusted according to desired levels. **WWTP-1**: Municipal Wastewater Treatment Plant-1. ND: Not Detected.

**Table 4**

Water characteristics for pH, ionic strength, and Ca<sup>2+</sup> experiments.

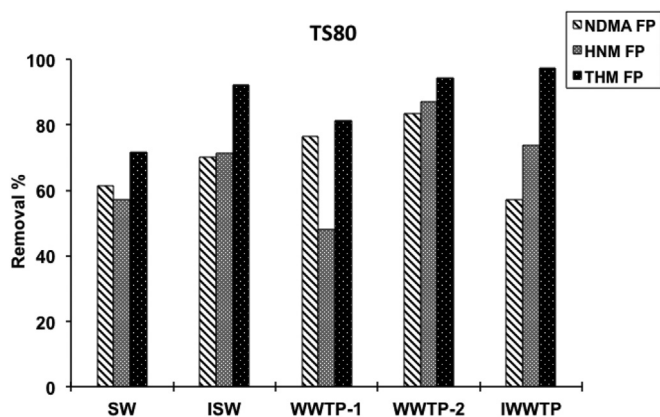
| Parameter                       | WWTP-1                | IWWTP |
|---------------------------------|-----------------------|-------|
| UV <sub>254nm</sub>             | 0.050                 | 0.337 |
| DOC (mg/L)                      | 1.9                   | 9.7   |
| SUVA <sub>254</sub> (L/mg/m)    | 2.6                   | 3.5   |
| DON (mg/L)                      | 2.3                   | 1     |
| *pH                             | 7.5 (6*–9*)           |       |
| *Ionic Strength (Molar as NaCl) | 0.0016 (0.005*–0.05*) |       |
| *Ca <sup>2+</sup> (mg/L)        | 6 (6–60*)             |       |
| NDMA FP (ng/L)                  | 576                   | 71    |
| HNM FP (μg/L)                   | 12                    | 52    |
| THM FP (μg/L)                   | 139                   | 695   |

\*Values were adjusted according to desired levels. **WWTP-1**: Municipal Wastewater Treatment Plant-1, **IWWTP**: Industrial Wastewater Treatment Plant.

(Tables 2 and 4). The observed levels of DBPs in municipal WWTP-1 ranged between 544 and 1078 ng/L, 139 and 308 μg/L, ND and 27 μg/L, while in IWWTP they were ranged from 71 to 193 ng/L, 695 to 1092 μg/L, and 16 to 52 μg/L for NDMA, THM, and HNM, respectively. These variations in water qualities suggests that not only the availability but also the reactivity of precursors in source waters may change based on the time of sample collection, which in turn results in variability in formation potential of DBPs.

### 3.2. Removal of NDMA, HNM and THM precursors

The removal efficiencies of the TS80 NF membrane for NDMA,



**Fig. 1.** The removal of NDMA, HNM, and THM precursors from different source waters using TS80 membrane. **SW**: Surface Water; **ISW**: Impacted Surface Water; **WWTP-1**: Municipal Wastewater Treatment Plant-1; **WWTP-2**: Municipal Wastewater Treatment Plant-2; **IWWTP**: Industrial Wastewater Treatment Plant.

HNM, and THM precursors are shown in Fig. 1; they were 57–83%, 48–87%, and 72–97%, respectively. In general, the removal of THM precursors was higher than those of NDMA and HNM precursors. This was attributed to the higher molecular weight of THM precursors (i.e., NOM) than NDMA precursors, which has been linked to small molecular weight compounds of anthropogenic origin (Gerecke and Sedlak, 2003; Krasner et al., 2013; Mitch and Sedlak, 2004). The focus of this analysis is on size exclusion as the main mechanism responsible for differences in transport among precursor types; however, it is recognized that other factors such as physicochemical characteristics of the precursors (i.e., hydrophilicity, hydrophobicity, charge, etc.) might also affect the overall removal process. Ascertaining the chemical structure and properties of precursors in a more detailed way is beyond the scope of this work, but is an interesting endeavor that should be pursued. More developments in structure and property knowledge will enable a better understanding of the mechanisms at play in membrane transport of DBP precursors.

