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REMOVAL OF N- NITROSODIMETHYLAMINE AND TRIHALOMETHANE PRECURSORS WITH POWDERED ACTIVATED CARBON

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REMOVAL OF N-NITROSODIMETHYLAMINE AND TRIHALOMETHANE
PRECURSORS WITH POWDERED ACTIVATED CARBON

A Thesis
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science
Environmental Engineering and Sciences

by
Wilson Beita Sandí
August 2013

Accepted by:
Dr. Tanju Karanfil, Committee Chair
Dr. Cindy M. Lee
Dr. David A. Ladner

ABSTRACT

N-nitrosodimethylamine (NDMA) has been used commercially in several applications, including the production of liquid rocket fuel, and a variety of foods, but gained more relevance when it was discovered as a drinking water disinfection by-product (DBP) in 1989. NDMA is a probable human carcinogen with 10^{-6} lifetime cancer risk associated with a drinking water concentration of 0.7 ng/L, and is listed as a priority pollutant in the Code of Federal Regulations; no federal maximum contaminant level has been established for drinking water yet. However, the United States Environmental Protection Agency is planning to make a preliminary regulatory determination in 2013 on regulating NDMA in drinking water.

The use of one or a combination of disinfectants is not likely to eliminate the formation of disinfection byproducts (DBPs), thus there is a need to apply treatment technologies to maximize the removal of DBP precursors from water before oxidant addition. Powdered activated carbon (PAC) is commonly added in water treatment plants (WTPs) at different locations for taste and odor control and/or removal of synthetic organic chemicals (SOCs) such as pesticides. Since PAC can adsorb different types of organic compounds, it might also be a promising option for removal of NDMA precursors.

The objectives of this project were (i) to examine the removal of NDMA FP by PACs in different waters and (ii) to examine the roles of PAC characteristics (e.g., raw material, surface chemistry, pore size distribution, and surface area) on the removal of

NDMA precursors. Due to regulatory and practical significance, the removal of THM precursors was also simultaneously investigated.

To address the objectives I collected wastewater-impacted and surface water sources to conduct adsorption experiments using powdered activated carbon and activated carbon fibers, showing a wide range of physicochemical characteristics. Also, I ran additional experiments with wastewater effluents to further understand the impact of changes in concentration and reactivity of NDMA precursors on their adsorption by PAC.

The results showed that the removal efficiency of NDMA formation potential (FP) precursors by PAC is significantly higher in samples from wastewater effluents and close proximity of wastewater influence than surface waters. The removal of NDMA FP by PAC was affected by the initial concentration of NDMA FP, and increased with increasing NDMA FP in water. The removal of THM FP was not greatly affected by the water source, due to the presence of large natural organic matter (NOM) molecules and short contact time during the adsorption experiments.

The adsorbability of NDMA precursors and effectiveness of PAC adsorption decreased with increasing distance from the wastewater discharges due to their natural attenuation through a combination of processes (biodegradation, photolysis and adsorption). Adsorbable NDMA precursors showed a size distribution in the waters tested, and the adsorbable fraction included more precursors in the size region of 10-20 Å than < 10 Å, and THM precursors were found to be much larger than the NDMA precursors (> 20 Å).

Basic carbons showed higher removal of NDMA FP and THM FP than acidic carbons. However, the overall removal on a mass basis will depend on the surface area, pore size distribution and pH_{PZC} . PACs with a basic surface and pores $> 10 \text{ \AA}$ are likely to be more effective for NDMA precursor control.

DEDICATION

This thesis is dedicated to my family.

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First and foremost, I would like to express my sincere gratitude to my advisor Dr. Tanju Karanfil, for his guidance, patience, motivation, and enthusiasm, and my committee members, Dr. Cindy M. Lee and Dr. David A. Ladner, for their insight and expertise.

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CHAPTER I

INTRODUCTION

NDMA and its formation

N-nitrosodimethylamine (NDMA) has been used commercially as an inhibitor of nitrification in soil, plasticizer for rubber and polymers, solvent in the fiber and plastics industry, antioxidant, softener of copolymers, additive to lubricants, and as intermediate in the production of 1,1-dimethylhydrazine, a liquid rocket fuel that contained approximately 0.1% NDMA as impurity (Najm and Trussel, 2001). NDMA is also present in a variety of foods: cured meats, fried bacon, marine products, flour and grain products, dairy and cheese products, and alcoholic beverages including beer and whisky (Tricker and Preussmann, 1991). NDMA is completely miscible in water and does not sorb onto solid particles or sediment (USEPA, 2013).

NDMA was discovered as a drinking water disinfection by-product (DBP) in Oshweken, Ontario, Canada, in 1989 (Jobb et al., 1993). Formation of NDMA is also promoted in wastewater effluents due to the presence of a wide range of NDMA precursors such as dimethylamine (DMA) and aliphatic tertiary amines with a DMA functional group (Mitch and Sedlak, 2004). During disinfection, NDMA formation is favorable in the presence of chloramines (Najm and Trussell, 2001; Sedlak et al., 2005). Thus, while chloramination generally results in lower levels of regulated disinfection byproducts such as trihalomethanes (THMs) and haloacetic acids (HAAs), NDMA formation is conversely promoted. NDMA formation mechanisms will be further reviewed later in this chapter.

Importance of NDMA and health effects

NDMA was classified as a probable human carcinogen with 10^{-6} lifetime cancer risk associated with a drinking water concentration of 0.7 ng/L by the U.S. Environmental Protection Agency (USEPA, 2002a), and as 2A, probably carcinogenic, by the International Agency for Research on Cancer of the World Health Organization (IARC, 2009).

In addition to ingestion through drinking water or food, nitrosamines may also be formed in the human body by nitrosation reactions (Fig. 1.1). Nitrosation depends on NO synthases (neuronal, endothelial, or inducible) that generate the nitrosating agent nitric oxide from arginine in a variety of tissues and the availability of amine precursors in various body compartments (Hrudey et al., 2013).

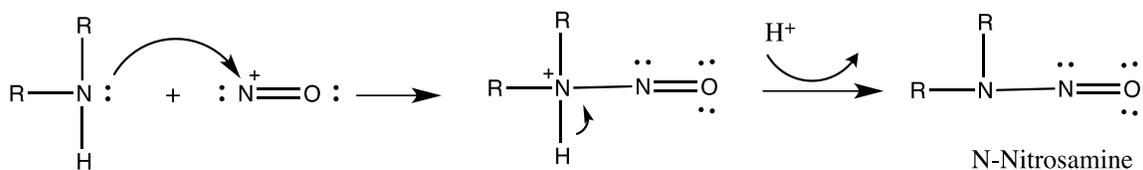


Figure 1.1. Nitrosation mechanism of secondary alkylamines.

A Monte Carlo modeling analysis was used to understand the exogenous contribution of drinking water to total human NDMA exposure (Fristachi and Rice, 2007). Results showed that drinking water contributed less than 2.8% of ingested NDMA and less than 0.02% of total NDMA exposure when estimated endogenous formation was considered. A recent Monte Carlo analysis by Hrudey et al. (2013) employing the UCMR2 database, to be discussed in the next section, showed that drinking water

contributes a mean proportion of the lifetime average daily NDMA dose ranging from between 0.0002% and 0.001% for surface water systems using free chlorine or between 0.001% and 0.01% for surface water systems using chloramines. Although the contribution of drinking water is such a negligible contributor to total human exposure to N-nitrosamines, other factors are considered by the U.S. EPA to develop a regulation for NDMA (adverse effect on the health of persons and occurrence in public water systems at frequency and levels of public health concern).

Occurrence of NDMA in U.S. drinking waters

NDMA detection in drinking water wells near rocket testing facilities in California, employing unsymmetrical dimethylhydrazine (UDMH)-based fuels, motivated the California Department of Health Services (DHS) to sponsor a survey of NDMA in California drinking waters. NDMA was detected in groundwater in concentrations as high as 400,000 ng/L. The results of this survey demonstrated that NDMA occurrence was not limited to regions proximal to facilities that used UDMH-based fuels, but also found that NDMA formed as a byproduct of chloramine disinfection of water and wastewater. Especially in locations where chlorinated wastewater effluent was used for aquifer recharge, NDMA was present at elevated concentrations (Mitch et al., 2003).

Over the last decade, interest has been growing about NDMA formation during drinking water treatment. Disinfection with chloramines is known to significantly reduce the formation of regulated THMs and HAAs as compared to disinfection with

chlorination. However, chloramination favors the formation of N-nitrosamines, including NDMA (Choi et al., 2002a; Mitch et al., 2003; Mitch and Sedlak, 2004; Le Roux et al., 2011).

The amendment of the Safe Drinking Water Act (SDWA) in 1996 required that once every five years, U.S. Environmental Protection Agency (USEPA) provides a new list of no more than 30 unregulated contaminants to be monitored by public water systems (PWSs). This monitoring provides a basis for future regulatory actions to protect public health. Since 1999, three Unregulated Contaminant Monitoring Rule (UCMR) programs, in coordination with the Contaminant Candidate List (CCL), have been issued (USEPA, 2006).

The analysis of nitrosamine data from samples collected under the UCMR2 revealed that NDMA was detected in U.S. drinking waters at concentrations > 2 ng/L in 10% of the samples surveyed, and 26% of systems detected NDMA in at least one sample (Russell et al., 2012). In contrast, NDMA occurrence in water systems in the United Kingdom showed a much lower frequency, only 7.3% in concentrations up to 5.8 ng/L (Dillon et al., 2008). Systems with NDMA concentrations below the minimum reporting levels (MRLs) tended not to use chloramines as either a primary or a secondary disinfectant.

However, other nitrosamines (e.g., N-nitrosodiethylamine (NDEA), N-nitroso-di-n-butylamine (NDBA), N-nitrosopyrrolidine (NPYR), and N-nitrosomethylethylamine (NMEA)) were rarely detected at levels above their MRLs. NDMA was primarily detected in systems using chloramines, and concentrations were higher, ranging from 4 to

15 ng/L (the maximum NDMA excursion measured was 630 ng/L), in water systems having long contact times with chloramines.

The same study also showed that systems using chloramine as disinfectant had 35% of the samples above its MRL, compared to 3% that used chlorine. The highest NDMA concentrations (i.e., > 50 ng/L) were observed in Community Water systems (CWSs) located in California, Florida, Minnesota, Oklahoma, and Texas; and these states reported the highest percent of chloramines use (Russell et al., 2012).

Additionally, Russell and collaborators (2012) observed NDMA above the MRL in chloraminated systems reporting pH of 7.4 to 8.1, whereas NDMA concentrations below the MRL was detected in systems with pH of 7.0. The latter is consistent with previous studies (Krasner et al., 2010; Schreiber & Mitch, 2006; Sacher et al., 2008), reporting increased NDMA formation at pH 8–9 compared with pH 7.

The results also highlighted chloramines use as the more important factor leading to NDMA formation and did not find significant differences between chloraminated CWSs using polyDADMAC or epi-DMA and systems using no cationic amine-based polymer or polyacrylamide only. Finally, results showed increased NDMA formation with decreased chlorine contact time along with increased wastewater impacts.

Nitrosamines and NDMA regulations in United States

Although NDMA is listed as a priority pollutant in the Code of Federal Regulations (CFR) (40 CFR 136.36), no federal maximum contaminant level (MCL) has been established in drinking water. However, six nitrosamines were monitored as part of

the UCMR2. Four of these nitrosamines—NDMA, NDEA, NDPA, and N-nitrosopyrrolidine (NPYR)—were included in the final Contaminant Candidate List 3, along with N-nitrosodiphenylamine (NDPhA; USEPA, 2009). The five nitrosamines included on the list were selected as a group of 32 constituents that have been shortlisted for further evaluation in USEPA regulatory determination process.

In California, the Department of Public Health (CDPH) set 10-ng/L notification levels for three nitrosamines (CDPH, 2013), and the Office of Environmental Health Hazard Assessment (OEHHA) set a 3-ng/L public health goal for N-nitrosodimethylamine (NDMA) (OEHHA, 2006). USEPA plans a preliminary regulatory determination for nitrosamines in 2013 and, if it intends to regulate, a regulation will be proposed in 2016.

NDMA formation during drinking water treatment

Several pathways have been proposed for the formation of nitrosamines during drinking water treatment: chloramination, ozonation, chlorination of nitrite-containing waters, breakpoint chlorination, activated carbon, and photolysis.

Chloramination

Formation of nitrosamines during chloramination is likely to be the most important pathway in drinking water. Early mechanistic research (Mitch et al., 2003) suggested the nucleophilic substitution reaction between unprotonated secondary amines and monochloramine, to form an UDMH intermediate that can be later oxidized by chloramines to form NDMA (Fig. 1.2).

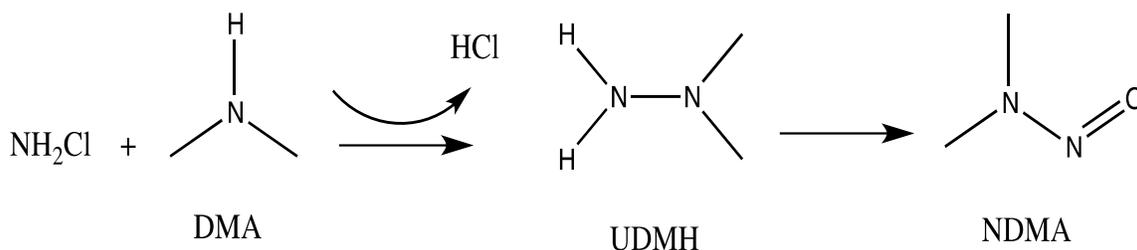


Figure 1.2. Nucleophilic substitution of secondary amines to form NDMA through UDMH intermediate (Mitch et al., 2003).

However, Schreiber and Mitch (2006) revised the proposed mechanism by Mitch and colleagues (2003) and suggested the formation of a chlorinated unsymmetrical dimethylhydrazine intermediate (Cl-UDMH) from a nucleophilic substitution reaction between DMA and dichloramine (NHCl₂) instead of monochloramine. Oxidation of Cl-UDMH by oxygen to form NDMA competes with its oxidation by chloramines to form other products (Fig. 1.3). The pathway was demonstrated to accurately model NDMA formation over a wide range of conditions during application of preformed NHCl₂ to DMA, and even preformed monochloramine (dichloramine could be present in traces due to equilibrium with monochloramine).

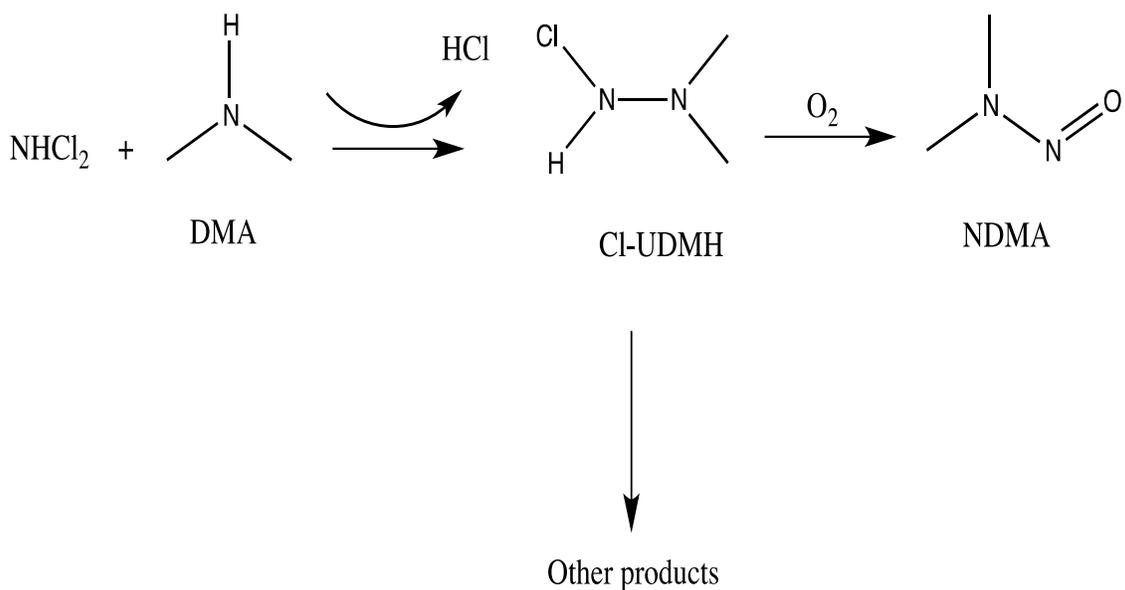


Figure 1.3. NDMA formation from dichloramine and DMA through Cl-UDMH intermediate (Schreiber and Mitch, 2006).

