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A Mixed Cation and Anion Exchange Resin System for the Simultaneous Removal of N-Nitrosodimethylamine and Trihalomethanes Precursors from Water

Wilson Beita Sandi
Clemson University, wbeita@g.clemson.edu

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A MIXED CATION AND ANION EXCHANGE RESIN SYSTEM FOR THE SIMULTANEOUS REMOVAL OF N-NITROSODIMETHYLAMINE AND TRIHALOMETHANES PRECURSORS FROM WATER

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by
Wilson Beita Sandí
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Accepted by:
Dr. Tanju Karanfil, Committee Chair
Dr. Cindy Lee
Dr. David Ladner
Dr. Brian Powell

ABSTRACT

Drinking water utilities are relying more than ever on water sources impacted by wastewater effluents. Disinfection of these waters during water treatment may lead to the formation of several disinfection by-products, including the probable human carcinogen *N*-nitrosodimethylamine (NDMA) and the regulated trihalomethanes (THMs).

The main objectives of this dissertation work were to investigate i) the potential of ion exchange resins to remove simultaneously both NDMA and THMs, ii) the factors (i.e., pH and competing ions) that may influence the capability of ion exchange resins, and iii) the effect of bromide on the formation of NDMA.

Two ion exchange resins were examined, a cation exchange resin (Plus) to target NDMA precursors and an anion exchange resin (MIEX) for THMs precursors control. The resins were applied individually and combined in the treatment of surface and wastewater effluent samples. The treatment with both resins removed simultaneously NDMA (43–85%) and THMs (39–65%) precursors. These results proved that the combined application of a cation and an anion exchange resins is a feasible treatment technique to control effectively NDMA and THMs precursors concomitantly since there were no interactions between the resins.

The treatment of fresh and naturally attenuated samples containing varying wastewater content showed that neither the wastewater content nor the attenuation of the precursor affected the removals of NDMA and THMs precursors with the ion exchange resins.

The hypothesis that the majority of NDMA precursors are amine–based compounds was tested by treating waters at different pH (5, 7 and 10). The speciation of NDMA precursors was expected to change as a function of pH and generally, amines have pKa values > 8. At a pH below their pKa values, NDMA precursors would be ionized (positively charged). The results of the treatment with the cation exchange resins validated the hypothesis as the majority of NDMA precursors were removed at pH 5 and 7 but not at pH 10. Additionally, basic conditions (pH 10) also promoted the release of NDMA precursors from the cation exchange resin.

Wastewater effluent samples with naturally occurring levels of inorganic ions (e.g., bicarbonate, bromide, calcium, nitrate and sulfate) were enhanced to simulate a challenging treatment scenario. The results showed that the presence of high concentrations of calcium promoted the release of NDMA precursors in the cation exchange resin. The release of NDMA increased as calcium concentration increased. Nonetheless, NDMA precursors levels subsided after several regeneration cycles. In these challenging conditions, bromide was not removed in either the ambient or the amended wastewater effluent sample. Given that bromide is not well removed, its presence in water is a cause of concern because it can lead to the formation of brominated DBPs that are more cytotoxic and genotoxic than the chlorinated analogs.

In this study bromide (0–1000 μg/L) increased the formation of NDMA only in aqueous solutions of NDMA model precursor compounds but not in surface waters. A different trend was observed in chloraminated wastewater effluent samples in which bromide suppressed the formation of NDMA with increasing bromide concentration. It is

likely that bromochloramine preferentially reacted with background natural organic matter (NOM) instead of NDMA precursors thus decreasing the formation of NDMA. More NDMA was formed at pH 8 compared to pH 6. However, bromide increased the formation of NDMA in waters containing dimethylamine (DMA), trimethylamine (TMA) and poly(diallyldimethylammonium chloride) (polyDADMAC) and dissolved organic carbon (DOC) levels around 2 mg/L.

DEDICATION

I dedicate my dissertation work to Juan Carlos and my family for their continued love and support.

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CHAPTER ONE

INTRODUCTION

The objective of this dissertation work was to investigate the removal of *N*-nitrosodimethylamine (NDMA) and trihalomethanes (THMs) precursors in a combined ion exchange process and the factors that control its efficiency. The research focused on the application of a fundamental physicochemical process, ion exchange, to simultaneously control the formation of both regulated THMs and unregulated NDMA. Balancing effective and efficient removal of both types of precursors has been a challenge for researchers and practitioners. This was the first study in the literature that showed the application of a mixed system of ion exchange resins that targeted different disinfection byproducts (DBPs) precursors in a single completely mixed flow reactor to control the formation of both NDMA and THMs.

Climate change would likely increase the severity of droughts throughout the world reducing the availability of water sources. Moreover, the continued increase in the world population generate stress on water supplies; as a result, pollution and scarcity of water are becoming commonplace. Water utilities face the challenge to meet water needs at the cost of increasing their reliance on water sources impacted by wastewater effluents. Under these conditions water utilities must remove not only natural components including natural organic matter but also multiple wastewater effluent constituents such as pharmaceuticals, personal care products, antibiotics, etc., before the water is disinfected. Otherwise, disinfection of these waters would lead to the formation of disinfection by products of health concern.

Ion exchange is a promising treatment technique because it provides the possibility of controlling NDMA and THMs precursors concurrently in a single completely mixed flow reactor or fluidized bed reactor. One of the main benefits is its versatility because it allows a dose of either one or two resins depending on the characteristics of the influent water. Also, both resins can be regenerated using a brine solution in a single process once the exchange capacity is exhausted.

1.1 Disinfection of water

Disinfection of drinking water and wastewater is a process intended to reduce or eliminate the concentration of pathogenic organisms including those causing cholera, polio, typhoid, hepatitis, and a number of other bacterial, viral, and parasitic diseases (Voukkali and Zorpas, 2015). Chlorine, chlorine dioxide, chloramines, ozone, and ultraviolet irradiation are the most common disinfectants. Ideally, the disinfectants should be able to destroy all pathogens in water within the time available for disinfection and not increase the toxicity of the treated water. Unfortunately, disinfectants are strong oxidants and not only interact with pathogens but with other water components (e.g., organic matter, bromide) and form undesired disinfection byproducts.

Chlorine has been used for the control of waterborne infectious diseases for nearly a century. The use of chloramines has increased during the last years. Both disinfectants provide effective residual disinfection; however, monochloramine is 200 times less effective as a disinfectant than chlorine (Guay et al., 2005) and forms a significantly lower amount of trihalomethanes and haloacetic acids, but it forms NDMA.

1.2 Removal of NDMA precursors

NDMA precursors and model precursor compounds are effectively removed (98–99%) with reverse osmosis (RO), nanofiltration (98.5%), and powdered and granular activated carbon (37–91%) (Beita-Sandí et al., 2016; Hanigan et al., 2015, 2012). Pre-oxidation of waters with chlorine, ozone, chlorine dioxide, permanganate, ferrate, hydrogen peroxide, and even sunlight is capable of reducing NDMA formation during subsequent chloramination by deactivating NDMA precursors (Charrois and Hrudey, 2007; Chen and Valentine, 2008; Lee et al., 2008, 2007; Selbes et al., 2014).

However, the NDMA precursors must be removed or minimized before leaving the treatment plant. Otherwise, NDMA will continue to form within the chloraminated distribution systems, as the kinetics of nitrosamine formation during chloramination is slow (Charrois and Hrudey, 2007; Wilczak et al., 2003).

A representative group of anion exchange resins was investigated as a source of nitrosamines [NDMA, *N*-nitrosodiethylamine (NDEA), *N*-nitrosodi-n-propylamine (NDPA), and *N*-nitrosodi-n-butylamine (NDBA)] and their precursors (Flowers and Singer, 2013). NDMA, NDEA, and NDBA precursors were released from the anion exchange resins over a wide range of concentrations, with NDMA and NDBA precursor released in excess of 2000 ng/L and NDEA precursor release reaching 1850 ng/L upon initial rinsing with lab-grade water, with levels subsiding within 50−100 bed volumes of rinsing (Flowers and Singer, 2013). Because cation exchange resins do not use amine-functional groups they did not release NDMA or NDMA precursors (Kemper et al., 2009).

In a water sample from one aquaculture-impacted lake in the Yangtze River Delta, China, the cation fraction separated by the polarity rapid assessment method (PRAM) (Rosario-Ortiz et al., 2007, 2004) proved to be the major contributor (63%) to NDMA FP (Liao et al., 2015a). The PRAM method was conducted with no pH modifications. This finding is in agreement with the fact that most of the known NDMA precursors have pKa values higher than 8 (Le Roux et al., 2012a; Selbes et al., 2014) and therefore are likely to carry a net positive charge at ambient pH values. Thus, there is a potential for exploring cation exchange resins for removal of NDMA precursors, especially in the combined application of both cation and anion exchange resin. The combination will allow simultaneous removal of NOM and NDMA precursors.

Anion exchange resins are another group of drinking water treatment polymers and are commonly used for the removal of anionic contaminants during drinking water treatment (Flowers and Singer, 2013). Early studies found that anion exchange resins used in deionized water systems released NDMA (Fiddler et al., 1977; Gough et al., 1977; Kimoto et al., 1980). Experiments with anion exchange resins used in drinking water treatment have found nitrosamines. In batch contact studies, resins containing trimethylamine (TMA) or dimethylethanolamine (DMEA) were found to release appreciable levels of NDMA (up to 140 ng/L) (Najm and Trussell, 2001). While some of the cationic polymers and ion exchange resins have been reported to release NDMA precursors (Gan et al., 2013a; Kohut and Andrews, 2003; Najm and Trussell, 2001; Wilczak et al., 2003). Most of the known NDMA precursors have pKa values higher than 8 (Le Roux et al., 2012b; Selbes et al., 2014), especially amines. Therefore, they are weakly cationic in their undissociated form at pH 7. This suggests that cation exchange resins could remove positively charged NDMA precursors at the pH of drinking water treatment operations. However, there are no publications so far to support this hypothesis.

Coagulation and polymer optimization: NDMA formation potential (FP) was poorly removed (<10%) during coagulation with multiple ferric chloride dosages and alum (40 or 80 mg/L) (Krasner et al., 2008; Sacher et al., 2008). Similarly, lime softening had no significant impact on NDMA FP (Mitch et al., 2009). The majority of NDMA precursors are <1 kDa, and the corresponding fraction of NOM was poorly removed by coagulation (Xu et al., 2011). Coagulation, due to the frequent inclusion of amine-based cationic polymers, typically increased NDMA FP (Bond et al., 2011). NDMA FP increased by 43–82% at plants using poly(diallyldimethylammonium chloride) (polyDADMAC) and was not changed (±18%) at the plants that did not use a cationic polymer (Krasner et al., 2012). High polymer doses can leave residual polymer in the effluent (Novak and Langford, 1977; Novak and Montgomery, 1975). PolyDADMAC used as a coagulant alone, can leave residuals at high concentrations levels; however, the residuals can be reduced if the dose is optimized in combination with alum. For example, the dosage of alum can be raised to compensate for a reduction in polyDADMAC dosage in order to maintain good turbidity removal and filter run lengths (Labernik et al., 2010).

Precursors pre-oxidation: Pre-oxidation of waters with chlorine, ozone, chlorine dioxide, permanganate, ferrate, hydrogen peroxide, and even sunlight can deactivate NDMA precursors and decrease NDMA formation during subsequent chloramination (Charrois and Hrudey, 2007; Chen and Valentine, 2008; Lee et al., 2008, 2007). Ozone achieved 50% reduction in NDMA formation for exposures of < 0.4 mg × min/L; chlorine achieved similar results at exposures of ~ 70 mg × min/L. However, reductions in NDMA precursors of only ~30% were observed for UV doses relevant to advanced oxidation (~1000 mJ/cm^2). In some waters, chlorine promoted NDMA formation at low exposures, but formation declined again at higher exposures (Shah et al., 2012). In other waters, chlorine dioxide promoted NDMA formation across a range of exposures (Shah and Mitch, 2012).

For secondary and tertiary amine precursors (pKa ~8–11), the deprotonated species is more reactive (Abia et al., 1998). For free chlorine, HOCl is the stronger oxidant (Abia et al., 1998). Accordingly, because chlorination of secondary or tertiary amines involves a reaction between HOCl and deprotonated amines, the maximum rate of reaction is anticipated at a pH intermediate between the pKa values of HOCl (pKa = 7.58) and the amine precursors (Abia et al., 1998; Lee and von Gunten, 2010; McCurry et al., 2015). Pre-treatment of model precursors or natural waters with free chlorine showed that NDMA formation decreased during subsequent chloramination (Charrois and Hrudey, 2007; Chen and Valentine, 2008; Selbes et al., 2014). However, increasing pre-oxidant exposures, for control of NDMA formation, promoted the formation of regulated and unregulated DBPs associated with each pre-oxidant, including THMs, HAAs, and chloral hydrate for chlorine; bromate, chloropicrin, and chloral hydrate for ozone; chlorite for chlorine dioxide; and chloropicrin and chloral hydrate for medium pressure UV treatment (Shah and Mitch, 2012).

NDMA was not produced when selected *N*-nitrosamines precursors (dimethylamine, trimethylamine, 3-(dimethylaminomethyl) indole, 4-dimethylaminoantipyrine, ethylmethylamine, diethylamine, and dipropylamine) were oxidized with peracetic acid (PAA) (West et al., 2016). However, the deactivation of NDMA precursors with PAA has not been fully investigated.

Powdered activated carbon: Powdered activated carbon (PAC) is widely used in drinking water treatment plants (DWTPs) mainly to remove taste and odor causing-compounds, as well as synthetic organic chemicals (SOCs). To date, only a small number of studies have examined the removal of NDMA precursors by PAC adsorption during water treatment. The reported NDMA FP removals were (i) >73% from a water influenced by effluent organic matter (EfOM) with 50 mg/L of PAC (F400, Calgon Carbon Corp., Pittsburgh, PA) and 7 d of contact time (Krasner et al., 2008); (ii) 50% in river waters with 5 mg/L of PAC (F300, Calgon Carbon Corp., Pittsburgh, PA) and 7 d of contact time, and ≥ 90% with 20 mg/L of PAC (Sacher et al., 2008); and (iii) 40% in a secondary wastewater effluent with 3 mg/L of PAC (WPH, Calgon Carbon Corp., Pittsburgh, PA) and 4 h of contact time (Hanigan et al., 2012). A dose of 75 mg/L of WPH had similar removals (~ 90%) in secondary wastewater effluents with different NDMA FP (544 and 1470 ng/L) (Hanigan et al., 2012). Recently, the same researchers found similar removals (17–34%) of watershed-derived NDMA precursors by 3 mg/L of WPH from blends of a treated secondary wastewater effluent and Colorado River water (Hanigan et al., 2015). Additionally, they reported that all PAC doses investigated (3–20 mg/L) with different contact times (15–120 min) decreased NDMA FP, but contact times longer than 15 min did not provide additional removal of watershed-derived precursors.

The removal efficiency of NDMA FP by PAC was significantly higher in wastewater-impacted (50-82%) than surface waters (10-30%) (Beita-Sandí et al., 2016). Basic carbons showed higher removal of NDMA FP than acidic carbons on a surface area basis. The overall removal of NDMA FP by PAC on a mass basis depended on the surface area, pore size distribution and pH_{PZC}. Thus, PACs with hybrid characteristics (micro and mesoporous), higher surface areas, and basic surface chemistry were more likely to be effective for NDMA precursor control by PAC adsorption. The application of PAC in DWTPs for taste and odor control resulted in an additional 20% removal of NDMA FP for the PAC doses of 7–10 mg/L (Beita-Sandí et al., 2016).

Modification of monochloramine application protocol: By adding pre-formed chloramines to wastewater less NDMA resulted than from addition of chlorine and ammonia in situ, a result attributed to lower dichloramine levels (Hayes-Larson and Mitch, 2010). Unequal distribution of chlorine and ammonia, especially around the point of chlorine addition, can lead to the formation of dichloramine which can also be alleviated by adding free chlorine before ammonia (Hayes-Larson and Mitch, 2010). In the presence of dichloramine, NDMA formation at neutral pH in treated municipal secondary wastewaters and from dimethylamine was approximately 1–2 orders of magnitude higher than from monochloramine (Schreiber and Mitch, 2007). While reactive nitrosating intermediates were thought to contribute to heightened NDMA formation when small amounts of free chlorine were present. Thus, to limit NDMA it was recommended that chloramination be conducted away from the breakpoint and with no free chlorine residual (Bond et al., 2011; Schreiber and Mitch, 2007).

Biofiltration: NDMA FP is dramatically reduced by biologically activated carbon (BAC) even in the absence of main ozonation prior to the filtration. BAC was able to reduce the NDMA FP by more than 85%, which is better than ozonation alone (66%), in full and pilot-scale biofilters treating the effluent from a municipal WWTP (Farré et al., 2011b). However, NDMA formation in was observed in ozone fed BAC columns during biofiltration (D. Li et al., 2017)

Membrane filtration: NDMA precursors and model precursor compounds were effectively removed (98–99%) with reverse osmosis (RO) treatment from different background waters (Farré et al., 2011a; Krauss et al., 2010; Mitch and Sedlak, 2004; Miyashita et al., 2009; Snyder et al., 2007), while rejections higher than 98.5% of nitrosamine precursors were reported with nanofiltration (Miyashita et al., 2009). Apart from larger molecules, RO also removed small charged precursors such as dimethylamine (DMA) and only small uncharged molecules such as dimethylsufamide or dimethylformamide likely can pass RO membranes to any great extent. Although RO does effectively remove the vast majority of NDMA precursors, the permeate can still contain significant concentrations of NDMA precursors resulting in additional NDMA formation during chloramination. Thus, it is possible for this advanced treatment system to produce water with NDMA levels higher than regional requirements for potable applications (10 ng/L) (Sgroi et al., 2015).

1.3 Removal of trihalomethanes precursors

Natural organic matter (NOM) in natural waters is a complex mixture of heterogeneous compounds derived from the decomposition of plant and animal tissue, including humic compounds, amino acids, proteins and carbohydrates with molecular weights ranging from a few hundred Da to over 5,000 Da (Stumm and Morgan, 1996; Tipping, 2002). Most NOM components are weak polyelectrolytes dissociated into negatively charged species as a result of the structure-bound carboxylic and phenolic groups such as found in humic and fulvic acids (Kim and Yu, 2005), while the rest of the NOM consist of neutral compounds, such as polysaccharides and proteins (Leenheer and Croué, 2003).

Water treatment processes to remove NOM include enhanced coagulation, granular and powdered activated carbon adsorption, nanofiltration, and ion exchange. The removal of NOM with ion exchange resins relies on the theoretical interaction expected between anion exchange resins and negatively charged NOM. Ion exchange resins remove NOM fractions to different extents. Since not all the fractions are negatively charged a complete removal of NOM is not anticipated. The removal of humic substances increased with increasing water content of the resins and with a decrease in the resin size (Cornelissen et al., 2008). Thus, separation of specific NOM fractions by ion exchange resins based on molecular weight and hydrophobicity is feasible.

The mechanisms for NOM removal by anion-exchange resins comprises (1) ion exchange, involving counterion displacement from the resin phase and electrostatic interaction between ionic functional groups (Allpike et al., 2005; Boyer et al., 2008; Boyer and Singer, 2008; Croué et al., 1999; Fearing et al., 2004; Humbert et al., 2005; Johnson and Singer, 2004), and (2) physical adsorption, involving van der Waals interactions between non-ionic (hydrophobic) moieties present on NOM molecules and the resin polymer backbone (Bolto et al., 2002; Cornelissen et al., 2008; Croué et al., 1999; Tan and Kilduff, 2007). Additionally, entropy-assisted sorption resulting from desolvation may occur (Li and Sengupta, 1998; Tan and Kilduff, 2007), and molecular association (i.e., van deer Waals interations) can also cause irregular sorption (Qi et al., 2012). Entropy is gained in large part from the first step in the organic ion sorption process, desolvation, which involves removal of the organic ion from a water cavity bounded by water molecules that have reorganized themselves in clusters via hydrogen bonding. Loss of water cluster structure and loss of organic ion confinement in the water cavity both result in an increase in entropy. The displacement of the counterion and the water of hydration from the resin phase also results in an increase in entropy.

Strongly basic anionic exchange resins are effective in removing NOM (Fearing et al., 2004; Martijn et al., 2010; Singer et al., 2007). Purolite A860, a strong base anion exchange resin, removed mainly humic (-like) (40–67%), whereas hydrophilic, non-ionic fractions such as biopolymers, neutrals, and building blocks were poorly removed (12–33%) (Bazri et al., 2016). However, strong base anion exchange resin can release *N*-DBPs precursors (e.g., alkylamines) and *N*-DBPs (Flowers and Singer, 2013; Gan et al., 2013a; Kemper et al., 2009; Kimoto et al., 1980; Najm and Trussell, 2001; Watson et al., 2015). For instance, when the magnetic ion exchange (MIEX) resin was used to treat three wastewater effluents, NDMA formation potential (FP) increased from 156–287 to 266–

344 ng/L, whereas the increase for three drinking waters was from 10–12 to 14–18 ng/L (Gan et al., 2013b). Manufacturing impurities in the resins (e.g., dimethylamine, trimethylamine) and/or organic precursors can be detached into the water during the first bed volumes (BV) of operation (Flowers and Singer, 2013; Kemper et al., 2009). Resins swelling (i.e., more open structure) facilitate the detachment of organic impurities.

Among strong basic anionic exchange resins, MIEX resin has gained a lot of attention. MIEX removed effluent organic matter fractions of both low and high molecular weight (MW) (Filloux et al., 2012; Nguyen et al., 2011; Wang et al., 2014). MIEX resin removed the majority of hydrophilic compounds and significant amounts of hydrophobic compounds within a short contact time (20 min) (Zhang et al., 2006). MIEX resin has traditional anion exchange properties, such as a polyacrylic matrix in the chloride form, a macroporous structure, and strong-base functional groups but with magnetic properties due to the high content of iron oxide integrated into its structure (Singer and Bilyk, 2002). The magnetic properties allow the resin beads to agglomerate and separate from the suspending solution by gravitational settling at relatively high overflow rates (Cornelissen et al., 2008; Singer and Bilyk, 2002). The MIEX resin beads (diameter ~ 180 mm) are 2–5 times smaller than traditional ion exchange resins and can be applied to raw water in a slurry form. MIEX is used in a suspended manner in a completely mixed flow reactor (CMFR), instead of a fixed-bed like traditional ion exchange resins. The suspension increases the turbulence around the resin and decreases resistance to liquid-phase mass transfer. The MIEX process removed NOM much faster than traditional ion exchange resins (Cornelissen et al., 2008; Singer and Bilyk, 2002).

The MIEX resin can be easily regenerated and even after several regenerations it yields significant organic matter removal (Matilainen et al., 2010). A further benefit of treatment with MIEX is that it has been shown to remove bromide (Johnson and Singer, 2004; Singer and Bilyk, 2002). Optimal characteristics of strong-base anion resins for NOM removal include fast kinetics, high chemical stability, physical stability in terms of mechanical strength and resistance to wear, effective and lasting ion exchange capacity, consistent particle size, and high effective surface area. MIEX resin showed similar removal of hydrophobic, transphilic, and hydrophilic fractions of DOC from biologically treated wastewater effluent (Boyer, 2015; Metcalfe et al., 2015).

1.4 Ion exchange process

The ion exchange process involves diffusion through the film of solution that is in close contact with the resins and diffusion within the resin particle. One of the benefits of ion exchange relies on the ability to use and reuse the ion exchange material for a number of cycles. For example, in water softening:

$$2R^{-}Na^{+} + Ca^{2+} \rightleftharpoons (R^{-})_2Ca^{2+} + 2Na^{+} \qquad \text{Eq. 1–1}$$

the exchanger R^- in the sodium ion form is able to exchange for calcium and thus, to remove calcium from the hard water and replace it with an equivalent quantity of sodium. Subsequently, the calcium loaded resin may be treated with a sodium chloride solution, regenerating it to the sodium form, so that it is ready for another cycle of operation. The regeneration reaction is reversible.

Conventional ion exchange resins consist of a cross-linked polymer matrix with a relatively uniform distribution of ion exchange sites throughout the structure. Ion exchange materials are sold as spheres or sometimes granules with specific size and uniformity. The majority are prepared in spherical (bead) form, either a conventional resin with polydispersed particle distribution from about 0.3 mm to 1.2 mm diameter (US Mesh Sieve size 50-16) or as uniform particle size (UPS) resin with all beads in a narrow particle size range. Conventional polymeric anion exchange resins and MIEX resin have been evaluated for removing DOC and controlling the formation of DBPs. The major difference between these two classes of resins is their mode of treatment, i.e., conventional polymeric resins are used in a fixed-bed to treat filtered water, whereas MIEX resin is used in a completely mixed flow reactor to treat raw water.

The MIEX resin is designed specifically to be used in a continuous ion exchange process in mixed or fluidized bed reactors. The magnetic properties of the resin beads result in the beads forming agglomerates that will settle rapidly or fluidize at high hydraulic loading rates. MIEX resin can be applied in two different reactor configurations.

High Rate Configuration: The raw water is fed to the base of the reactor vessel and mixed with the MIEX resin and the ion exchange process occurs in a fluidized bed (Figure 1–1). In the fluidized bed the magnetic particles are attracted to each other to form large agglomerates that form a stable resin suspension at hydraulic loading rates of up to 12 gpm/ft^2. An agitator operating at slow speeds keeps the resin/water suspension uniformly mixed. A small stream of resin is withdrawn from the reactor vessel, regenerated with a 12% NaCl solution and returned to maintain the ion exchange capacity of the process. A series of plates (or tube settlers) at the top of the reactor vessel separate the resin from the water and treated effluent overflows into collection tanks to downstream treatment processes.

Dual Stage Configuration: Ion exchange occurs in a flow-through mixed tank (contactor) where the resin particles are dispersed to provide a high surface area for ion exchange to occur. The magnetic resin particles then agglomerate and settle rapidly in a gravity separator designed for a hydraulic loading rate of 6 gpm/ft^2. In the separator, the resin is recovered and most is recycled back to the contactor while a small side-stream is regenerated with a 12% NaCl solution and then returned to the contactor to maintain the ion exchange capacity of the process. Treated water overflows the resin separator to downstream treatment processes.

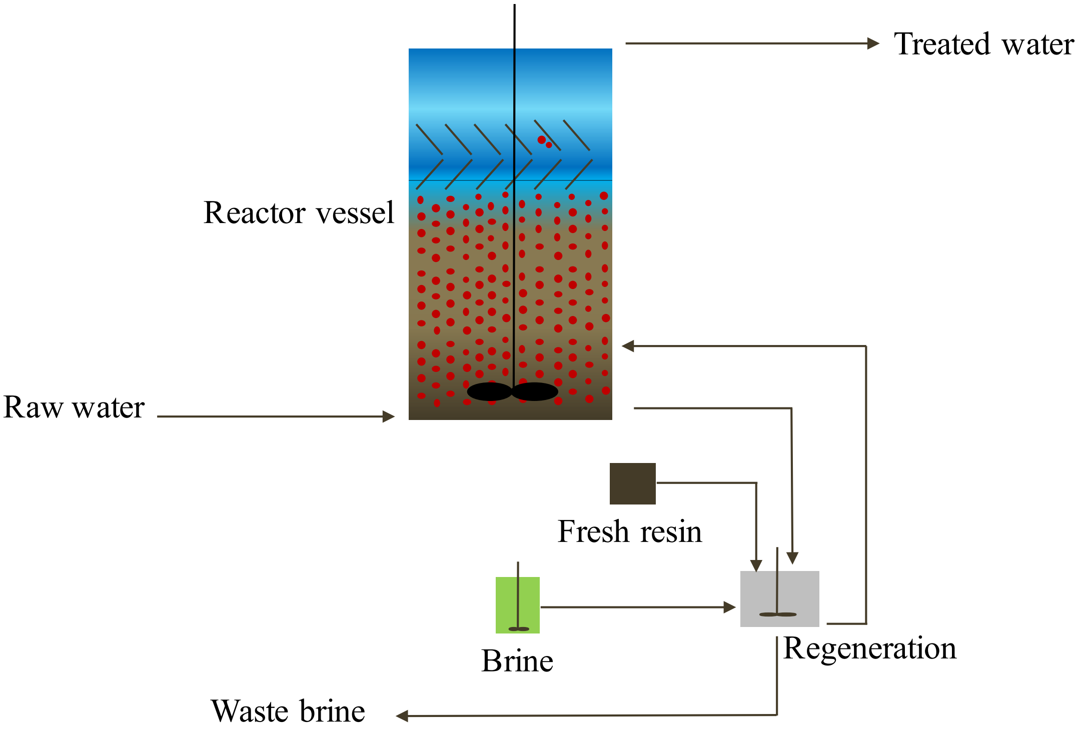


Figure 1–1. Schematic of MIEX process treatment in the high rate configuration system.