Focusing on the NDMA data in Fig. 1, precursor removals from different sources varied according to the following sequence: WWTP-2 > WWTP-1 > ISW > SW > IWWTP. Higher NDMA precursor removals were observed for the effluents of two municipal wastewater treatment plants (WWTP-2 and WWTP-1) and for the impacted surface water (ISW) than for the non-impacted surface water (SW) and industrial wastewater effluent (IWWTP). This suggests that municipal wastewater effluents and impacted surface waters tested in this study either contained relatively larger precursors or some particle-associated NDMA precursors (Mitch and Sedlak, 2004). The lower NDMA precursor removal observed for the industrial wastewater effluent and the non-impacted surface water was attributed to the presence of small molecular sized NDMA precursors. These results suggest that NDMA precursors originating from different sources can be different in terms of their molecular sizes (or perhaps other properties), which in turn affects their rejection by NF membranes.

Focusing on the HNM data in Fig. 1, precursor removals varied according to the following sequence WWTP-2 > IWWTP > ISW > SW > WWTP-1. It is notable that in one case the HNM precursor removal was much lower than NDMA precursor removal, while in the other cases HNM precursors were removed similarly to or higher than NDMA precursors. This finding indicates that the size and/or chemical characteristics of HNM precursors varied from source to source, and the size and types of HNM precursors were different than those of NDMA.

Focusing on the THM data in Fig. 1, the precursor removal sequence was as follows: IWWTP > WWTP-2 > ISW > WWTP-1 > SW. In all studied water sources, the removal of THM precursors by the NF membrane was higher than NDMA or HNM precursors. This suggests that THM precursors are relatively large as compared to NDMA and HNM precursors. The largest THM precursors were apparently in the industrial wastewater (IWWTP), with the impacted source water (ISW) and one of the municipal wastewater effluents (WWTP-2) also having fairly large THM precursors. The other municipal wastewater effluent (WWTP-1) and the non-impacted surface water (SW) apparently had smaller THM precursors. Previous studies have shown that the removal of THM precursors by NF membranes ranged between 41 and 98% (Ángeles et al., 2008; Chellam, 2000; Golea et al., 2016; Lin et al., 2006); which is comparable with the values observed in this study.

Most of the data presented here are comparisons between feed and permeate precursor formation potentials. It would also be useful to measure the precursors directly rather than relying on formation potential tests alone. The molecular structure of the precursors is not known, so direct measurements are not possible, but we were able to measure bulk DOC and DON in an effort to draw



correlations. Overall the removal of DOC and DON from the studied source waters ranged between 77 to 97% and 37 to 80%, respectively (Fig. S2). When percent removal of DBPs were plotted as a function of DOC removal (Fig. S3), there was a good correlation between THMFP and DOC removal ( $r^2 = 0.90$ ) (Fig. S3-a), which suggest that percent DOC removals can be used as a surrogate parameter for THM precursor removals. On the other hand, a much weaker correlation ( $r^2 = 0.46$ ) was observed for HNM precursor removals (Fig. S3-b) while no correlation was seen for NDMA precursor removal (Fig. S3-c). As far as correlations between DBP and DON removals, a negative correlation was obtained for THM ( $r^2 = 0.40$ ) and HNM ( $r^2 = 0.66$ ) precursor removals while no correlation was observed for NDMA precursor removals. The lack of observed correlations suggests that most of the NDMA and HNM precursors are diverse and different than THM precursors.

On the other hand, we also looked at the ratios of DBPFP/DOC in both treated and raw waters to see the possible changes in the reactivity of precursors on the permeate and feed sides of the membrane. Here we are using the term “reactivity” to describe the degree to which precursors are converted to DBPs upon oxidation; a higher reactivity means a higher yield of DBPs. In this sense, DBPFP/DOC ratios in raw water were plotted as a function of DBPFP/DOC ratios in treated waters (Fig. S4), where the solid line (1:1) in the graph indicates that DBPFP/DOC remains the same after NF membrane treatment. If the reactivity of precursors is higher after the treatment, we would expect the data points to be higher than the solid line (1:1) or vice versa. In Fig. S4-A, the squares falling under the line (for IWWTP and WWTP-2) suggest that the reactivity of THM precursors were lower in the permeate NF membrane

in these waters while opposite was observed for ISW and SW. As for HNM precursors (Fig. S4-b), reactivity of precursors per DOC was higher in the permeate as opposed to raw water.

### 3.3. The effect of membrane type on the removal of NDMA and THM precursors

The effect of membrane type on NDMA and THM precursor removals at different pH (6–9) and ionic strength (0.005–0.05 M) conditions from a municipal WWTP effluent was investigated using three different commercially available NF membranes (TS80, NF270, and ESNA) (Table S3). The results showed that while the removal efficiencies for NDMA precursors were within the range of 78–82%, 51–58%, and 57–62%, for TS80, NF270 and ESNA, respectively, the removals of THM precursors were 83–87%, 72–80%, and 87–91% for TS80, NF270 and ESNA, respectively (Fig. 2).