However, a comprehensive study by Selbes and colleagues (2013) demonstrated that tertiary amine precursor compounds react with both mono- and dichloramine to form NDMA, and the preference of chloramine species depends on the structure of the leaving group attached to the nitrogen atom of the DMA moiety.

In this mechanism, there is a nucleophilic attack of amines on chloramines and the preference of chloramine species depends on electron densities of precursors and oxidants (Fig. 1.4). Tertiary amines with electron withdrawing groups (EWG) react with monochloramine; meanwhile the presence of electron donating groups (EDG) favors the reaction with dichloramine (Selbes et al., 2013).

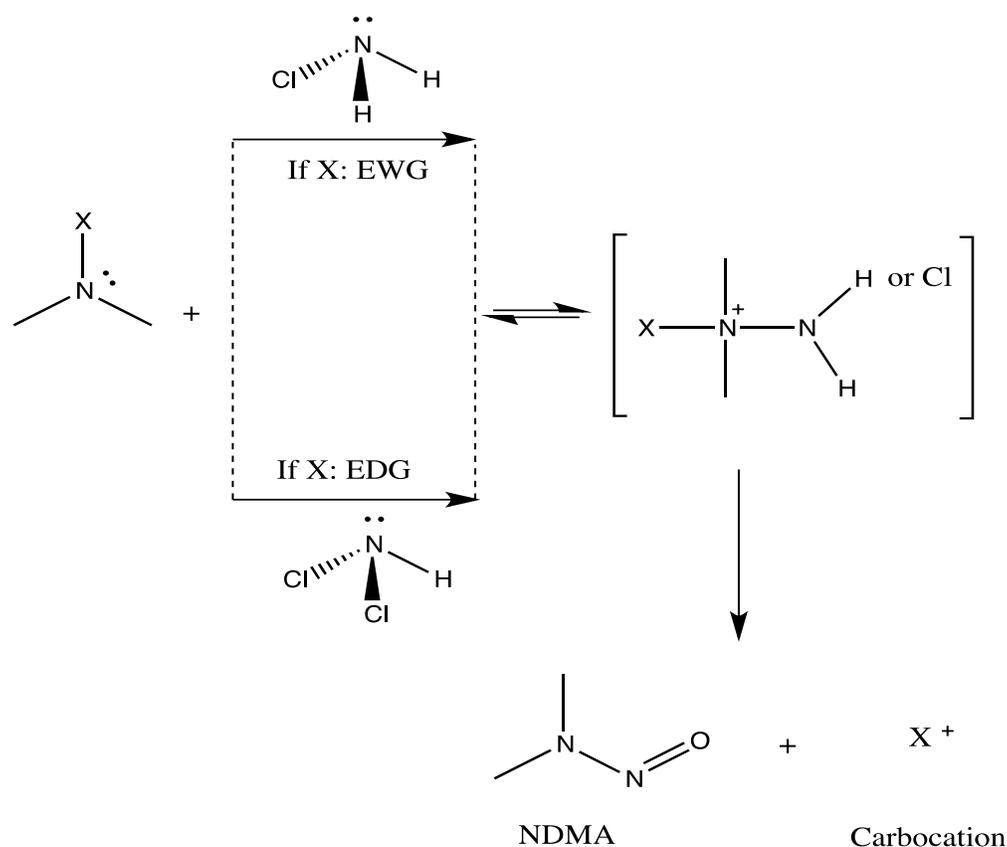


Figure 1.4. Mechanism of nucleophilic substitution of tertiary amine with monochloramine and dichloramine to form NDMA and intermediate carbocation.

Either the reaction of tertiary amines with monochloramine or dichloramine lead to the formation of a carbocation (X⁺) that is prone to react with other nucleophiles such as water. Particularly, the carbocation resulting from the chloramination of ranitidine has been documented (Le Roux et al., 2012b). Overall, this research provided a new insight in the role of monochloramine speciation in the formation of NDMA, and highlighted that both electronegativity and stability of the leaving group in tertiary amines are closely related with the reactivity of NDMA precursors and the preferred chloramine species involved in the NDMA formation reaction.

Ozonation

Ozonation of DMA, concentrations in natural waters or wastewaters typically are < 10 nM, forms NDMA but yields generally are < 0.02% at neutral pH (Andrzejewski et al., 2008). However, ozonation of UDMH, daminozide and semicarbazide, both of which have UDMH-like functional groups, formed NDMA at yields > 50% (Schmidt et al., 2008; Shah and Mitch, 2012). Ozonation of N,N-Dimethylsulfamide (DMS), a newly identified microbial transformation product of the fungicide tolylfluanide, formed NDMA at 52% yield (von Gunten et al., 2010). NDMA formation from ozonation of DMS is particularly important in Europe, as DMS was detected in 94% of German groundwater samples; with half of DMS concentrations > 100 ng/L (tolylfluanide was prohibited in Europe in Plant Protection Products in 2010). Tolyfluanid is not registered for use in United States (USEPA, 2002b), DMS is not on the EPA Toxic Substances Control Act (TSCA) inventory, and is supplied solely for use in research and development.

Chlorination of nitrite-containing waters

Choi and Valentine (2003) noted that NDMA forms during chlorination of nitrite-containing waters. Formation has been attributed to a dinitrogen tetroxide (N_2O_4) intermediate, which can nitrosate amines. The reaction is rapid (i.e., < 1 h), but the yields are approximately two orders of magnitude lower than for the chloramination pathway. NDMA formation increased with pH and sharply increased above about pH 8, nevertheless the reaction appears to be to be complex not only for the speciation of hypochlorous acid and DMA but also for other factors such as stability of intermediates.

This pathway has been implicated in nitrosamine formation in chlorinated wastewater effluents and recreational waters (Shah and Mitch, 2012; Walse and Mitch, 2008).

Breakpoint chlorination

Breakpoint chlorination and increase in the chlorine to ammonia molar ratio to reduce available ammonia in distribution systems are two control strategies practiced by WTPs experiencing nitrification during chloramination (Schreiber and Mitch, 2007). However, the former strategy will form a series of potentially reactive, but poorly characterized, breakpoint chlorination intermediates (e.g. N_2O_4), whereas the latter will increase the formation of dichloramine (Muellner et al., 2007).

The breakpoint chlorination enhanced NDMA formation from DMA in the presence of nitrite and chlorine (Choi and Valentine, 2003), via breakpoint chlorination intermediates. Active pathways in the breakpoint chlorination region could explain the formation of NDMA: (i) a relatively slow reaction of dichloramine with amine precursors in the presence of dissolved oxygen, and (ii) a fast reaction involving reactive breakpoint chlorination intermediates.

However, this enhancement was observed at a limited range of chlorine to ammonia molar ratios near 1.7:1, where negligible residual chlorine was measured. With a sufficient chlorine dosage to maintain free chlorine residual (e.g., 2:1 molar ratio), the enhancement in NDMA formation was not significant. Nonetheless, this pathway is likely to be important for drinking water treatment, only when free chlorine residual during breakpoint chlorination is not achieved, or poorly-controlled breakpoint

chlorination during blending of chlorinated and chloraminated waters (Krasner et al., 2013).

Formation catalyzed by activated carbon

N-nitrosamines can be formed from catalytic transformation of secondary amines on activated carbon (AC) with yields lower than 0.3% (Padhye et al., 2010). The heterogeneous catalysis requires the presence of both atmospheric oxygen and nitrogen. First, O_2 reacts with reactive sites on the AC surface and form reactive oxygen species (ROS), such as superoxide, hydroxyl radical, and hydrogen peroxide (Fig. 1.5). Next, ROS facilitate the fixation of N_2 on the AC surfaces to generate reactive nitrogen species (RNS) like N_2O or diazo intermediates (Vorob'ev-Desyatovskii et al., 2006). Later, N_2O is converted into ammonia via an H_2N_2O intermediate. Finally, the reduction of H_2N_2O can provide hydroxylamine (NH_2OH) that can react with adsorbed amines to form nitrosamines (Padhye et al., 2011b).

However, this pathway is unlikely to be important during drinking water treatment due to the combination of the low yields of the reaction from secondary amine precursors and the low importance in drinking waters of secondary amines (Krasner et al., 2013).

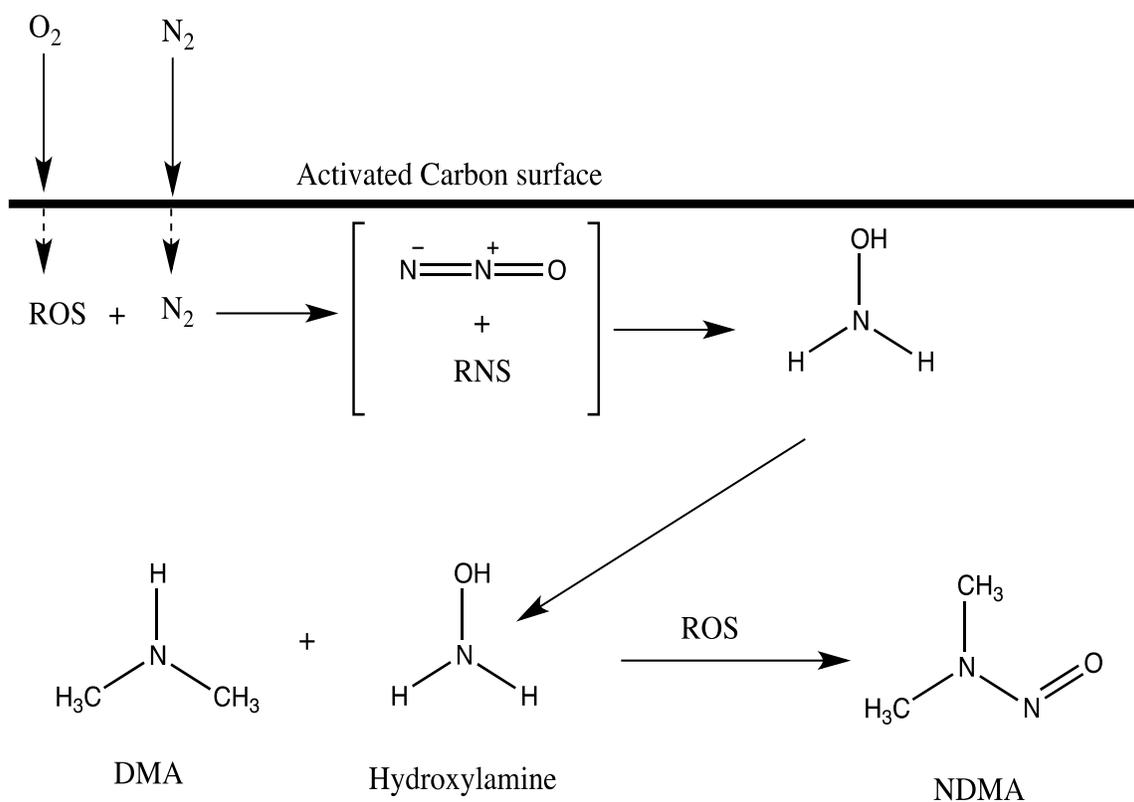


Figure 1.5. Formation of NDMA catalyzed by Activated Carbon.

Formation catalyzed by UV or sunlight photolysis

Sunlight photolysis of nitrite at $\lambda < 400$ nm forms $\text{NO}\cdot$ and $\cdot\text{OH}$. Formation of RNS can occur following $\cdot\text{OH}$ oxidation of $\text{NO}\cdot$ to $\text{NO}_2\cdot$, including the nitrosating species N_2O_3 and N_2O_4 (Shah and Mitch, 2012). Sunlight photolysis of 4 mM DMA and 1 mM nitrite formed NDMA with a yield of 0.015% (Lee and Yoon, 2007). Due to the low concentrations of nitrite and dimethylamine present in natural waters, this formation pathway is likely not important in practice.

Factors affecting NDMA formation

Several factors affect the formation of NDMA during drinking water treatment, including (i) chloramine speciation, (ii) disinfectant dose and contact time, (iii) pH level, and (iv) bromide concentration, among others.

Chloramine speciation

In aqueous solutions at pH 7.0 to 8.5, chlorine (i.e. HOCl) reacts rapidly with ammonia to form a mixture of inorganic chloramines that may contain monochloramine (NH₂Cl), dichloramine (NHCl₂), or nitrogen trichloride (NCl₃), according to the following reactions:

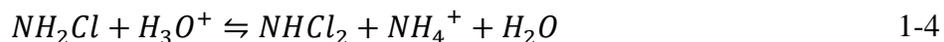


These competing reactions depend upon pH, chlorine to ammonia ratio, temperature, and contact time. At pH higher than 8, and 5:1 Cl₂:N ratio monochloramine is the dominant species. Conversely, NHCl₂ is favored as the pH decreases (4 to 6) and the Cl₂:N ratio increases (5:1 to 7.9:1) (Diehl et al., 2000). NH₂Cl is generally the chemical of interest in drinking water disinfection since dichloramine and nitrogen trichloride are too unstable to be useful, and highly malodorous. Under practical drinking water treatment operating conditions chloramination is designed to produce mostly monochloramine (USEPA, 1999).

The role of chloramine speciation in the formation of NDMA was initially reported indicating the participation of monochloramine in the nucleophilic substitution

of unprotonated secondary amines to form UDMH intermediates (Mitch and Sedlak, 2002; Choi and Valentine, 2002b). Further research showed that dichloramine enhanced NDMA formation from DMA through the formation of a chlorinated UDMH (Mitch et al., 2009).

Nonetheless, chloramination of DMA at pH 6.9 formed more NDMA with dichloramine compared to pre-formed monochloramine (Farré et al., 2010). Meanwhile studies with ranitidine (Le Roux et al., 2011) showed an increase in NDMA formation when switched from dichloramine to monochloramine (from 46.8% to 80.2%). Overall, these results suggest that NDMA formation may not always be limited to only one chloramine species; they both could be present due to the equilibrium reaction:



Disinfectant dose and contact time

Experiments conducted in natural waters (Sacher et al., 2008) and secondary wastewater effluent (Hatt et al., 2013) showed an increase in NDMA formation with increasing chloramine dose. For natural water the effect was more pronounced if only small amounts of NDMA were formed. If higher amounts of NDMA were formed, the impact of chloramine dose appeared to become negligible.

pH concentration

The effect of pH on NDMA formation in drinking water has been found to increase with increasing pH levels (Mitch and Sedlak, 2002; Sacher et al., 2008; Schreiber and Mitch, 2005; Schreiber and Mitch, 2006; Valentine et al., 2005). For

example, Schreiber and Mitch (2006) found that reaction was higher at pH 8–9, than at pH 7, and chloramination of DMA at pH 8.8 had higher NDMA yield than at pH 6.9 and 5.1 (Schreiber and Mitch, 2005). A similar trend was observed for natural waters (Krasner et al., 2012).

Bromide concentration

Bromide enhanced NDMA formation with monochloramine at pH values of 8 and 9, after 24 h of reaction time. However, at low to neutral pH (6 to 7), the presence of bromide resulted in lower NDMA formation as compared to results obtained in the absence of bromide (Luh and Mariñas, 2012). Similarly, NDMA formation from reactive 5-(dimethylaminomethyl)furfuryl alcohol (Fig. 1.6) was enhanced in the presence of bromide due to the formation of brominated oxidant species (e.g. NHBrCl , NHBr_2) and the hypothetical UDMH-Br as an intermediate (Le Roux et al., 2012a).