CHAPTER II

MATERIALS AND METHODS

2.1 NDMA Analysis

NDMA standards were prepared from a nitrosamine mix in methylene chloride (40035-U, Supelco, min. 99.6%). The calibration curves included at least six standards in the range of 0.5–400 ng/L, and the minimum reporting level (MRL) was 0.5 ng/L. The temperature program for the front multimode inlet was 35 °C for 0.1 min, then ramped to 265 °C at a rate of 600 °C/min. The GC inlet was held at 280 °C and lined with an Agilent dimpled ultra-inert liner (2 mm id). The oven temperature program was 50 °C held for 1 min then raised to 80 °C at a rate of 10 °C/min, increased to 130 °C at 20 °C/min, increased to 230 °C at a rate of 60 °C/min and finally held for 2 min (total run time 10.17 min). The GC-MS/MS transfer line temperature was maintained at 280 °C. The helium carrier gas flow rate was 1.2 mL/min. Ionization was carried out by electron impact (EI) with an EI voltage of 70 eV and a source temperature of 280 °C. The triple quadrupole MS detector was operated in multiple reaction monitoring (MRM) mode and two MRM transitions were monitored for NDMA, NDMA-d6, and NDPA-d14 for quantification and confirmation of molecular identification. All samples were run with a solvent delay of 4.3 min. The MRM transitions monitored for all analytes, dwell times and the collision energies (CE) are presented in Table 2–1. Every sample was injected twice in the GC-MS/MS and the standard deviation of the two injections was calculated. The NDMA stock solution was used to prepare two samples in DDI water at 10 ng/L and 50 ng/L. These two samples were extracted along with the rest of the batch, and measured in the GC-MS/MS. The NDMA recoveries were between 80–120%. An additional quality control consisted in analyzing the 10 ng/L calibration standard every 10 samples.

Table 2–1. Acquisition data for GC-MS/MS analysis of NDMA (target), NDMA-d6 (surrogate), and NDPA-d14 (internal standard).

Analyte	Ret. time (min)	MRM transitions (*m/z*)*	CE (V)	Dwell (ms)
NDMA	6.65	1: 74.0 → 44.0	3	130
		2: 74.0 → 42.0	7	140
NDMA-d6	6.66	1: 80.0 → 50.0	3	30
		2: 80.0 → 48.0	7	30
NDPA-d14	8.8	1: 144.0 → 126.0	5	20
		2: 144.0 → 50.0	5	20

*1: Quantifier (Precursor ion → Product ion), 2: Qualifier (Precursor ion → Product ion)

2.2 THMs Analysis

Briefly, samples (20 mL) were extracted with methyl-*t*-butyl ether (8 mL) containing the internal standard 1,2-dibromopropane and 8.5 g anhydrous sodium sulfate. Samples were shaken horizontally on a shaker table (15 min, 300 rpm). The vials rested for 15 min, and then the methyl-*t*-butyl ether extract was transferred to glass inserts inside amber glass vials. Standards were prepared in DDI water from a THMs calibration mix (4M8140-U, Supelco, min. 99.4%), then the aqueous standards were extracted in methyl t-butyl ether (Omnisolv, min. 99.5%). The calibration curves included six standards and the MRL was 1 μg/L.

Two microliters of the extracted samples and the standards were injected on an Agilent 6890 GC in splitless mode and separated on a Phenomenex ZB-1 (30 m x 0.25 mm x 1.00 μm) column. The GC was coupled with an electron capture detector. The oven temperature program was initially held at 35 °C for 15 min then raised to 145 °C at a rate of 25 °C/min and held for three min, then increased to 240 °C at a rate of 35 °C/min and finally held for five min (total run time 30.11 min). The hydrogen carrier gas flow rate was 1.5 mL/min, and the nitrogen make-up gas flow rate was 30 mL/min. The temperature of the injector was 230 °C and the detector 260 °C.

2.3 Other analytical methods

Standard Methods (SM) (APHA et al., 2005) were followed to measure dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) using a Shimadzu Total Organic Carbon (TOC)-V_{CSH} coupled with the TNM-1 (SM 5310 B). Free chlorine and monochloramine were measured using the *N,N*-diethyl-*p*-phenylenediamine (DPD) ferrous titrimetric method (SM 4500-Cl F). UV absorbance was measured using a Varian Cary 50 (SM 5910), and pH using a VWR Symphony pH meter (SM 4500-H^+). Calcium was measured using a titration method (SM 2340C). Anions were measured with a Dionex ICS-2100 Ion Chromatograph according to the US EPA Method 300.0 (US EPA, 1993a). Analytical methods and their minimum reporting levels (MRLs) for water characterization parameters are given in Table 2–2.

Table 2–2. Analytical methods and minimum reporting levels (MRL).

Parameter	Method	MRL or accuracy[a]
Bromide	EPA 300.0	10 μg/L
Calcium	SM 2340C	---
Dissolved nitrogen	SM 5310 B	0.1 mg/L
Dissolved organic carbon	SM 5310 B	0.1 mg/L
NDMA	EPA 521	0.5 ng/L
pH	SM 4500-H^+	± 0.01 pH units
Residual combined chlorine	SM 4500-Cl F	0.05 mg Cl_2/L
Residual free chlorine	SM 4500-Cl F	0.05 mg Cl_2/L
THM	EPA 551.1	1 μg/L
UV absorbance	SM 5910	± 0.004 Absorbance unites

[a] Reported by the manufacturer

SM: Standard Methods (APHA, 2005).

UV Absorbance: measured at $\lambda = 254$ nm using a 1 cm cell

Chapter III

REMOVAL OF BOTH N-NITROSODIMETHYLAMINE AND TRIHALOMETHANES PRECURSORS IN A SINGLE TREATMENT USING ION EXCHANGE RESINS

3.1 Abstract

Drinking water utilities are relying more than ever on water sources impacted by wastewater effluents. Disinfection/oxidation of these waters during water treatment may lead to the formation of several disinfection by-products, including the probable human carcinogen *N*-nitrosodimethylamine (NDMA) and the regulated trihalomethanes (THMs). In this study, the potential of ion exchange resins to control both NDMA and THMs precursors in a single treatment is presented. Two ion exchange resins were examined, a cation exchange resin (Plus) to target NDMA precursors and an anion exchange resin (MIEX) for THMs precursors control. The resins were applied individually and combined in the treatment of two surface and two wastewater effluent samples. The treatment with MIEX and Plus resins combined removed simultaneously NDMA (43–85%) and THMs (39–65%) precursors. However, no removal of NDMA precursors was observed in the surface water (SW–2) with low initial NDMA FP (14 ng/L). The removals of NDMA FP and THMs FP with Plus and MIEX resins applied alone were (49–90%) and (41–69%), respectively. These results suggest no interaction between the resins, and thus the feasibility of effectively controlling NDMA and THMs precursors concomitantly. Additionally, the effects of the wastewater impact and the natural attenuation of precursors were studied. The results showed that neither the wastewater content nor the attenuation of the precursor affected the removals of NDMA and THMs precursors. Finally, experiments

using a wastewater effluent sample showed that an increase in the calcium concentration resulted in a reduction in the removal of NDMA precursors of about 50%.

3.2 Introduction

The continued increase in the world population combined with a low availability of pristine water sources generate stress on water supplies; pollution and scarcity of water are becoming commonplace (McCurry et al., 2016). To meet these challenges, drinking water utilities are increasing their reliance on water sources impacted by wastewater effluents (Chen et al., 2009; Mitch and Sedlak, 2004; Morehouse et al., 2000; Rice et al., 2013; Rice and Westerhoff, 2015), which are rich in disinfection by-products (DBPs) precursors (Beita-Sandí et al., 2016; Krasner et al., 2009; Watson et al., 2012b).

To minimize the formation of regulated DBPs, some drinking water utilities in the United States have been changing disinfection practices from chlorine to chloramines (Li, 2011). Unfortunately, one of the unintended consequences of using chloramines is the formation of *N*-nitrosamines, including *N*-nitrosodimethylamine (NDMA) (J. Choi and Valentine, 2002; Le Roux et al., 2011; Mitch et al., 2003b; Mitch and Sedlak, 2004). NDMA is a probable human carcinogen and has a lifetime cancer risk of one in a million for 0.7 ng/L in drinking water (US EPA, 1993b). NDMA formation is promoted in wastewater effluents due to a wide range of its precursors being present (Mitch and Sedlak, 2004). Therefore, drinking water utilities face the challenge of controlling either the formation of regulated (e.g. trihalomethanes [THMs]) or emerging (e.g. NDMA) DBPs.

An approach to control the formation of DBPs is to remove the precursors before the oxidant additions. However, NDMA and THMs are formed from an ensemble of constituents in water and wastewater that differ in their nature. For example, NDMA precursors include amine based compounds (pKa ≥ 8) that are protonated at the typical pH range (6–8) of water treatment operations, hence they are weakly cationic (Hanigan et al., 2016; Le Roux et al., 2012b; Liao et al., 2015b; Selbes et al., 2014). On the other hand, natural organic matter (NOM) is considered as the main precursor of THMs. The bulk components of natural organic matter are weak polyelectrolytes with carboxylic and phenolic moieties present in humic and fulvic acids (Karanfil et al., 1996; Kim and Yu, 2005). Thus, at the pH of natural waters most NOM corresponds to dissociated negatively charged species.

NDMA precursors can be removed or deactivated by a wide variety of strategies, including riverbank filtration (Krasner et al., 2012; Sacher et al., 2008), reverse osmosis (RO) (Farré et al., 2011a; Krauss et al., 2010; Mitch and Sedlak, 2004; Miyashita et al., 2009; Sgroi et al., 2015; Snyder et al., 2007), nanofiltration (Miyashita et al., 2009), biofilters (Farré et al., 2011b; Selbes et al., 2016), activated carbon adsorption (Beita-Sandí et al., 2016; Hanigan et al., 2015, 2012), pre-oxidation with different oxidants (Charrois and Hrudey, 2007; Chen and Valentine, 2008; Lee et al., 2008, 2007; Selbes et al., 2014), and even natural attenuation (Beita-Sandí et al., 2016; Woods and Dickenson, 2016).

NOM is removed well during drinking water treatment by enhanced coagulation (Bazri et al., 2016; Fearing et al., 2004), activated carbon adsorption (Gur-Reznik et al., 2008; Karanfil, 2006), nanofiltration (Zhang et al., 2009), and ion exchange (Bazri et al., 2016; Filloux et al., 2012; Gan et al., 2013a, 2013b; Nguyen et al., 2011; Singer et al., 2007; Wang et al., 2014). NOM is removed by anion exchange through two main mechanisms: (1) ion exchange, involving counterion displacement from the resin phase and electrostatic interaction between ionic functional groups (Allpike et al., 2005; Boyer et al., 2008; Boyer and Singer, 2008; Croué et al., 1999; Fearing et al., 2004; Humbert et al., 2005; Johnson and Singer, 2004), and (2) physical adsorption, involving van der Waals interactions between NOM non-ionic hydrophobic moieties and the polymer backbone of the resin (Bolto et al., 2002; Cornelissen et al., 2008; Croué et al., 1999; Tan and Kilduff, 2007). Ion exchange resins remove NOM fractions to different extents because not all the of fractions are negatively charged (Cornelissen et al., 2008). It has also been reported that nitrosamines and nitrosamine precursors may be released into water during the first bed volumes (BV) of operation due to the detachment of manufacturing impurities from the resins (Fiddler et al., 1977; Flowers and Singer, 2013; Gan et al., 2013a, 2013b; Gough et al., 1977; Kemper et al., 2009; Kimoto et al., 1980; Najm and Trussell, 2001; Watson et al., 2015).

Some previous studies have documented the cationic behavior of NDMA precursors. For instance, Chen and collaborators used solid phase extraction (SPE) columns and the polarity rapid assessment method (PRAM) to characterize NDMA precursors, and found that a cartridge containing a cation exchanger (sulfonate functional groups), retained 45–90% of the NDMA FP in secondary and tertiary wastewater effluents (Chen et al., 2014; Rosario-Ortiz et al., 2007). In a later study using an impacted lake water in China, the cationic fraction of NDMA FP was retained in the cationic SPE cartridge (sulfonate functional groups) by >60% (Liao et al., 2015b). Similar SPE cartridges were used also to demonstrate the recovery of NDMA precursors adsorbed in the cation exchanger; NDMA precursors were recovered efficiently by elution with 5% NH_4OH in methanol at pH 3 (Hanigan et al., 2016). More recently, the application of cation exchange resins to remove dimethylamine and ranitidine, and seven other NDMA model precursors compounds was reported (S. Li et al., 2017). Overall, these studies documented that an important fraction of NDMA precursors has a cation exchange behavior that is imposed by the protonation of the amine moiety at pH below the respective pKa values of the precursors.

NDMA and THMs pose health effects for humans due to their toxicity; ion exchange is a promising treatment technique to remove the precursors of both types of DBPs. The benefit of a mixed resin (anionic and cationic) ion exchange treatment relies on the ability of simultaneously targeting different precursors in a single completely mixed flow reactor or fluidized bed reactor to control the formation of both NDMA and THMs, and the possibility of regenerating both resins using a brine solution in a single process after the resins have exhausted their exchange capacity. In this study, the potential of ion exchange resins to simultaneously control NDMA and THMs precursors was explored. The approach was based on the ionic nature of NDMA and THMs precursors. The magnetic ion exchange resin (MIEX) was selected for removing NOM while Plus, a cation exchange resin, was chosen to control NDMA precursors. Both resins are manufactured by IXOM Watercare (Centennial, CO, USA). The simultaneous application of a cation and an anion exchange mixed resin system to control NDMA and THMs precursors has not yet been investigated. A water treatment process capable of dealing simultaneously with both type of precursors is of great importance for the water industry due to its versatility because it allows to dose either one or two resins depending on the characteristics of the influent water and the DBPs that need to be addressed.

In this work, the goals were to explore the potential of ion exchange resins to simultaneously control NDMA and THMs precursors, the effect of the concentration and the natural attenuation of precursors, and the competing effect of background ions on the efficiency of the ion exchange process. To the best of my knowledge, this is the first study that investigated the simultaneous removal of both NDMA and THMs precursors in a single mixed-resin treatment system.

3.3 Materials and methods

3.3.1 Water samples

Water samples were collected in South Carolina, USA, from two surface waters (SW-1 and SW-2) used by drinking water utilities, and wastewater effluents (WW-1, WW-2, WW-A and WW-B) from four municipal wastewater treatment plants. The wastewater effluents were sampled at the secondary effluent but before UV disinfection. Upon arrival in the laboratory, all samples were filtered with 0.45 µm pore size Whatman™ Polycap 150 TC filters, and kept at 4 °C until experiments were conducted (usually a maximum of 2–3 days).

3.3.2 Ion exchange resins

The anionic (MIEX) and the cationic (Plus) resins were obtained from IXOM Watercare (Centennial, CO, USA). Plus is a strong acid cation exchange resin composed of polystyrene with sulfonic acid functional groups; the total exchange capacity is 1.9

meq/mL; and it is used in the sodium form. MIEX is a macroporous strong base resin with quaternary ammonia functional groups, in the chloride form and made of polyacrylic matrix. Its total exchange capacity is 0.42 meq/mL. The presence of high amounts of iron oxide in its structure gives magnetic properties to the resin (Singer and Bilyk, 2002), allowing the resin beads to agglomerate and separate from the suspending solution by gravity, settling at relatively high overflow rates (Cornelissen et al., 2008; Singer and Bilyk, 2002). The MIEX resin particles (diameter ~ 180 μm) are 2–5 times smaller than traditional ion exchange resins. Both resins can be applied to raw water in the form of a slurry.

3.3.3 Bench-scale experiments

Bench-scale removal experiments were conducted at 600 bed volumes (BV = volume of treated water / volume of resin). To achieve the desired settled resin volume, doses of 5 mL of the resin were measured at least 30 min before each experiment and placed in a 2 L plastic square beaker, followed by the addition of 1 L of untreated water. The pH the water was adjusted to 7 with NaOH/HCl and mixed in a Phipps & Bird jar tester (Richmond, VA, USA) at the rate of 150 rpm for 15 min. The mixer was then turned off and the resin was allowed to settle for 2 min. The treated water was carefully decanted into a 5 L glass carboy, retaining the resin in the beaker. Two additional cycles were conducted to attain 600 BV. The composite sample was filtered through a pre-rinsed 0.45 μm membrane filter to remove any resin particles. Samples of both the untreated and treated water were collected.

3.3.4 Chemical reagents

Monochloramine with a chlorine to nitrogen mass ratio of 4.75:1 was prepared fresh daily. In brief, sodium hypochlorite (Baker Analyzed Reagent, 5% available free chlorine) was added slowly to a rapidly stirred solution of ammonium sulfate (BDH, 99%). Before mixing, the pH of sodium hypochlorite and ammonium sulfate was adjusted to 9 with NaOH and/or HCl (Hong et al., 2007). Chlorine stock solutions were also prepared fresh daily by the dilution of sodium hypochlorite in DDI water. A borate buffer solution (800 mM, pH 8.0) was prepared by dissolving sodium tetraborate decahydrate (Sigma-Aldrich, 99%) and boric acid (Beantown Chemical, 99%) in DDI water. The pH of the buffer solution was adjusted to 8 with either NaOH or HCl.

3.3.5 NDMA and THMs formation tests

The formation potential (FP) test was used as a measure of the concentration of the precursors present in water samples. Excess amounts of the oxidants, 100 mg Cl_2/L chlorine for THMs and 50 mg Cl_2/L chloramine for NDMA were added to react with the precursors. In both tests, the samples were adjusted to pH 8 with borate buffer at 8 mM concentration. All samples were stored in the dark at room temperature. The reactions were stopped after five days by the addition of stoichiometric amounts of sodium thiosulfate anhydrous to the chloraminated samples, and sodium sulfite to the chlorinated samples. NDMA and THMs formation were also evaluated under uniform formation conditions (UFC) for selected experiments. Briefly, samples were chloraminated at room temperature at pH 8 and held for 3 d. The monochloramine doses were selected to achieve a residual of ~2.0 mg Cl_2/L after 3 d of reaction time. During chlorination experiments the reaction time was 24 h and the residual was 1 mg Cl_2/L. Before extraction, 40 ng/L of deuterated NDMA (NDMA-d6) (Restek, 99%) was added as a surrogate standard to the chloraminated quenched samples. Additional details about the FP tests may be found elsewhere (Uzun et al., 2016).

3.3.6 Simulated natural attenuation of precursors

Wastewater effluents containing DBPs precursors are discharged in natural systems. Precursors in the environment may be attenuated by a series of complex photolytic and biological reactions. The effect of natural attenuation of precursors on their removal by ion exchange process has not been investigated. To simulate the natural attenuation process, unfiltered wastewater effluent samples were placed in 15 L borosilicate glass carboys (Pyrex No. 1596, Corning, NY, USA) covered with Parafilm™, and exposed to direct sunlight (approximately 14 h of sunlight per day) outside of the laboratory with continuous stirring for seven days.

3.3.7 Effect of background ions

The affinity of the cation exchange resins for cations increase with the charge and the size of the ions. Calcium was selected to conduct the cation competition experiments because is relatively more abundant than other cations in natural waters. It was hypothesized that calcium ions and NDMA precursors compete for exchange sites in the resin. To investigate this competition effect, a wastewater sample was collected after the clarifier in a municipal wastewater treatment plant. The ambient calcium concentration in the wastewater sample was 11.2 mg /L. Half of this sample was later fortified with calcium chloride (Mallinckrodt, >99.95%) to reach approximately 92 mg//L. Both samples were treated in the jar tester with a) the cation resin, b) the anion resin, and c) both resins simultaneously.

3.3.8 Analytical methods

NDMA was extracted using SPE cartridges, additional details are provided in section 2.1. Briefly, the internal standard deuterated *N*-nitroso-di-n-propylamine (NDPA-d14) was spiked (40 ng/L) in the extracted samples, and the volume was adjusted to 1 mL with methylene chloride. The concentrated samples were transferred to glass inserts in amber vials. One microliter of the extracted samples and the standards were injected on a Agilent 7890B (Santa Clara, CA, USA) Gas Chromatograph (GC) equipped with an Agilent DB-1701 (30 m x 0.25 mm x 1.00 μm) column, and coupled with an Agilent 7000C triple quadrupole mass spectrometer (MS/MS) (McDonald et al., 2012).

Chloroform, bromodichloromethane, dibromochloromethane, and bromoform were analyzed following the US EPA Method 551.1 (US EPA, 1990), and their sum was reported as THMs. A detailed procedure is given in section 2.2. Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were measured using a Shimadzu Total Organic Carbon (TOC)-V_{CSH} coupled with the TNM-1. Free chlorine and monochloramine were measured using the *N,N*-diethyl-*p*-phenylenediamine (DPD) ferrous titrimetric method. UV absorbance was measured using a Varian Cary 50, and pH using a VWR Symphony pH meter. Calcium was measured using a titration method. Analytical methods and their minimum reporting levels (MRLs) for water characterization parameters are given in Table 2–2.

3.4 Results and discussion

3.4.1 Efficiency of precursors removal by combined application of Plus and MIEX resins

The water quality parameters of the samples used in this study are presented in Table 3–1. The NDMA FP in the surface water (SW) and the wastewater effluent (WW) samples, both untreated and treated with the ion exchange resins, are presented in Figure 3–1.

Table 3–1. Selected characteristics of the untreated water used for ion exchange experiments.

Parameter	Units	SW-1	SW-2	WW-1	WW-2
Calcium	mg/L	8	7.2	12.8	59.2
DOC	mg/L	2.7	4.6	4.5	5.1
NDMA FP	ng/L	31	14	6,269	919
pH	pH units	7.1	6.9	7.4	7.3
$SUVA_{254}$	L/mg-m	2.5	3.1	1.9	2.5
THMs FP	µg/L	351	556	448	285

The initial concentration of NDMA FP varied substantially among individual samples, and the concentrations were at least 30 times higher in the wastewater effluent samples (919–6,269 ng/L) than in the surface waters (14-31 ng/L). In contrast, the concentrations of THMs FP did not vary greatly among the water types and ranged from 285 µg/L to 556 µg/L (Figure 3–2). Plus resin removed NDMA FP in the wastewater effluent samples and the removals were 90% and 51% for WW-1 and WW-2, respectively.

In the surface water SW-1 sample, the removal was 51%; however, no removal was observed for the SW-2 sample.

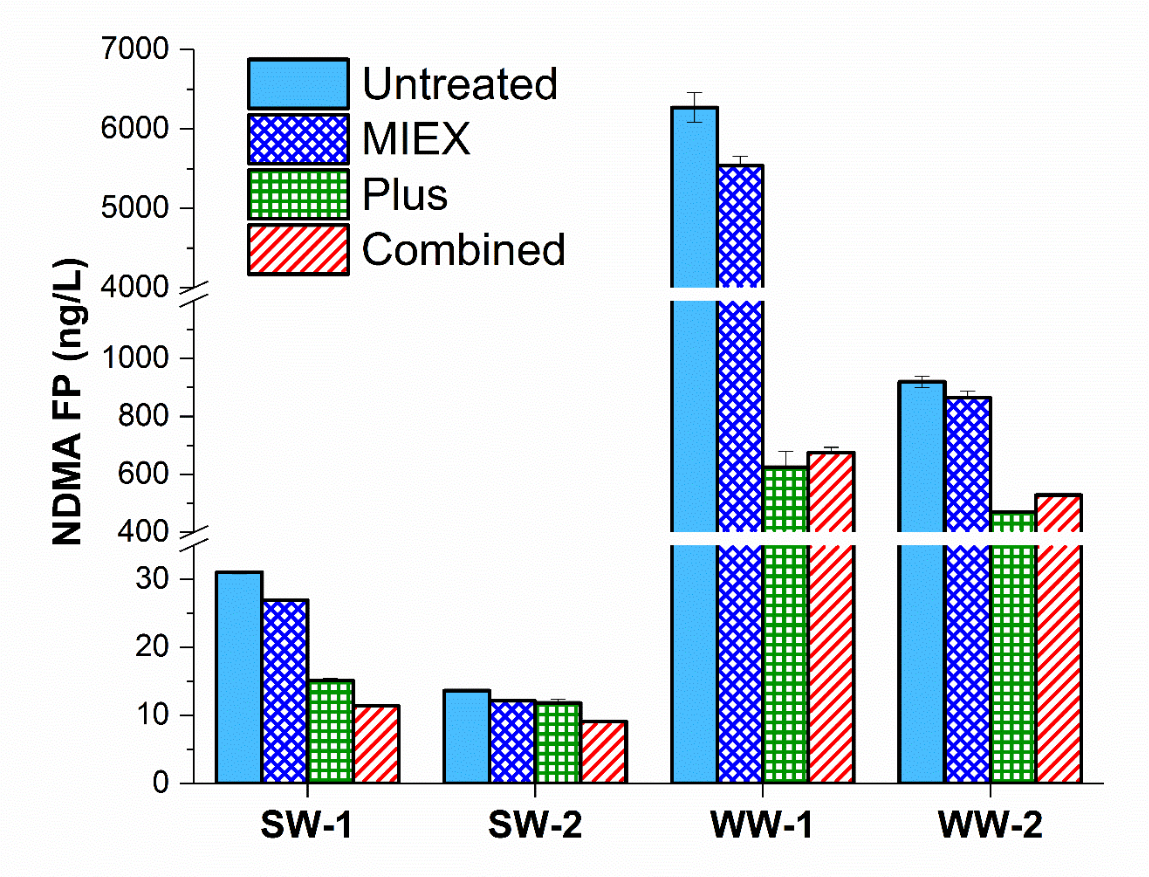


Figure 3–1. Control of NDMA FP with ion exchange resins in wastewater effluent and surface water samples. Error bars represent the standard deviation of two injections of one sample.

These results provide evidence that in the examined waters as much as 50% or more of the NDMA precursors are positively charged, in agreement with literature findings (Chen et al., 2014; Hanigan et al., 2016; S. Li et al., 2017; Liao et al., 2015b). Hence, the positively charged NDMA precursors can be exchanged by sodium ions in the cation exchange resin. During the ion exchange process cations or positively charged molecules (e.g., NDMA precursors) in the aqueous phase are exchanged for the mobile counter ions (i.e., Na^+) associated with the fixed charged functional groups in the three-dimensional, crosslinked polymer matrix. The counter ions are associated by electrostatic attraction to each of the charged functional groups to satisfy the criterion that electro-neutrality is maintained at all times within the exchange material as well as in the bulk aqueous solution. The schematic framework of a synthetic organic cation exchange resin immersed in an aqueous solution containing cation B^+ with its counter ion X^- is illustrated in Eq. 3–1:

$$R^-A^+ + B^+X^- \leftrightharpoons R^-B^+ + A^+X^- \qquad \text{Eq. 3–1}$$

The cation B^+ in water is exchanged by the cation A^+ on the resin. The driving force of the ion exchange process is the electric potential difference between the bulk solution and the resin, called the *Donnan* potential (Helfferich, 1962). The competition effect rises from the presence of different cations in the water that show different affinity for the exchange sites in the cation exchange resin.

The concentrations of calcium in WW-1 and WW-2 samples were 12 and 60 mg Ca^{2+}/L, respectively, which may explain the lower removal of NDMA FP observed in WW-2 compared to WW-1. A high concentration of calcium ions in the background water increased the competition effect for exchange sites in the Plus resin. This will be further discussed in section 3.3.4. The lack of NDMA FP removal observed after the Plus resin treatment for SW-2 was likely related to the absence of cationic precursors, and also very small initial NDMA FP concentration (14 ng /L, Table 3–1).

Applying Plus resin simultaneously with MIEX produced similar NDMA FP removals (43-85%) to Plus alone (51–90%) (Figure 3–1). In contrast, MIEX resin alone barely removed NDMA precursors (<5%). MIEX lowered the THMs precursors concentration ranging from 41% to 69%, similar to the reduction after the combined resins treatment (39-65%) (Figure 3–2). These results are consistent with previously reported THMs precursors removals achieved by MIEX (Boyer and Singer, 2005; Gan et al., 2013a; Singer et al., 2007; Wert et al., 2005).