For the membranes studied, the removal of NDMA precursors decreased with the increasing average molecular weight cut off and negative surface charge (Table 1), which was attributed to the low molecular weight nature of NDMA precursors, while the removal of THM precursors (i.e., NOM) was only slightly affected by the membrane characteristics. Statistical analysis of the results also revealed that the membrane type is an important factor that significantly affects the removal of NDMA and THM precursors ( $p$ -values = 0.0001 and 0.0004). As far as water chemistry effects, while the pH and ionic strength had a significant effect on the removal of NDMA ( $p$ -value = 0.006), the effect of pH and ionic strength on THM precursor removal was insignificant ( $p$ -value = 0.0829 and 0.2929) (Fig. 2).

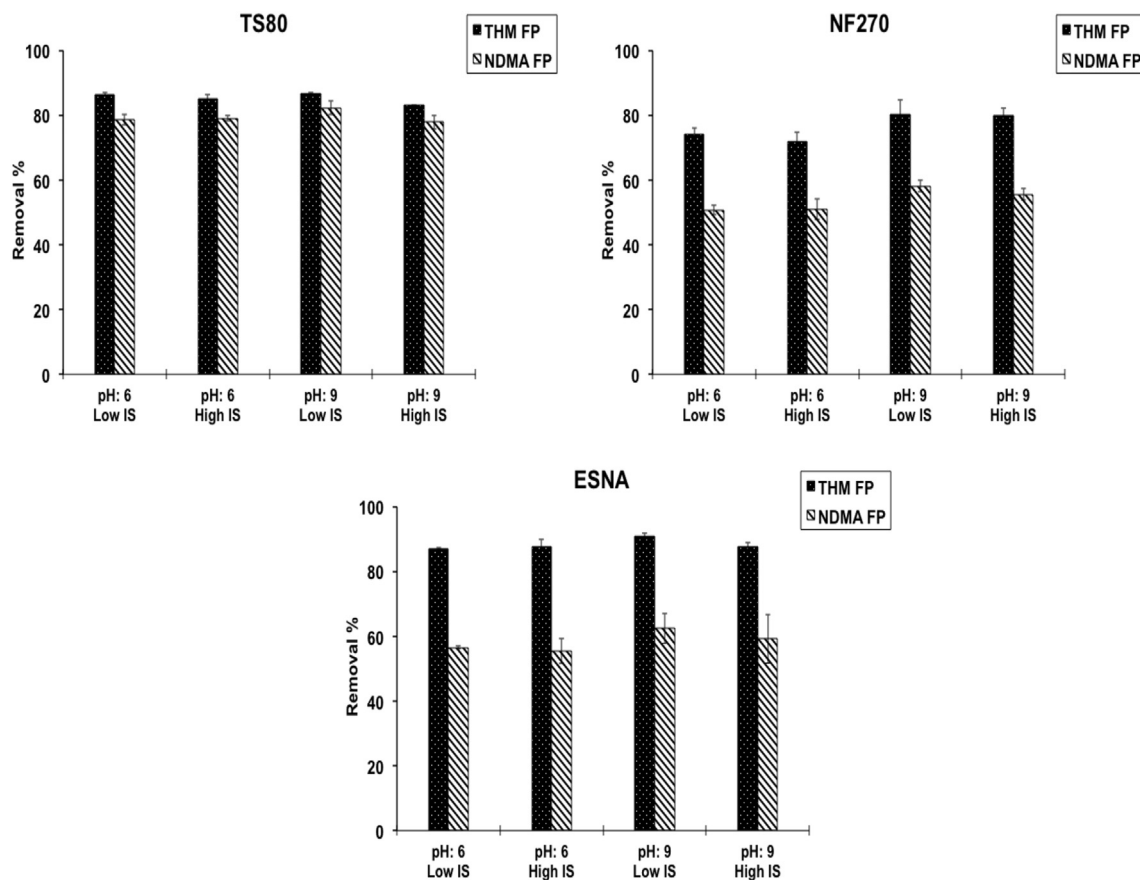


Fig. 2. The effect of Membrane Type on the removal of NDMA and THM precursors from Municipal Wastewater Treatment Plant Effluent.