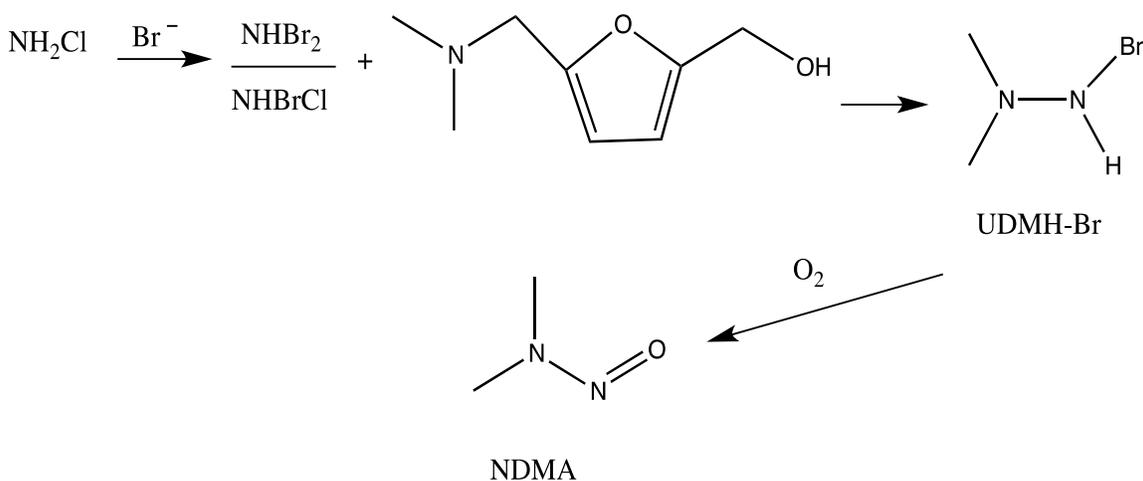


Figure 1.6. NDMA formation from 5-(dimethylaminomethyl)furfuryl alcohol enhanced by bromide.

NDMA precursors

Several sources have been identified to contain NDMA precursors, the most significant being (i) amine-containing coagulation polymers, (ii) effluent-impacted source waters, (iii) pharmaceuticals and personal care products, (iv) distribution system materials, and (v) anion exchange resins. Although limited NDMA formation has been observed for soluble microbial products, agricultural chemicals, bulk DON, and algae.

Dimethylamine (DMA) is the most studied model precursor of NDMA (Andrzejewski et al., 2008; Choi and Valentine, 2003; Lv et al., 2009; Mitch et al. and Sedlak, 2002; Mitch et al., 2003) and ubiquitous in natural waters, but molar yield of NDMA formation is low, < 3% (Lee et al., 2007; Mitch et al., 2009; Le Roux et al., 2012a; Selbes et al., 2013).

Amine-containing coagulation polymers

Cationic polymers (e.g., polyamines and polyDADMAC) used as coagulant or dewatering aids in drinking water treatment can degrade and release NDMA precursors (Kohut and Andrews, 2003; Najm and Trussell, 2001; Wilczak et al., 2003). The NDMA formation from these polymers was strongly related to polymer degradation and DMA release during chloramination. In polyamines, the tertiary amine chain ends play a major role in the NDMA formation, whereas with polyDADMAC it is the quaternary ammonium ring group (Park et al., 2009). Also, polyamines have been found to produce more NDMA than polyDADMAC around pH 8 during chloramination. Additionally, ozonation of polyDADMAC yielded three and four times more NDMA compared to polyacrylamide (PAM) and polyamine (Padhye et al., 2011a).

Wastewater impacted source waters

Wastewater-impaired waters are also a source of NDMA precursors (Guo and Krasner, 2009; Krasner, 2009; Schreiber and Mitch, 2006; Shah and Mitch, 2012). Specific precursors in wastewater-impacted water supplies have not been characterized but may include tertiary amine-based pharmaceuticals and pesticides (Le Roux et al., 2011; Shen and Andrews, 2011a) or quaternary amine-based constituents of shampoos and other personal care products (Kemper et al., 2009). The herbicide diuron has been identified as a nitrosamine precursor that can occur in wastewater or agriculturally affected source waters (Chen and Young, 2008; Kemper et al., 2009; Le Roux et al., 2011; Sacher et al., 2008).

Pharmaceuticals and personal care products

Chloramination of pharmaceutical and personal care products (PPCPs) has led to the formation of nitrosamine in water (Shen and Andrews, 2011a, 2011b). Amine groups in PPCP molecules could serve as nitrosamine precursors in the chloramination process. Among the tested pharmaceuticals, ranitidine showed the highest molar conversion (40.2%) to NDMA (five days of contact time at pH 8.5), and the formation increased as the pH decreased to 7.9 (59.6%), indicating the importance of the pH (Le Roux et al., 2011; Le Roux et al., 2012b).

These results (Le Roux et al., 2011) revealed that the investigated compounds (ranitidine, minocycline, doxepine, amitriptyline, mifepristone, isotretinoin, trifluralin, and diuron) formed NDMA in greater amounts than DMA, and highlighted the importance of structural characteristics of tertiary amines for NDMA formation.

Compounds with a heterocyclic ring in their structure (e.g. ranitidine) produced more NDMA than compounds with DMA functions near carbonyl groups (i.e. diuron and isoproturon) and compounds with aromatic rings (e.g. minocycline or mifepristone). Likewise, NDMA formation from a number of aliphatic and aromatic tertiary amines demonstrated the importance of the chemical structure, and both stability and electron distribution of the leaving group of tertiary amines (Selbes et al., 2013).

Distribution system materials

Certain rubber seals (pipe rubber ring joint lubricant, natural rubber seal rings, ethylene propylene diene terpolymers and styrene-butadiene rubber) and gaskets (ethylene propylene diene monomer M class rubber) leached NDMA in chlorine-free water and formed NDMA after chloramination (Morran et al., 2011; Teefy et al., 2011). Periods of stagnation resulted in significant increases in NDMA levels. NDMA levels resulting from sealing ring leaching, on the order of 10-25 ng/L, would undermine any NDMA-reduction processes at the water treatment plant (Morran et al., 2011).

Anion exchange resins

Anion exchange units employ strong (quaternary amine) or weak (tertiary amine) base polymeric resins. Anion exchange resins (fresh trimethylamine, tributylamine-based, and dimethylethanolamine based) released NDMA and their corresponding nitrosamines (e.g., N-nitrosodibutylamine from tributylamine-based resins), likely due to shedding of manufacturing impurities (Kemper et al., 2009). Resins also shed organic precursors that might contribute to nitrosamine formation within distribution systems when chloramines

are applied downstream of the column. The application of free chlorine or chloramine upstream of the column produced more nitrosamine concentrations as compared to downstream (Kemper et al., 2009). The resins can also degrade over time releasing organic precursors that might contribute to nitrosamine formation in the presence of chloramines (Nawrocki and Andrzejewski, 2011). Higher levels of nitrosamine precursors were observed after regeneration cycles (Singer and Flower, 2012). Exposure of resins to chlorinated tap water produced NDMA in the effluents (Kimoto et al., 1980; Najm and Trussell, 2001). When magnetic ion exchange resin (MIEX) was used to treat three wastewater effluents, NDMA FP increased from 156-287 to 266-344 ng/L, whereas the increase for three drinking waters was from 10-12 ng/L to 14-18 ng/L (Gan et al., 2013).

Other sources of NDMA precursors

Other identified precursors include natural organic matter (NOM) (Chen and Valentine, 2007; Dotson et al., 2007; Gerecke and Sedlak, 2003; Mitch and Sedlak, 2004), but generally the NDMA yield from the chloramination is low.

Strategies for control of NDMA precursors

The nature of NDMA precursors in natural waters is still not clearly understood, but they are believed to be predominantly hydrophilic, and low molecular weight compounds (Chen and Valentine, 2007; Pehlivanoglu-Mantas and Sedlak, 2008; Van Huy et al., 2011; Xu et al., 2011).

To remove or minimize NDMA precursors, different strategies may be considered, namely, (i) coagulation and polymer optimization, (ii) adsorption on activated carbon, (iii) magnetic ion exchange process (MIEX), and (iv) membrane filtration.

Coagulation and polymer optimization

Coagulation experiments with ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) conducted in either drinking water sources, or river waters with different impacts of wastewater showed that NDMA precursors were unaffected by the coagulation process (Knight et al., 2012; Krasner et al., 2008; Sacher et al., 2008). Likewise, lime softening had no significant impact on NDMA FP (Mitch et al., 2009). It has been shown that the majority of NDMA precursors are < 1 kDa, and that this fraction of NOM is poorly removed by coagulation (Lee and Westerhoff, 2006; Xu et al., 2011).

Cationic polymers (e.g., polyamines and polyDADMAC) used as coagulant or dewatering aids in drinking water treatment can degrade and release NDMA precursors (Kohut and Andrews, 2003; Najm and Trussell, 2001; Wilczak et al., 2003).

Adsorption on activated carbon

Powdered activated carbons (PAC) and granular activated carbon (GAC) for water treatment typically exhibit a heterogeneous pore structure with micropores (pore width < 2 nm), mesopores (pore width 2-50 nm) and macropores (pore width > 50 nm), and are typically manufactured from base materials such as bituminous coal, lignite, coconut shells, or wood (Pelekani and Snoeyink, 2000). The activation process for the

manufacture of activated carbon creates highly porous material with a distribution of pore sizes and surface areas. Pore structure has a large influence on both adsorption capacity and adsorption kinetics (Snyder et al., 2007). Depending on the activation process and base material, activated carbons also have a distribution of surface functional groups that influence their adsorption characteristics.

The chemical characteristics of the activated carbon (AC) are influenced to a large extent by the foreign elements fixed on the surface, in particular by heteroatoms (Boehm, 1994). Oxygen is an important heteroatom found at the edges of the condensed, polyaromatic sheets that constitute the building blocks of activated carbons, and commonly occurs in the form of carboxylic acids groups, phenolic hydroxyl groups, and quinone carbonyl group. The increased acidity is explained by the formation of these functional groups during the activation of the carbon surface. The net positive charge on the surface of basic PACs arose primarily from delocalized π electrons on the condensed polyaromatic sheets (Li et al., 2002).

PAC is widely used in WTPs in the United States to minimize taste and odor causing-compounds as well as synthetic organic chemicals (SOCs), and can simply be turned on or off as complaints warrant (Najm et al., 1991). Dosages can also be easily altered to accommodate severity, although a problem can outstrip the dosing capability of a utility (Suffet et al., 1996).

Initial experiments investigating removal of NDMA precursors with PAC demonstrated NDMA FP removals in wastewater $> 73\%$ with 50 mg/L after seven days contact time (Krasner et al., 2008). Experiments in surface waters with the same contact

time exposed to 5 mg/L of PAC (Calgon F300) showed 50% of NDMA FP reduction, and 90% or greater with 20 mg/L (Sacher et al., 2008).

Recently, Hanigan et al. (2012) reported the removal of 40% NDMA FP in a secondary wastewater effluent at 3 mg/L of PAC (WPH) dose and 4 h contact time. A dose of 75 mg/L of WPH had similar removals in secondary wastewater effluents with different NDMA concentrations, 90% (NDMA FP 544 ng/L), and 91% (NDMA FP 1470 ng/L).

MIEX

The magnetic ion exchange (MIEX) process has been increasingly used in recent years for DBP precursor control. It is applied as a pretreatment before oxidant addition to remove dissolved organic matter, thus reducing the formation of DBPs. While the effectiveness of MIEX for the removal of C-DBP precursors has been well established in many surface waters (Boyer and Singer, 2005; Fearing et al., 2004), the effectiveness for removing NDMA precursors is quite limited. Results by Gan et al. (2013) showed that NDMA FP in effluent impacted waters and drinking waters increased upon exposure to MIEX. The average increase in the drinking waters was 5 ng/L, whereas the effluent impacted waters exhibited a more significant increase ranging from 57 to 110 ng/L.

Membrane filtration

As NDMA precursors are associated with low molecular weight compounds, ultrafiltration (UF) exhibited negligible removal (Pehlivanoglu-Mantas and Sedlak, 2008). Reverse osmosis (RO) demonstrated complete removal at selected wastewater

treatment plants in California (Mitch and Sedlak, 2004). Steady-state nitrosamine precursors (dimethylamine, methylethylamine, diethylamine, and dipropylamine,) rejections at feed concentrations of 5500 ppb by nanofiltration (NF) Saehan NE90 membrane (at 70 psi) were > 98.5% (Miyashita et al., 2009).

Research objectives

Although very limited, the results available so far in literature warrant further investigations on the removal of NDMA precursors by activated carbons. Understanding of the factors controlling the removal of NDMA precursors by activated carbons is lacking. The objectives of this project were (i) to examine the removal of NDMA FP by PACs in different waters and (ii) to examine the roles of PAC characteristics (e.g., raw material, surface chemistry, pore size distribution, and surface area) on the removal of NDMA precursors. Due to regulatory and practical significance, the removal of THM precursors was also simultaneously investigated.

CHAPTER II
MATERIALS AND METHODS

Water samples

In this study, water samples were obtained from six different sources in South Carolina (SC), three surface water (SW) samples used as water sources for WTPs, and three treated effluents (IW) obtained from municipal wastewater treatment plants (WWTPs) located in Anderson, Greenville, and Pendleton (Table 2.1). All samples were immediately filtered through 0.2 μm membrane filters upon arrival at the laboratory, and kept at 4 °C.

Table 2.1. Water sources used in adsorption experiments with PAC.

Sample	Water Type	Source
SW1	Surface	Reservoir
SW2	Surface	River
SW3	Surface	River
IW1-Oct	Wastewater impacted	WWTP effluent-lab prepared
IW1-Jan	Wastewater impacted	WWTP effluent-lab prepared
IW2	Wastewater impacted	WWTP effluent
IW3	Wastewater impacted	WWTP effluent

Sampling Location: SW1

This surface water source was a small reservoir. Historically, there has been high level of biological activities (i.e., algae growth during summer).

Sampling Location: SW2

This sample was collected in the inlet of a DWTP, which has a capacity of 71 MGD and daily average operational flow rate of 35 MGD. The water treatment process consists of raw water intake, pre-treatment, coagulation-flocculation, sedimentation, filtration, post-oxidation and storage.

The source water of SW2 is a river that is approximately 441 km long. The river watershed occupies 148,599 acres. Land use/land cover in the watershed includes: 59.4% forested land, 21.4% urban land, 13.0% agricultural land, 3.0% forested wetland, 2.0% water, 0.8% barren land, and 0.4% scrub/shrub land. In this watershed, point sources are primarily WWTPs and industrial dischargers.

The river receives one major industrial discharge from a nuclear station and several minor industrial discharges from a hydro station, quarry, nuclear training center, brick, and vulcan materials. Two major and one minor discharges are coming from domestic wastewater treatment utilities. The closest upstream wastewater discharges are a county WWTP (16 km upstream) and a city WWTP (21 km upstream) with about 6 MGD and 1.5 MGD permitted flow, respectively. The non-point sources include land disposal and mining activities.

Sampling Location: SW3

The source of the SW3 reservoir is an upstream river whose watershed occupies 49,168 acres. Land use/land cover in the watershed includes 70.7% forested land, 11.9% urban land, 7.5% forested wetland, 5.1% agricultural land, 3.0% scrub/shrub land, 1.4% water, and 0.3% barren land. There are both point and nonpoint sources, including three natural pollutant discharge elimination system (NPDES) permits classified as minor (i.e., < 1 MGD) industrial and domestic discharges.