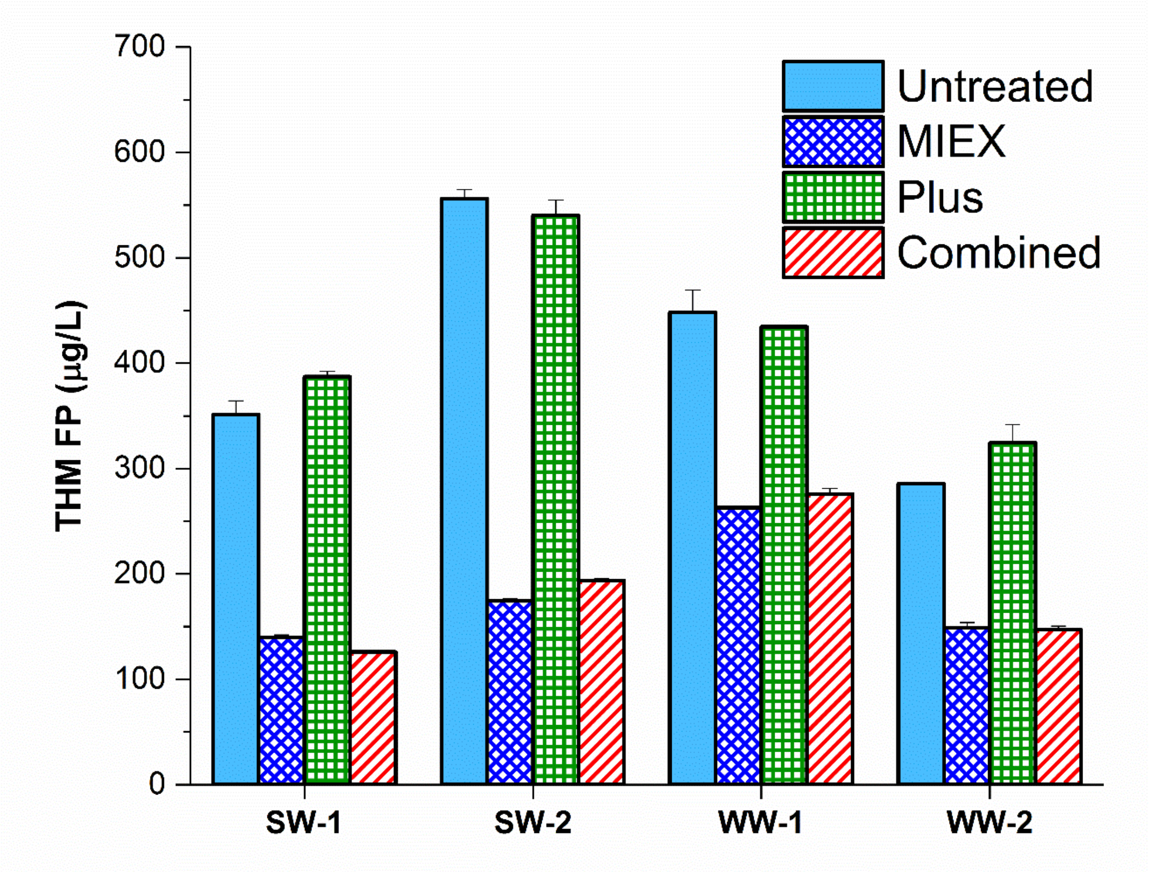


Figure 3–2. Control of THMs FP with ion exchange resins in wastewater effluent and surface water samples. Error bars represent the standard deviation of two injections of one sample.

These results showed that there was no interaction between the anionic and cationic resins in the tested waters, suggesting that Plus and MIEX resins can be used to effectively control NDMA and THMs precursors concurrently. Additional experiments were conducted and the precursors were measured under UFC and FP conditions. Selected characteristics of the waters, as well as NDMA and THM formation are presented in Table A–1. The removals of NDMA precursors were 25–27% (UFC) and 44–48% (FP) while for those of THMs were 42–48% (UFC) and 25–31% (FP). Overall the results confirm that in practical drinking water treatment disinfection conditions the mixed system of resins is effective in controlling both NDMA and THM precursors. The extent of the removal of NDMA precursors with Plus resin may also be determined by other factors, such as the nature of the precursors, and the presence of cations that are able to compete for the exchange sites in the resin. These factors are discussed in the following sections.

3.4.2 Effect of the wastewater content

Another objective was to assess the impact of wastewater content on the efficiency of the ion exchange process to remove both NDMA and THM precursors. For this purpose, two sets of samples were prepared in the laboratory by mixing wastewater effluent with surface water at different ratios (0%, 10%, 50% and 100% wastewater). One set of samples was treated the same day with the ion exchange resins, and the second group was used for the simulated natural attenuation of precursors experiment. The measured NDMA FPs in the fresh samples were 11, 706, 3113, and 6544 ng/L, respectively, and the results including the resin treatments are presented in Figure 3–3.

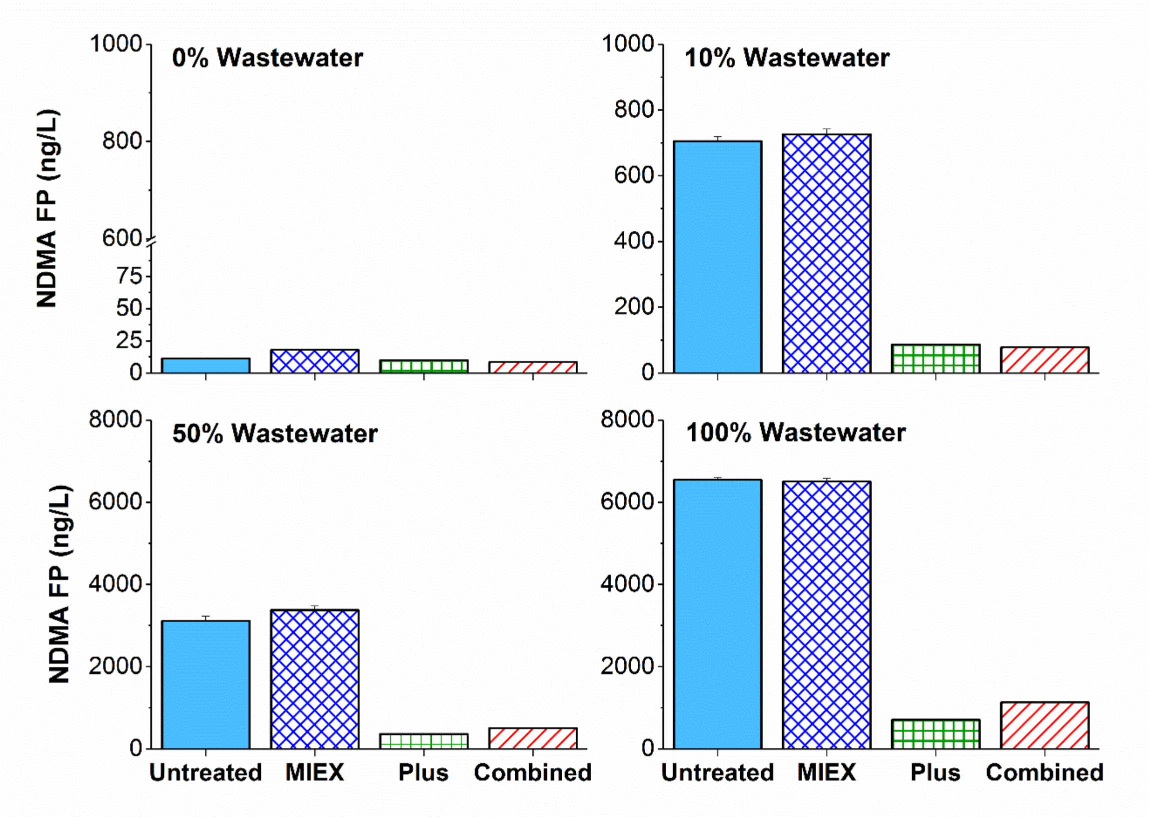


Figure 3–3. Effect of wastewater impact on the control of NDMA FP with ion exchange resins. Error bars represent the standard deviation of two injections of one sample.

The treatment of samples containing wastewater effluent with Plus resin, both alone and combined with MIEX resin, decreased the concentration of NDMA precursors regardless of the initial concentration of the precursors. The removal rate was higher than 88% for Plus resin, and ranged from 83% to 89% for the combined resins. However, Plus resin, both alone and combined with MIEX resin, had no effect on the surface water (0% wastewater). This indicates an absence of a significant amount of positively charged NDMA precursors in the surface water sample tested. The concentration of calcium ion in the wastewater effluent (100% wastewater) was 12.8 mg/L which means that the cation exchange capacity occupied was 1.8 meq. The available cation exchange capacity is orders or magnitude larger than the levels of concentration of the NDMA precursors that are in the range of ng/L, hence the available cation exchange capacity of 7.7 meq was high enough in all the cases to remove the amenable fraction of NDMA precursors in the wastewater effluent and the blended samples.

MIEX resin alone increased the measured NDMA FP to 6 ng/L in the surface water and up to 266 ng/L in the wastewater and wastewater impacted samples (10, 50 and 100%). Previous studies found that manufacturing impurities present in fresh anion exchange resins released NDMA precursor but the levels subsided with increasing bed volumes of rinsing with DDI (Flowers and Singer, 2013; Gan et al., 2013a, 2013b). Since experiments were conducted with 600 BV rinsed resins, the increase in NDMA precursors after the treatment of the wastewater effluents with the rinsed MIEX resin is not clear yet. Elucidating the factors that contribute to the increase in NDMA precursors after MIEX treatment was beyond the scope of this study.

Figure 3–4 shows the results of the ion exchange treatments on THMs precursors. The initial concentrations of THMs ranged from 118 to 285 μg/L. As previously reported (Boyer and Singer, 2005; Gan et al., 2013a; Singer et al., 2007; Wert et al., 2005), MIEX resin substantially lowered THMs precursors in the examined waters, and the removals ranged from 41% to 58%. Similarly, MIEX resin combined with Plus resin reduced THMs precursors (48-57%). Plus resin had no impact on negatively charged precursors.

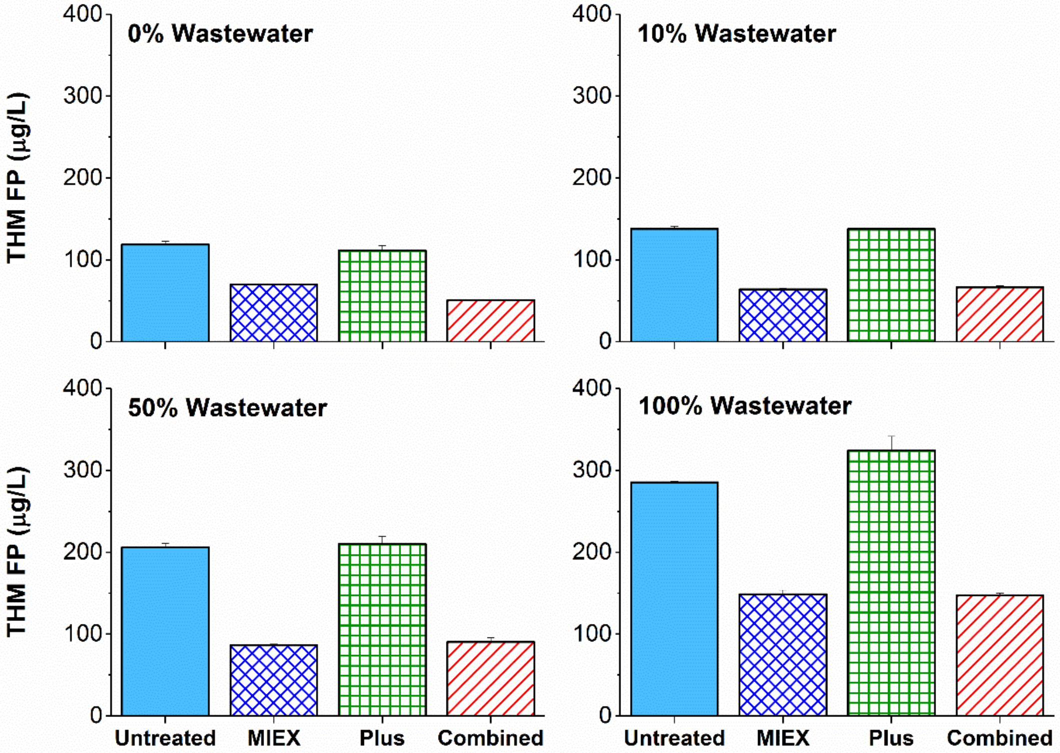


Figure 3–4. Effect of wastewater impact on the control of THMs FP with ion exchange resins. Error bars represent the standard deviation of two injections of one sample.

3.4.3 Effect of the simulated natural attenuation of DBPs precursors

NDMA precursors in fresh wastewater effluents experience photolytic reactions and microbial degradation (Beita-Sandí et al., 2016; Chen et al., 2009; Krasner et al., 2008; Pehlivanoglu-Mantas and Sedlak, 2006; Woods and Dickenson, 2016) that lead to less reactive precursors found in most surface waters. These changes may influence the removal of NDMA precursors by a cation exchange resin.

The natural attenuation of NDMA precursors and their removal with Plus resin were evaluated with samples with different WW impacts (0%–100%) exposed to sunlight. First, the concentration of NDMA FPs decreased after the attenuation experiment, ranging from

35% to 65% in the wastewater effluent samples. NDMA FP removals with Plus resin in the WW-impacted samples (73%–85%) (Figure 3–5), both alone and combined with MIEX resin were similar to the removals in the fresh wastewater effluent samples. Previous natural attenuation experiments, in similar conditions as conducted here (Beita-Sandí et al., 2016), showed that the reactivity of NDMA precursors decreased with increasing exposure to sunlight and formed less NDMA. Therefore, the small increase (7 ng/L) in the NDMA FP observed in the surface water (0% wastewater) after the natural attenuation experiment was attributed to the experimental variability.

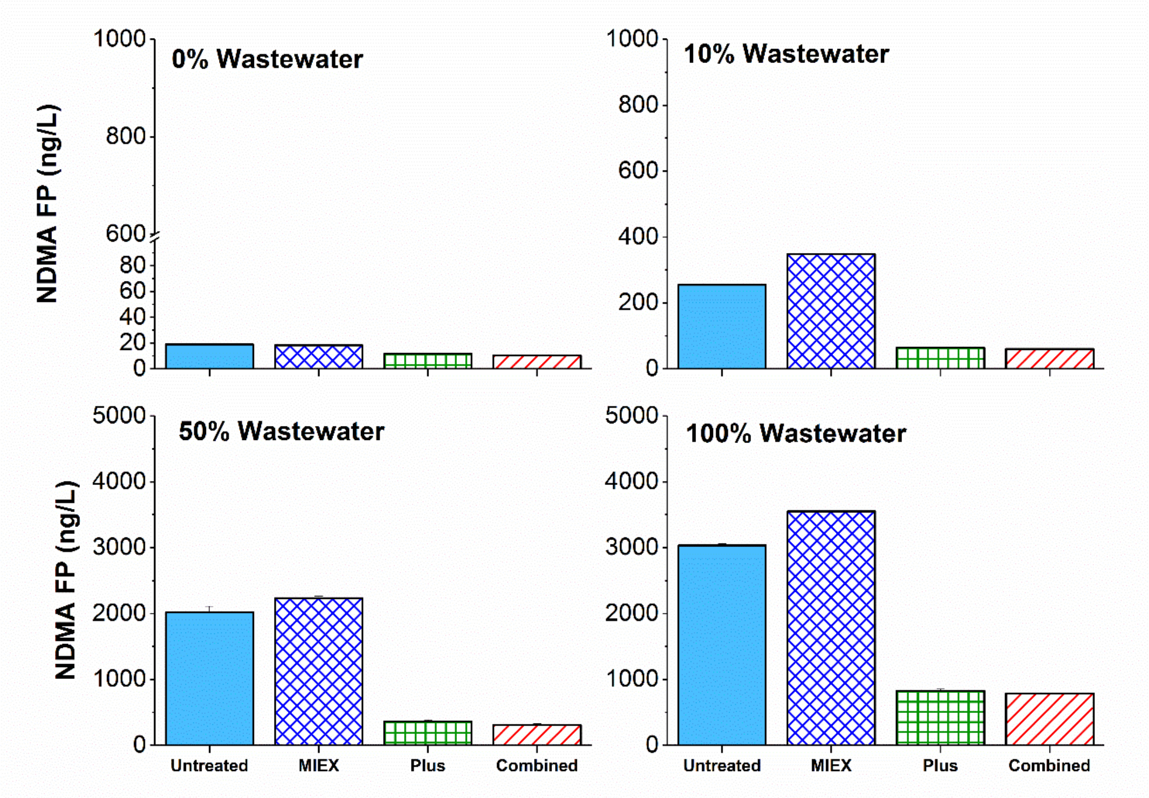


Figure 3–5. Effect of natural attenuation of wastewater-derived NDMA precursors on the control of NDMA FP with ion exchange resins. Error bars represent the standard deviation of two injections of one sample.

Though overall the reactivity of NDMA precursors decreased, the results demonstrated that a substantial portion of the naturally attenuated precursors preserved their cationic nature. The possibility of removing NDMA precursors with the cation exchange resin relies on the cation nature of the precursors. The protonation of the nitrogen in the $(CH_3)_2$–N moiety impose the positive charge to the precursors. Therefore, the similar removals of NDMA precursors in the fresh and attenuated experiments suggest that the dimethylamine moiety [$(CH_3)_2$–N] is conserved after the transformation of the precursors. In a previous study, irradiation of ranitidine, a potential NDMA precursor, in environmental-like conditions yielded two main photoproducts and both kept the $(CH_3)_2$–N moiety (Isidori et al., 2009).

The wastewater effluent comprises components that are not removed during the wastewater treatment included the organic nitrogen-containing NDMA precursors and the more recalcitrant non-biodegradable organic matter (Imai et al., 2002; Shon et al., 2006). Consequently, natural attenuation had minimal effect on the reactivity of the highly refractory NOM fraction (THMs precursors) (Figure 3–6). Similar removals were achieved either with MIEX resin alone or the combined resins (43-59%). Overall, the results indicated that even after some natural attenuation processes NDMA and THMs precursors can be simultaneously removed in a single ion exchange process that combines both cationic and anionic exchange resins.

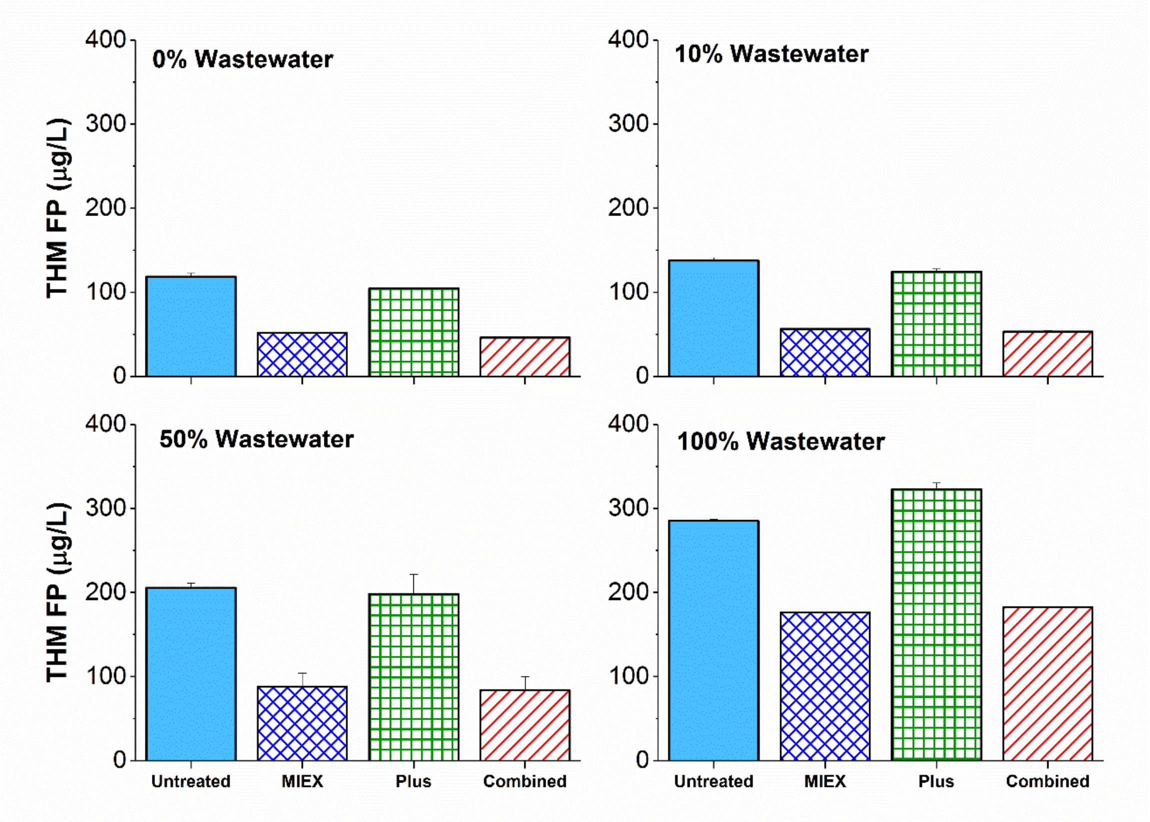


Figure 3–6. Effect of natural attenuation of wastewater-derived THMs precursors on the control of THMs FP with ion exchange resins. Error bars represent the standard deviation of two injections of one sample.

3.4.4 Effect of competing ions on the removal of NDMA precursors

The effect of background water containing competing ions on the removal of NDMA precursors with the cation exchange resin was investigated; calcium was selected as the main cation because is a prevalent constituent in most surface waters and is more abundant than other common cations (e.g., Mg^{2+}, K^{+}, Na^{+}). NDMA precursors in the presence of calcium ions are of concern because of the competition effect for exchange sites in the cation exchange resin. To assess the competing effect of calcium ion on the removal of NDMA precursors with Plus resin, a wastewater effluent sample was used. The ambient calcium concentration in the wastewater effluent samples was 8.8 mg /L and was later enriched with calcium chloride to 91.2 mg/L.

Based on the total ion exchange capacity of Plus resin, the estimated concentration of calcium that could be removed in 600 BV treatment was 63.2 mg/L. Since the initial concentration of calcium was 91.2 mg /L, then the predicted concentration of calcium after Plus treatment was 28 mg/L. The total hardness concentrations in the hard water sample after treatment with both Plus resin alone and combined with MIEX resin were 32 and 25.6 mg/L, respectively. The difference between the predicted and measured calcium concentration (± 4 mg/L) is due to the assumption that all sites in the resin are available for exchanging sodium ions for calcium, but in reality, the operational capacity is smaller than the total exchange capacity.

The effect of increasing the concentration of calcium in the wastewater effluent during the removal of NDMA FP with the ion exchange resins is presented in Figure 3‒7. The Plus resin removed 52% of NDMA FP alone and 58% in combination with MIEX resin at 8.8 mg Ca/L. The increase in the calcium concentration from 8.8 to 91.2 mg/L lowered the removal of NDMA FP from 52-58% to 24%. This indicates that the Plus resin preferentially removed calcium over the NDMA precursors. The usage of the cation exchange capacity of Plus resin was estimated based on the ion exchange capacity reported by the manufacturer (1.9 meq/mL). At the higher calcium concentration, there was little capacity for NDMA precursors removal (7%) (Figure 3–8).

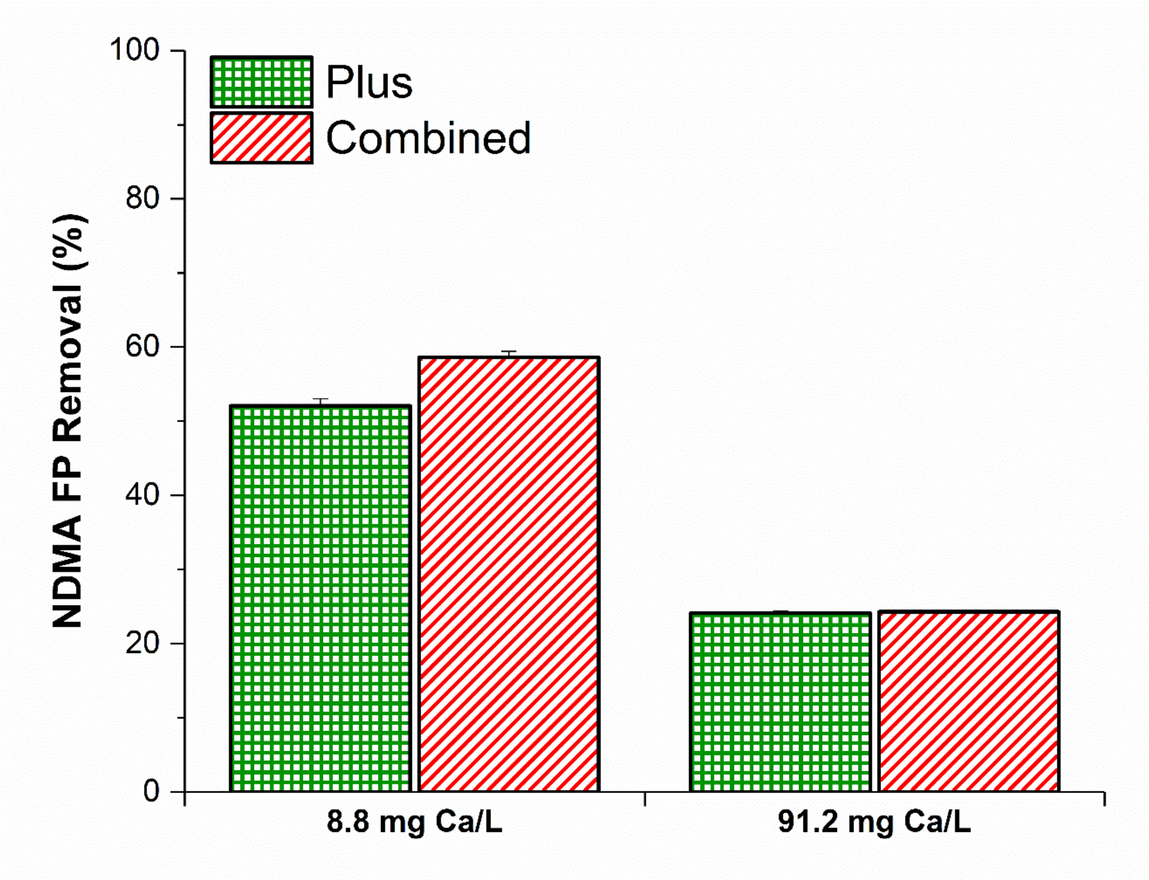


Figure 3–7. Effect of calcium ion on the control of NDMA FP with cation exchange resin in wastewater effluent. NDMA FP removals are compared to the untreated water. Error bars represent the standard deviation of two injections of one sample.

The percent of the available capacity that was used by NDMA precursors exchange cannot be estimated since NDMA FP represents a complex mixture of NDMA precursors with an unknown charge distribution required to estimate the concentration in meq. The cation exchange capacity used in the enriched wastewater sample by calcium was 93%, leaving only 7% available for NDMA precursors control. Despite the concentration of calcium ions being orders of magnitude higher than the NDMA precursors (mg vs. ng), still, some exchange sites in the cation exchange resin were available to exchange NDMA precursors. Although not tested in this study, reducing NDMA FP in hard waters will likely require either using elevated resin levels to remove both calcium and NDMA precursors or reducing the hardness level prior to using Plus resin for the NDMA precursor removals.