### 3.4. Effect of background water components on the removal of NDMA, HNM, and THM precursors

As discussed above, differences in precursor characteristics as well as membrane type were contributing factors to the differences in removal efficiencies by NF observed in Figs. 1 and 2. However, some of these effects could also be attributed to the characteristics of the water matrix, such as pH, ionic strength, and calcium content. A detailed evaluation of these parameters was performed using the factorial experimental design, with the data shown in Fig. 3. The observed removal efficiencies for municipal WWTP effluent (Fig. 3A) ranged from 69 to 79% for NDMA, 40 to 64% for HNM, and 87 to 93% for THM precursors. The removal of DBP precursors from the industrial WWTP effluent (Fig. 3B) ranged from 52 to 66% for NDMA, 92 to 96% for HNM, and 94 to 98% for THM precursors. Observations regarding pH, ionic strength, and calcium are described separately below.

#### 3.4.1. The effect of pH

Investigation of eight different water background conditions showed that, for the tested municipal wastewater effluent, increasing the pH from 6 to 9 increased NDMA precursor removal. This is shown by comparing the pH 6 and pH 9 bars in Fig. 3A. Statistical analysis reveals that the pH effect was significant, having a p-value of 0.0036. For HNM and THM precursor removals in the municipal wastewater effluent, there were no significant effects of pH (p-value = 0.8114 and p-value = 0.2245).

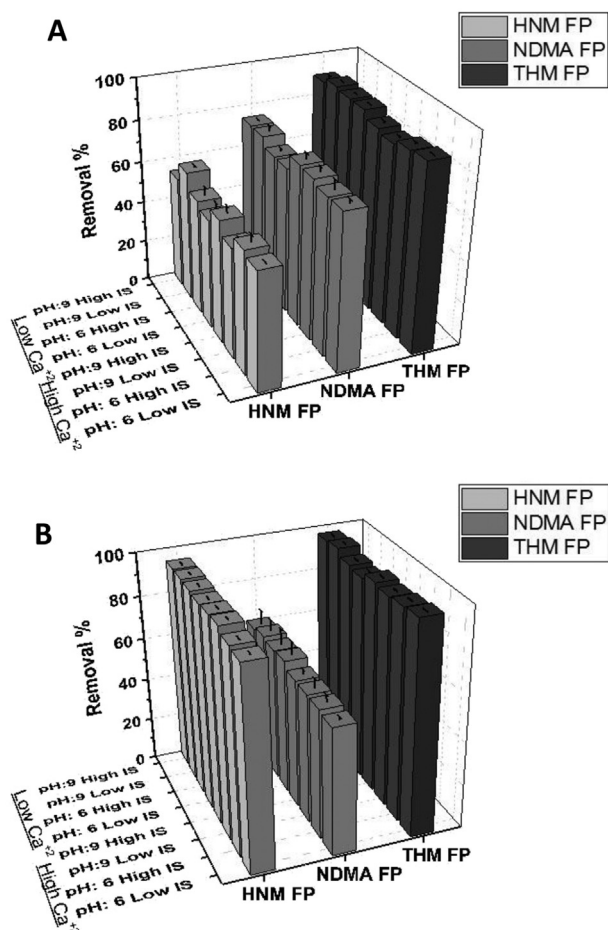


Fig. 3. The effect of Water Chemistry on the removal of NDMA, HNM, and THM precursors using TS80 membrane with A) Municipal wastewater effluent (WWTP-1) and B) Industrial wastewater effluent (IWWTP). \*IS: Ionic Strength.

As for industrial wastewater effluent, increasing the pH from 6 to 9 did not show any significant effect on NDMA, HNM, or THM precursor removals (p-values = 0.0973, 0.6326, 0.3692, respectively) (Fig. 3B).

Two mechanisms, or a combination of them, are proposed to explain the observed variations in DBP precursor removal with changing background conditions: i) electrostatic charge repulsion based on the acidity constants (pKa) of DBP precursors in different sources and ii) size exclusion. For instance, NDMA precursors must have been altered such that their charge repulsion was reduced and/or their molecular size was reduced at pH 6 compared to pH 9. On the contrary, THM precursor removals were not affected by pH changes in both municipal and industrial WWTP effluent. This suggests that the controlling mechanism for THM precursor removal was size exclusion rather than charge repulsion. pH is an important factor that affects the size of ionizable THM precursors (i.e. NOM) and also affects the membrane matrix. More specifically, at pH 9, ionizable macromolecules will be in a linear form due to charge repulsion, while at pH 6, the molecules will be in more compact and spherocolloidal form due to reduced charge repulsion. At the same time, the membrane will be in a more expanded form at pH 9 as opposed to pH 6 (Braghetta et al., 1997). Previous studies have found that THM precursors are mostly large molecules and their removal increased with increasing pH (Ángeles et al., 2008; Chellam, 2000; Lin et al., 2006). However, in this study, the results suggest that the removal of THM precursors was mainly controlled by size exclusion. Thus, no pH effect was observed for both wastewater effluents tested.