Sampling Location: IW1

The IW1 sampling point is in a small watershed, which is 32,883 acres with only one municipal WWTP. About 58% of the watershed is forested, and the remaining is composed of urban area (6%), cropland (19%), pastureland (16%), and a small mix of water (0.2%) and barren (0.32%) land uses. A 1.2 million gallon/day (MGD) municipal WWTP incorporating tertiary treatment and UV disinfection is the major discharger to the stream. A USGS gauge station is available approximately 1.6 km upstream of the WWTP. The sample was collected 8 km downstream of the WWTP on two different dates, October 2012 (IW1-Oct) and January 2013 (IW1-Jan). The contribution of the WWTP effluent to the creek flow was determined by mass balance calculations using bromide as a conservative tracer, which was estimated to be 25% during the sampling days.

Sampling Location: IW2

The effluent of the second WWTP was used to prepare a blended sample in the laboratory. The treated effluent was mixed in a 0.6:0.4 ratio with water coming from an upstream location from the same creek that the WWTP discharges. This WWTP has an installed capacity of 9.5 MGD and is a conventional secondary activated sludge plant.

Sampling Location: IW3

The effluent of the third WWTP was used to prepare a blended sample in the laboratory. The treated effluent was mixed in a 0.6:0.4 ratio with water coming from an upstream location from the same creek to which the WWTP discharges. This WWTP has an installed capacity of 2.0 MGD, and the process train consists of a primary clarifier, trickling filters, rotating biological contactors, and sand filters. The phosphorus removal system consists of chemical treatment and rapid mixing. The WWTP has ultraviolet disinfection and post aeration prior to its discharge.

Powdered activated carbons (PACs) and activated carbon fibers (ACFs)

Four different PACs were selected for the adsorption experiments (Table 2.2): two acidic PACs with high surface areas (A1 and A2), and two basic PACs with lower surface areas (B1 and B2). The acidic carbons were more mesoporous, whereas the basic carbons had higher micropore volume. Three of the PACs, A1, A2, and B2, were obtained from WTPs in South Carolina, and they are used for taste and odor control on a need basis. B1 was available in our laboratory from previous research. The PACs with different physical and chemical characteristics were used to assess the role of carbon

characteristics on the NDMA FP removal. All the carbons were sieved through U.S. Mesh Sieve size No.400 (37 μm diameter opening) prior to use.

Two ACFs were previously characterized in our research group (Shaikh et al., 2004). ACF10 consists mostly of primary micropores, with 91% of pores $< 10 \text{ \AA}$. The pores size distribution of ACF20H is shifted toward larger pore sizes (10–20 \AA), and an important fraction is in the range of 10–20 \AA (50%). Both fibers have basic pH_{pzc} but ACF20H has twice the surface area of ACF10 (Table 2.2).

ACFs are prepared from homogeneous polymeric base materials such as polyacrylonitrile, cellulose or phenolic resin (Li et al., 2002), have high surface area, and uniform and controllable micropore structure. Larger molecules that cannot access the micropores do not experience the adsorption phenomenon, even when there are multiple contact points between the adsorbate and adsorbent (Pelekani and Snoeyink, 2000).

Table 2.2. Physicochemical characteristics of activated carbons.

Adsorbent	Base Material	BET Surface Area, m^2/g	Pore Size Distribution, %			pH_{pzc}
			$< 10 \text{ \AA}$	10-20 \AA	$> 20 \text{ \AA}$	
A1	Coal	1748	0	23	77	5.4
A2	Wood	1727	0	24	76	5.6
B1	Coal	849	36	26	38	9.2
B2	Coal	713	32	15	53	10.4
ACF10*	Phenolic Resin	963	91	9	0	8.6
ACF20H*	Phenolic Resin	1983	47	50	3	9.6

*Shaikh et al., 2004.

Experimental procedures and analytical methods

NDMA Analysis

NDMA was analyzed following USEPA method 521 (USEPA, 2004). Calibration solutions were prepared from an NDMA stock. Typical calibration curves were generated from nine standard solutions and the MRL was 3 ng/L. For the sample analysis, a stoichiometric amount of sodium thiosulfate anhydrous was added to 500 mL of chloraminated sample to quench NH_2Cl and prevent further unintended reactions. N-nitrosodimethylamine-d6 (NDMA-d6) was added to the samples as a surrogate before extraction. Environ-Clean 521 (UCT) solid phase extraction (SPE) columns pre-packed with 2000 mg of coconut charcoal were preconditioned with dichloromethane (DCM), methanol (MEOH), and finally deionized (DI) water. Samples were passed through the SPE columns. The columns were dried with air, and then the adsorbed NDMA was eluted with DCM. The eluent was dried using a drying cartridge containing 6 g of sodium sulfate anhydrous. The sample was evaporated to 1 mL under ultrahigh-purity nitrogen gas. Samples were transferred to GC vials and spiked with N-nitrosodi-n-propylamine-d14 (NDPA-d14) as an internal standard, and analyzed using a Varian GC 3800-MS/MS 4000 equipped with RTX-5MS (Restek 30 m x 0.25 mm x 0.25 mm) column and under the chemical ionization mode (Selbes et al., 2013).

Trihalomethane Analysis

Trihalomethanes (THM) species (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) were analyzed following US EPA Method

551.1 (USEPA, 1990). Standards were prepared by spiking different volumes of a stock solution of THM into 20 mL of DDI. Typical calibration curves were generated from seven standard solutions and the MRL was 1 µg/L. THM stock solution was obtained from Sigma Aldrich. Eight mL of a solution containing MTBE and 1,2-dibromopropane as internal standard, and then 8.5 g of Na₂SO₄ were added to each vial. The extraction vials were shaken horizontally at 300 rpm for 15 min on the shaker table. The vials sat for 15 min, and the MTBE extract was transferred to 2 mL GC vials.

The MTBE extract was analyzed with an Agilent 6890 gas chromatograph (GC) equipped with a ZB-1 column (J &W Scientific 30 m x 0.25 mm x 0.001 mm), and an electron capture detector (ECD). The GC temperature program was 35 °C for 22 min, 10 °C/min to 125 °C and held for 1 min, 30 °C/min to 300 °C and held for 4 min. A 2-µL injection volume was used in splitless mode. The make-up and carrier gases were high purity nitrogen and ultra-high purity hydrogen, respectively. The injector temperature was set at 250 °C, while the detector temperature was set at 290 °C.

Chlorine and Monochloramine Measurements

Free chlorine and monochloramine were measured with the N,N-diethyl-p-phenylenediamine (DPD) method according to Standard Method 4500-Cl Chlorine G. Briefly, 5 mL each of buffer reagent and DPD indicator solution were placed in a constantly stirred titration flask. Then, 100 mL of the sample was added and rapidly titrated with standard ferrous ammonium sulfate (FAS) titrant until the disappearance of the red color. For monochloramine, one very small crystal of KI was added to the mixing sample, and the titration was continued until the red color was discharged again.

Characterization of the Activated Carbons

Surface area and pore size distribution of samples were determined from adsorption isotherms of nitrogen from relative pressure of 10^{-6} to 1 at 77 K. The surface area of activated carbon samples was calculated by the BET equation. The pore size distribution of activated carbon samples was determined from the nitrogen isotherms using Micromeritics' Density Functional Theory (DFT) software.

For the determination of the pH of the point of zero charge (pH_{pzc}), 0.1 M NaCl solutions having different initial pH values (2–11) were prepared using deionized water that was boiled for removal of dissolved CO_2 (Dastgheib et al., 2004). Solutions of 0.5 N HCl or NaOH were used in pH adjustment. One hundred mg of carbon samples were contacted with 20 mL of 0.1 M NaCl solutions at different initial pH values. Sealed vials were shaken for 48 h at 200 rpm at room temperature, and then left for settling of carbons. The final pH of the solution was measured in a glove box. The pH_{PZC} was determined as the pH of the NaCl solution that did not change after the contact with the samples.

Adsorption Experiments

A dose of 30 mg/L of each one of the PAC was added to 1-L amber borosilicate bottles and filled to 1000 mL with water sample, and then the bottles were agitated in a tumbler for 4 hours. Next, the PAC was removed using 0.45 μm membrane pre-washed filters. Formation potential (FP) tests were carried out with filtered sample. The rather higher PAC dose was intentionally selected to magnify the removal of NDMA precursors

and better evaluate the trends. Such high PAC doses are used to combat excessive taste and odor problem in practice.

Formation Potential Tests

FP tests were used to determine the DBP precursor levels in a sample under favorable disinfection conditions and an excess amount of disinfectant for each DBP group: (1) THMs under chlorination, and (2) NDMA under chloramination. Chlorine stock solutions (6250 mg/L) were prepared by diluting sodium hypochlorite (Baker Analyzed Reagent, 5% available free chlorine). Preformed monochloramine stock solutions (2500 mg/L) were generated by slowly mixing sodium hypochlorite in an ammonium sulfate solution at Cl₂/N mass ratio of 4:1 at pH 9 (Hong et al., 2007). All the disinfectant stock solutions were freshly prepared on the day of use.

NDMA FP was conducted in 500-mL amber borosilicate bottles and THM FP in 125-mL amber borosilicate. The pH of the samples was adjusted to 7.8 with a phosphate buffer solution. NDMA samples were spiked with 100 mg/L as Cl₂ of a monochloramine stock solution, and THM samples with 50 mg/L of a chlorine stock solution. All samples were stored for five days in the dark.

All samples were prepared and analyzed in duplicates, raw water in triplicates. Then each extract was analyzed on GC/MS/MS or GC-ECD with multiple injections. Error bars in all the graphs show the variability (one standard deviation) due to multiple extractions and analysis (n = 4) under the same conditions.

Water Characterization

Dissolved organic carbon (DOC) and dissolved nitrogen (DN) were measured using a Shimadzu Total Organic Carbon (TOC)-VCSH & TNM-1 by applying Standard Method 5310 B (2005). UV absorbance was measured with a Varian Carry 50. Bromide, was measured by ion chromatography (ICS-2100, Dionex Corp.), pH was measured with a VWR Symphony pH meter (Table 2.3). Residual chlorine and monochloramine were measured using the DPD Ferrous Titrimetric Method.

Table 2.3. Analytical methods and minimum reporting levels (MRL).

Parameter		Method	Equipment	MRL or Accuracy ^a
Bromide	µg/L	EPA 300.0	Dionex ICS-2100	10
DN	mg/L	High Temp. Combustion	Shimadzu TOC-V _{CHS} & TNM-1	0.1
DOC	mg/L	SM 5310 B	Shimadzu TOC-V _{CHS}	0.1
NDMA	ng/L	EPA 521	Varian GC 3800-MS/MS 4000	3.0
NH ₃	mg/L	Salicylate Method	Hach DR/890	0.02
pH	pH	SM 4500-H ⁺	VWR Symphony	± 0.01
Residual Combined Chlorine	mg/L	SM 4500-C1 F	N/A	0.05
Residual Free Chlorine	mg/L	SM 4500-C1 F	N/A	0.05
THM	µg/L	EPA 551.1	Agilent 6890 GC-ECD	1.0
UV Absorbance	cm ⁻¹	SM 5910	Varian Carry 50	± 0.004

a: Reported by the manufacturer

SM: Standard Methods (APHA, 2005).

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

CHAPTER III

RESULTS AND DISCUSSION

Source water characteristics

The selected physicochemical characteristics of the water samples used in this study are presented in Table 3.1. The results showed that the DOC and SUVA₂₅₄ values ranged from 2.3 up to 7.1 mg/L and 1.7 to 3.6 L · (mg · m)⁻¹, respectively. SW3 had a particular high THM FP value corresponding to the high level of DOC. Meanwhile the rest of the water samples had relatively comparable values of THM FP. In contrast to THM FP results, the NDMA FP values were always higher in the wastewater-impacted sources (IW) than the surface water sources (SW). The latter is consistent with a previous study conducted by Hanigan et al. (2012). The researchers tested several blends of surface and wastewater, and showed an increase of NDMA FP as the contribution of wastewater in the blended water was increased. IW samples had higher total dissolved nitrogen (DN) than SW samples, but similar bromide levels.

Table 3.1. Selected water quality characteristics, THM and NDMA FPs of surface and wastewater impacted waters.

Parameter	Units	Source						
		IW1-Oct	IW1-Jan	IW-2	IW-3	SW1	SW2	SW3
DOC	mg/L	2.6	2.4	3.7	2.9	2.3	2.6	7.1
UV ₂₅₄	cm ⁻¹	0.0714	0.0433	0.0854	0.0668	0.0582	0.0633	0.2561
SUVA ₂₅₄	L/mg · m	2.8	1.7	2.3	2.3	2.5	2.4	3.6
THM FP	µg/L	190	170	194	241	227	173	552
NDMA FP	ng/L	146	145	569	412	42	70	20
DN	mg/L	3.3	2.9	8.3	2.6	0.64	0.63	0.34
Bromide	µg/L	62	35	27	49	23	93	74

Effect of source water characteristics on the removal of NDMA and THM precursors

It was hypothesized that the removal of NDMA and THM precursors by PAC is affected by the characteristics of the source waters. Therefore, water samples with different characteristics were selected for testing. Three of them were wastewater-impacted samples (IWs). Two samples (IW-1) were collected downstream of a municipal WWTP (~ 8 km from the discharge) in October 2012 and January 2013. For the other two WWTP effluents, since there were no suitable sampling locations close to the effluent, wastewater-impacted samples were prepared in the laboratory by mixing the effluent with the upstream water at a 1:1 ratio. These samples represented freshly impacted water sources. Additional samples were also collected from three surface waters (SWs) including a small reservoir, and two large rivers where samples were collected at the influent of drinking water plants (DWP). At these sources, sucralose concentrations were measured twice during 2012 in another project in our research group. Sucralose is an artificial sweetener that has been linked to anthropogenic influences including wastewater discharges on source waters (Buerge et al., 2009; Loos et al., 2009; Mead et al., 2009; Scheurer et al., 2009; Ferrer and Thurman, 2010; Oppenheimer et al., 2011). The sucralose values were < MRL at SW1, 600-960 at SW2 and 680-1000 ng/L at SW3. This indicates the presence of some anthropogenic inputs to SW2 and SW3, while SW1 did not have any impact. SW2 and SW3 are large rivers with NPDES permits well above the WTP intakes. SW1 is small reservoir surrounded by forests and rural areas without any public residences.

Natural water samples are heterogeneous mixtures of different types of organic materials, and the fraction of absorbable NDMA precursor(s) in a sample will determine the reduction of NDMA FP by PAC. Figure 3.1 shows the adsorption experiment results. Independent of carbon types and characteristics, higher removals of NDMA FP were observed from IWs (50-60%) than SWs (10-30%). It appears that IW samples contained more absorbable NDMA precursors as compared to SWs. These results suggest three possibilities. (i) Fresh wastewater effluents are rich in NDMA FP, and PAC is effective in removing those NDMA precursors. As a result, the effectiveness of PAC increased with increasing degree and proximity of wastewater influence. (ii) Some NDMA precursors naturally attenuate in natural waters through a combination of photolysis, adsorption, and biodegradation. As a result, lower degree of adsorption observed for SW than IW may be due to the loss of some adsorbable NDMA precursors in the source waters through natural attenuation processes. This may also explain the low degree of NDMA FP removal by PACs in SW1 and SW3 despite the influence of some anthropogenic inputs as indicated by the sucralose values. (iii) The concentration effect may play role in adsorption because the higher NDMA FP may impact the adsorption kinetics; the higher the initial concentration is, the higher the concentration gradient. These and other factors influencing the adsorption of NDMA FPs by PAC will be discussed in the following sections.