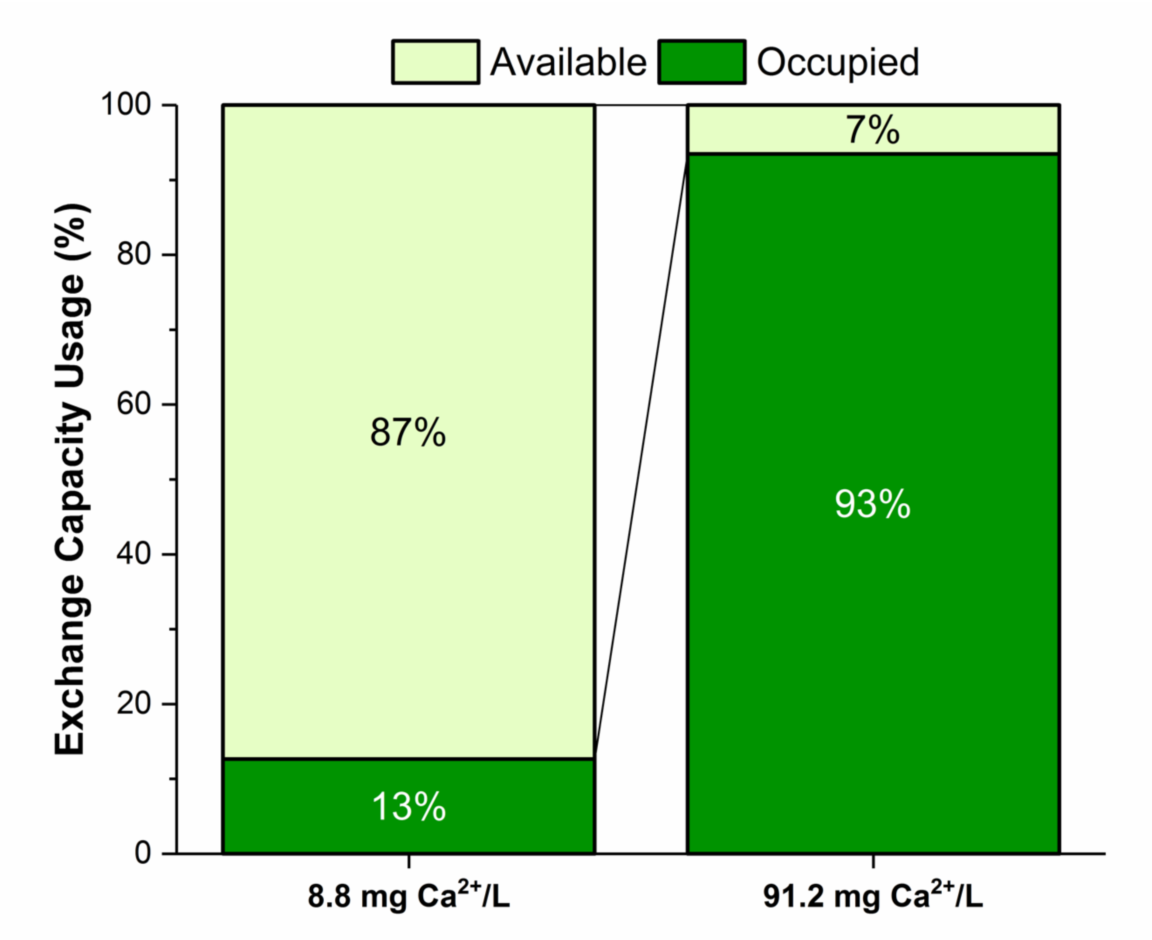


Figure 3–8. Effect of calcium ion on the control of NDMA FP with cation exchange resin (Plus) in a wastewater effluent. The exchange capacity usage is determined based on the total ion exchange capacity of the Plus resin reported by the manufacturer (1.9 meq/mL) and the resin dose used in this experiment (5 mL).

3.5 Conclusions

The simultaneous control of NDMA and THMs precursors with ion exchange resins was investigated. The combined application of Plus and MIEX resins effectively controlled concurrently NDMA and THMs precursors, under the test conditions no interaction between the ion exchange resins was found. Plus resin removed NDMA precursors to a different extent in surface and wastewater effluent samples and produced similar results when it was simultaneously applied with MIEX resin. MIEX resin alone and combined with Plus resin lowered the THMs precursors concentration ranging from of 39% to 69%. Plus resin alone and combined with MIEX resin reduced the concentration of NDMA precursors regardless of the initial concentration of the precursors. In naturally attenuated wastewater effluents, the fraction of precursors removed with both the Plus alone and combined was similar to the fresh wastewater effluent samples. Natural attenuation decreased the reactivity of NDMA precursors but their cationic nature was preserved. I found that a high concentration of calcium in the wastewater effluent reduced the ability of the cation exchange resin to remove NDMA precursors.

CHAPTER FOUR

FACTORS AFFECTING THE CONTROL OF *N*-NITROSODIMETHYLAMINE AND TRIHALOMETHANES PRECURSORS WITH ION EXCHANGE RESINS

4.1 Abstract

The main goal was to investigate the factors that may influence the capability of ion exchange resins (i.e., pH and competing ions) to control NDMA and THM precursors. Further experiments were conducted to address the release of NDMA precursors from the cation exchange resin. NDMA precursors were removed at both acidic and neutral conditions, indicating that the precursors were protonated at these pH ranges. In contrast, NDMA precursors were not removed at pH 10. Also, increasing the pH to 10 promoted the release of NDMA precursors from the Plus resin either in distilled deionized water or natural waters. Plus resin and the combined treatment removed NDMA precursors in the wastewater with naturally occurring levels of the selected inorganic ions. However, NDMA FP increased in the enriched wastewater after the treatment with the cation exchange resin. This effect was specific to the Plus resin since similar experiments with the commercial Purolite® cation exchange resins did not increase the NDMA FP after treatment. The removals of THM precursors by the anion exchange resin were affected by the elevated sulfate concentrations in the amended water. Bromide was not removed in either the ambient or the enriched wastewater effluent sample while nitrate was removed only in the unamended wastewater sample. In the presence of high levels of calcium, the Plus exchange resin released NDMA precursors. The amount of NDMA precursors that were released from the Plus resin increased with the calcium concentration. However, NDMA

FP levels subsided with increasing the number of regeneration cycles and approached the level of the DDI water.

4.2 Introduction

Disinfection of drinking water and wastewater has been proven to be one of the largest public health achievements by reducing cholera, polio, typhoid, hepatitis, and a number of other bacterial, viral, and other waterborne parasitic diseases (Voukkali and Zorpas, 2015). Unfortunately, the unintended consequence is the formation of undesired disinfection byproducts (DBPs) owing to the reactions between disinfectants and natural organic matter (NOM) in water (Liu and Croué, 2016; Richardson et al., 2007). Among the various DBPs, the most recognized species are trihalomethanes (THMs) and haloacetic acids (HAAs) which are currently regulated by the US Environmental Protection Agency (EPA). Due to stringent THM and HAA regulations, the use of chloramines has increased during the last years (Diehl et al., 2000; Li, 2011). Although chloramine can effectively control the formation of both THMs and HAAs DBPs, chloramine forms its own suite of DBPs, e.g., *N*-nitrosamines including *N*-nitrosodimethylamine (NDMA) (Choi and Valentine, 2002; Le Roux et al., 2011; Mitch et al., 2003a; Mitch and Sedlak, 2004). NDMA is a probable human carcinogen with a calculated lifetime cancer risk of 10^{-6} at a concentration of 0.7 ng/L in drinking water (US EPA, 1993b). NDMA is included in the U.S. EPA fourth Contaminant Candidate List in consideration for its potential regulatory determination (Khiari, 2017; Russell et al., 2017)

The pool of NDMA precursors includes amine-containing coagulation polymers, effluent-impacted waters, pharmaceuticals, personal care products, herbicides, insecticides and pesticides, anion exchange resins, and gasket materials in the distribution systems (Krasner et al., 2013). All of these precursors have dimethylamino (DMA) as a common moiety that can lead to formation of NDMA during chloramination (Li et al., 2017; Spahr et al., 2015). During a typical water treatment, common strategies to control NDMA formation require removing NDMA precursors directly or transforming NDMA precursors with alternate oxidants prior to chloramination.

Natural organic matter (NOM) in aquatic environments is mainly composed of humic substances (Leenheer and Croué, 2003). Humic substances include refractory anionic macromolecules that contain both aromatic and aliphatic components with primarily carboxylic (accounting for 60–90% of all functional groups) and phenolic functional groups. Hence at the pH range of natural waters (6–8), humic substances are negatively charged (Hong and Elimelech, 1997). In contrast, most NDMA precursors are amine-based compounds that under environmentally relevant pH conditions are positively charged due to the protonation of the DMA moiety (Beita-Sandí et al., 2016; Hanigan et al., 2016; Le Roux et al., 2012a; Li et al., 2017; Liao et al., 2015b; Liu et al., 2014; Selbes et al., 2014). Therefore, the use of anion exchange resins would provide ineffective removals of such NDMA precursors (Gan et al., 2013a, 2013b). On the other hand, the use of cation exchange resins can be a promising treatment technique to remove amine–based NDMA precursors.

Ion exchange processes play an important role in water treatment; particularly, the use of anion exchange resins is an efficient technique for the removal of NOM, which is the major component of sources of THMs and HAAs precursors. The effectiveness of the treatment is strongly influenced by the available exchange capacity of the resins, the presence of competing ions, and the source water pH. Magnetic ion exchange (MIEX) resins can selectively remove NOM (Bolto et al., 2004; Cornelissen et al., 2008; Gan et al., 2013a; Kitis et al., 2007), particularly in raw waters with a high aromaticity (high specific UV absorbance (SUVA) values) and low anionic strength (Boyer and Singer, 2005; Singer and Bilyk, 2002). MIEX resins showed the greatest affinity for NOM fractions with high charge density (Boyer et al., 2008). However, NOM removal by MIEX resins was affected by the presence of sulfate due to the high selectivity of MIEX resins for sulfate (Fu and Symons, 1990). For instance, the removal of NOM in low SUVA waters decreased from 60% to 20% as sulfate increased from 17 to 600 mg/L (Ates and Incetan, 2013). Monovalent ions such as bicarbonate, nitrate, and bromide did not influence the NOM removal during the MIEX process (Ates and Incetan, 2013).

NDMA precursors found in secondary and tertiary wastewater effluents have proven to behave to some extent as organic cations (Chen et al., 2014; Hanigan et al., 2016; Liao et al., 2015b). The cationic behavior is due to the protonation of the DMA moiety that occurs in the amine–based NDMA precursors at pH below the corresponding pKa values. It was reported that a strong cation exchange resin removed DMA and ranitidine, and seven other NDMA model precursors compounds (S. Li et al., 2017) in distilled and deionized (DDI) water, which might suggest that at neutral pHs these precursors are positively charged. Recently, Beita-Sandí and Karanfil (2017) reported that the use of mixed cation and anion exchange resins can efficiently control simultaneously NDMA and THM precursors. However, further research is needed for understanding the factors affecting their performance. The main goal of the present work was to investigate the factors that may influence the capability of ion exchange resins (i.e., pH and competing ions) to control NDMA and THM precursors. First, the impact of the pH on the removal of NDMA precursors using ion exchange resins in different water matrices was assessed. Second, a secondary wastewater effluent sample with ambient and enhanced concentrations of calcium, bicarbonate, bromide, and sulfate was used to challenge the performance of the ion exchange treatment. Further experiments were conducted to address the release of NDMA precursors from the cation exchange resins.

4.3 Materials and methods

4.3.1 Source water

Water samples were collected from two municipal wastewater treatment plants (WW-1 and WW-2) located in South Carolina, USA. At each wastewater treatment plant, wastewater samples were collected following secondary stage treatment and prior to disinfection by UV. Upon collection, samples were transported to the laboratory, filtered with 0.45 µm pore size Whatman™ Polycap 150 TC filters (Pittsburgh, PA, USA), and stored at 4 °C until experiments were conducted (maximum storage time of three days).

4.3.2 Chemicals and reagents

NDMA calibration solutions were prepared with a certified reference material containing nine *N*-nitrosamines (2000 μg/mL each component in methanol, 502138, Supelco, 99.9%). Calibration curves for NDMA included at least seven calibration standards in the range of 0.5–800 ng/L, and the minimum reporting level (MRL) was 0.5 ng/L. THM calibration standards were prepared in DDI water with a THMs calibration mix (2000 μg/mL each component in methanol, 4M8140-U, Supelco, min. 99.4%), then the aqueous standards were extracted in methyl t-butyl ether (MTBE) (Omnisolv, min. 99.5%). Calibration curves for THMs included six standards, ranging from 1 to 500 μg/L and the MRL was 1 μg/L.

Chlorine stock solutions were prepared by diluting Baker Analyzed® Reagent sodium hypochlorite solution (Center Valley, PA, USA) in DDI, and preformed monochloramine stock solutions were generated by slowly mixing sodium hypochlorite in an ammonium sulfate solution at a chlorine to nitrogen mass ratio of 4.75:1 at pH 9 (Hong et al., 2007). All the disinfectant stock solutions were prepared on the day of use and used immediately after preparation.

Sodium sulfite (Na_2SO_3) solutions were prepared by dissolving 10 g of Na_2SO_3 (Mallinckrodt 99.9%) in 100 mL DDI water. Sodium thiosulfate anhydrous (Amresco, min. 98.3%) was used to quench the residual monochloramine. $CaCl_2.2H_2O$ (>99.0%), $NaHCO_3$ (99.5–100.5%), NaBr (min. 99.0%), $NaNO_3$ (>99.0%) and Na_2SO_4 (>99.0%) purchased from Sigma–Aldrich (St. Louis, MO, USA) were used to prepare aqueous solutions of Ca^{2+}, HCO_3^-, Br^-, NO_3^- and SO_4^{2-} respectively.

4.3.3 Ion exchange treatments

Two types of resins were used in the experiments, a strong acid cation (Plus) and a strong base anion (MIEX) exchange resin obtained from Ixom Watercare Inc. (Centennial, CO, USA). The characterization of the ion exchange resins is presented in Table 4–1.

The waters were treated with 5 mL of the resins. The resin doses were measured at least 30 min before each experiment to achieve the 5 mL settled resin volume. A multiple–loading approach was conducted using a Phipps & Bird jar tester (Richmond, VA, USA). Initially, the resin was mixed with one liter of sample water at the rate of 150 rpm for 15 min. After stopping the mixer, the resin was allowed to settle for 2 min. The treated water was decanted into a 5 L glass carboy while the resin was retained in the beaker. During the first cycle, a 200 bed volume (BV = 1000 mL / 5 mL = 200) treatment was achieved. Two additional cycles were repeated to complete 600 BV. A composite sample was prepared by mixing the water of each treatment cycle. Samples were filtered through pre-rinsed 0.45 µm Pall membrane filters (Port Washington, NY, USA) to remove any resin particles.

Table 4–1. Characterization of the ion exchange resins.

Parameter	Cation Exchange Resin	Anion Exchange Resin
Commercial name	Plus	MIEX
Type	Strong acid	Strong base
Functional group	Sulfonate	Quaternary ammonia
Polymer	Polystyrene	Polyacrylate
Exchange capacity (meq/mL)	1.9	0.42
Form	Sodium	Chloride
Matrix	Macroporous	Macroporous

4.3.4 Experimental procedure

Ion exchange experiments were conducted with secondary wastewater effluents, blends of surface water and secondary wastewater effluents, and with DDI water. Unless specified otherwise, the pH of the samples was adjusted to 7 with NaOH (1 M) or HCl (1 M) and treated in 600 BV. Further details are provided as follows.

- **Effect of pH:** The pH of the secondary wastewater effluents and the blended samples was adjusted to 5, 7 and 10 with NaOH (1 M) or HCl (1 M). The pH was monitored during the treatment and adjusted as needed. NDMA FPs in the samples treated with MIEX and Plus were measured after five days of contact time with 100 mg Cl_2/L preformed monochloramine. The samples were treated with MIEX and Plus; NDMA formation potential (FP) was measured after the treatments. Similar experiments also were conducted in DDI water with both resins.
- **Challenged treatment scenario:** In this experiment, a secondary wastewater effluent sample with naturally occurring concentrations of calcium, bicarbonate, bromide and sulfate was enriched at the levels shown in Table 4–2. The samples were treated with Plus, MIEX, and both resins combined. NDMA FP and THM FP were measured after the treatments. Additional experiments were conducted with Purolite® (Bala Cynwyd, PA, USA) cation exchange resins in a secondary wastewater effluent with ambient and enriched concentrations of calcium.
- **NDMA precursors released from ion exchange resins**: Experiments were conducted in DDI water with naturally occurring and amended concentrations of calcium, bromide, nitrate and sulfate as shown in Table 4–2. The samples were treated with Plus

and MIEX. NDMA FP was measured after the treatments. Additional experiments were carried out to evaluate the release of NDMA precursors from the cation exchange resin with calcium concentrations ranging from 0 to 10 meq Ca^{2+}/L and treated only with Plus resin. Kinetics experiments of the release of NDMA were run in DDI water with calcium at 5 meq Ca^{2+}/L. The samples were treated in 200 BV with Plus and the release of NDMA FP was monitored within one hour of contact time. Finally, the effect of the regeneration of the cation exchange resin was performed in DDI water with calcium at 2 and 10 meq Ca^{2+}/L. The samples were treated with Plus and the release of NDMA FP was measured after the treatment. After each cycle the resin was regenerated with 10% w/v NaCl.

4.3.5 DBP formation potential tests

Formation potential tests were conducted to determine the THM and NDMA precursor levels in the water samples under excess amounts of oxidant concentrations. The oxidant concentrations for THM FP were 50 mg Cl_2/L chlorine, and for NDMA FP 100 mg Cl_2/L monochloramine. In both FP tests, 8 mM phosphate buffer solution was used to adjust the pH at 8. All samples during the FP test were stored in the dark at room temperature (22 °C ± 1 °C). After five days, the residual disinfectants were quenched adding stoichiometric amounts of sodium sulfite to the chlorinated samples and sodium thiosulfate to the chloraminated samples.

4.3.6 DBP extractions and analytical methods

For NDMA analysis, samples were fortified with 40 ng/L deuterated NDMA (NDMA-d6) (Restek, 99%) as a surrogate standard before extraction. NDMA was extracted using solid phase extraction (Beita-Sandí et al., 2016). Briefly, deuterated *N*-nitroso-di-n-propylamine (NDPA-d14) was spiked in the extracted samples as an internal standard (40 ng/L), and the volume was adjusted to 1 mL with methylene chloride. The concentrated samples were transferred to glass inserts in amber vials. One microliter of the extracted samples was injected on an Agilent 7890B (Santa Clara, CA, USA) Gas Chromatograph (GC) with DB-1701 (30 m x 0.25 mm x 1.00 μm) column coupled with an Agilent 7000C triple quadrupole mass spectrometer (MS/MS) (McDonald et al., 2012).

THMs were analyzed following the US EPA Method 551.1 (US EPA, 1990), and were reported as the sum of chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Briefly, 20 mL of each sample was extracted with 8 mL of MTBE containing the internal standard 1,2-dibromopropane and 8.5 g anhydrous sodium sulfate. Samples were shaken for 15 min at 300 rpm in a Lab–Line Orbit Shaker (Melrose Park, IL, USA). The water and MTBE phases were allowed to separate and a portion of the MTBE extract was transferred to glass inserts inside amber glass vials. Two microliters of the extracted samples and the standards were injected on an Agilent 6890 GC in splitless mode and separated on a Phenomenex ZB-1 (30 m x 0.25 mm x 1.00 μm) column.

According to Standard Methods (SM) (APHA et al., 2005), dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were measured using a Shimadzu Total Organic Carbon (TOC)-V_{CSH} coupled with a TNM-1 (SM 5310 B). Free chlorine and monochloramine were measured using the *N,N*-diethyl-*p*-phenylenediamine (DPD) ferrous titrimetric method (SM 4500-Cl F). UV absorbance was measured using a Varian Cary 50 (SM 5910), and pH using a VWR Symphony pH meter (SM 4500-H^+). Total hardness was measured using a titration method (SM 2340C). Anions were measured with a Dionex ICS-2100 Ion Chromatograph according to the US EPA Method 300.0 (US EPA, 1993a). Error bars in figures represent the standard deviation of two injections form one sample

4.4 Results and discussion

4.4.1 Effect of pH on the removal of NDMA and THMs precursors with ion exchange resins

The influence of pH on the removal of NDMA and THM precursors with ion exchange resins was investigated with secondary wastewater effluent (W1 and W2) and blended (B1 and B2) samples at pH 5, 7 and 10 (Figure 4–1). Negative NDMA FP removals occurred where the NDMA FP increased after the resin treatment.

The pH is a major factor affecting the efficiency of the ion exchange process because it determines the form of the precursor species present. Amine–based precursors would be protonated at pH below their pKa values and thus positively charged, and increasing pH over their pKa would result in deprotonated precursors in the. NDMA precursors were removed at both acidic and neutral conditions, indicating that the precursors were protonated at these pH ranges. NDMA FPs were removed after the cationic ion exchange resin (Plus) treatment at pH 5 and 7 (up to 50%). There was no significant difference in the removals of NDMA FP at pH 5 and 7 ($p > 0.05$). At pH 10, however, Plus resin was not effective in removing NDMA precursors, probably because amine-based precursors may not be positively charged, and therefore, cannot be exchanged for sodium ions in Plus resin. Instead, at pH 10, NDMA precursors were released from the Plus resins increasing NDMA

FPs. This tendency was more noticeable in the blended samples (B1 and B2) than in the secondary wastewater effluent samples.

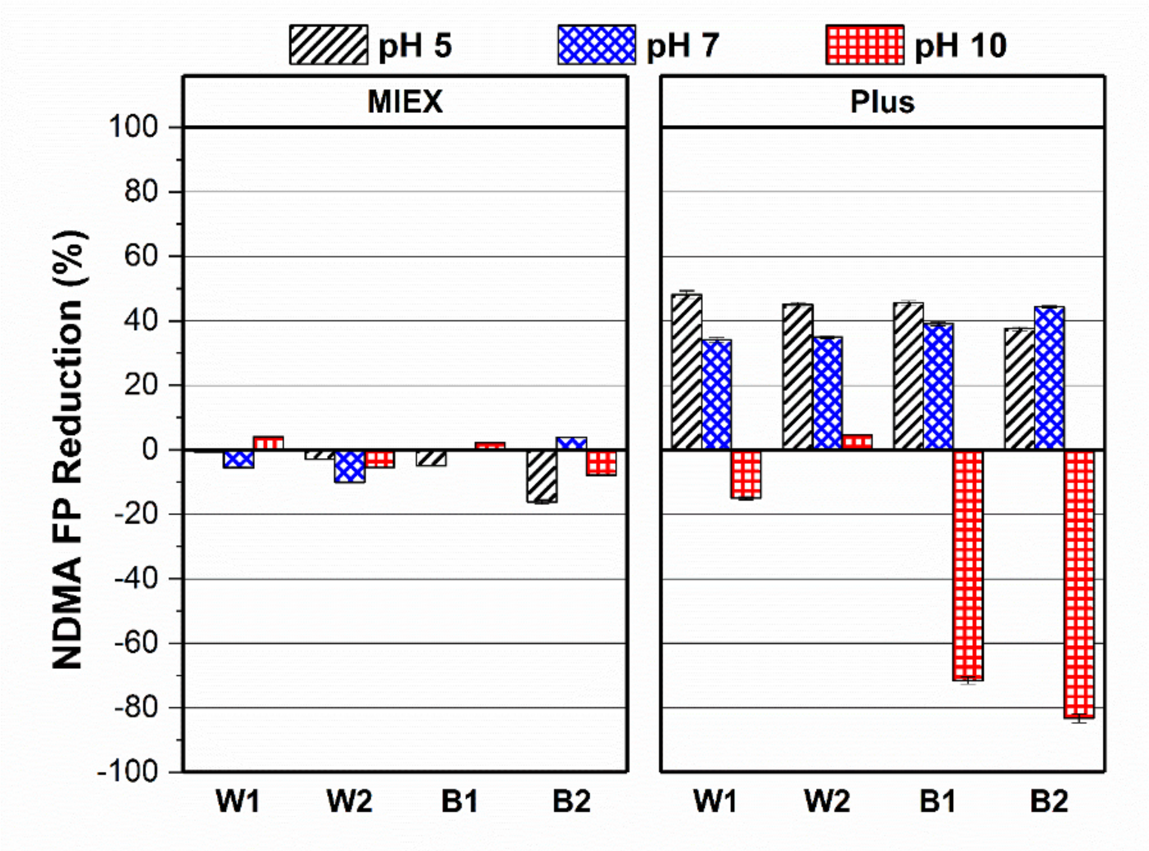


Figure 4–1. Effect of pH on the control of NDMA precursors with ion exchange resins in secondary wastewater effluent (W1 and W2) and blended (B1 and B2) samples. $[\text{NDMA FP}]_{0,\,W1}$ = 612 ng/L, $[\text{NDMA FP}]_{0,\,W2}$ = 923 ng/L, $[\text{NDMA FP}]_{0,\,B1}$ = 88 ng/L, $[\text{NDMA FP}]_{0,\,B2}$ = 144 ng/L. Experimental conditions: resin dose = 5 mL, contact time = 15 min, BV = 600. Error bars represent the standard deviation of two injections of one sample.

NDMA precursors were released from the resin, if the leaching of precursors was constant then the effect would be more prominent in waters with a low NDMA precursors background such as that in the blended samples (88–144 ng/L) as compared to the secondary wastewater effluent samples (612–923 ng/L). NDMA FP was as high as 83% of the initial concentration in B2. Unlike Plus resin, MIEX did not remove NDMA precursors effectively, and in some instances NDMA FP increased after the treatment, in agreement with previous studies (Flowers and Singer, 2013; Gan et al., 2013a, 2013b).

Since it is likely that considerable amounts of NDMA precursors are released from Plus resins at pH 10, NDMA precursor leaching from MIEX and Plus resins were further investigated in DDI water. For this purpose, DDI water was contacted with 5 mL of each resin and the pH was adjusted to 5, 7 and 10. The NDMA FPs of the DDI water were measured before (Blank) and after (Treated) the resin treatments and the results are shown in Figure 4–2. NDMA FPs measured in the blanks were in all cases < 5 ng/L. NDMA precursors (about 20 ng/L NDMA FP) also were released at pH 10 from the cation exchange resin. At pH 5 and 7 NDMA FPs were not different from the NDMA FPs in the blanks. MIEX only increased NDMA FP at pH 10 by 5 ng/L. Since the removal at pH 7 was not significantly different ($p > 0.05$) from the removal at pH 5, the former pH was selected to conduct further experiments.

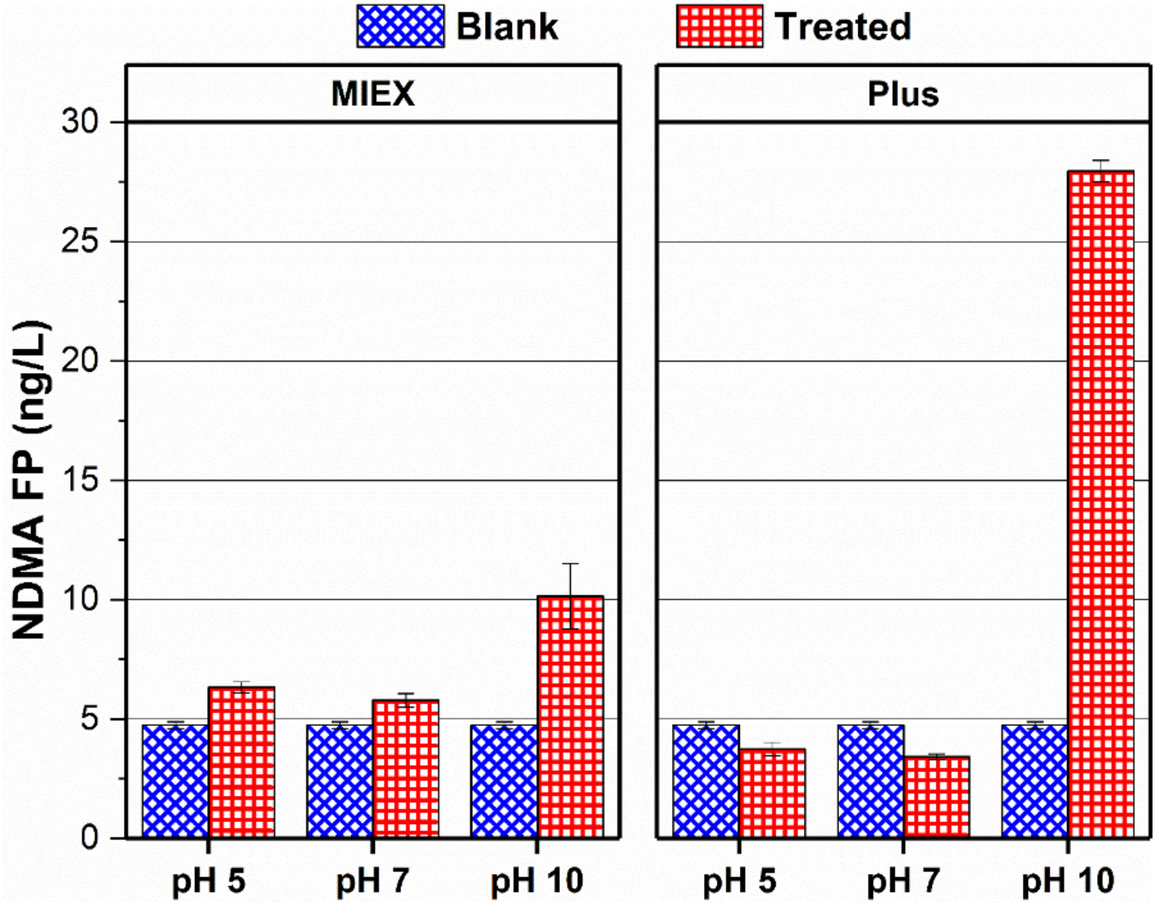


Figure 4–2. Effect of pH on the formation of NDMA FP in DDI water contacted with ion exchange resins. Experimental conditions: resin dose = 5 mL, contact time = 15 min, BV = 600. Error bars represent the standard deviation of two injections of one sample.

