

REMOVAL OF DISINFECTION BY-PRODUCT PRECURSORS BY ACTIVATED
CARBON AND MIEX®

A Thesis

presented to

the Faculty of the Graduate School

at the University of Missouri-Columbia

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

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JULY 2011

The undersigned, appointed by the dean of the Graduate School, have examined the thesis entitled

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ACKNOWLEDGEMENTS

I would like to express my thanks to Dr. Tom Clevenger for his encouragement and advice throughout this research. Also, to the Missouri Water Resources Research Center, who provided funding for the project. To my committee, Dr. Enos Inniss and Dr. Allen Thompson, thank you for the time you have invested in me while providing guidance. I would also like to acknowledge my fellow students Lisa Wulff , Laetitia Ramolino, Dan David, and Ted Grimes for their help with instrumentation, planning, and a set of extra hands. The staff of the Missouri Water Resources Research Center, specifically Dr. Jing Cheng, provided training on the instrumentation. I would also like to thank my family for their support and assistance.

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LIST OF ABBREVIATIONS

AC – Activated carbon

BCAA – Bromochloroacetic acid

BDCAA – Bromodichloroacetic acid

BDCM – Bromodichloromethane

CDBAA – Chlorodibromoacetic acid

CDBM – Chlorodibromomethane

CNT – Carbon nanotubes

COOH – Carboxyl group

COOR – Ester group

DBAA – Dibromoacetic acid

DBP – Disinfection by-product

DBP FP – Disinfection by-product formation potential

DCAA – Dichloroacetic acid

DI – Deionized

DOC – Dissolved organic carbon

DOM – Dissolved organic matter

EPA – Environmental Protection Agency

GC/MS – Gas chromatograph / mass spectrometer

GFH – Granular ferric hydroxide

HAA – Haloacetic acid

HAA5 FP – Total of 5 haloacetic acid's formation potentials

HPI – Hydrophilic

HPO – Hydrophobic

HPO-A – Hydrophobic Acid

HPO-N – Hydrophobic Neutral

MBAA – Monobromoacetic acid
MCAA – Monochloroacetic acid
MTBE – Methyl tertiary-butyl ether
NH₂ – Amine group
NO₂ – Amide group
NOM – Natural organic matter
OH – Alcohol group
OR – Ether group
R – Alkyl group
SUVA – Specific ultraviolet absorbance
TBAA – Tribromoacetic acid
TBM – Bromoform
TCAA – Trichloroacetic acid
TCM – Chloroform
THM – Trihalomethane
TTHM FP – Total trihalomethane formation potential
TOC – Total organic carbon
TPI- Transphilic
TPH-A – Transphilic acid
TPH-N – Transphilic neutral
X – Halogen group
µg/L – Micrograms per liter
≥ - Greater than or equal to
≤ - Less than or equal to
< - Less than
> - Greater than

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ABSTRACT

The objective of this research was to investigate NOM removal with activated carbon and MIEX®. Hydrophilic (HPI), hydrophobic (HPO), and transphilic (TPI) NOM was fractionated and subsequent DBP formation from these fractions was studied.

Several new adsorptive materials (greensand, carbon nanotubes, iron impregnated activated carbon) were tested for DBP reduction potential. Reductions by the materials were poor and therefore the materials were not investigated further.

Activated carbons, although similar in structure, perform differently from each other. Aqua Nuchar® and Hawkins Sabre Series® had greater than 30% difference in TTHM FP reduction under the same test conditions. None of the activated carbons investigated were found to have potential for brominated DBP precursor removal.

When MIEX® (magnetic ion exchange) was compared to activated carbon with respect to NOM fraction removal, it was found that MIEX® removed more of the HPI and TPI fractions. This was represented well in DBP FP reductions specifically derived from reactions with NOM in these fractions. In particular, MIEX® decreased NOM in the HPI fraction only 10% more than activated carbon but decreased TTHM FP 34% greater than activated carbon. This suggests that MIEX® preferentially removes DBP precursors to a greater extent than activated carbon. MIEX® was also found to decrease formation of brominated DBPs.

SUVA, UV254, DOC, and chlorine demand were all investigated as surrogate parameters for DBPs. UV254 was found to correlate best with DBP formation with $0.56 < R^2 < 0.80$. UV254 absorbed by HPO NOM was found to correlate best with TTHM FP ($R^2=0.88$) with HPI being poorly correlated ($R^2=0.20$). THMs resulting from reactions with HPI NOM accounted for between 40% and 55% of THMs from all fractions.

1 INTRODUCTION

1.1 DBPS AND POTABLE WATER

As the world population continues to grow, there is an ever increasing demand for potable water. Due to this demand, a modern treatment and distribution system has been established in almost all major urban centers. The oxidative properties of chlorine have made it a primary form of disinfection in many of these facilities. However, because of chlorine's chemical properties, it has the potential to create disinfection by-products (DBPs). Disinfection by-products are generated following a reaction with natural organic matter (NOM) and chlorine (Bull *et al.*, 1995; Jacangelo *et al.*, 1995). Natural organic matter has been found in all surface and ground waters in varying amounts, but has been found in greater concentrations in surface water.