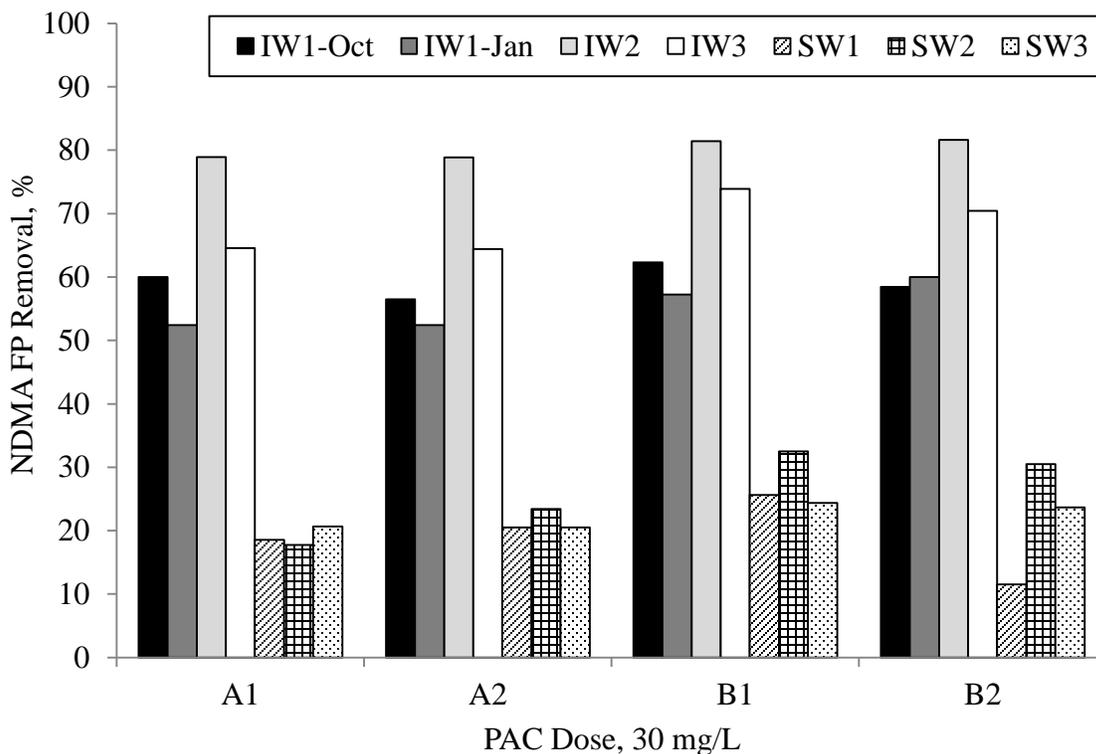


Figure 3.1. Effect of water source on the removal of NDMA FP precursors with four different PACs.

In contrast to NDMA FP, the removal efficiency of THM precursors was not greatly affected by the water source type and remained between 30-45% (Fig. 3.2). The removal efficiency for SW3 was lower than other water samples. SW3 had higher DOC and $SUVA_{254}$ values as compared to other waters (Table 3.1). Higher $SUVA_{254}$ values are linked to higher molecular weight of NOM in natural waters (White et al., 1997; Archer and Singer, 2006). One possibility is that the presence of large NOM molecules and the short contact time of four hours during the adsorption experiments resulted in a lower degree of adsorption for SW3. The different removal patterns of NDMA FP and THM FP by PAC also indicate that their major precursors are different.

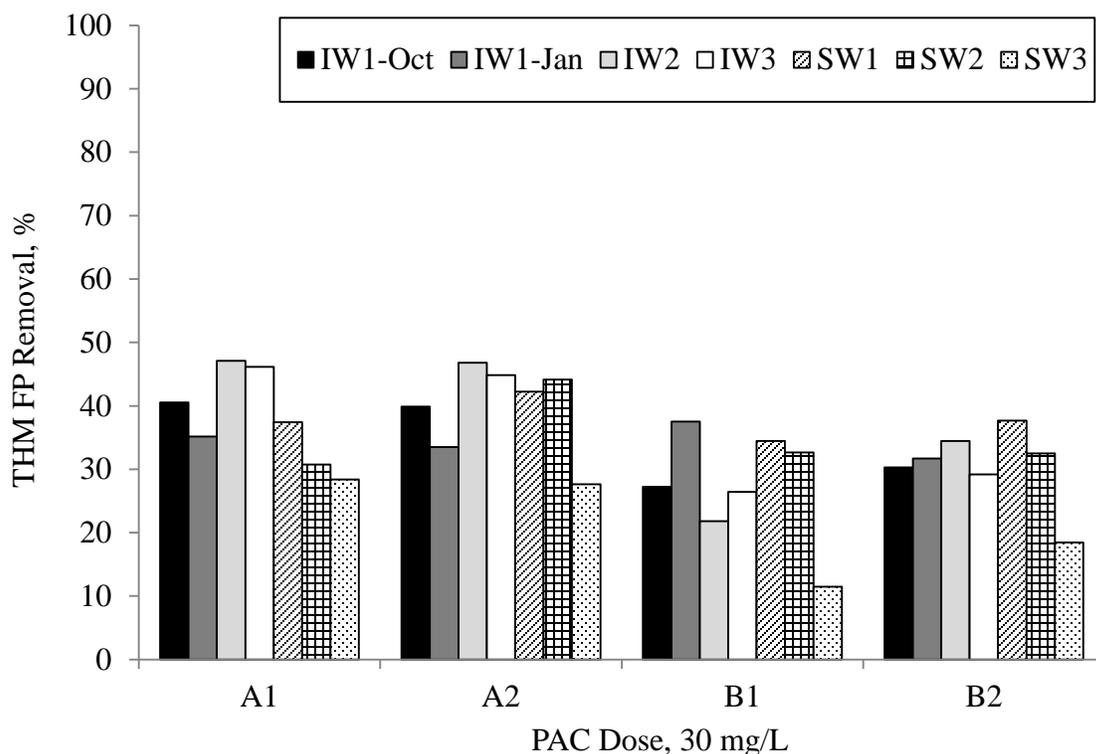


Figure 3.2. Effect of water source on the removal of THM precursors with four different PAC.

The effect of PAC type

On a mass basis, the type of PAC did not affect the removal efficiency of NDMA FPs (Figure 3.1). Nonetheless, the PACs had different surface areas and surface chemistry (e.g. pH_{pzc}). To isolate the effect of the surface chemistry from the surface area, the NDMA FP uptakes were normalized with the surface areas of PACs, as given in Eq. 3.1:

$$\text{NDMA removal} = \frac{1000 \times (C_0 - C_{\text{sample}})}{(\text{mass PAC} \times \text{Surface Area})} \quad 3.1$$

Where:

C_o = NDMA FP before adsorption
 C_{sample} = NDMA after adsorption
 Mass PAC = Dose of PAC used in the adsorption experiments
 Surface Area = BET surface area of the PAC

The surface-area normalized uptakes are presented in Figure 3.3. Assuming the BET surface area is accessible to all NDMA precursors, the normalized uptakes were used to examine the effect of carbon surface acidity on NDMA precursor adsorption. The results showed that the NDMA FP removal by basic carbons was higher as compared to acidic carbons (Fig. 3.3). The two lab prepared wastewater impacted source waters, IW2 and IW3, showed significantly higher uptakes than the other waters

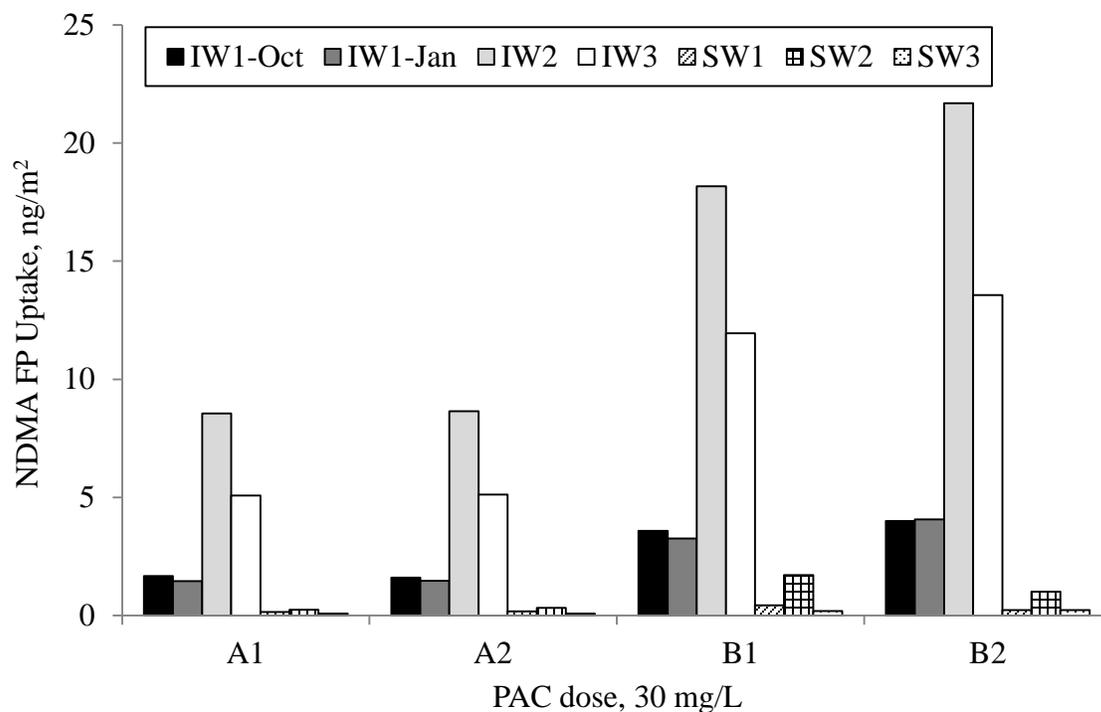


Figure 3.3. Surface area-normalization of the removal of NDMA FP precursors with PAC.

Upon surface area-normalization, slightly higher THM FP removals were observed on basic than acidic PACs (Fig. 3.4), the effect was not as pronounced as in NDMA. Typically, NOM, the main THM precursors, molecules carry a net negative charge at neutral pH values (Newcombe and Drikas, 1997; Kim et al., 2010), which is the pH of adsorption experiments (pH 6.2). Consequently, adsorption of negatively NOM molecules is more favorable to basic carbon surfaces, which carry a net positive charge.

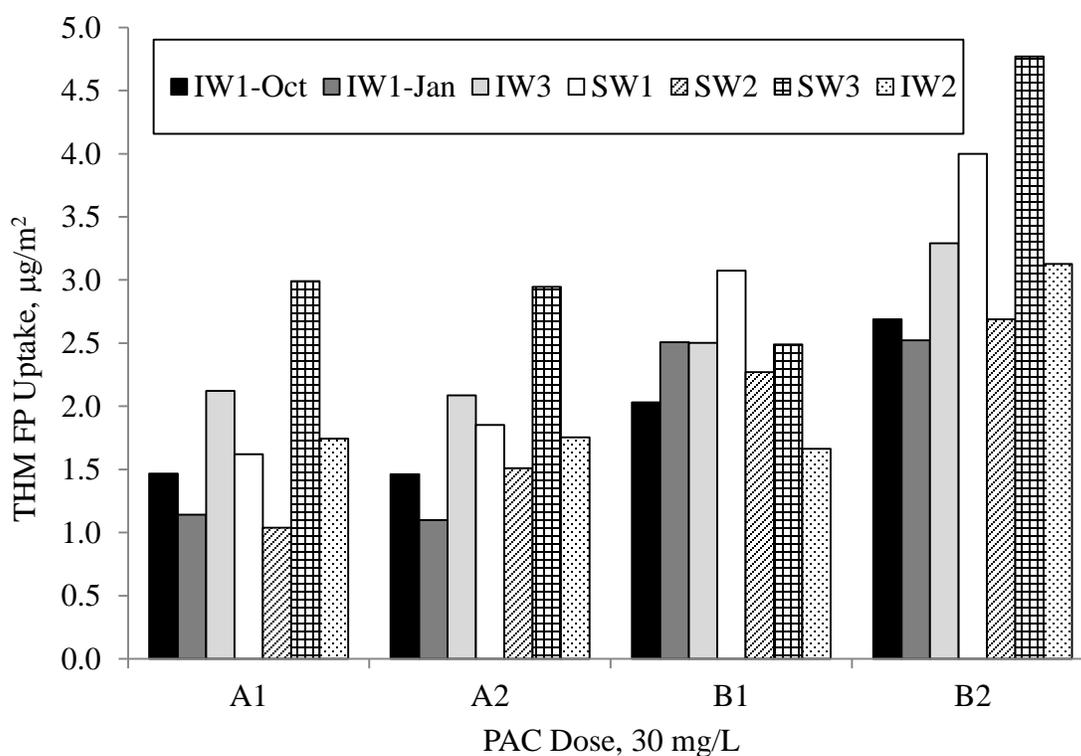


Figure 3.4. Surface area-normalization of the removal of THM FP precursors with PAC.

One of the assumptions made during the surface area normalization was the fact that all BET surface area was available. BET surface area is measured using nitrogen gas molecules that have an effective diameter about 3Å. Therefore, pores larger than 3Å can

be characterized using N₂ gas adsorption measurements and the BET equation. However, NDMA or THM precursors are likely to have a range of size distributions and not all carbon pores may be accessible to them. To examine the pore size regions that NDMA and THM precursors can access, additional experiments were conducted using two activated carbon fibers ACF10 and ACF20H (American Kynol, Inc.) (Table 2.2). Adsorption experiments were conducted using three fresh municipal wastewater effluents and one surface water samples. The results are presented in Figure 3.5.

The NDMA FP precursors removal by ACF20H ranged from 20 to 60%, while it was from 4.5 to 27% by ACF10 (Fig. 3.5). These results indicate that there was a size distribution of adsorbable NDMA precursors in the waters tested, and the adsorbable fraction included more precursors in the size region of 10-20 Å than <10 Å. PACs with hybrid characteristics (micro & mesoporous) or mainly mesoporous characteristics are likely to be more effective for NDMA precursor control. The results also provided some additional explanations for the trends observed with acidic and basic PAC tested in this study. One possibility for acidic carbons showing a high degree of NDMA precursor uptake on a mass basis is likely related to their mesoporous nature in addition to their larger surface areas. On the other hand, basic carbons showing higher uptakes on a surface-area normalized basis despite their more microporous nature and lower surface area further indicate the favorable nature of basic carbon surface for the adsorption of NDMA precursors. Since the exact structure of NDMA precursors in natural waters and wastewater are not fully understood, it is not possible to further speculate on the nature of interactions responsible for adsorption

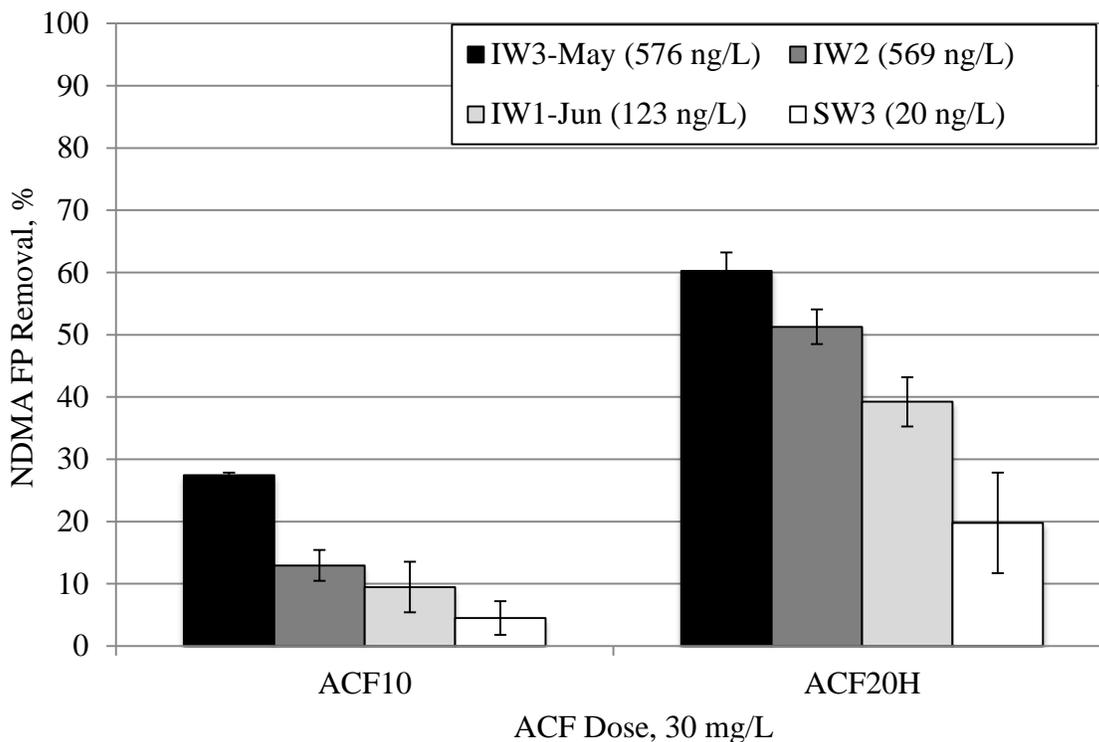


Figure 3.5. NDMA FP removal with activated carbon fibers ACF10, and ACF20H.