4.4.2 Evaluation of the ion exchange treatment in a simulated challenged treatment scenario

The simultaneous application of cation and anion exchange resins demonstrated that both NDMA and THMs precursors can be removed concurrently (Beita-Sandí and Karanfil, 2017). Here, the performance of Plus and MIEX resins in the presence of various ionic species was investigated. For that purpose, a secondary wastewater effluent sample was enriched with calcium, bicarbonate, bromide and sulfate at levels that are shown in

Table 4–2. The natural occurring concentrations of the ions were increased to challenge the performance of the resins.

Table 4–2. Selected characteristics of the secondary wastewater effluent water sample used for the ion exchange experiments.

Parameter	Naturally Occurring	Enriched
Alkalinity (mg $CaCO_3$/L)	38	120
Bromide (mg/L)	0.021	0.257
Calcium (mg Ca^{2+}/L)	15.2	112.8
DN (mg/L)	7.1	7.1
DOC (mg/L)	3.2	3.2
NDMA FP (ng/L)	715	752
Nitrate (mg/L)	20	22
pH	7.6	7.6
Specific absorbance (254 nm)	0.0859	0.0859
$SUVA_{254}$	2.68	2.68
Sulfate (mg/L)	13	265
TTHM FP (µg/L)	0.255	0.345

The samples were treated with i) Plus resin alone, ii) MIEX resin alone, and iii) both resins combined. The removals of DBP FPs as a result of these treatments are shown in Figure 4–3.

The treatment with either Plus resin alone or the combined resins removed NDMA precursors in the wastewater with naturally occurring levels of the ionic species, and the results are consistent with those in our previous study (Beita-Sandí and Karanfil, 2017). In the unamended wastewater effluent sample, 40% NDMA FP was removed by Plus alone and the combined resins; however, NDMA FP increased after the treatment of the wastewater effluent sample with higher levels of the spiked ions.

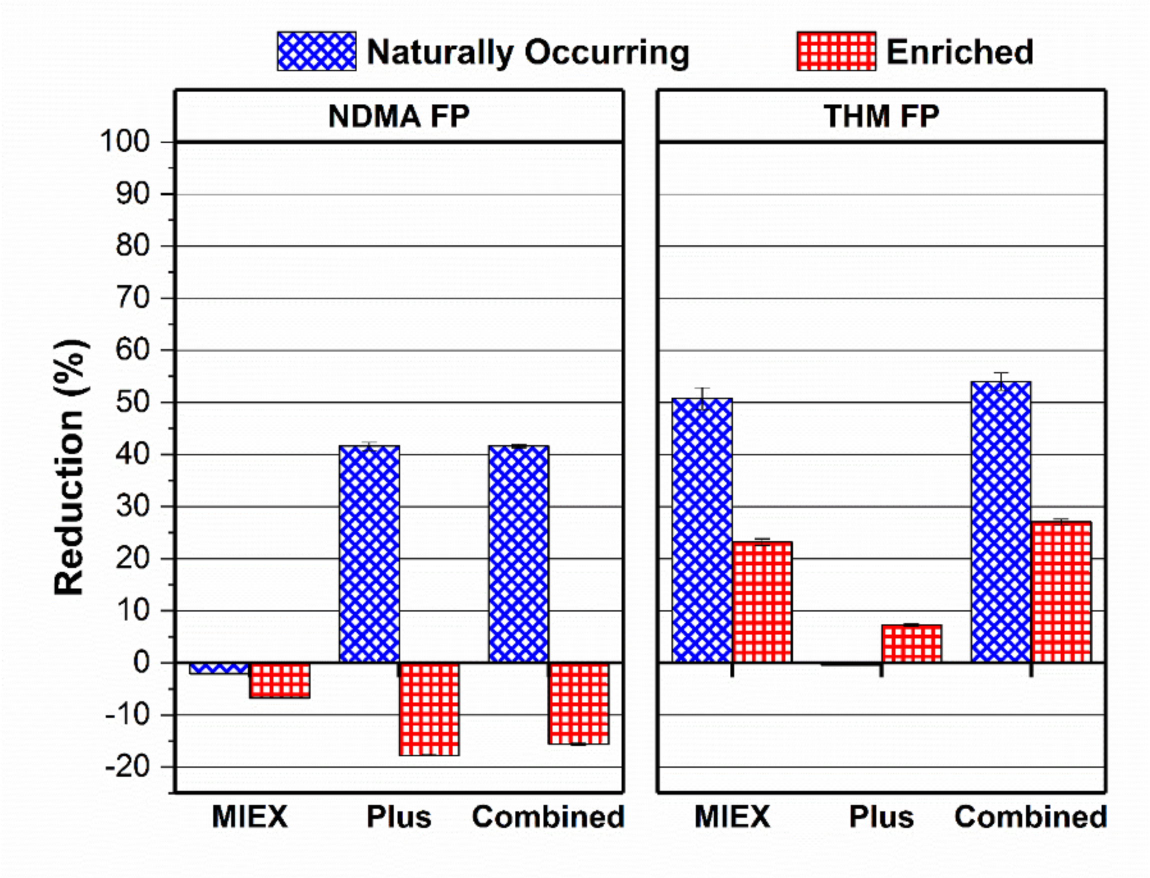


Figure 4–3. Control of NDMA and THM precursors with ion exchange resins in a secondary wastewater effluent with naturally occurring and enriched concentrations of ions (challenge treatment). $[\text{NDMA FP}]_{0,\ \text{ambient}}$ = 715 ng/L, $[\text{NDMA FP}]_{0,\ \text{enriched}}$ = 752 ng/L. Experimental conditions: resin dose = 5 mL, contact time = 15 min, BV = 600. Error bars represent the standard deviation of two injections of one sample.

The results indicate that in the presence of abundant ionic species NDMA precursors were not effectively removed and interaction between ionic species and Plus resin led to increases in NDMA precursors which may be released from resins. The naturally occurring concentration of calcium was 0.76 meq Ca^{2+}/L and decreased to < 0.1 meq Ca^{2+}/L after the treatment with Plus resin. Similarly, the spiked calcium concentration was 5.64 meq Ca^{2+}/L and decreased to 2.48 meq Ca^{2+}/L. Based on the ion exchange capacity of the Plus resin (1.9 meq/mL), the concentration of calcium after the Plus treatment was estimated as 2.47 meq Ca^{2+}/L. Therefore, one can expect that NDMA precursors are not able to be removed since most of the exchange sites in the Plus resin would be occupied by calcium ions. However, in both wastewater effluent samples the concentration of calcium was orders of magnitude higher than the NDMA precursors, and the assumption that all the sites in the resin were exchanged by calcium ions is based on the theoretical exchange capacity that might differ from the operational capacity. In practical operational conditions the capacity could be higher than the theoretical and hence some NDMA precursors removal can still occur.

THM FPs removal by MIEX and the combined resins were over 50% in the water sample with naturally occurring levels of ionic species, while only 20–30% of THM FPs removals were achieved in the enriched wastewater effluent sample. The initial DOC concentration in both samples was 3.2 mg/L, and after MIEX treatment it decreased to 1.7 and 0.7 mg/L in the ambient and the enriched wastewater effluent samples, respectively. Elevated sulfate concentrations inhibited the DOC removal by ion exchange. In this experiment, sulfate concentration was increased from 0.26 to 5.5 meq SO_4^{2-}/L and it observed that most of the exchange sites in the MIEX resin were occupied by sulfate (0.67 meq SO_4^{2-}/L) (Figure A-1). Bromide was not removed in either the ambient or the enriched wastewater effluent sample. The naturally occurring concentration of nitrate was 22 mg NO_3^-/L and was not amended in the water samples; however, nitrate was removed in the sample with ambient concentrations of ionic species but not in the enriched wastewater sample due to the high competition of sulfate. However, bicarbonate was marginally removed. The competition between NOM and sulfate is consistent with other studies that showed that anion exchange resins tend to have higher sulfate selectivity (Ates and Incetan, 2013; Boyer and Singer, 2006; Wert et al., 2005).

The increase in the NDMA FP after the resin treatment was further investigated and will be discussed in the following sections. In another experiment, a different secondary wastewater effluent with a naturally occurring concentration of calcium of 0.72 meq Ca^{2+}/L was fortified to 4.54 meq Ca^{2+}/L. Both samples were treated with different cation exchange resins available in the laboratory (C100E, C150 and SST60) from a different manufacturer (Purolite®, Bala Cynwyd, PA, USA). These resins have the same cation exchange capacity (1.9 meq/mL) and sulfonate functional group as Plus resin. Although Plus resin exhibited higher NDMA FP removal than C100E, C150 and SST60 in the sample with naturally occurring levels of calcium, Plus resin increase the NDMA FP after the treatment of the enriched sample. In contrast, the release of NDMA precursors was not observed with the C100E, C150 and SST60 cation exchange resins for the enriched sample (Figure 4–4).

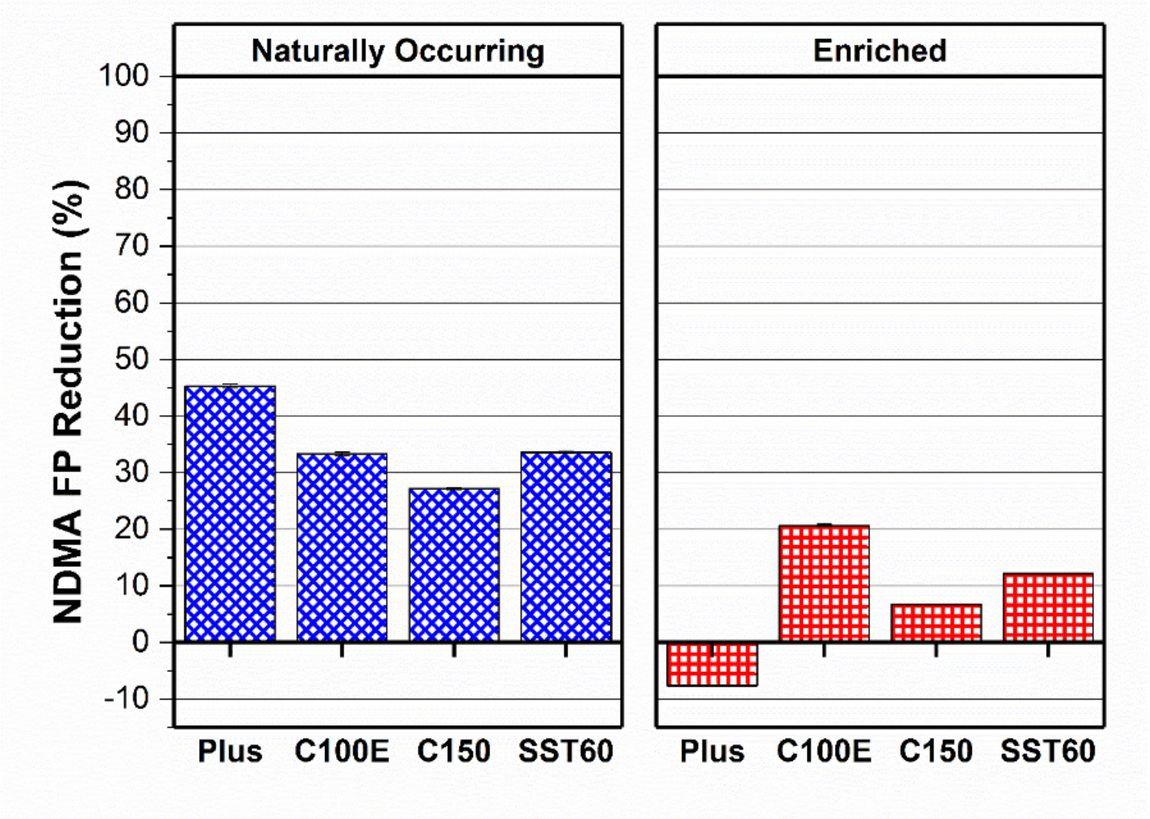


Figure 4–4. Control of NDMA precursors with cation exchange resins in a secondary wastewater effluent with naturally occurring and enriched levels of calcium ion (challenged treatment). $[\text{NDMA FP}]_{0,\text{ ambient}}$ = 582 ng/L, $[\text{NDMA FP}]_{0,\text{ enriched}}$ = 606 ng/L. Experimental conditions: $[\text{Ca}^{2+}]_{0,\text{ ambient}}$ = 0.72 meq Ca^{2+}/L, $[\text{Ca}^{2+}]_{0,\text{ enriched}}$ = 4.54 meq Ca^{2+}/L, resin dose = 5 mL, contact time = 15 min, BV = 600. Error bars represent the standard deviation of two injections of one sample.

4.4.3 NDMA precursors released from Plus resin

To further investigate the release of NDMA precursors from Plus resin, the chemical reagents used and the cation exchange resin were examined as possible sources of NDMA precursors. Solutions in DDI water containing bromide, calcium, nitrate, and sulfate were prepared individually and combined at the same concentration levels as in the enriched secondary wastewater effluent sample as shown in Table 4–2. Only NDMA FP was measured since THM precursors would not be released from the resins. NDMA FPs were measured before and after the treatment with the Plus resin, and the results are shown in Figure 4–5.

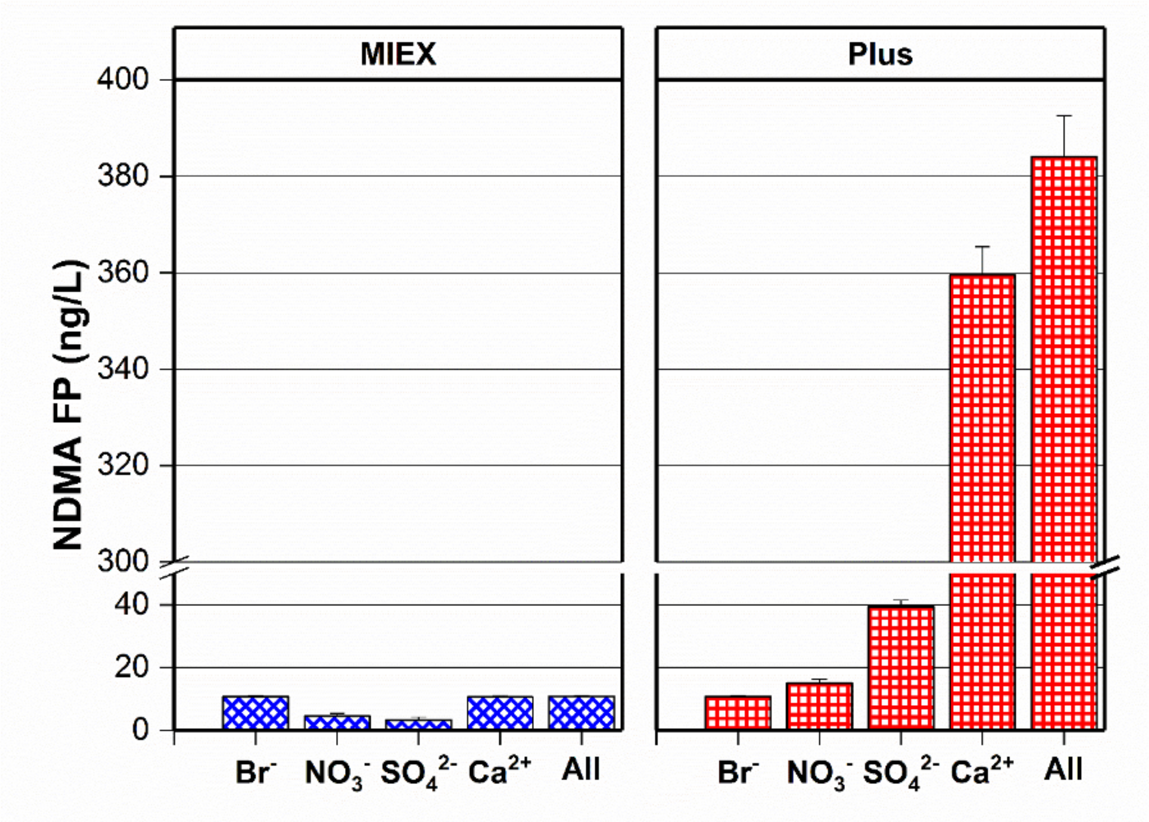


Figure 4–5. Release of NDMA precursors from the anion and cation exchange resins in contact with DDI water containing different inorganic ions. Experimental conditions: resin dose = 5 mL, contact time = 15 min, BV= 600, [Br^-] = 0.257 mg/L, [NO_3^-] = 22 mg/L, [SO_4^{2-}] = 265 mg/L, [Ca^{2+}] = 112.8 mg/L. Error bars represent the standard deviation of two injections of one sample.

NDMA FPs were measured before any treatment with the resins and there was no significant difference ($p > 0.05$) between NDMA FPs measured in the DDI water with added ions and without (NDMA FP 15 ng/L). Hence, it is not likely that the chemical reagents used to prepare the solutions were contaminated and constituted a source of

NDMA precursors. NDMA FPs measured in the DDI water after the treatment with MIEX were significantly different from those in the presence of ionic species ($p < 0.05$). MIEX resin released about 8 ng/L NDMA FP (Figure 4–5). However, NDMA precursors were apparently released from Plus resin. NDMA FP was 360 ng/L in the solution containing calcium after the Plus resin treatment. Sulfate also promoted to a lesser extent the release of NDMA precursors from the resins (i.e., 40 ng/L of NDMA FP). Anion exchange resins could release a wide range of concentrations of nitrosamines and nitrosamine precursors (Flowers and Singer, 2013; Gan et al., 2013a, 2013b; Gough et al., 1977; Kemper et al., 2009), which is attributed to amines used in the functionalization of the resins. Generally, the release of nitrosamines and nitrosamines precursors subsided as bed volumes rinsing increased. However, the release of nitrosamines or nitrosamines precursors from cation exchange resins has not been reported since cation exchange resins do not have amine-functional groups. Amine-functional groups which would increase NDMA FPs, especially in the presence of calcium ions may be due to the presence of manufacturing impurities. It is possible that those impurities were retained within the polymer structure of the cation exchange resins, and eventually changes in the volume of the resin (i.e., resin swelling), exerted by calcium ions, result in NDMA precursors released to the liquid solution.

4.4.4 The effect of the calcium on the release of NDMA precursor from Plus resin

The aim of this experiment was to study the effect of calcium concentration on the release of NDMA precursors from Plus resin. For this purpose, calcium solutions were prepared in DDI water with concentrations ranging from 0 to 9.6 meq Ca^{2+}/L and treated with Plus resin. The solutions were contacted with 5 mL of Plus resin for 15 min (BV =

600). The treated samples were chloraminated to measure NDMA FPs and the results are plotted in Figure 4–6. Calcium was measured before and after the treatment with Plus resin.

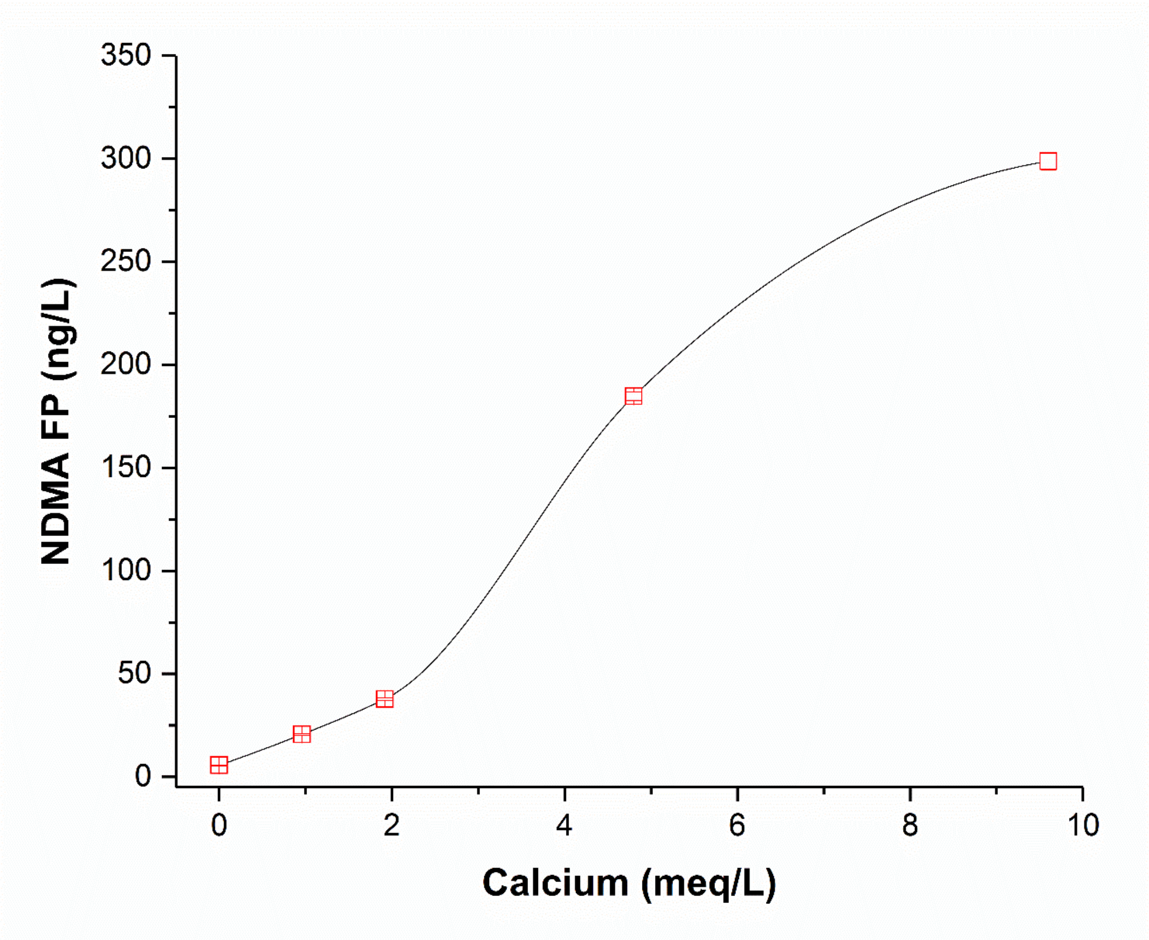


Figure 4–6. Release of NDMA precursors from the Plus resin in contact with DDI water containing calcium at different concentration levels. Experimental conditions: resin dose = 5 mL, contact time = 15 min, BV= 600. Error bars represent the standard deviation of two injections of one sample.

NDMA FP increased with increasing calcium concentration in the studied range. For instance, NDMA FP was 6 ng/L in the absence of calcium and was 299 ng/L at 9.6 meq Ca^{2+}/L. These results demonstrated that calcium was solely the cause of the release of precursors from Plus resin. I also determined the removal of calcium with Plus resin (Figure A–2). While Plus resin released NDMA precursors, it also removed calcium. One can estimate the theoretical amount of calcium that would be removed based on the ion exchange capacity. Particularly, Plus resin has an exchange capacity of 1.9 meq/mL. Thus, 5 mL of resin contains an expected total exchange capacity of 9.5 meq (1.9 meq/mL x 5 mL = 9.5 meq). The removal of calcium reached a plateau at 4.8 mg Ca^{2+}/L, indicating that the resin was completely exhausted and no more calcium could be loaded. However, even in these conditions the NDMA FP continued to increase.

The interaction of calcium specifically with the Plus resin was found to be the cause of the release of NDMA precursors. Unlike Plus, the other cation exchange resins (C100E, C150 and SST60) did not release NDMA precursors (Figure 4–4). Although all of these resins included Plus resin have a polymer backbone structure based on polystyrene crosslinked with divinylbenzene and sulfonate as functional group, the release of NDMA precursor is a specific phenomenon associated to the Plus resin.

The exchange of ions between calcium in the solution and sodium in the resin exerts swelling and shrinking of the ion exchange resins (Helfferich, 1962) . The magnitude of the changes depends on several factors including nature of the solvent, degree of cross-linking, nature of the fixed ionic groups, capacity, and nature of the counter ion (Helfferich, 1962). Some studies have reported a decrease of ~6% in the polymeric network (i.e., volume of resin) when calcium occupied the exchange sites in one type of cation exchange resin in the sodium form (Lafond et al., 2015; Wilson et al., 2017). Calcium ions have a solvated ionic radius close to that of sodium ions (~4 Å) (Helfferich, 1962), but since they are divalent cations, two equivalents of sodium are replaced by one equivalent of calcium reducing the concentration by a factor of two.

In this work, the swelling of the resin was not estimated; however, increased NDMA precursors in the presence of calcium indicated that Plus resin is the solely conceivable source of these precursors. The increase in the resin volume can explain the release of impurities, which are probably amine-based compounds, within the structure that were encapsulated during the manufacturing process.

Solutions containing 5 meq Ca^{2+}/L in DDI water were contacted with Plus resin, and NDMA FPs were determined as a function of time (Figure 4–7). The concentrations of calcium removed by Plus resin were also measured. A contact time of 15 min was long enough to remove over 90% of calcium. NDMA FP was 48 ng/L at 15 min and continued to increase up to 71 ng/L at 60 min. Overall, the increase in the NDMA FP was dependent both on the calcium concentration and the contact time. Swelling proceeds from the outer shells of the resin particle towards its center (Helfferich, 1962). Hence, the solvated cations take more time to reach the core of the resin. Consequently, equilibrium can be reached when the calcium ions finally approach the contracted core (Helfferich, 1962). This may explain the release of NDMA precursors even after the resin was fully loaded with calcium.

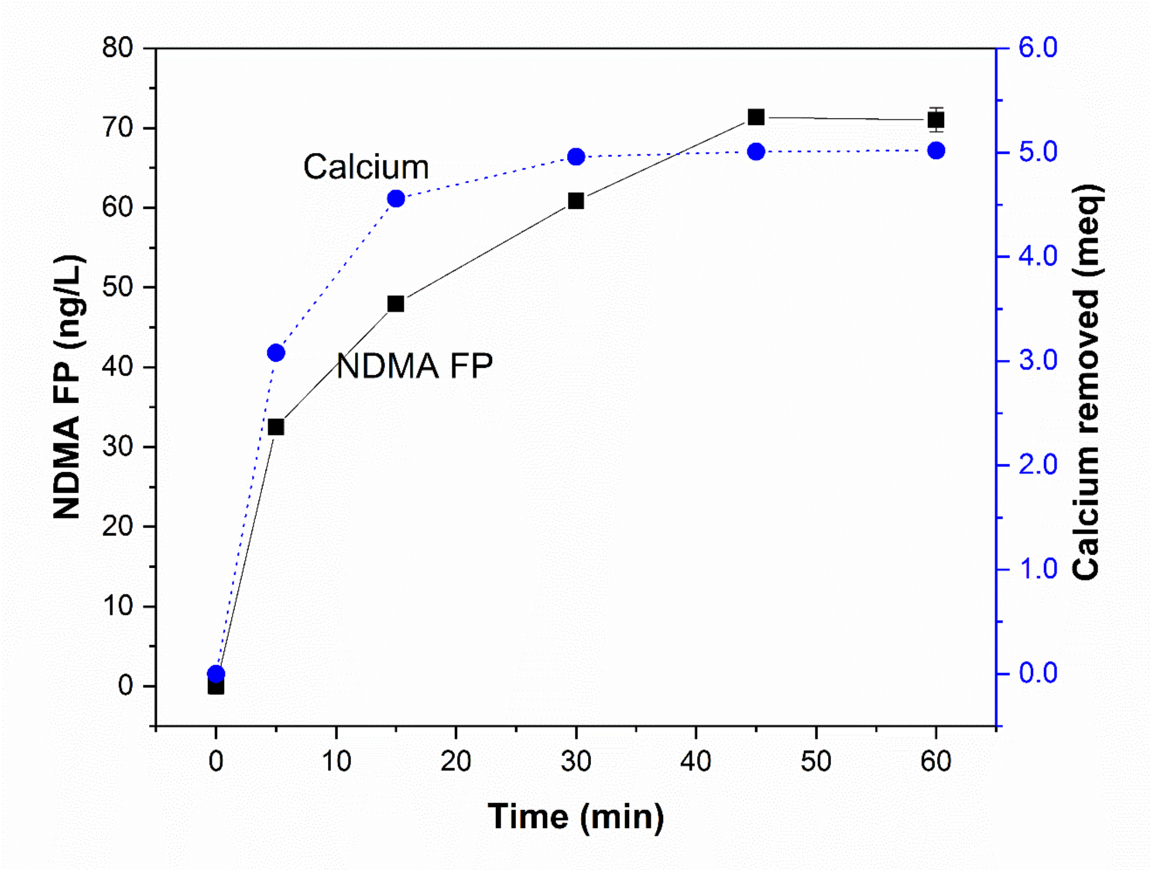


Figure 4–7. Kinetics of the release of NDMA precursors from Plus cation exchange resin in DDI water. Experimental conditions: resin dose = 5 mL, BV= 200, $[Ca^{2+}]_0$ = 5 meq/L. Error bars for NDMA represent the standard deviation of two injections of one sample.