Chlorinated disinfection systems are closely regulated by the United States Environmental Protection Agency (EPA). Most recently, EPA placed regulations on disinfection by-products due to their potential carcinogenicity (McGeehin, 1993; Villanueva *et al.*, 2003). Trihalomethanes (THMs) and haloacetic acids (HAAs) have been shown to be the two largest contributors to DBPs on a by weight basis (Krasner *et al.*, 1989; Adams *et al.*, 2005). Their contributions are regulated by the Stage 2 Disinfectants and Disinfection By Products Rule at 80 and 60 $\mu\text{g/L}$, respectively (U.S. EPA, 2006).

Trihalomethanes form as the substitution of any halogen such as fluorine, chlorine, bromine, and iodine, for three of the four hydrogen atoms in methane. Haloacetic acids form when a halogen atom takes the place of hydrogen in acetic acid. Waters high in bromide have been shown to generate more THMs and HAAs, specifically the brominated species such as bromoform, as bromide tends to catalyze these reactions (Richardson *et al.*, 1999; Hua *et al.*, 2006).

Trihalomethane and HAA concentrations are measurements of several combined compounds. In bench scale studies, DBPs are generally reported as total trihalomethane formation potential (TTHM FP) and haloacetic acid formation potential (HAA5 FP). Stage 2 Disinfectants and Disinfection By Products Rule requires that the total of the four THMs and the total of 5 HAAs (MCAA, DCAA, TCAA, MBAA, DBAA) listed in Table 1-1 to be below the standard values to be in compliance.

Table 1-1 Disinfection by-product common abbreviations (adapted from Shorney, 1998)

	Compound	Abbreviation	Structure
THMs	Chloroform	TCM	CHCl_3
	Bromodichloromethane	BDCM	CHBrCl_2
	Chlorodibromomethane	CDBM	CHBr_2Cl
	Bromoform	TBM	CHBr_3
HAAs	Monochloroacetic acid	MCAA	CH_2ClCOOH
	Monobromoacetic acid	MBAA	CH_2BrCOOH
	Dichloroacetic acid	DCAA	CHCl_2COOH
	Trichloroacetic acid	TCAA	CCl_3COOH
	Bromochloroacetic acid	BCAA	CHBrClCOOH
	Dibromoacetic acid	DBAA	CHBr_2COOH
	Bromodichloroacetic acid	BDCAA	$\text{CHBrCl}_2\text{COOH}$
	Chlorodibromoacetic acid	CDBAA	$\text{CBr}_2\text{ClCOOH}$
	Tribromoacetic acid	TBAA	CBr_3COOH

1.2 RESEARCH OBJECTIVES

The objectives of this research were; 1) To investigate THM and HAA formation reduction with activated carbon and ion exchange, 2) Investigate possible surrogates for DBP formation of Boonville, MO treatment facility water, 3) Investigate NOM fractions that were removed using activated carbon and ion exchange treatments, 4) Test performance of several new adsorptive materials for DBP precursor removal.

2 CURRENT STATE OF KNOWLEDGE

2.1 HEALTH EFFECTS

Research has been conducted regarding the toxic effects of DBPs. A large amount of conclusive direct work has been conducted on animals while case-control studies have been performed concerning human toxicity with generally less conclusive findings.

2.1.1 Animal

It has been shown that both THMs and HAAs are carcinogenic in rodents (Dunnick *et al.*, 1985; National Toxicology Program, 1987; National Toxicology Program, 1989; Bull *et al.*, 1990). The U.S. National Cancer Institute confirmed early findings (Eschenbrenner, 1945; Eschenbrenner and Miller, 1946) regarding carcinogenic properties of TCM. Up to a 92% increase of hepatocellular carcinoma could be found in male mice dosed 180 mg/kg five times a week for 78 weeks and a 95% increase for female mice with the same dosing schedule. Rats in the study were less susceptible to increased cancer risk having only 24% increase in male and 4% in female (National Cancer Institute, 1976).

More recently, in rats, liver toxic effects, specifically cytoplasmic vacuolization, chronic inflammation, necrosis and fatty change, have been observed after administration of CDBM, BDCM, and TBM. Similar effects were found in mice with the exception of

female mice, which were only susceptible to fatty change after exposure to THMs. Chlorodibromomethane, BDCM, and TBM also caused liver neoplasms in mice, kidney neoplasms in mice and rats, and colon or rectal neoplasms in rats (Dunnick and Melnick, 1993).

2.1.2 Case Studies

Much of the aforementioned research studied individual DBPs rather than ingestion of common mixtures of DBPs found in modern water supply systems. Also, doses were much higher than an average person would receive from a properly functioning water treatment facility. Epidemiological studies have been conducted to gain knowledge on the toxicity to humans.