The removal of THM precursors in the same water samples by carbon fibers are shown in Figure 3.6. The THM FP precursor removals ranged from 2.7 to 15%, and 0 to 9% for ACF20H and ACF10, respectively. Much lower reductions in THM FP than NDMA FP despite the basic nature of ACFs favoring adsorption of NOM indicate that THM precursors were much larger than the NDMA precursors. These findings are consistent with our experiences with NOM in other water sources (Cheng et al., 2005).

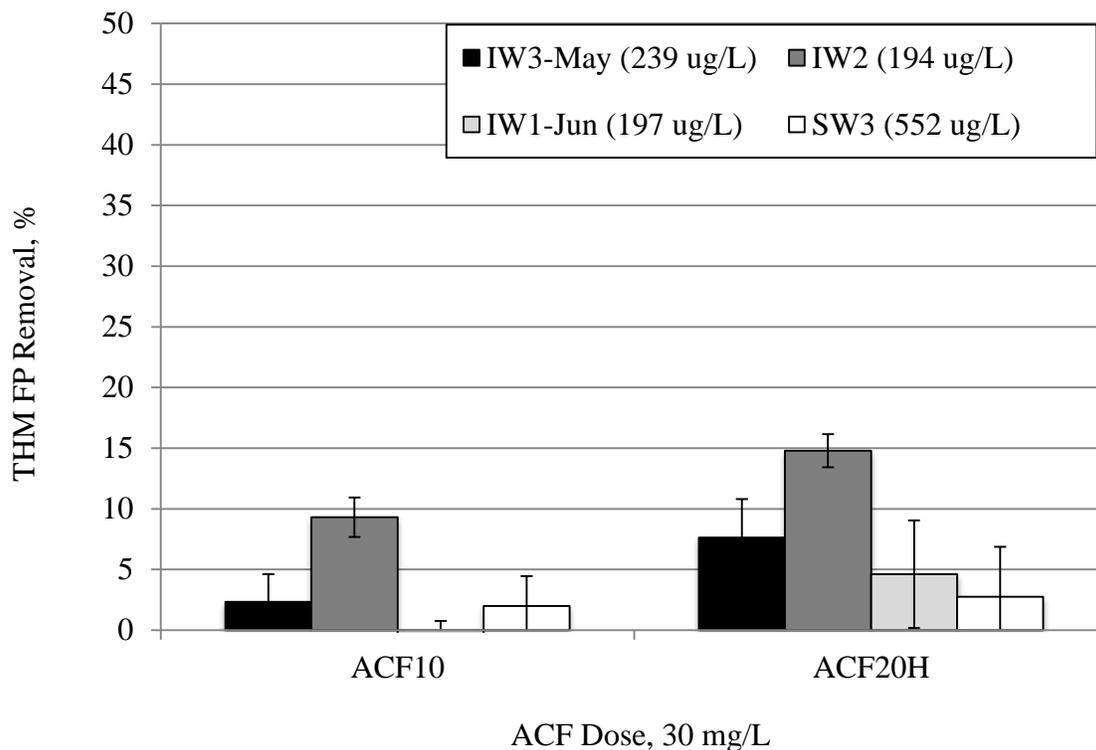


Figure 3.6. THM FP removal with activated carbon fibers (ACF10, and ACF20H).

Effect of NDMA FP precursors concentration on their removal by PAC

One possibility of higher NDMA FP removal in the wastewater-impacted samples than surface waters may be related to the difference in the initial NDMA FP concentrations. Therefore, to further investigate the effect of the NDMA precursor concentration on the removal by PAC, one fresh sample collected from the effluent of a WWTP was diluted using sun-exposed deionized water to about half its initial concentration. The adsorption experiments were conducted under the same conditions described previously and results are shown in Figure. 3.7.

The removal efficiency for the high initial concentration sample (NDMA FP = 252 ng/L) was higher for all PAC ranging from 50 to 75% than the low initial

concentration sample (NDMAFP = 82 ng/L), which ranged from 23 to 38%. The trends are consistent with the difference observed between the impacted-wastewater (55-80%) and surface water (20-25%) samples (Figure 3.1). All the results obtained with different water samples are compiled in Figure 3.8. Consistently, samples with high levels of NDMA FP exhibited the highest removal (52-82%). Therefore, NDMA precursor levels play a role in their removal by PAC. It is likely that this is due to the impact of initial concentration, initially higher driving force for adsorption in the high concentration solutions resulted in higher removals.

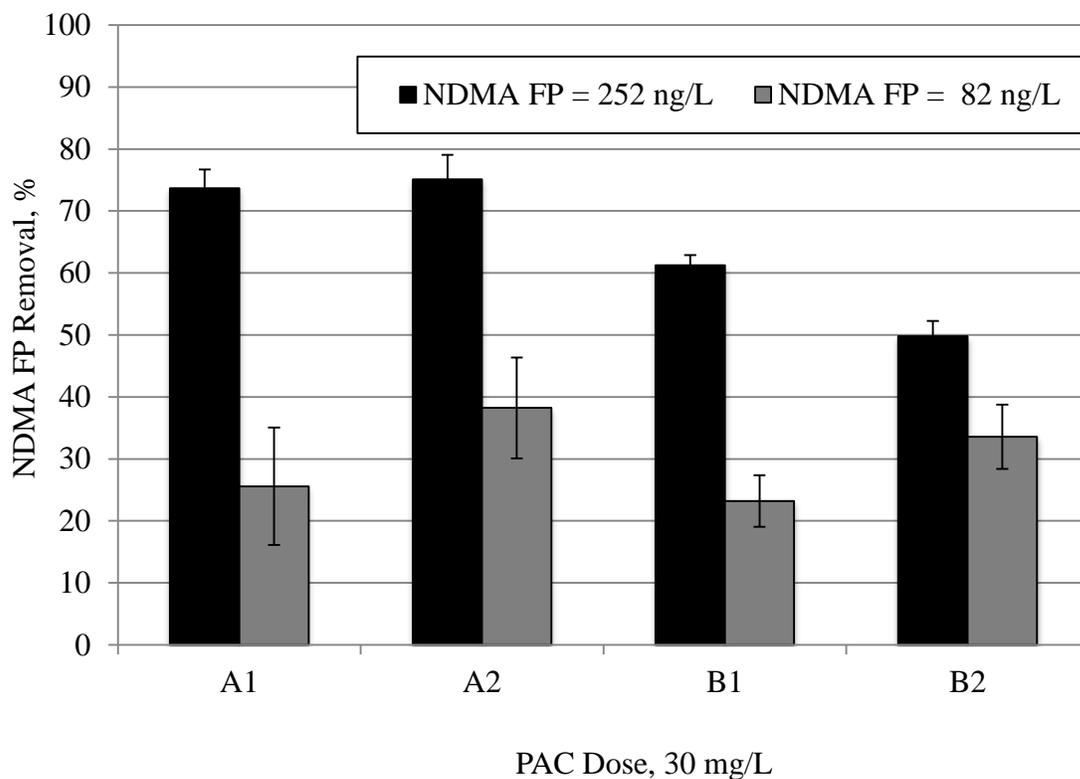


Figure 3.7. Effect of the concentration of NDMA FP precursors on its removal with PAC.

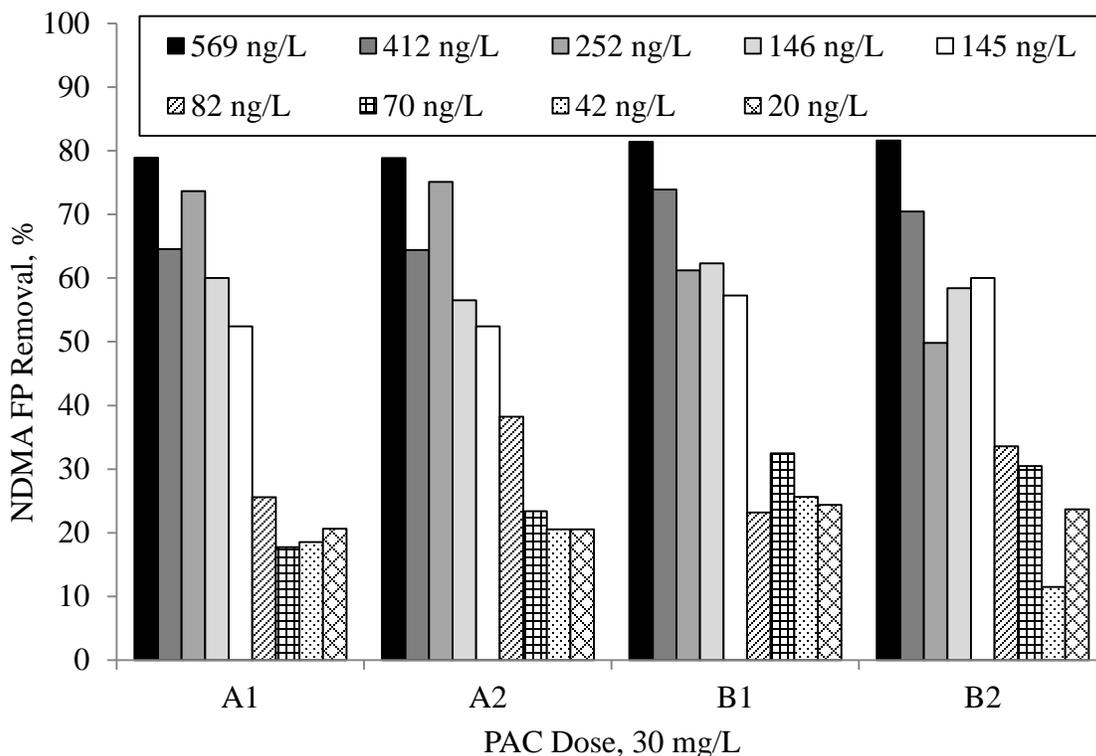


Figure 3.8. NDMA FP removal with PAC in several wastewaters effluents.

The impact of changes in NDMA precursors reactivity in natural waters on their adsorption by PAC

The observed higher removal of NDMA FP in wastewater-impacted sources than surface water samples may also relate to changes in the reactivity of NDMA precursors in source water with residence times in the discharge environment (lake or rivers). Since in natural systems, it has been observed that NDMA precursors decreases with travel or residence time through photolytic and microbial degradation and sorption reactions (Pehlivanoglu-Mantas and Sedlak, 2006; Krasner et al., 2008; Gan et al., 2013), it is important to examine the impact of such changes on their adsorbability by PAC. A new

wastewater-impacted sample was prepared by mixing the effluent of a WWTP (i.e., after clarifier before the UV treatment system) with the upstream water at a ratio of 1:1 (IW2-Apr). The NDMA FP test was carried out with this sample ($C_0 = 626$ ng/L). Then, a 20 L clear bottle with the unfiltered sample and covered with Parafilm[®] was left outside of the laboratory under sunlight and continuous stirring for over 23 days. Samples were collected during this period for testing NDMA FP and THM FP. Figure 3.9 shows the change in NDMA FP in the bottle during the course of the experiments. Initially, the NDMA FP did not change for two days, but after four days, a decrease of 20% was observed. At the end of the seven days, NDMA FP in the bottle decreased overall by 60%, which remained almost constant up to 23 days.

The high decrease in NDMA FP precursors (60%) observed could be due to a combination of loss mechanisms including photolysis, sorption and biodegradation (Chen et al., 2009; Krasner et al., 2008; Pehlivanoglu-Mantas and Sedlak, 2006). Inoculation of wastewater effluent samples with activated sludge mixed liquor for over 30 days reduced NDMA FP by less than 30%.

Chen et al. (2009) investigated the fate and transport of DBP precursors in a natural river (Santa Cruz River, CA, USA), a 100% effluent-dominated stream that served to study the fate and transport of effluent organic matter (EfOM) and DBP precursors in a natural river. They found that NDMA FP decreased exponentially (from 682–804 to 280–347 ng/L) along the length of the stream, meanwhile THM precursors were relatively unchanged because they were more associated with non-biodegradable organic matter.

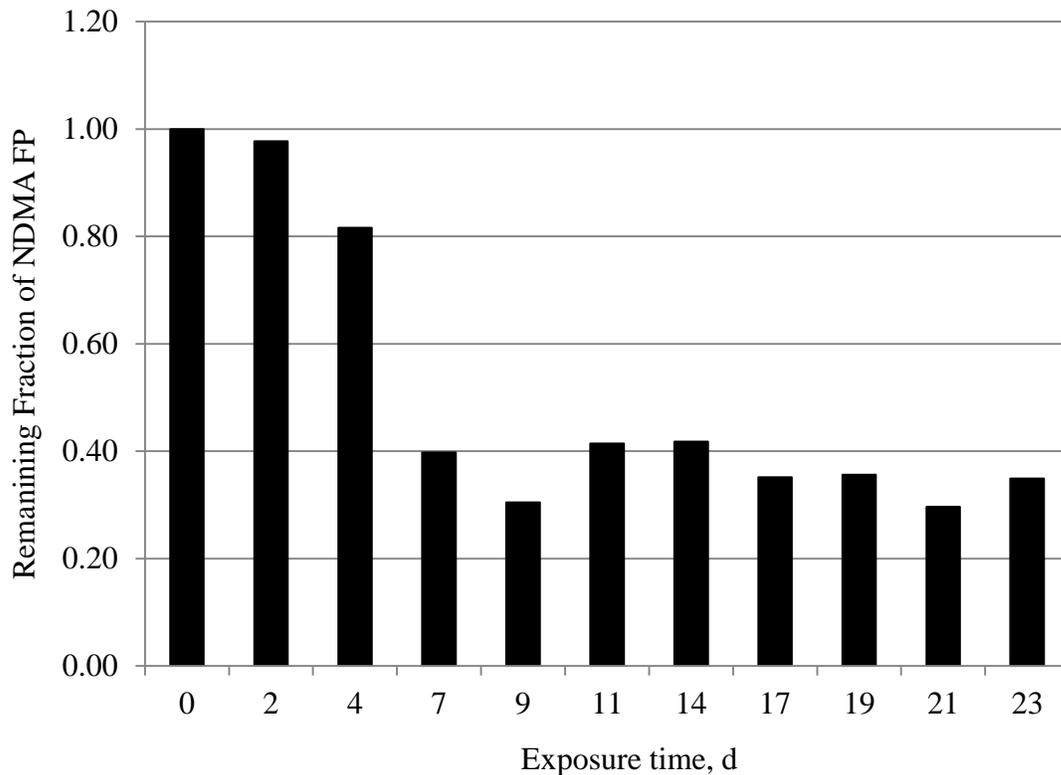


Figure 3.9. Remaining fraction of NDMA FP in a wastewater effluent during 23 d of exposure to sunlight ($C_0 = 626$ ng/L).