4.4.5 Effect of the resin regeneration on the removal of NDMA precursors

The influence of the resin regeneration on the NDMA precursors release was examined with aqueous solutions of calcium at 2 meq Ca^{2+}/L and 10 meq Ca^{2+}/L. Plus resin was regenerated using 10% NaCl (w/v), followed by rinsing with 600 BV of DDI water and NDMA FPs measured after each regeneration cycle (regeneration cycles =1, 2 and 3). NDMA FPs subsided with increasing the number of regeneration cycles and approached the base line (i.e., NDMA FP formed in DDI water) (Figure 4–8).

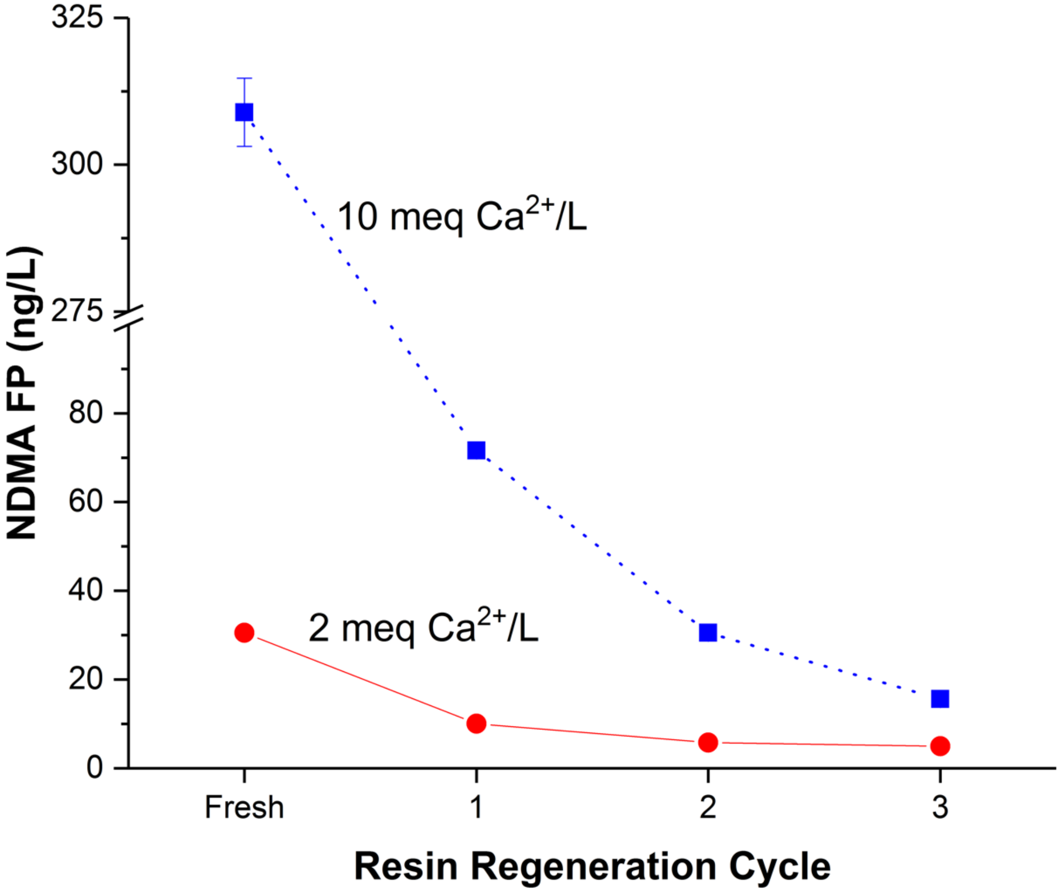


Figure 4–8. Effect of the regeneration on the release of NDMA precursors in deionized water. Experimental conditions: resin dose = 5 mL, contact time = 15 minutes, BV = 600, $[Ca^{2+}]_0$ = 2 meq/L and 10 meq/L, regenerant = 10% w/v NaCl. Error bars represent the standard deviation of two injections of one sample.

The efficiency of regeneration was controlled after each cycle by comparing the removal of calcium. After the third regeneration cycle the interference caused by the release of precursors from the Plus resin was minimized. The cation exchange resin was regenerated one more time (regeneration cycle = 4). A new secondary wastewater effluent sample with naturally occurring concentration of calcium (0.44 meq Ca^{2+}/L) was enriched

(4.56 meq Ca^{2+}/L); both samples were treated with Plus resin and the NDMA FP was measured.

The NDMA FP removed in the secondary wastewater effluent with ambient levels of calcium was 208 ng/L, and decreased to 104 ng/L in the enriched sample (Figure 4–9). The results suggest that to remove NDMA precursors in waters with elevated concentrations of calcium, the concentration of calcium must be decreased before the cation exchange treatment. This can be achieved either by chemical softening before the ion exchange treatment or by increasing the resin doses. If enough ion exchange capacity is provided, the demand of calcium should be satisfied first and then NDMA precursors can be removed as well.

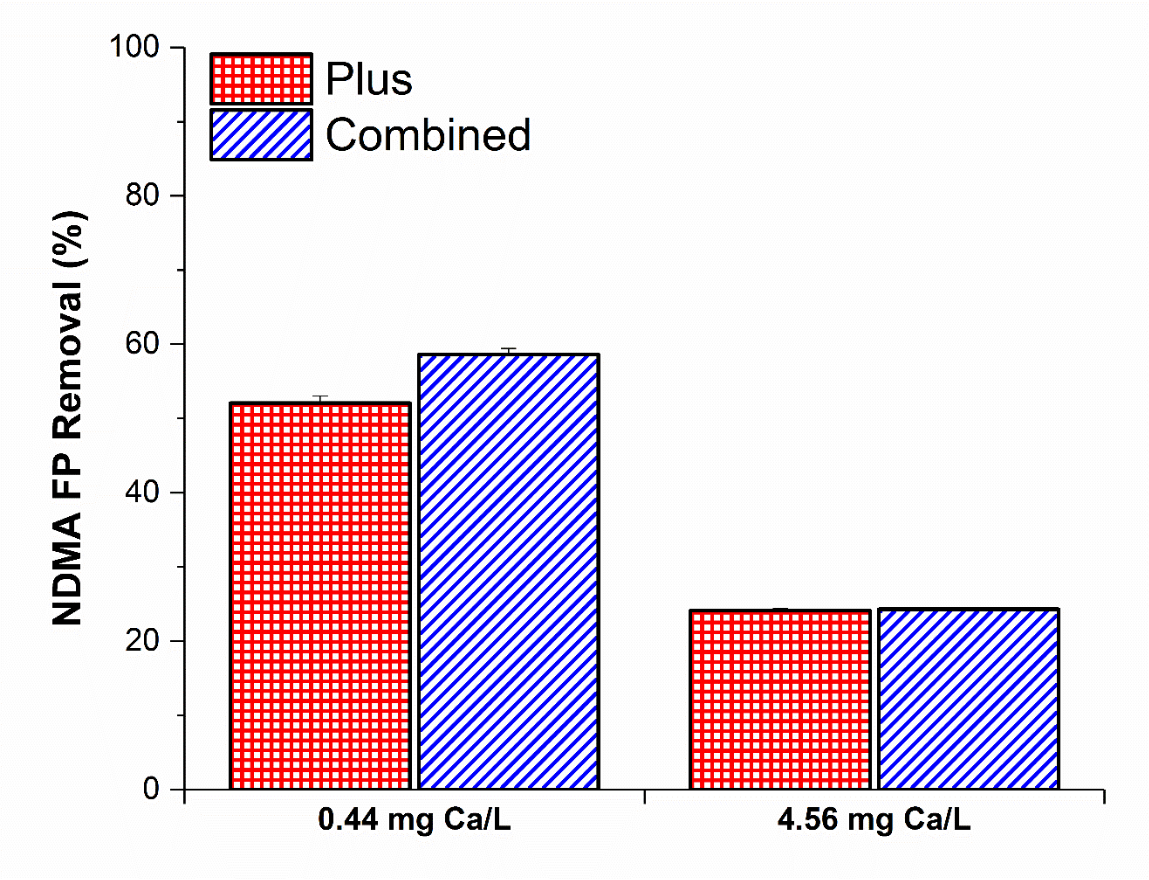


Figure 4–9. Effect of calcium ion on the control of NDMA FP with cation exchange resin in wastewater effluent. NDMA FP removals are compared to the untreated water. Error bars represent the standard deviation of two injections of one sample.

4.5 Conclusions

In this study, the factors that may influence the capability of ion exchange resins (i.e., pH and competing ions) used to control NDMA and THM precursors were investigated. Also experiments to investigate the release of NDMA precursors from Plus (i.e., cation exchange) resin were conducted. The pH is a major factor affecting the efficiency of the ion exchange process because it determines the form of the precursor species. NDMA precursors were removed at both acidic and neutral conditions, indicating that the precursors were protonated at these pH ranges. In contrast, increasing the pH to 10 not only changed the speciation of the amine–based NDMA precursors but promoted the release of NDMA precursors from the Plus resin. Experiments conducted in DDI water showed that NDMA precursors were released in the same conditions as the natural waters.

Plus resin and the combined treatment removed NDMA precursors in the wastewater with naturally occurring levels of the selected inorganic ions. However, NDMA FP increased in the enriched wastewater after the treatment with the cation exchange resin. This effect was specific to the Plus resin because similar experiments with other commercial Purolite® cation exchange resins did not increase the NDMA FP after treatment. The removals of THM precursors by the anion exchange resin were affected by the elevated sulfate concentrations in the amended water. Bromide was not removed in either the ambient or the enriched wastewater effluent sample, while nitrate was removed only in the unamended wastewater sample.

It was found that in the presence of high levels of calcium, the Plus exchange resin released NDMA precursors. The amount of NDMA precursors that were released from the Plus resin increased with the calcium concentration. However, NDMA FP levels subsided by increasing the number of regeneration cycles and approached background levels.

CHAPTER V

EFFECT OF BROMIDE ON THE FORMATION OF NDMA FROM NDMA MODEL PRECURSOR COMPOUNDS AND NATURAL WATERS

5.1 Abstract

The increasing demand on water resources will inevitably require increasing use of impaired and alternative water sources, including wastewater impacted source waters. Bromide, which is typically a trace component, is a cause of concern because it can lead to the formation of brominated DBPs that are more cytotoxic and genotoxic than their chlorinated analogs. The removal of bromide with current water treatment techniques is challenging. For instance, the removal of bromide with anion exchange resins is limited due to high competition of NOM and other inorganic ions present in the raw waters.

Bromide is a ubiquitous trace component of seawater but rarely occurs naturally at high concentrations, in surface waters and wastewaters usually ranging from 50 to 300 μg/L. The enhancement in the formation of NDMA during chloramination that has been reported is attributed to the presence of bromide. Bromide is readily oxidized by chloramines and form bromamines and bromochloramine but bromochloramine rather than bromamines is responsible for the increase in the formation of NDMA.

The effect of bromide on the formation of NDMA in a selected group of NDMA model precursor compounds and polymers commonly used in water treatment at environmentally relevant concentrations was investigated. Experiments were conducted in DDI water, secondary wastewater effluent and surface water samples. The effects of the pH and the background DOC were also investigated. It was found that increasing the bromide concentration (0–1000 μg/L) in surface water samples caused no enhancement in

the formation of NDMA either with 3 or 100 mg Cl_2/L monochloramine. In contrast, bromide suppressed the formation of NDMA with increasing bromide concentration in wastewater effluent samples treated with 3 mg Cl_2/L of monochloramine. Suppression was not observed with monochloramine at 100 mg Cl_2/L. It is possible that bromochloramine reacted with NOM rather than with NDMA precursors and consequently decreased the formation of NDMA. In DDI water, bromide enhanced the formation of NDMA in the NDMA model precursors compounds, and more NDMA was formed at pH 8 compared to pH 6. In the presence of 1 mg/L bromide, increasing the DOC concentration (0–15 mg/L) suppressed the formation of NDMA in the presence of NDMA model precursor compounds. However, the presence of bromide increased the formation of NDMA in waters with DOC levels around 2 mg/L and containing DMA, TMA and polyDADMAC.

5.2 Introduction

N-nitrosodimethylamine (NDMA) is a disinfection byproduct (DBP) formed mainly during the chloramination of water and wastewater (J. Choi and Valentine, 2002; Le Roux et al., 2011; Mitch et al., 2003b; Mitch and Sedlak, 2004). NDMA is a probable (B2) human carcinogen and has a lifetime cancer risk of one in a million for 0.7 ng/L in drinking water (US EPA, 1993b).

In aqueous solutions chlorine reacts rapidly with ammonia to form a mixture of monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and trichloramine (NCl_3) (Kovacic et al., 1970). The formation of a specific chloramine depends upon the pH, the chlorine to ammonia ratio, and the temperature. However, monochloramine is the predominant chloramine species under the conditions typically found in drinking water treatment and is produced at pH higher than 8, and Cl_2 to N weigh ratio of 5:1 (US EPA, 1993b; Vikesland et al., 2001). In addition to the chloramine speciation several other factors affect the formation of NDMA during drinking water treatment, including disinfectant dose, contact time, pH, temperature, bromide, among others (Chen and Valentine, 2006; Junghoon Choi and Valentine, 2002; Hatt et al., 2013; Schreiber and Mitch, 2005; Selbes et al., 2014, 2013; Sgroi et al., 2014; Shen and Andrews, 2011).

The presence of bromide ion is of particular concern because it can lead to the formation of brominated DBPs that are more cytotoxic and genotoxic than their chlorinated analogs (Heller-Grossman et al., 1999; Muellner et al., 2007; Richardson et al., 2003). Bromide is an inorganic ion that is an ubiquitous trace component of seawater but rarely occurs naturally at high concentrations in fresh surface water sources in the United States (Mctigue et al., 2014).

In seawater the concentration of bromide, 66–68 mg/L, is completely overshadowed by the typical concentration of chloride that is around 19,000 mg/L (Magazinovic et al., 2004; Stumm and Morgan, 1996; Wilson et al., 2014). Its concentration in surface waters and wastewaters is usually very small ranging from 50 to 300 μg/L (Flury and Papritz, 1993). The sources of bromide in water include naturally occurring process like seawater intrusion and dissolution of geologic sources, but also anthropogenic activities such as seawater desalination, generation of mining tailings, chemical production, production of sewage and industrial effluents, road salt, some fertilizers, natural gas production with hydraulic fracturing, air pollution control methods in coal fired power plants, and textile production (Flury and Papritz, 1993; Mctigue et al., 2014; Watson et al., 2012a).

Bromide ion is readily oxidized by chloramines and form bromamines and bromochloramine (NHBrCl). Although the chemistry of bromamines has been shown to have some similarity with chloramines, bromamines are less stable than chloramines and generally show a higher reactivity. Bromide reacts as catalyts in the reaction of NHBrCl with NH_2Cl [$NHBrCl + NH_2Cl \rightarrow N_2 + Br^- + 2Cl^- + 3H^+$] (Le Roux et al., 2012a).

Bromide has been shown to enhance the formation of NDMA during chloramination (Chen et al., 2010; Luh and Mariñas, 2012). However, most of those studies have been conducted with high concentrations of bromide that are not likely to represent relevant environmental concentrations. For instance, bromide enhanced the formation of NDMA from DMA (300,000 nM) under chloramination conditions ($[NH_2Cl]_0$ = 21 mg Cl_2/L) at pH 7 when the bromide concentrations were increased from 0 to 23,970 μg/L (Chen et al., 2010). However, an opposite effect was observed for TMA in similar disinfection conditions with bromide ranging from 0 to 79,900 μg/L (Chen et al., 2010). Chen and colleagues also showed that the formation rate of NDMA during chloramination of DMA was higher in the presence of 2,500 μg/L bromide ion during the first 12 h of reaction time. When the authors investigated the effect of pH (4, 7, 9 and 12) they found that the greatest NDMA formation was at neutral pH, regardless of the absence or the presence of bromide. In another study by Luo (Luo, 2006), an experiment in natural water with bromide ion ranging from 0 to 160,000 μg/L, an initial monochloramine concentration of 70 mg Cl_2/L and a reaction time of 48 hours showed an increase in the NDMA formation of only 6 ng/L (from 23 to 29 ng/L).

Chloramination ($[NH_2Cl]_0 = 14$ mg Cl_2/L) of a lower concentration of DMA (500 nM) in the presence of bromide ion (31,960 μg/L) also showed an enhancement in the formation of NDMA at pH 8 and 9 after 24 h of contact time (Luh and Mariñas, 2012). However, at pH 6 and 7 the yields of NDMA in the presence of the same concentration of bromide were lower compared to those in the absence of bromide. Luh and Mariñas (2012) indicated that possibly a mixed dihaloamine bromochloramine rather than bromamines were responsible for the enhance of NDMA by the bromide ion.

The studies in the literature on the effect of bromide ion in the formation of NDMA have used high concentrations of bromide that are not likely to represent relevant environmental concentrations. The number of model precursors investigated is limited and focused mainly on DMA. In this study, the aim was to investigate the effect of bromide on the formation of NDMA. A group of NDMA model precursor compounds and polymers commonly used in water treatment was selected to study the effect of bromide at environmentally relevant concentrations. Experiments were conducted in distilled deionized (DDI) water, secondary wastewater effluent and surface water samples. The effects of the pH and the background DOC were also investigated.

5.3 Materials and methods

5.3.1 Source waters

Water samples were obtained from five different sources in South Carolina, USA, and classified as surface waters (SW) or secondary wastewater effluents (WW). SW-1 was collected from Lake Hartwell, SW-2 and SW-3 were sampled from a drinking water treatment plant (DWTP). SW-2 was collected after the conventional clarification processes while SW-3 in the influent of the DWTP. The WW samples were collected from the secondary effluent of (i) a municipal wastewater treatment plant (WWTP) (WW-1); (ii) a municipal/industrial WWTP (WW-2); and (iii) a municipal WWTP (WW-3). Upon arrival to the laboratory, samples were filtered with 0.2 μm pore size Whatman™ Polycap 150 TC filters (Pittsburgh, PA, USA), and stored at 4 °C until experiments were conducted (maximum storage time of 3 days).

5.3.2 Chemicals

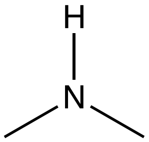
Dimethylamine (DMA), trimethylamine (TMA), *N,N*-dimethyl-isopropylamine (DMiPA), *N,N*-dimethylaniline (DMAN), *N,N*-dimethylbenzylamine (DMBzA), ranitidine (RNTD) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Water treatment polymers that were used included poly(diallyldimethylammonium chloride) (polyDADMAC) solution 20% w/v, in water, poly(dimethylamine-co-epichlorohydrin) quaternized (polyAMINE) 37.66% w/v in water and were bought from Sigma–Aldrich (St. Louis, MO, USA) and Scientific Polymer Products, Inc. (Ontario, NY, USA), respectively. Also, Sedifloc 400C polyacrylamide polymer (polyaACRYL) was provided by the DWTP. These compounds contain the DMA moiety and were selected to examine the influence of the molecular structures (Table 5–1).

A *N*-nitrosamines certified reference material (purity 99.9%) was purchased from Sigma–Aldrich (St. Louis, MO, U.S.) and used to prepare NDMA calibration solutions. Deuterated NDMA (NDMA-d6) (purity 99%) and deuterated *N*-nitroso-di-n-propylamine

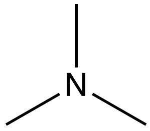
(NDPA-d14) (purity 99%) were purchased from Restek (Bellefonte, PA, USA) and added at 40 ng/L to the calibration solutions as surrogate and internal standard, respectively. Calibration curves included at least seven calibration standards in the range of 0.5–800 ng/L, and the minimum reporting level (MRL) was 0.5 ng/L.

Sodium hypochlorite (NaOCl) solution (5% available chlorine) and ammonium sulfate [$(NH_4)_2SO_4$)] were obtained from Fisher Scientific (Center Valley, PA, USA) and VWR (Radnor, PA, USA), respectively.

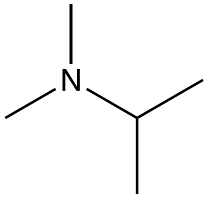
Table 5–1. Molecular structures of selected precursors.



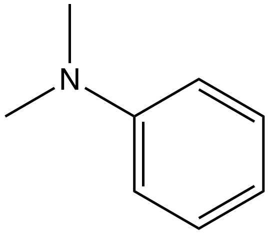
Dimethylamine (DMA)



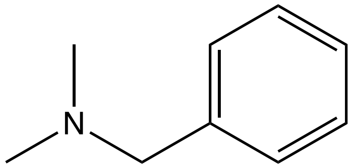
Trimethylamine (TMA)



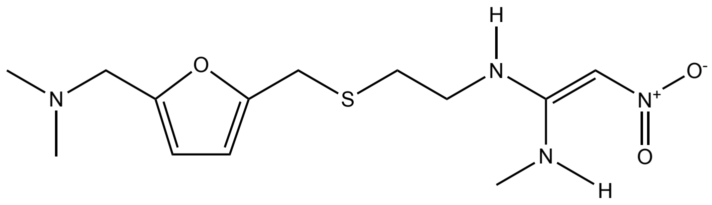
N,N-dimethyl-isopropylamine (DMiPA)



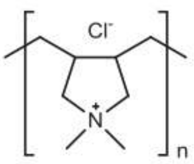
N,N-dimethylaniline (DMAN)



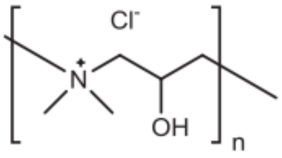
N,N-dimethylbenzylamine (DMBzA)



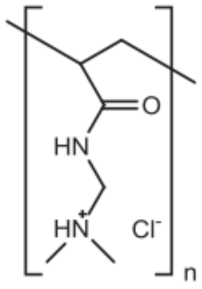
Ranitidine (RNTD)



PolyDADMAC



Polyamine



Polyacrylamide

5.3.3 Chloramination experiments

Stock solutions of monochloramine were prepared on the day of use. Sodium hypochlorite solution was slowly added into an ammonium sulfate solution at a Cl/N ratio of 4.75:1 (Hong et al., 2007). Before mixing, the pH of both solutions was adjusted to 9 with 1 M NaOH or 1 M HCl.

Stock solutions with a concentration of 200 nM of each of the NDMA model precursor compounds and the polymers (Table 5–1) were prepared in DDI water. Two hundred fifty mL amber bottles containing the stock solutions were amended with bromide (0, 100, 250, 500 and 1,000 μg/L). The solutions were buffered at pH 8 with 0.002 M phosphate buffer and chloraminated at an initial concentration of monochloramine of 3.0 mg Cl_2/L. The samples were stored in the dark at room temperature (21 °C ± 2°C) for three days. A second batch of samples was buffered at pH 8 with 0.008 M phosphate buffer, an initial monochloramine concentration of 100 mg Cl_2/L and five days of contact time. These two monochloramine doses were selected to represent chloramination conditions such as those found during uniform formation conditions (UFC) and formation potential tests. The reactions were stopped by quenching the residual monochloramine with stoichiometric amounts of sodium thiosulfate anhydrous. The surrogate standard was added (40 ng/L) to the quenched samples before extraction.

5.3.4 NDMA extraction and analysis

NDMA was analyzed following US EPA method 521 (US EPA, 2004). Environ-Clean 521 (UCT) solid phase extraction (SPE) columns packed with 2000 mg of coconut charcoal were conditioned with dichloromethane, methanol and DDI water. Then samples were passed through the SPE columns at an approximate flow rate of 10 mL/min (Beita-Sandí et al., 2016). The columns were dried in a vacuum and under atmospheric pressure air, sequentially, and then the adsorbed NDMA was eluted with dichloromethane. The eluent passed through a drying cartridge containing 6 g of sodium sulfate anhydrous. The samples were concentrated to approximately 0.9 mL under a gentle stream of ultrahigh-purity nitrogen. The internal standard was spiked (40 ng/L) in the samples before transferring a portion to glass inserts in amber vials. One microliter of the samples and the standards were injected on a Agilent 7890B (Santa Clara, CA, USA) Gas Chromatograph (GC) equipped with an Agilent DB-1701 (30 m x 0.25 mm x 1.00 μm) column, and coupled with an Agilent 7000C triple quadrupole mass spectrometer (MS/MS) (McDonald et al., 2012). The concentration of NDMA was normalized to the NDMA-d6 recovery.

5.4 Results and discussion

5.4.1 Effect of bromide on NDMA formation in secondary wastewater effluent and surface water samples

The aim of this first experiment was to investigate the effect of bromide on the formation of NDMA during chloramination. The effect of bromide with surface water (SW) and wastewater effluent (WW) samples was investigated. The selected characteristics of these water are summarized in Table 5–2.

Samples were amended with bromide ranging from naturally occurring concentrations (<100 μg/L) up to 1000 μg/L. Then, waters were buffered at pH 8 and oxidized with monochloramine at 3 and 100 mg Cl_2/L. NDMA was measured after three and five days. Chloramination was carried out with preformed monochloramine at 3 mg

Cl_2/L and 100 mg Cl_2/L and reaction times of 3 d and 5 d, respectively. NDMA (C) was normalized to the concentration of NDMA in the absence of bromide (C_0). The results are shown in Figures 5–1 (SW) and 5–2 (WW).

Table 5–2. Characterization of wastewater effluent and surface water samples.