As for HNM precursors, although their removal patterns were different in both municipal and industrial WWTP effluents (~55% vs 95%), the change in pH from 6 to 9 was not significant. This could also suggest that the molecular structure of HNM precursors was not altered significantly by the change in pH to affect their removal by the NF membrane.

#### 3.4.2. The effect of ionic strength

The effects of ionic strength on the removal of NDMA, HNM, and THM precursors from municipal and industrial WWTP effluent sources are shown in Fig. 3A and B, respectively. In both water types and under all studied conditions, the flux and osmotic pressure have been altered by an increase in ionic strength from 0.005 M to 0.05 M, which influences the ion transport across the NF membrane pores (Park et al., 2010). The flux data suggest that the membrane matrix was in a more expanded state at high pH or low ionic strength and a less expanded state at low pH or high ionic strength conditions with respect to intra-membrane electrostatic repulsion forces (Braghetta et al., 1997; Hong and Elimelech, 1997) (Figs. S5–S6). Although there were changes in membrane matrix and precursor charge density, the removal of NDMA, HNM, and THM precursors were not affected by an increase in ionic strength in both examined waters. Statistical analysis of results from the municipal and industrial WWTP effluents also shows that the effect of ionic strength on the removal of DBPs is insignificant (0.05 < p-values).

#### 3.4.3. The effects of calcium

The effect of  $\text{Ca}^{2+}$  on the removal of NDMA, HNM, and THM precursors was studied in municipal and industrial WWTP effluent under eight different background conditions and results are shown in Fig. 3A and B. It is plausible that the presence of  $\text{Ca}^{2+}$  ions in source waters may influence the removal of DBP precursors by either changing the precursor stability in the water or altering the flux of the membrane filters (Kabsch-Korbutowicz et al., 1999). Under all studied conditions for industrial WWTP effluent, the results indicated that increasing the  $\text{Ca}^{2+}$  concentration did not show any significant change on the removal of NDMA, HNM, and THM

precursors ( $p$ -values = 0.1686, 0.2258, and 0.1709, respectively) (Fig. 3B). However, for municipal WWTP effluent, while the removal of HNM precursors was not significantly affected by a change in background  $\text{Ca}^{2+}$  concentration ( $p$ -values = 0.2059), the removal of NDMA was increased and the removal of THM precursors was decreased. When the  $\text{Ca}^{2+}$  content of source waters were increased, a severe flux decline was observed due to formation and/or accumulation of  $\text{Ca}^{2+}$ -NOM complexes onto the NF membrane surface (Figs. S3–S4). Therefore, the abundance of positively charged divalent ions on the membrane surface might act as a barrier for the small-sized NDMA precursors thus favoring their rejection by NF membranes. Statistical analysis of examined conditions for municipal WWTP effluent also suggested that an increase in  $\text{Ca}^{2+}$  concentration had a significant effect on the removal of NDMA and THM precursors ( $p$ -value = 0.0013 and  $p$ -value = 0.0346).

#### 4. Conclusions

In this study, the removal of NDMA, HNM, and THM precursors from different types of water/background matrices were investigated using different NF membranes. A cumulative summary of important findings is as follows:

- Based on the characteristics of the NF membranes used, the removal of NDMA precursors decreased with the increases in average molecular weight cut off and negative surface charge, while the removal of THM precursors (i.e., NOM) was slightly affected by the membrane characteristics.
- Among the studied waters, THM precursor removals were always higher than those of NDMA and HNM precursors. The overall precursor removal efficiencies ranged between 57 and 83%, 48–87%, and 72–97% for NDMA, HNM, and THM precursors, respectively.
- The variation in background  $\text{Ca}^{2+}$ , pH and ionic strength concentrations not only leads to a change in membrane conformation (i.e., surface charge, pore size) but also affects the physicochemical properties of precursors (i.e., charge and size). However, these changes were specific to the membrane type and/or water type.
- The removal of NDMA precursors under varying  $\text{Ca}^{2+}$  and pH conditions were shown to be different from two sources; increase in background  $\text{Ca}^{2+}$  and pH increased the removal of NDMA precursors from municipal wastewater effluent, while little or no effect was observed in industrial wastewater effluent.
- Regardless of the background water characteristics and membrane type, change in ionic strength did not show any impact on the removal of all the studied DBPs.
- Although there were differences in the removal efficiencies under varying background water characteristics, which affected flux levels, the variability of removal efficiencies remained within ~10–15%. This suggests relatively stable performance of NF membranes under varying background conditions.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2016.08.065>.

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