Krasner et al. (2008) conducted experiments with filtered EfOM to understand the photolytic degradation of DBP precursors (THM FP and NDMA FP, among others). After six hours of natural sunlight exposure, the change in concentration of THM FP was within $\pm 21\%$, and NDMA FP concentrations did not change significantly (-2 to 10%). In our experiment, we observed a variation of $< 2\%$ for both THM FP and NDMA FP after two days. However, for the 23 d period of exposure to sunlight the results showed a variation within $\pm 15\%$ for THM FP (Fig. 3.10) and a decrease about 60% in NDMA FP (Fig. 3.9).

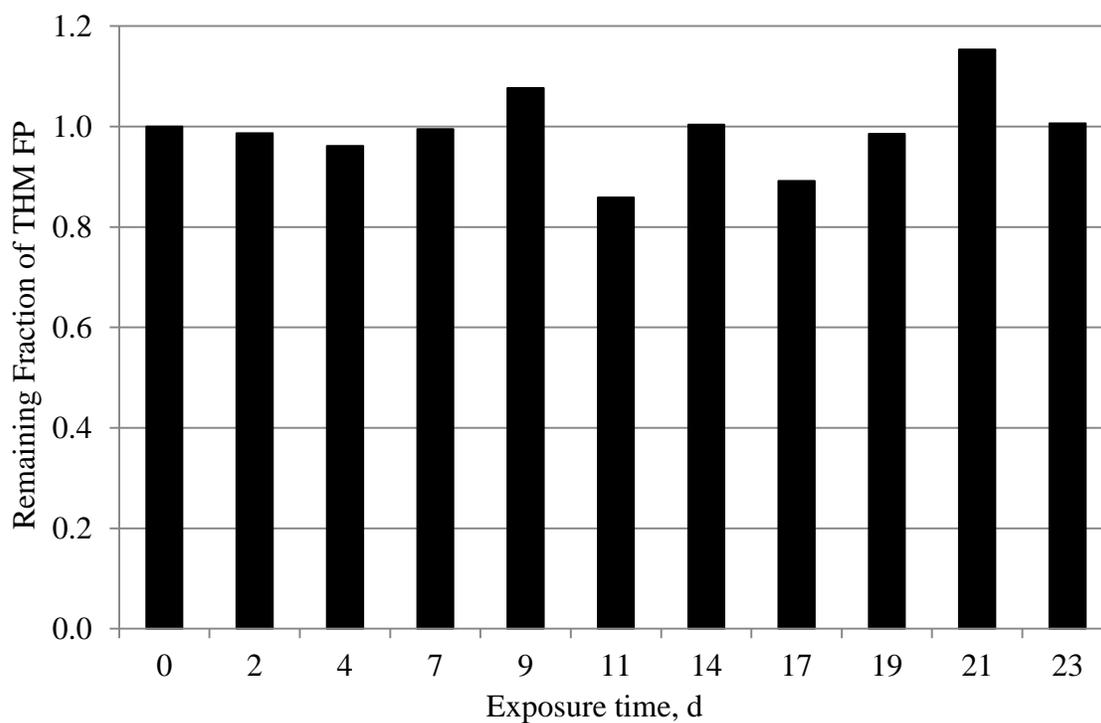


Figure 3.10. Remaining fraction of THM FP in a wastewater effluent during 23 d of exposure to sunlight.

During the same experiment, DOC increased by 61% (Fig. 3.11) while $SUVA_{254}$ decreased by 53% (Fig. 3.12) over time, which was attributed to the die-off of the cells and release of some soluble microbial products (SMPs) in water. DN decreased by 80% (Fig. 3.11).

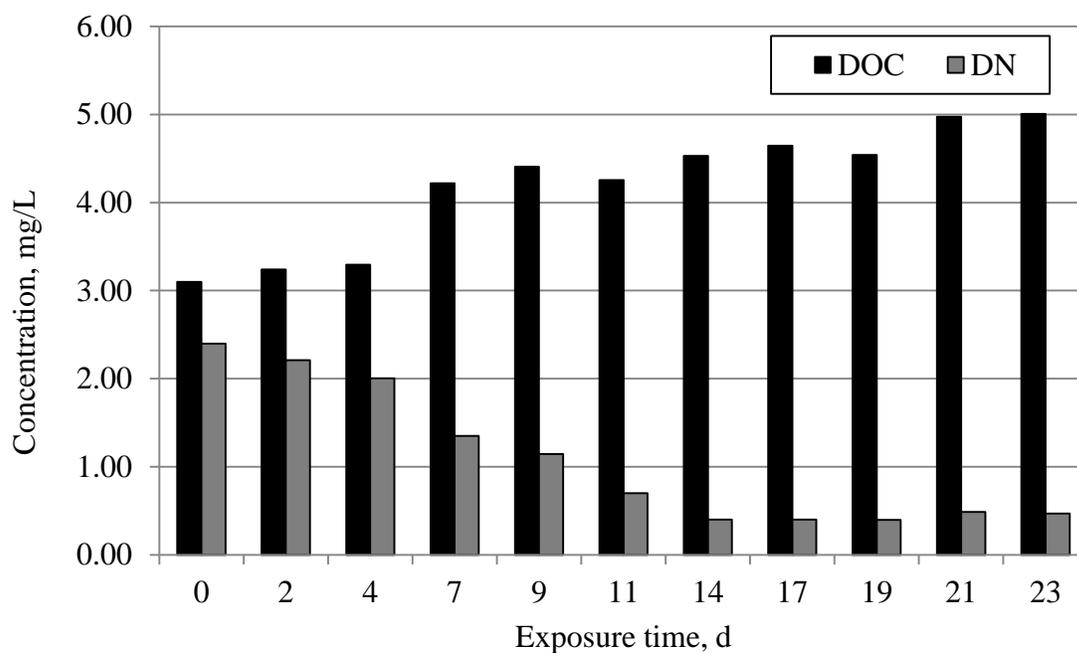


Figure 3.11. DOC and DN in wastewater effluent exposed to sunlight.

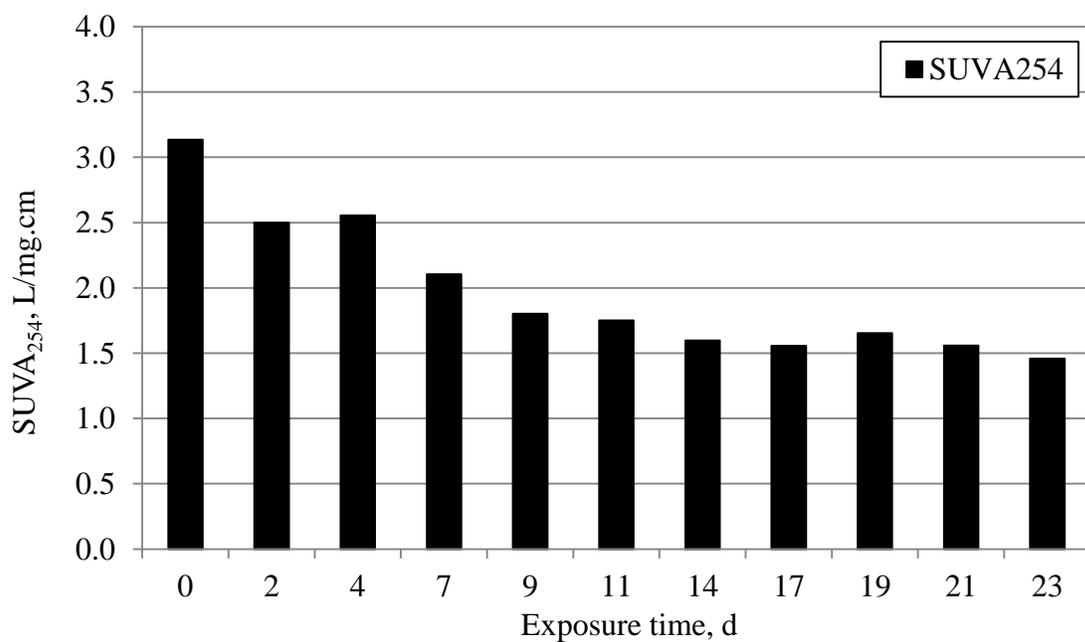


Figure 3.12. SUVA₂₅₄ in wastewater effluent exposed to sunlight.

Then a fresh sample (IW2-May) of 40 L was prepared, as previously described, for conducting adsorption experiments using the four PACs. The stock solution was exposed to sunlight outside of the lab as in the previous experiment. Samples were obtained after seven and 14 d for conducting adsorption experiments. The results for NDMA FP are presented in Figure 3.13. Initially, the NDMA FP precursors removal was within 63-68% (NDMA FP 576 ng/L) at $t = 0$ d. After seven days of exposure to sunlight, the concentrations of NDMA FP precursor exhibited a pronounced decrease (45%), from 576 to 318 ng/L. The removal by PACs at seven days decreased to 20 and 47% depending on carbon type (Fig. 3.14). After 14 d, although NDMA FP further decreased to 161 ng/L, NDMAFP removal by PAC adsorption did not change. Therefore, it appears that the difference in concentration did not play a role here; however, the decrease in the NDMA precursors reactivity (Fig. A-1) reduced their adsorbability by PAC adsorption. These results indicate that PAC adsorption is the most effective for the fresh NDMA precursors from wastewater treatment plant effluents where the FP level is the highest. Residence time of NDMA precursors in the source waters will lower NDMA FP through a combination of processes (biodegradation, adsorption, photolysis), and reduce the adsorbability of NDMA precursors. The effect of PAC type did not appear to play a major role; the only exception was the PAC B2 that showed lower removals for seven days and 14 d samples.

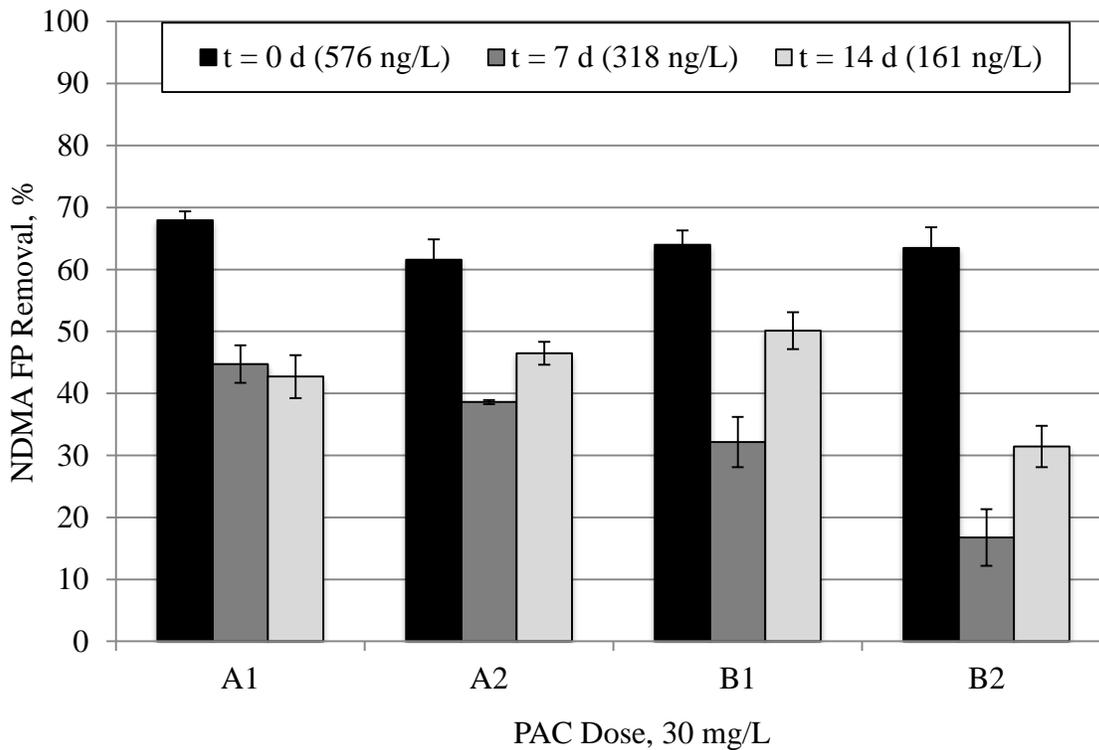


Figure 3.13. Removal of NDMA FP with PAC in a wastewater effluent exposed to sunlight.

The change in the adsorption of THM FP during the test is shown in Figure 3.14. THM FP removals remained between 18-31% during the test and was not affected by 7 d or 14 d exposure periods. One likely explanation for the THM trend is that the formation of THM was controlled mainly by the non-biodegradable natural organic matter, which was not affected by photolysis; therefore no major change was observed on the adsorption patterns of THM FP.

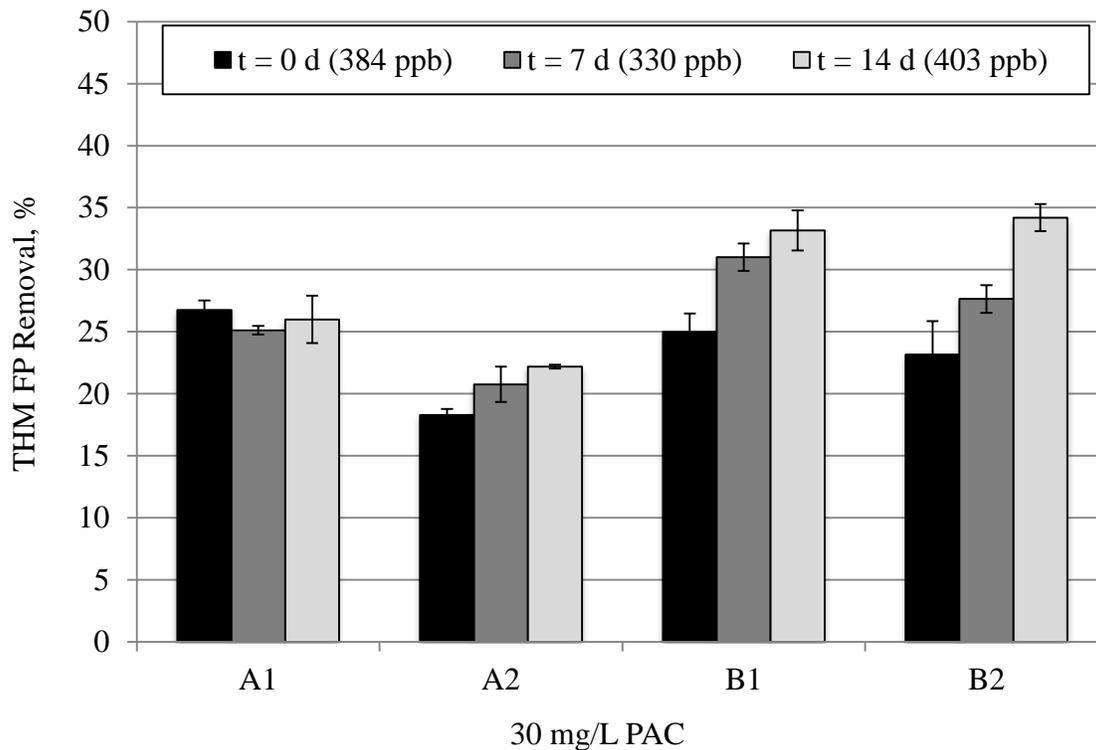


Figure 3.14. Removal of THM FP with PAC in a wastewater effluent exposed to sunlight.

Effect of carbon dose on NDMA and THM precursors removal by PAC

Hanigan and colleagues (2012) studied the effect of PAC dose on the removal of NDMA precursors. A secondary WWTP effluent with a NDMA FP of 544 ng/L was exposed to PAC doses ranging from 15-210 mg/L, with four hours contact time. The lowest dose (15 mg/L) of PAC removed 70% of the NDMA FP, and the removal continued as the dose was increased up to 75 mg/L (90% NDMA FP removal). Addition of PAC doses higher than 75 mg/L achieved incrementally little additional NDMA FP removal.