Parameter	WW-1	WW-2	SW-1	SW-2	SW-3
Bromide (µg/L)	43	62	17	52	52
Calcium (mg/L)	13	47	7	20	18
DN (mg/L)	4.3	23.5	0.2	0.6	0.4
DOC (mg/L)	3.5	5.5	1.9	4.8	15
Nitrate (mg/L)	17	12	8	0.7	0.8
pH	7.8	6.7	7.4	7.5	7.8
Sulfate (mg/L)	20	22	24	63	11
$SUVA_{254}$ (L/mg-cm)	2.1	2.1	1.4	1.4	4.0

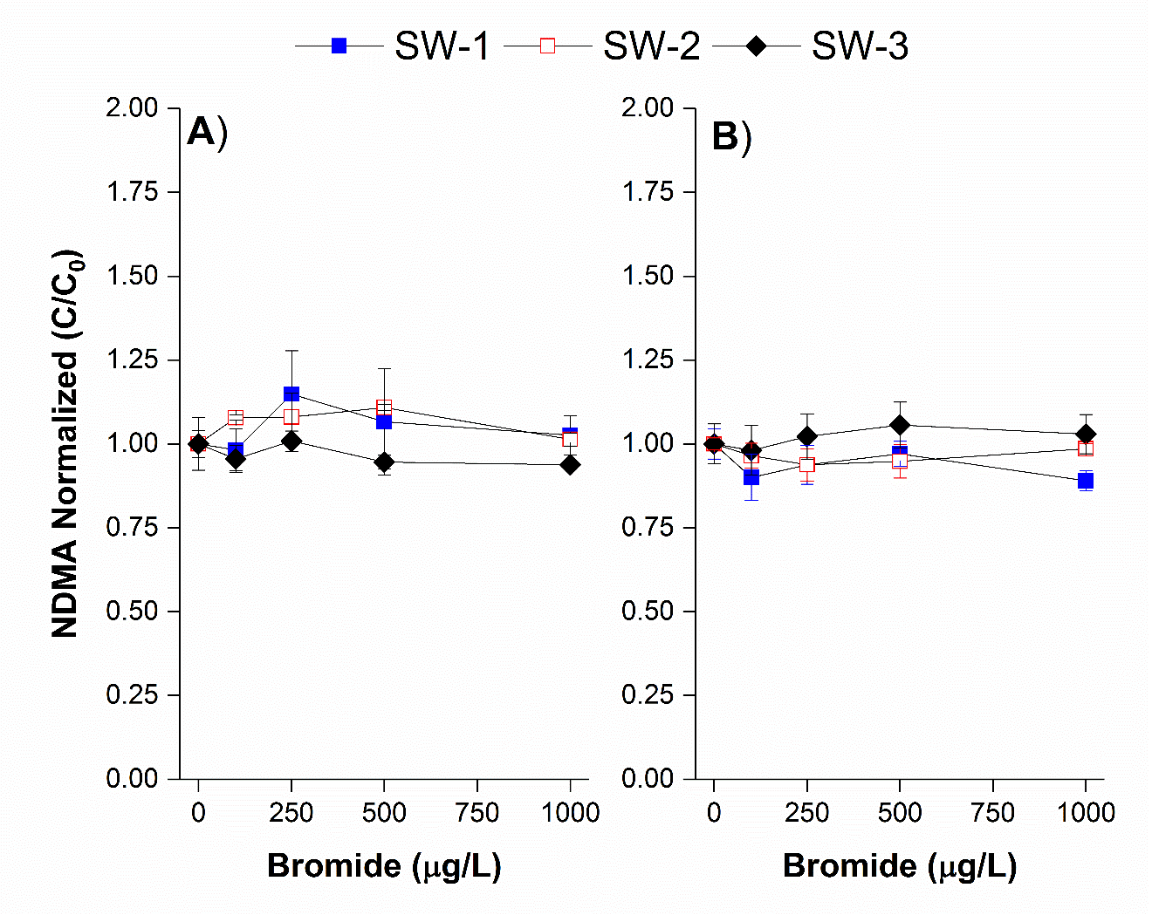


Figure 5–1. Effect of bromide on the formation of NDMA in surface water (SW) samples. Experimental conditions **A)** $[NH_2Cl]_0$ = 3 mg Cl_2/L, phosphate buffer = 0.002 M, contact time = 3 d and **B)** $[NH_2Cl]_0$ = 100 mg Cl_2/L, phosphate buffer = 0.008 M, contact time = 5 d. In both experiments the temperature was (21 ± 2) °C and the pH = 8. Error bars represent the standard deviation of two injections of one sample.

NDMA concentrations measured in the presence of 3 mg Cl_2/L (no bromide) in the surface waters were relatively low (< 10 ng/L), indicating the lack of a significant amount of NDMA precursors. On the other hand, NDMA concentrations (no bromide) with monochloramine at 100 mg Cl_2/L were higher than with 3 mg Cl_2/L and those NDMA concentrations were 30 ng/L (SW–1), 21 ng/L (SW–2) and 42 ng/L (SW–2). However, increasing the bromide concentration in the surface water samples caused no enhancement of the formation of NDMA (Figure 5–1) either with 3 or 100 mg Cl_2/L monochloramine.

In contrast, NDMA concentrations (no bromide) in the wastewater effluent samples (Figure 5–2) were higher than the surface water, ranging from 145–190 ng/L and 433–1620 ng/L with 3 and 100 mg Cl_2/L, respectively. In the presence of 3 mg Cl_2/L of monochloramine bromide suppressed the formation of NDMA with increasing bromide concentration. However, no effect was observed when the monochloramine was 100 mg Cl_2/L.

Previous studies have shown that bromide enhanced the formation of NDMA during chloramination of DMA (Chen et al., 2010; Luh and Mariñas, 2012). However, those studies have been conducted in DDI water, limiting the competition of background NOM. The opposite trend observed in this study to that reported in the literature may be explained by the presence of not only NOM and but also a wider range of NDMA precursors. As shown before, bromide only decreased the NDMA formation in the wastewater effluent samples and caused no effect on the surface waters. Since the monochloramine to bromide ratio was the same in the surface water and wastewater effluent samples, other factors are responsible for the bromide effect on the wastewater effluent samples.

In the presence of bromide, monochloramine (NH_2Cl) decays as bromide ion is oxidized by NH_2Cl to bromochloramine (NHBrCl) (Bousher et al., 1989; Gazda and Margerum, 1994; Le Roux et al., 2012a; Trofe et al., 1980). Firstly, the ionization of monochloramine forms the monochlorammonium ion (NH_3Cl^+) (Eq. 5–1, Table 5–3).

NH_3Cl^+, an intermediate compound, oxidizes bromide and leads to the production of bromamines (Eq. 5–2, Table 5–3) (Vikesland et al., 2001). Additionally, the hydrolysis of monochloramine forms free chlorine that can also further oxidize bromide to hypobromous (HOBr) (Eq. 5–4, 5–5 in Table 5–3). Nonetheless, in typical chloramination conditions the oxidation of bromide by NH_3Cl^+ usually dominates. Both NH_2Br and HOBr undergo further rapid reactions to produce mixed bromochloramines, primarily bromochloramine (NHBrCl) (Eq. 5–3, Table 5–3). Further fast decomposition reactions of NHBrCl lead to formation of bromide (Eq. 5–6) (Bousher et al., 1989). Overall, bromide acts as a catalytic in the decomposition of monochloramine. Increasing bromide results in less monochloramine available and more highly reactive NHBrCl formed.

Table 5-3. Chloramine and bromamines reactions.

Reaction	Equation
$NH_2Cl + H^+ \leftrightharpoons NH_3Cl^+$	5–1
$NH_3Cl^+ + Br^- \leftrightharpoons NH_3Br^+ + Cl^-$	5–2
$NH_3Br^+ + NH_2Cl \leftrightharpoons NHBrCl + {NH_4}^+$	5–3
$NH_2Cl + H_2O \leftrightharpoons HOCl + NH_3$	5–4
$HOCl + Br^- \leftrightharpoons HOBr + Cl^-$	5–5
$NHBrCl + NH_2Cl \longrightarrow N_2 + Br^- + 2Cl^- + 3H^+$	5–6

However, in the presence of NOM a series of reactions of monochloramine with NOM provides a more complex scenario. Wastewater effluent samples contain more reactive NDMA reactive precursors than the surface water. It has been demonstrated that monochloramine decay rate increases with increasing bromide concentration at the same time that bromochloramine increases (Luh and Mariñas, 2014). NHBrCl is expected to produce more NDMA than NH_2Cl due to the higher electronegativity of the brominated nitrogen atom, thus favoring the nucleophilic substitution with the DMA moiety (Le Roux et al., 2012a). However, an increase in the bromochloramine concentrations did not form more NDMA in the wastewater effluent samples. It is then reasonable to think that bromochloramine reacted with NOM rather than with NDMA precursors and consequently decreased the formation of NDMA.

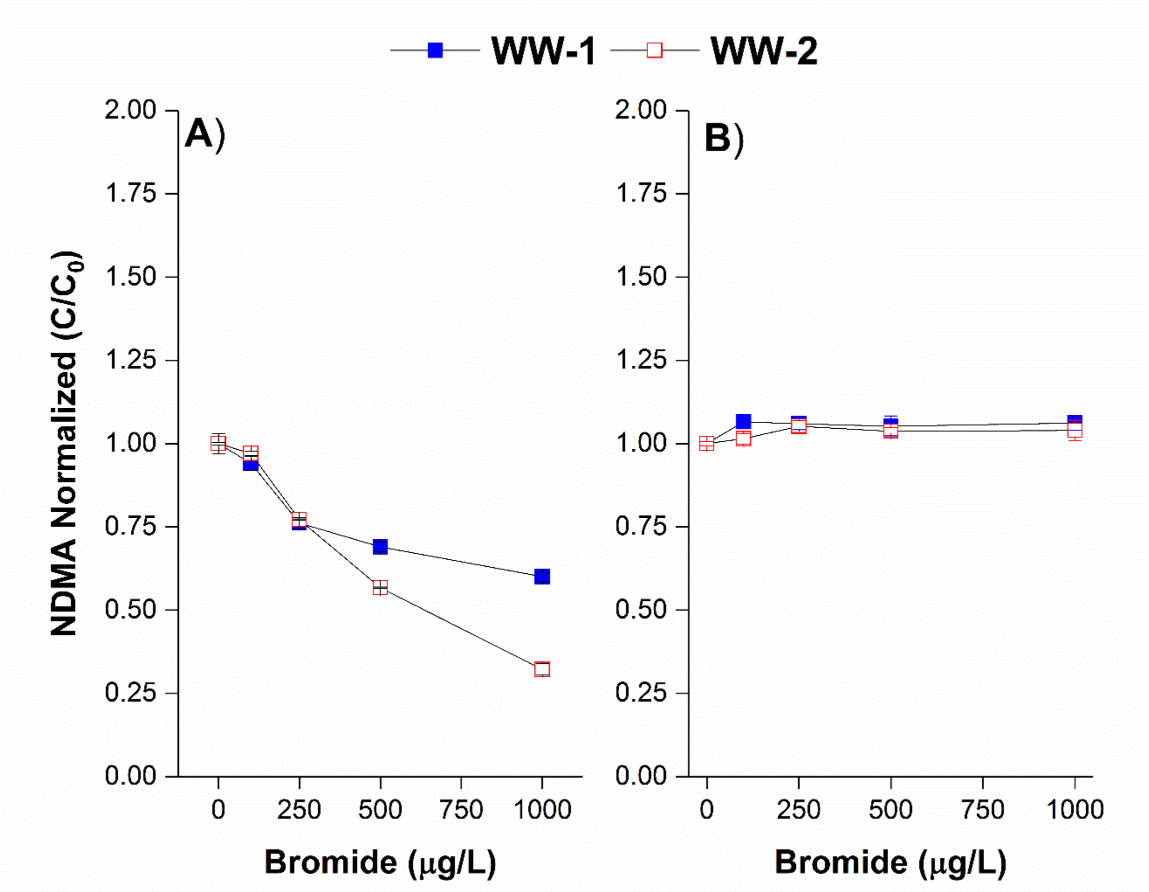


Figure 5–2. Effect of bromide on the formation of NDMA in secondary wastewater effluents (WW) samples. Experimental conditions **A)** $[NH_2Cl]_0$ = 3 mg Cl_2/L, phosphate buffer = 0.002 M, contact time = 3 d and **B)** $[NH_2Cl]_0$ = 100 mg Cl_2/L, phosphate buffer = 0.008 M, contact time = 5 d. In both experiments the temperature was (21 ± 2) °C and the pH = 8. Error bars represent the standard deviation of two injections of one sample.

5.4.2 Effect of bromide on the formation of NDMA from model precursor compounds

The goal of this experiment was to assess the effect of bromide on the formation of NDMA from nine NDMA model precursors compounds in two chloramination conditions, 3 mg Cl_2/L and 100 mg Cl_2/L monochloramine, at pH 8 during three and five days of reaction time, respectively. The concentrations of the precursor compounds were 200 nM, in these experimental conditions it was expected that monochloramine predominantly decayed by self-decomposition and bromide oxidation (Figures A-3 and A-4). Moreover, since the experiments were carried out in DDI water the NOM background competition was minimized and the formation of NDMA from the precursors was due to the reaction with haloamines added or formed during the reaction.

NDMA was normalized to the concentration of NDMA formed in the absence of bromide as shown in Figure 5–3 (3 mg Cl_2/L monochloramine). The presence of bromide enhanced the formation of NDMA in solutions of the selected NDMA model precursors compounds in the range of bromide concentrations studied (0–1000 μg/L). DMiPA, DMBzA and RNTD exhibited the highest NDMA molar conversion yield 37.9%, 73.1% and 78.8%, respectively. Low yield NDMA precursor compounds such as DMA, TMA and DMAN had molar conversion rates (< 1%) similar to that found in literature (Selbes et al., 2013). However, of the three compounds DMA and TMA rendered the higher increase of NDMA in the presence of bromide which was about two–fold. NHBrCl is expected to form more NDMA than NH_2Cl due to the higher electronegativity of the brominated nitrogen atom, consequently favoring the nucleophilic substitution with DMA (Le Roux et al., 2012a).

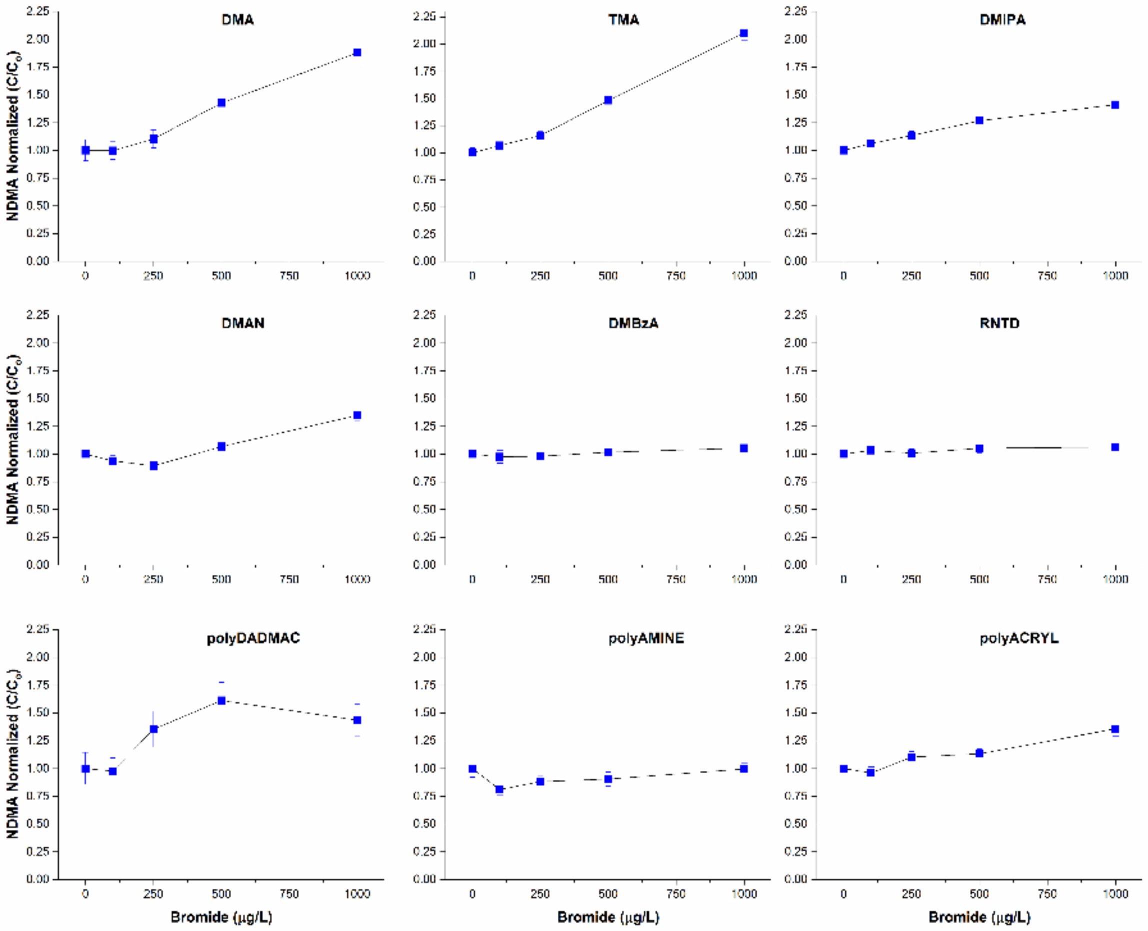


Figure 5–3. Effect of bromide on the formation of NDMA from model precursors compounds. Experimental conditions: $[DMA]_0$ = $[TMA]_0$ = $[DMiPA]_0$ = $[DMAN]_0$ = $[DMBzA]_0$ = $[RNTD]_0$ = 0.0002 mM, $[polyDADMAC]_0$ = $[polyAMINE]_0$ = 0.2 mg/L, $[polyACRYL]_0$ = 1 mg/L, $[NH_2Cl]_0$ = 3 mg Cl_2/L, pH = 8, phosphate buffer = 0.002 M, contact time = 3 d, temperature = (21 ± 2) °C. Error bars represent the standard deviation of two injections of one sample.

Despite the high conversion rate to NDMA of *N,N*-dimethylbenzylamine (DMBzA) and ranitidine (RNTD), bromide did not enhance the formation of NDMA. This can be explained by the fast and high molar conversion rate into NDMA upon chloramination of these two compounds (Le Roux et al., 2012a, 2011; Shen and Andrews, 2011; Spahr et al., 2017). From the three commonly used polymers in water treatment, only polyDADMAC and polyACRYL were impacted by the presence of bromide.

A second set of experiments was conducted with the NDMA model precursors compounds but the concentration of monochloramine was increased to 100 mg Cl_2/L and the reaction time to five days. The results are presented in Figure 5–4 and indicate that the formation of NDMA from the selected precursors is not likely to be enhanced or suppressed when the monochloramine to bromide ratio was increased.

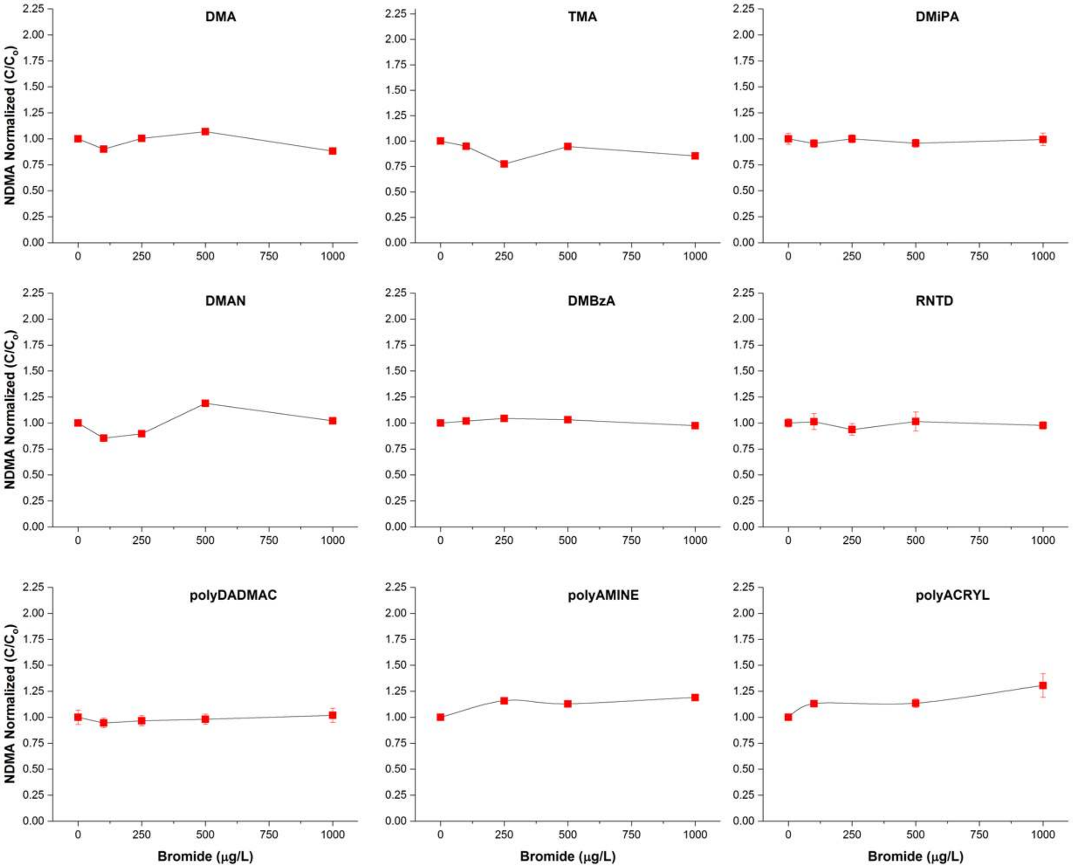


Figure 5–4. Effect of bromide on the formation of NDMA from model precursors compounds. Experimental conditions: $[DMA]_0 = [TMA]_0 = [DMiPA]_0 = [DMAN]_0 = [DMBzA]_0 = [RNTD]_0 = 200$ nM, $[polyDADMAC]_0 = [polyAMINE]_0 = 0.2$ mg/L, $[polyACRYL]_0 = 1$ mg/L, $[NH_2Cl]_0 = 100$ mg Cl_2/L, pH = 8, phosphate buffer = 0.008 M, contact time = 5 d, temperature = (21 ± 2) °C. Error bars represent the standard deviation of two injections of one sample.

Under these conditions, although the formation of NDMA is increased compared to 3 mg Cl_2/L of monochloramine the overall trend appeared to be unaffected as the bromide is increased. Even though bromochloramine is more reactive than monochloramine, it is also less stable than monochloramine. Due to the abundance of monochloramine, the bromamines and bromochloramine can be deactivated by reacting with monochloramine (Le Roux et al., 2012a).

Le Roux et al. (2012) found that formation of NDMA from DMA was almost double when the concentration of bromide was 1 mM (~79,900 µg/L) and 2.5 mM $NHCl_2$ ($NHCl_2$:Br^- molar ratio of 2.5:1) and the reaction time 24 h. In contrast, in my study the $NHCl_2$:Br^- molar ratios were 3.4:1 (i.e., 3 mg Cl_2/L and 1000 µg/L Br^-) and 114:1 (i.e., 100 mg Cl_2/L and 1000 µg/L Br^-) for the reaction times of 3 and 5 days. These results emphasize the importance of the monochloramine to bromide ratio.

An additional experiment was conducted with only DMA and TMA. The solutions containing the amines were oxidized with monochloramine at 3.0 mg Cl_2/L and three days of reaction time. The bromide concentration ranged from 0 to 32 mg/L (Figure 5–5). Such high concentrations of bromide are not expected to occur in source waters but were used to illustrate how bromide can increase the formation of NDMA in waters that contain precursors that generally have low NDMA conversion yield. Under these conditions, NDMA rose linearly as the bromide concentration increased. NDMA formation from DMA was enhanced by 25-fold and by 45-fold from TMA

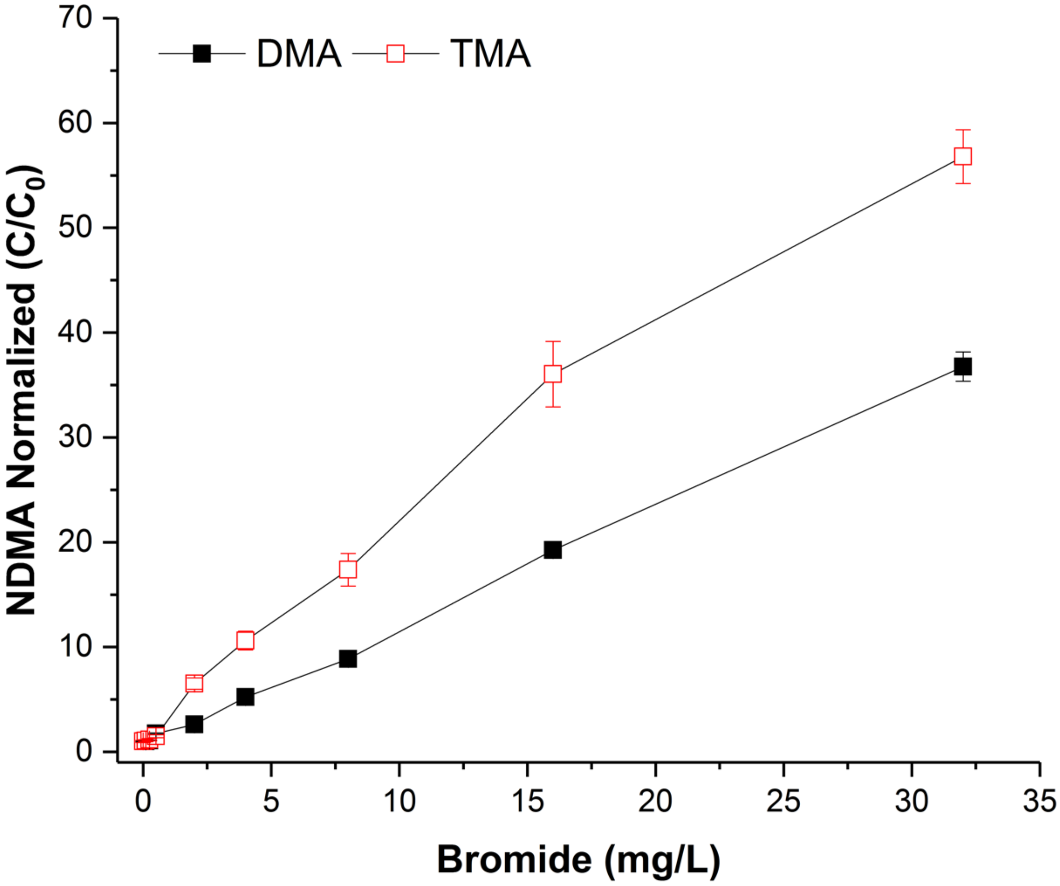


Figure 5–5. Effect of the bromide at high concentrations on the formation of NDMA in two selected model precursors compounds. Experimental conditions: $[DMA]_0 = [TMA]_0 = 200$ nM, $[NH_2Cl]_0 = 3.0$ mg Cl_2/L, phosphate buffer = 0.002 M, contact time = 3 d, temperature = (21 ± 2) °C. Error bars represent the standard deviation of two injections of one sample.

5.4.3 Effect of the pH on NDMA formation in the presence of bromide in selected model precursors compounds

The objective of this experiment was to evaluate the effect of pH on the formation of NDMA from DMA, TMA, polyDADMAC and polyACRYL in the presence of 1000 mg/L bromide and 3 mg Cl_2/L monochloramine. The pH was controlled with 0.002 M phosphate buffer at 6, 7 and 8. NDMA was normalized relative to the concentration at pH 6 and the results are shown in Figure 5–6. All the investigated compounds exhibited an increase in the concentration of NDMA formed as the pH was increased to a different extent. Particularly TMA and polyDADMAC showed the higher rate of formation of NDMA while polyACRYL was not considerably affected by the changes in the pH.

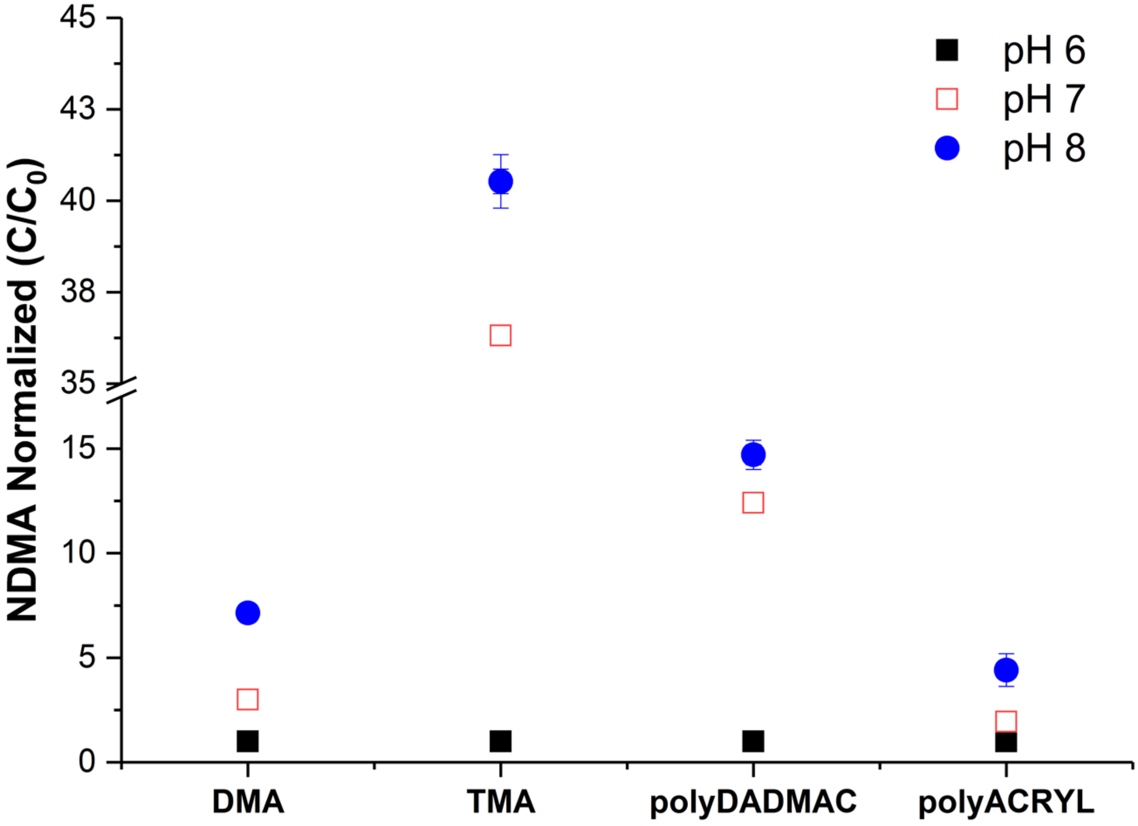


Figure 5–6. Effect of pH and bromide on the formation of NDMA from selected model precursors compounds. Experimental conditions: $[DMA]_0$ = $[TMA]_0$ = 200 nM, $[polyDADMAC]_0$ = 0.2 mg/L, $[polyACRYL]_0$ = 1 mg/L, $[Bromide]_0$ = 1 mg/L, $[NH_2Cl]_0$ = 3 mg Cl_2/L, phosphate buffer = 0.008 M, contact time = 3 d, temperature = (21 ± 2) °C. Error bars represent the standard deviation of two injections of one sample.