In this study, the effect of carbon dose was evaluated by selecting a surface water source (SW2, NDMA FP 70 ng/L) and two different doses (15 mg/L and 30 mg/L) of A1 and B1 PACs with four hours contact time. Doubling the PAC dose from 15 mg/L to 30 mg/L did not increase the NDMA precursor removal for both types of carbons (Fig. 3.15). The decrease in the NDMA FP remained about 30%; this finding is in agreement with the removals observed in other surface waters investigated in this study (Fig 3.1). The results indicated that 15 mg/L was sufficient to remove all the absorbable NDMA precursors. On the other hand, in the secondary wastewater effluent tested by Hanigan et al. (2012), the same dosages resulted in an increment of almost 15% in the removal of NDMA FP precursors.

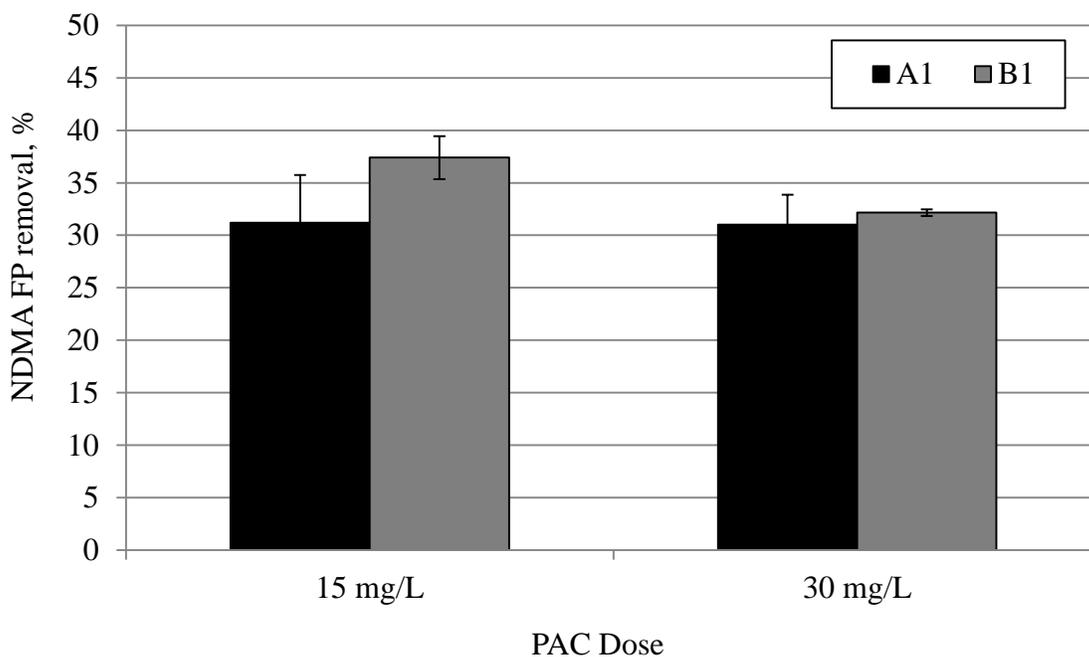


Figure 3.15. Effect of PAC dose on the removal of NDMA FP precursors in a surface water source (SW2).

The removal of THM FP precursors during the experiments showed an increase of about 10% when the PAC dose was doubled from 15 mg/L to 30 mg/L (Fig. 3.16). Removal of NOM, the major THM precursor, requires high PAC doses (Najm et al., 2001). Consequently, an increase in the PAC dose provided additional adsorption sites for THM precursor removal.

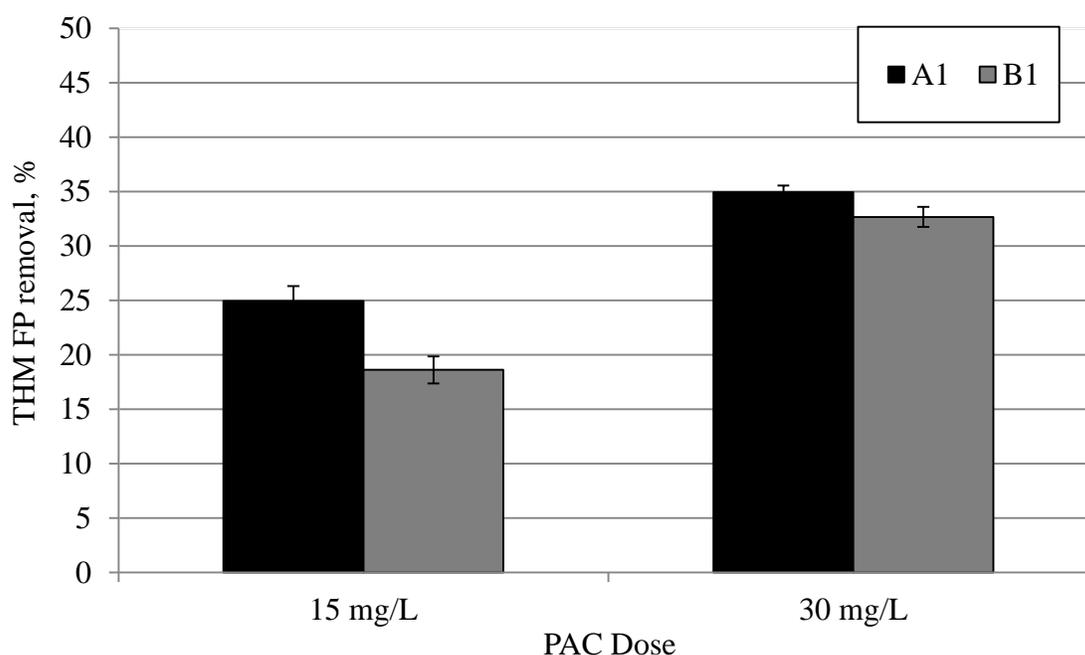


Figure 3.16. Effect of PAC dose on the removal of THM FP precursors in a surface water source (SW2).

Effect of combined addition of PAC on the removal of NDMA and THM precursors by

PAC

Additional experiments were conducted to examine if there would be any benefit to use acidic and basic carbon together. First, adsorption experiments with A1 and B1

were run at individual doses of 15 mg/L, and four hours contact time. Then, A1 and B1 were combined in 1:1 ratio and a total dose of 30 mg/L and four hours contact time.

The removal of NDMA FP by individual PACs was 31-37% (Fig. 3.17). The mixture of A1 and B1 removed 43% of NDMA FP precursors. For comparison purposes the theoretical removal of the mixture, the sum of the individual removals, was also plotted (70%).

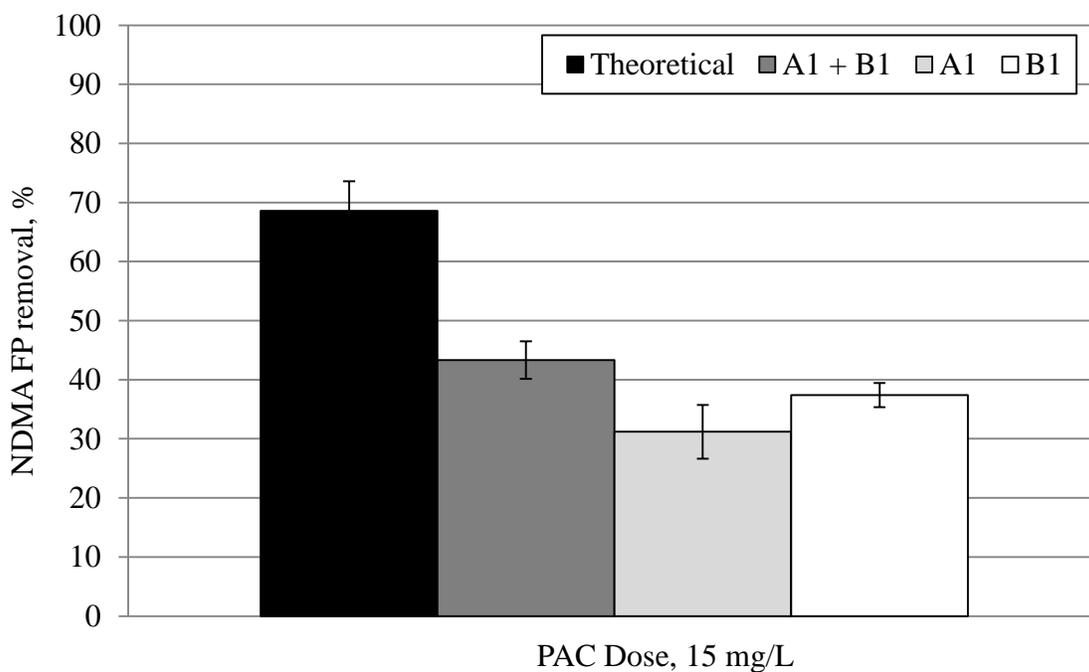


Figure 3.17. Effect of the combined addition of two different PAC on the removal of NDMA precursors (SW2).

If A1 and B1 removed different precursors, the combined removal should be close to 70% (not all the precursors can be removed). Perhaps, the mixture of A1 and B1 removed only 43% of NDMA FP precursors because these PACs remove a similar fraction of NDMA FP precursors.

The removal of THM FP by individual PACs was 19-25% (Fig. 3.18). The mixture of A1 and B1 removed 42% of THM FP precursors. Also, for comparison purposes the theoretical removal of the mixture, the sum of individual removals, was plotted (44%). It is likely that doubling the PAC dose almost doubled the removal of THM FP precursors.

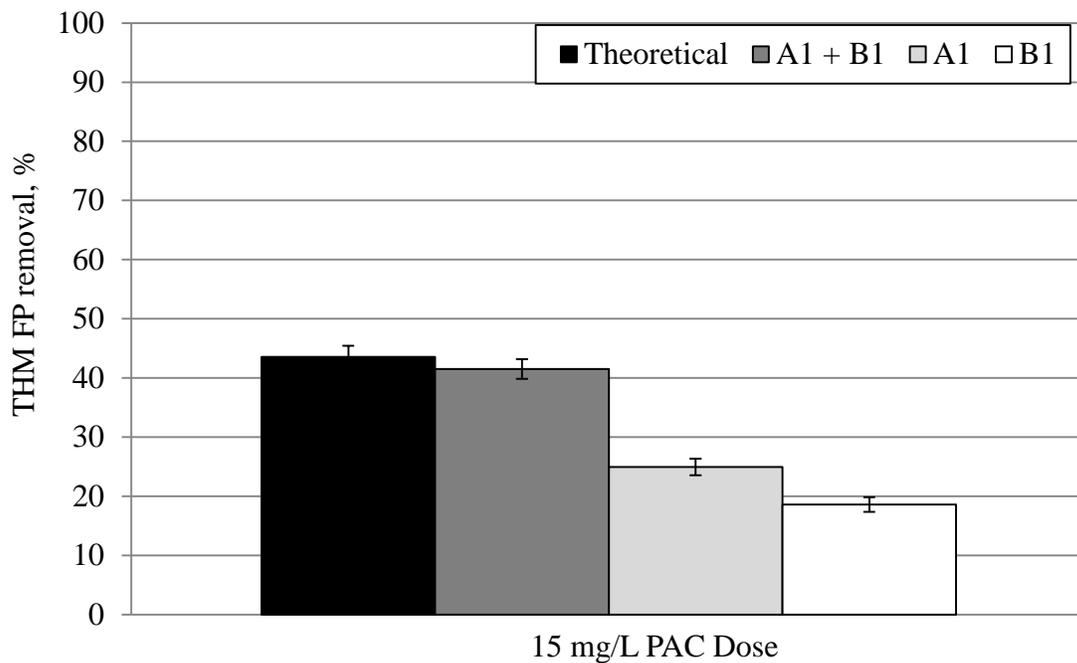


Figure 3.18. Effect of the combined addition of two different PAC on the removal of THM precursors (SW2).

CHAPTER IV

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

- The removal efficiency of NDMA FP precursors by PAC is significantly higher for samples from wastewater effluents and samples collected in close proximity to wastewater influence than for samples from surface water not influenced by wastewater. The adsorbability of NDMA precursors and effectiveness of PAC adsorption will decrease with increasing distance from the wastewater discharges due to the natural attenuation of precursors through a combination of processes (biodegradation, photolysis and adsorption).
- Adsorbable NDMA precursors showed a size distribution in the waters tested, and the adsorbable fraction included more precursors in the size region of 10-20 Å than < 10 Å.
- Basic carbons showed higher removal of NDMA FP than acidic carbons. However, the overall removal on a mass basis will depend on the surface area, pore size distribution and pH_{PZC} . PACs with basic surface with pores > 10 Å are likely to be more effective for NDMA precursor control.
- Adsorption of NDMA precursors by PAC for four hours contact time was affected by the initial concentration of NDMA FP. The removal increased with increasing NDMA FP in water.

- The removal efficiency of THM FP precursors was not greatly affected by the water source, due to the presence of large NOM molecules and the short contact time during the adsorption experiments.
- Adsorbable THM precursors were found to be much larger than the NDMA precursors ($> 20 \text{ \AA}$).
- Basic carbons showed higher removal of THM FP than acidic carbons. However, the overall removal on a mass basis will depend on the surface area, pore size distribution and pH_{PZC} . PACs with basic surface with pores $> 20 \text{ \AA}$ are likely to be more effective for THM precursor control.

Recommendations

- Further confirm the finding that adsorption of NDMA precursors is affected by the initial concentration of NDMA FP with samples from more sources.
- Full-or pilot-scale experiments to investigate practical use of PAC for control of NDMA precursors.
- Conduct more experiments with basic carbons (high surface area and mesoporous).
- Evaluate the effect of polymers on PAC adsorption.
- Evaluate the use GAC on NDMA precursors removal.

APPENDICES

Appendix A

Changes in Reactivity of Wastewater-impacted Sources

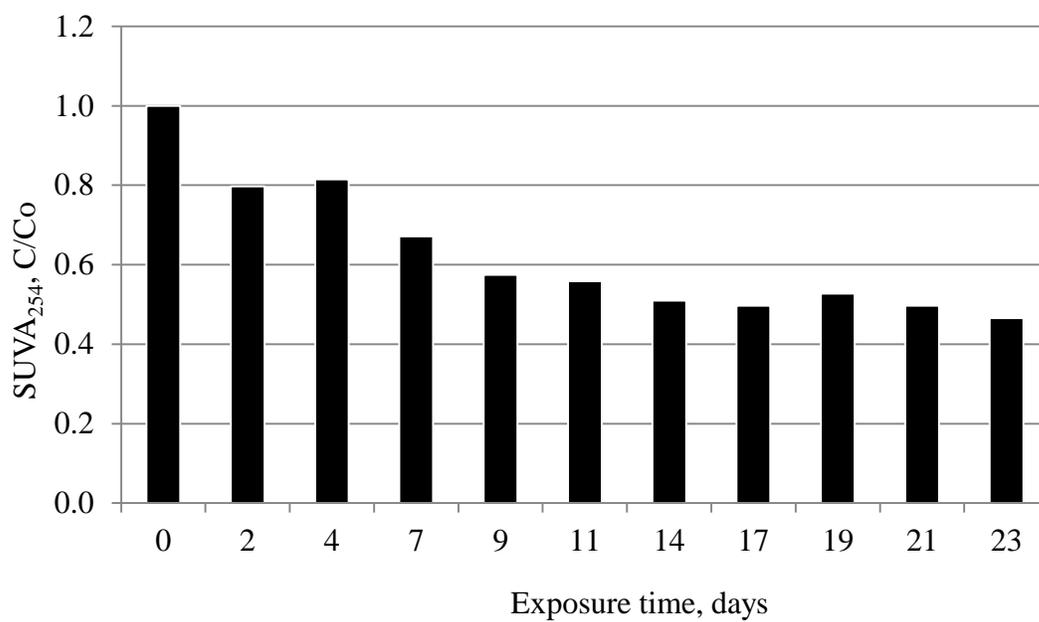


Figure A-1: Change in SUVA₂₅₄ in IW2 collected in April 2013 and subjected to sunlight.

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