The enhancement of NMDA in the presence of bromide during chloramination is due to formation of the highly reactive bromochloramine. Increasing the pH from 6 to 8 formed more NDMA. Bromochloramine was found to be more stable at pH 8 than 6 (Luh and Mariñas, 2014). Thus, the higher formation of NDMA at pH 8 compared to pH 6 can be explained by the increased stability of bromochloramine. At pH 6, bromochloramine rapidly decomposes, decreasing the conversion rate of NDMA precursors to NDMA.

5.4.4 Effect of NOM on the formation of NDMA in selected model precursor compounds and treated water

The goal of this experiment was to investigate the effect of NOM on the formation of NDMA from DMA, TMA, polyDADMAC, polyACRYL in the presence of 1000 μg/L bromide during chloramination. The initial concentration of DMA and THM was 200 nM, while concentrations of polyDADMAC and polyACRYL were 0.2 mg/L and 1.0 mg/L, respectively. DOC was adjusted by diluting DWTP raw water with DDI water. Understanding of the effect of bromide on the formation of NDMA from selected NDMA model precursors in the presence of NOM is important due to the practical implications for water treatment. The results of this experiment are shown in Figure 5–7.

NDMA formation was normalized to the concentration of NDMA in the presence of bromide and no DOC. The formation of NDMA from DMA, TMA and polyDADMAC was suppressed by >70% at 0.94 mg C/L. While polyACRYL was less impacted (~25%) by the presence of NOM. After 1.9 mg C/L the formation of NDMA remained constant for the four compounds.

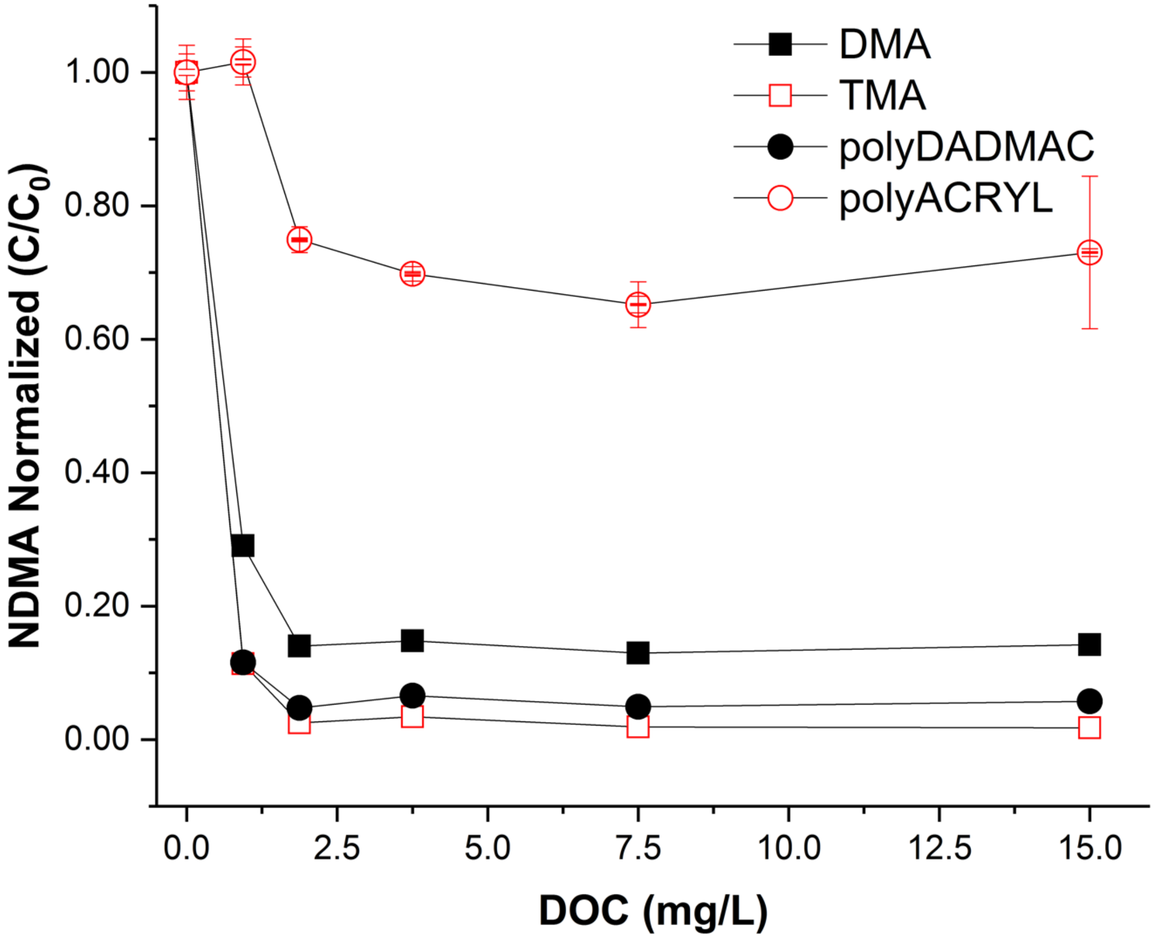


Figure 5–7. Effect of DOC on the formation of NDMA from selected model precursors compounds. Experimental conditions: $[DMA]_0 = [TMA]_0 = 200$ nM, $[polyDADMAC]_0 = 0.2$ mg/L, $[polyACRYL]_0 = 1$ mg/L, $[Bromide]_0 = 1$ mg/L, $[NH_2Cl]_0 = 3$ mg Cl_2/L, phosphate buffer = 0.008 M, contact time = 3 d, temperature = (21 ± 2) °C. Error bars represent the standard deviation of two injections of one sample.

The difference in the molecular structures of the model precursors did not cause changes in the pattern of NDMA formation. Under the experimental conditions, it was clear that increasing the DOC concentration suppressed the formation of NDMA from the selected NDMA precursor compound but the effect was stronger for DMA, TMA and polyDADMAC. Bromide enhanced the formation of NDMA from the selected compounds

(Figure 5–3) in the absence of NOM. However, such conditions are not expected to happen during water treatment. NOM is a ubiquitous component of natural waters. In the presence of NOM, monochloramine loss can happen. It occurs in two different pathways via auto decomposition and oxidation of NOM (Chen and Valentine, 2006). In the conditions of this experiment, bromamines species and to a lesser extent hypobromous acid (HOBr) may form through the oxidation of bromide by monochloramine. In the presence of NOM, HOBr participates in oxidation/substitution reactions resulting in a mixture of halogenated DBPs that leads to the loss of monochloramine (Duirk and Valentine, 2007).

The oxidation of bromide by monochloramine forms different active forms of bromine in the +1 valence state. These bromine active species may also react with NOM resulting in the formation of brominated and mixed chlorinated-brominated DBPs. Two major reactions in the oxidation of bromide are of importance. First, the ionization of monochloramine forms the monochlorammonium ion (NH_3Cl^+) that later oxidizes bromide to bromochloramine (NHBrCl) (Duirk and Valentine, 2007; Le Roux et al., 2012a; Trofe et al., 1980). Second, the hydrolysis of monochloramine forms hypochlorous acid that further oxidize bromide to HOBr (Valentine and Jafvert, 1988).

All bromine species formed as a consequence of the oxidation of bromide either by monochloramine or hypochlorous acid can oxidize NOM (Duirk et al., 2005; Duirk and Valentine, 2007; Vikesland et al., 2001). The oxidation of NOM by active bromine species is a major factor in the competition between NDMA precursors and NOM for the monochloramine or the bromine active species. Consequently, it is very likely that the increase in the DOC concentration led to the formation of more chlorinated/brominated DBPs and a decrease in the overall formation of NDMA.

An additional experiment was carried out with the treated water (SW–2) to investigate the effect of bromide in the presence of NOM in the formation of NDMA during chloramination. The treated water was diluted with DDI water to reach a DOC of 2.0 mg C/L to simulate the conditions of a finished water. The samples were amended with DMA, TMA, polyDADMAC and polyACRYL at 200 nM, 200 nM, 0.2 mg/L and 1 mg/L, respectively. The formation of NDMA was measured in the absence and in the presence of 1000 μg/L bromide and the results are presented in Figure 5–8.

NDMA formation was enhanced in the presence of bromide and increased by 20%, 20% and 10% for DMA, TMA and polyDADMAC, respectively. However, the presence or absence of bromide in solution with polyACRYL was not a factor affecting the formation of NDMA. In contrast, under the same conditions and in the absence of NOM the formation of NDMA was increased by 88%, 110%, 44% and 36% for DMA, TMA, polyDADMAC and polyACRYL, respectively. Bromide is not removed during conventional water treatment processes and its presence is of concern because it leads to higher formation of NDMA as demonstrated here. Overall, the results of this experiment shows that even though NOM promotes the decay of monochloramine in bromide containing waters, the formation of NDMA may be enhanced.

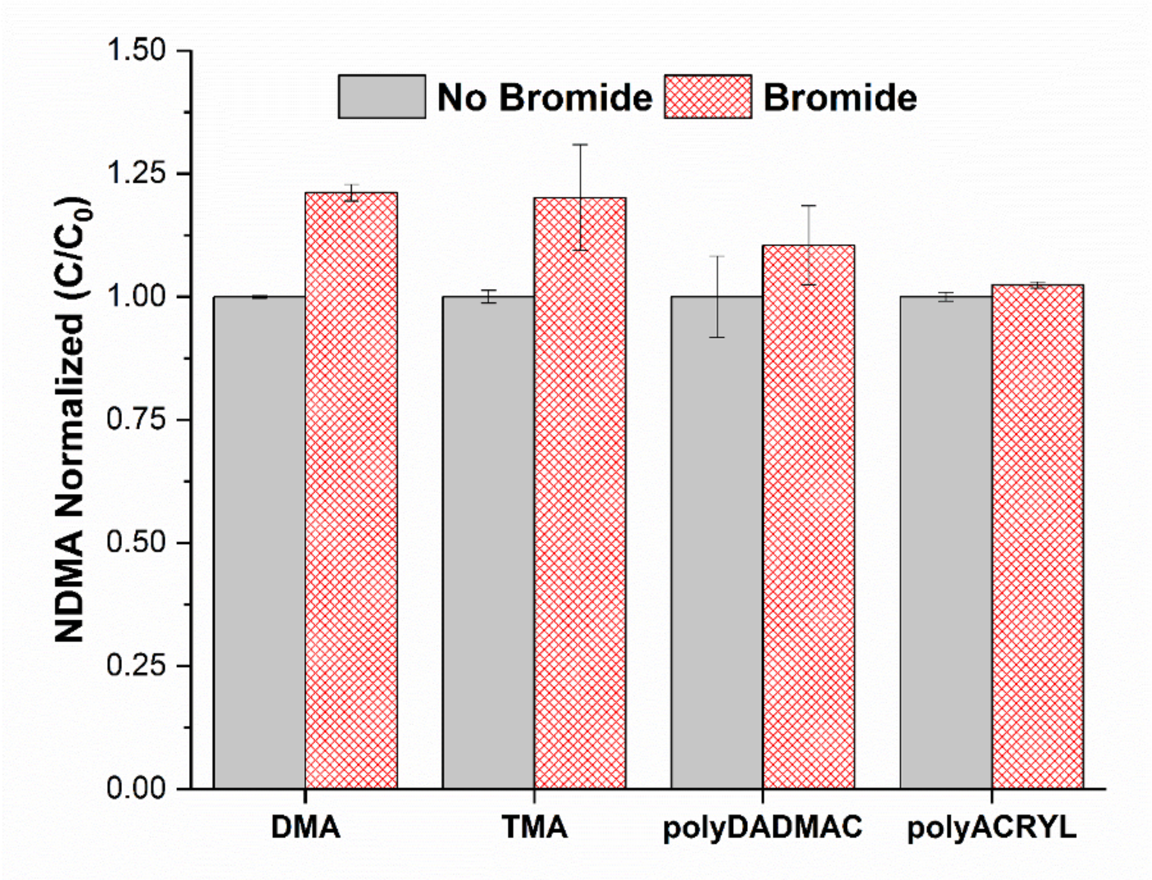


Figure 5–8. Effect of bromide on the formation of NDMA in a treated source water in the presence of selected NDMA model precursors compounds. Experimental conditions: $[DOC]_0$ = 2 mg C/L, $[DMA]_0$ = $[TMA]_0$ = 200 nM, $[polyDADMAC]_0$ = 0.2 mg/L, $[polyACRYL]_0$ = 1 mg/L, $[Bromide]_0$ = 1 mg/L, $[NH_2Cl]_0$ = 3 mg Cl_2/L, phosphate buffer = 0.008 M, contact time = 3 d, temperature = (21 ± 2) °C. Error bars represent the standard deviation of two injections of one sample.

5.5 Conclusions

I investigated the effect of bromide on the formation of NDMA for a selected group of NDMA model precursor compounds and polymers commonly used in water treatment. Experiments were conducted in DDI water, secondary wastewater effluent and surface water samples. I found that increasing the bromide concentration (0–1000 μg/L) in surface water samples caused no enhancement on the formation of NDMA either with 3 or 100 mg Cl_2/L monochloramine. In contrast, bromide suppressed the formation of NDMA with increasing bromide concentration in wastewater effluent samples at 3 mg Cl_2/L monochloramine. But no effect was observed with monochloramine at 100 mg Cl_2/L. It is possible that bromochloramine reacted with NOM rather than with NDMA precursors and consequently decreased the formation of NDMA. In DDI water, bromide enhanced the formation of NDMA in the NDMA model precursors compounds, and more NDMA was formed at pH 8 compared to pH 6. In the presence of 1 mg/L bromide, increasing the DOC concentration (0–15 mg/L) suppressed the formation of NDMA in the NDMA model precursor compounds. However, in a water with DOC levels around 2 mg/L the presence of 1 mg/L bromide and DMA, TMA and polyDADMAC increased the formation of NDMA compared to the water in the absence of bromide.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

I studied the potential of ion exchange resins to control NDMA and THMs precursors in a single treatment is presented. Particularly, two ion exchange resins were examined, a cation exchange resin (Plus) to target NDMA precursors and an anion exchange resin (MIEX) for THMs precursors control. The treatment of surface and wastewater effluent samples with both resins removed simultaneously NDMA (43–85%) and THMs (39–65%) precursors. I also found that in the presence of high levels of calcium, the Plus exchange resin released NDMA precursors. The amount of NDMA precursors that was released from the Plus resin increased with the calcium concentration and the regeneration of the resin decreased. Given that bromide is not well removed, its presence in water is a cause of concern because it can lead to the formation of brominated DBPs that are more cytotoxic and genotoxic than the chlorinated analogs. I found that bromide (0–1000 μg/L) increased the formation of NDMA only in aqueous solutions of NDMA model precursor compounds but not in surface waters. In wastewater effluent samples, bromide suppressed the formation of NDMA with increasing bromide concentration. Additional conclusions for each chapter are summarized as well as some recommendations for future research.

Chapter Three

REMOVAL OF BOTH *N*-NITROSODIMETHYLAMINE AND TRIHALOMETHANES PRECURSORS IN A SINGLE TREATMENT USING ION EXCHANGE RESINS.

- The combined application of Plus and MIEX resins effectively controlled concurrently NDMA and THMs precursors, and no interaction between the resins was found.
- Plus resin removed NDMA FPs (45–90%) in surface and wastewater effluent samples and produced similar results when it was simultaneously applied with MIEX resin (43–85%).
- MIEX resin alone and combined with Plus resin lowered the THMs FPs ranging from 39% to 69%.
- Plus resin alone and combined with MIEX resin reduced the concentration of NDMA precursors regardless of the initial concentration of the precursors (NDMA FPs 706–6544 ng/L).
- In naturally attenuated wastewater effluents, the fraction of precursors removed with both the Plus alone and combined was similar to the fresh wastewater effluent samples (73–85%).
- Natural attenuation decreased the reactivity of NDMA precursors but their cationic nature was preserved. I found that a increasing the concentration of calcium from 8.8 mg $\mathrm{Ca}^{2+/}$L to 91.2 mg $\mathrm{Ca}^{2+/}$L in the wastewater effluent reduced the ability of the cation exchange resin to remove NDMA precursors by 50%.

Chapter Four

FACTORS AFFECTING THE CONTROL OF *N*-NITROSODIMETHYLAMINE AND TRIHALOMETHANES PRECURSORS WITH ION EXCHANGE RESINS.

- The pH is a major factor affecting the efficiency of the ion exchange process because it determines the form of the precursor species present. NDMA precursors were removed at both acidic and neutral conditions with cation exchange resin, indicating that the precursors were protonated at these pH ranges. At pH to 10 NDMA precursors not only were not removed but the cation exchange resin leached NDMA precursors.
- Experiments conducted in distilled deionized water showed that NDMA precursors released in the same conditions as the natural waters.
- Plus resin and the combined treatment removed NDMA FPs (40%) and THM FPs (50%) in the wastewater with naturally occurring levels of the selected inorganic ions (bicarbonate, bromide, calcium, nitrate and sulfate).
- However, NDMA FP increased in the enriched wastewater after the treatment with the cation exchange resin (20%). This effect was specific of the Plus resin since similar experiments with the commercial Purolite® cation exchange resins did not increase the NDMA FP after treatment.
- The removals of THM precursors by the anion exchange resin were affected by the elevated sulfate concentrations in the amended water and were lowered from 50% to 20–30%.

- Bromide was not removed in either the ambient or the enriched wastewater effluent sample. While nitrate was removed only in the unamended wastewater sample.
- In the presence of high levels of calcium (112.8 mg Ca^{2+}/L), the Plus exchange resin released NDMA precursors.
- The amount of NDMA precursors that were released from the Plus resin increased with the calcium concentration (in the range of 0–192 mg Ca^{2+}/L).
- However, NDMA FP levels subsided with increasing the number of regeneration cycles and approached the level of the DDI water (10 ng/L).

Chapter Five

EFFECT OF BROMIDE ON THE FORMATION OF NDMA IN MODEL PRECURSOR COMPOUNDS AND NATURAL WATERS.

- Increasing the bromide concentration (0–1000 μg/L) in surface water samples caused no enhancement on the formation of NDMA either with 3 or 100 mg Cl_2/L monochloramine.
- Bromide suppressed the formation of NDMA with increasing bromide concentration in wastewater effluent samples at 3 mg Cl_2/L monochloramine. But no effect was observed with monochloramine at 100 mg Cl_2/L. It is possible that bromochloramine reacted with NOM rather than with NDMA precursors and consequently decreased the formation of NDMA.
- In DDI water, bromide enhanced the formation of NDMA in the NDMA model precursors compounds (up to two-fold), and more NDMA was formed at pH 8 compared to pH 6.
- In the presence of 1 mg/L bromide, increasing the DOC concentration (0–15 mg/L) suppressed the formation of NDMA in the NDMA model precursor compounds.
- In a water with DOC levels around 2 mg/L the presence of 1 mg/L bromide and DMA, TMA and polyDADMAC increased the formation of NDMA compared to the water in the absence of bromide.

Recommendations

Although in this work, I have only investigated the removal of NDMA and THM precursors; it is expected that the formation of precursors of regulated haloacetic acids can also be controlled since NOM is a common precursor for both of them.

Bromide is not efficiently removed with anion exchange resins unlike NOM. This increases the NOM to bromide ratios after the ion exchange treatment which changes the speciation of the formed trihalomethanes. In that sense, future research needs call for examining the speciation of chloraminated and brominated.

Also, future research needs could be directed to design and evaluate ion exchange resins with an increased selectivity for bromide. In this dissertation, the combination of two ion exchange resins was studied; however, multiple possibilities exist in the mixing of ion exchange resins that target specific contaminants while decreasing the competition of background organic and inorganic compounds. For example, mixed resin systems including three or more resins that target specific components can be investigated.

In the third chapter, it was demonstrated that a majority of NDMA precursors in the studied water samples behave as cation molecules. Thus, the removal of NDMA precursors occurs via an ion exchange mechanism. A variable fraction of NDMA precursor was not subjected to ionization and thus was not amenable to removal with cation exchange resins. Providing other materials with the cation exchange resins during the treatment that are capable of targeting non-ionized NDMA precursors is an area of study that could benefit by further research. Cation exchange resins investigated in this work had sulfonate functional group, the effect of other functional groups in the cation exchange resin merits more effort.

In the fourth chapter, it was found that a cation exchange resin exposed to high concentrations of calcium released a significant amount of NDMA precursors. This is an important finding since most studies in the literature have reported the release of NDMA and NDMA precursors from anion exchange resins but not cation exchange resins. The mechanism by which calcium promotes the release of NDMA precursors from the cation exchange resin needs further research as well.

In the fifth chapter, the experiments conducted showed that bromide enhanced the formation of NDMA from NDMA model precursor compounds in the absence of NOM and suppressed the formation of NDMA in wastewater effluent samples. Bromide caused no effect in surface waters with low levels of NDMA. To further address these findings additional experiments are needed. More insight can be gained on the effect of bromide on the formation of NDMA due to changes in the concentration and the reactivity of NDMA precursors. This can be addressed by diluting wastewater effluents samples in DDI water at different ratios, and running simulated natural attenuation experiments.

APPENDICES

APPENDIX A

Table A–1. Selected characteristics of the unamended wastewater effluent used for ion exchange experiments.

Parameter	Units	WW-A	WW-B
Calcium	mg/L	47.2	12.8
DOC	mg/L	5.6	3.5
NDMA FP	ng/L	2,104	922
NDMA UFC	ng/L	607	175
pH	pH units	6.7	7.8
$SUVA_{254}$	L/mg-m	2.0	2.1
THMs FP	µg/L	29	67
THMs UFC	µg/L	185	155

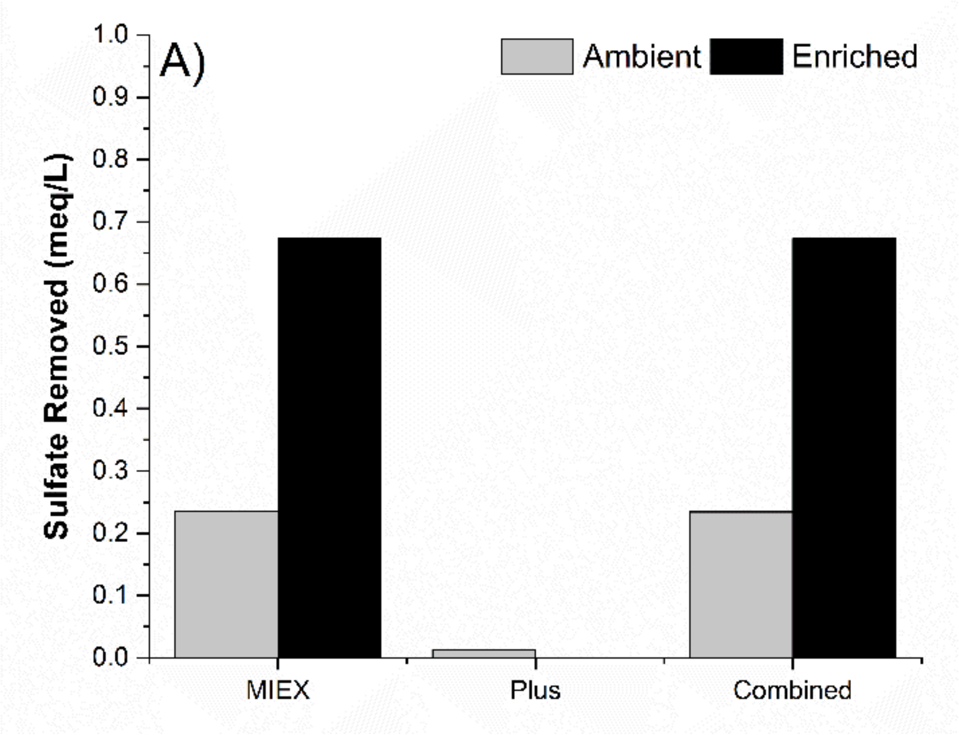


Figure A–1. Removal of sulfate in a secondary wastewater effluent sample with ambient (0.26 meq SO_4^{2-}/L) and enriched (5.5 meq SO_4^{2-}/L) concentrations of sulfate by ion exchange resins.

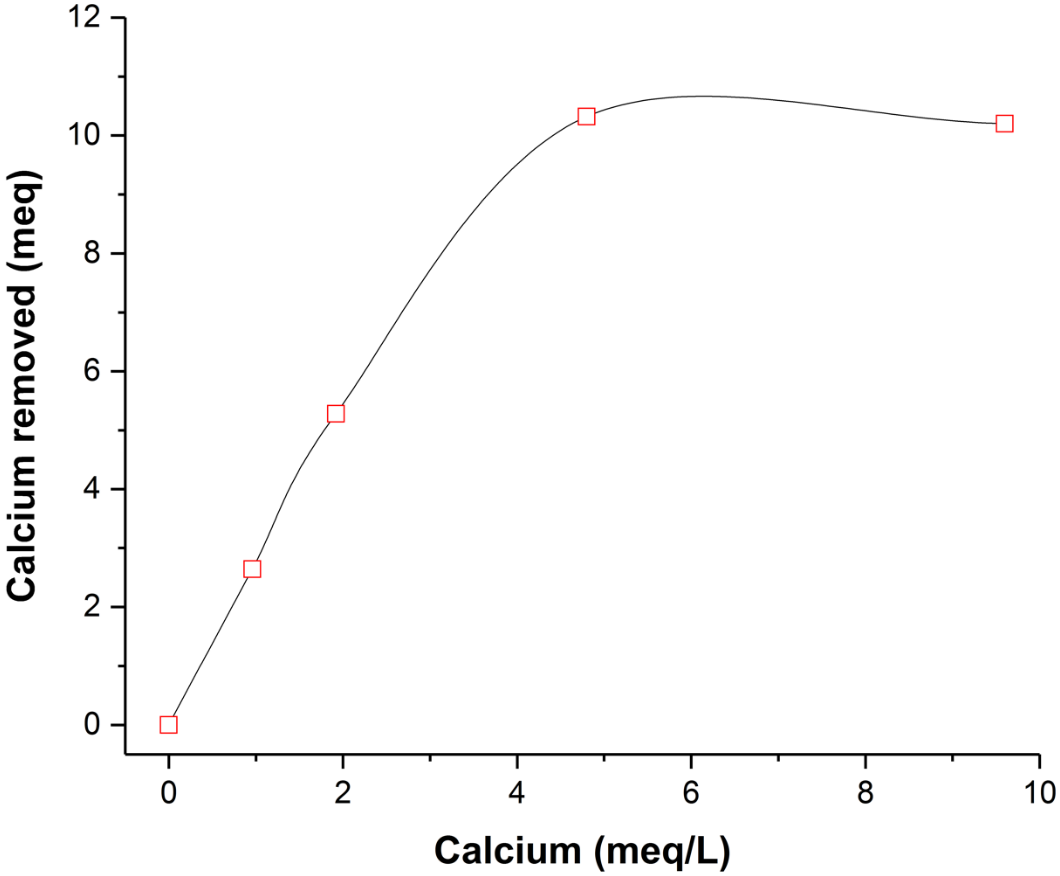


Figure A–2. Removal of calcium with Plus resin in contact with DDI water containing calcium at different concentration levels. Experimental conditions: resin dose = 5 mL, contact time = 15 min, BV= 600.

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