Early studies regarding exposure to chlorination by-products were conclusive individually, but often disagreed conjunctively. A meta-analysis encompassing 10 DBP/cancer related studies was conducted in 1992 (Morris *et al.*). Meta-analysis was based on the quality of the researcher's selection of subjects, confounding variables adjustment, exposure assessment, and statistical analysis. Bladder and rectal cancer were deemed to be of the highest quality by the author and are shown in Table 2-1. A positive correlation between exposure and risk was found.

Table 2-1 Meta-analytic estimates of the association between bladder and colon cancer at specified levels of cumulative exposure to chlorination by-products (from Morris *et al.*, 1992)

Site	Level of Exposure	Relative Risk	95% CI
Bladder	Low	1.03	0.85, 1.24
	Moderate ^a	1.2	1.05, 1.37
	Moderate ^b	1.2	1.04, 1.38
	High	1.41	1.24, 1.62
Rectum	Low	1.13	0.61, 2.09
	Moderate ^a	1.29	1.00, 1.67
	Moderate ^b	1.49	1.10, 2.01
	High	2.04	1.18, 3.53
^a This Category includes only data from those studies that ranked a middle level of exposure.			
^b This category includes all studies for which exposure was dichotomous, in addition to studies ranked a middle level of exposure.			

Cancer sites such as brain, breast, kidney, liver, and others were also included in the meta-analysis. All were found to have positive correlations with DBP exposure level.

More recent studies agreed with the above findings regarding bladder and rectal cancer (Cantor *et al.*, 1998; Hildesheim *et al.*, 1998; Cantor *et al.*, 1999) and added that men appeared to be more susceptible to THM influence for bladder cancer than women, finding a negative odds ratio for women no matter the length of exposure (Cantor *et al.*, 1998). Another study found odds ratios for brain cancer of 1.0, 1.1, 1.6, and 1.3 for exposure to chlorinated surface water of 0, 1-19, 20-39, and ≥ 40 years (Cantor *et al.*, 1999).

Toxicity has also been shown to be affected by quantity both in respect to consumption as well as concentration. Spontaneous abortion was shown to increase 3%

for women drinking water containing ≥ 75 $\mu\text{g/L}$ THM. Odds ratios increased from 1.1 to 2.0 when number of glasses consumed of ≥ 75 $\mu\text{g/L}$ THM increased to greater than 5 daily (Waller *et al.*, 1998).

2.2 DBP FORMATION

Disinfection by-product formation occurs as a reaction between NOM and any halogen. Due to the makeup of NOM, there are several pathways for the formation of DBPs.

2.2.1 NOM

Natural organic matter is an extremely complex heterogeneous material made up of hydrophilic acids, humic substances, proteins, lipids, carboxylic acids, polysaccharides, amino acids, and hydrocarbons (Wei *et al.*, 2008). Humic substances have been found to make up 50-70% of NOM in water (Baker and Spencer, 2004). Disinfection is generally a final process, after coagulation and filtration, for potable water, and therefore disinfectants react with only little or no particulate organic matter. Subsequently, the majority of DBP formation potential (DBP FP) research regarding organic matter in natural water has been conducted with interest in dissolved organic matter (DOM). Dissolved organic matter is measured with the surrogate parameter, dissolved organic carbon (DOC). Dissolved organic carbon is defined similarly to DOM as the fraction of total organic carbon (TOC) that passes a 0.45 μm filter, or the nonparticulate fraction. It is measured with a TOC analyzer after filtration.

XAD resin has been used to fractionate several distinct groups of DOM. These groups are; hydrophobic (HPO), containing the hydrophobic acid (HPO-A) and hydrophobic neutral (HPO-N) fractions, transphilic (TPI), also containing acid and neutral fractions (TPHA and TPHN, respectively), and hydrophilic (HPI). The hydrophobic fraction generally contains humic substances such as humic and fulvic acids (Cheng, 2007). Both TPH and HPI are mostly nonhumic containing fractions and are often referred to together as HPI.

Natural organic matter is considered highly aromatic as indicated by its high ultraviolet absorbance at a wavelength of 254 nm (UV254) (Reckhow *et al.*, 2004). This property can be attributed to unsaturated bonds in functional groups contained in humic substances common in NOM (Nikolaou and Lekkas, 2001). Specific ultraviolet absorbance (SUVA) is defined as UV254 divided by the DOC concentration. It has been shown to be a good indicator of the aromaticity of NOM (Reckhow *et al.*, 1990; Croue *et al.*, 2000; Kitis *et al.*, 2001; Liang and Singer, 2003).

2.2.2 Formation Mechanics

Trihalomethanes and HAAs form as the substitution of a halogen for one or more hydrogen atoms. However, the kinetics of such substitutions are extremely complex as the composition of NOM is not entirely known. Several pathways for the formation of DBPs are possible and therefore, it is difficult to be sure which is occurring.

pH may have an effect on DBP generation and governs the mechanics of formation of DBPs as well as their fate after formation. It has been shown that not only may HAA decompose at elevated pH (Krasner *et al.*, 1989), but that there is also more

potential for THM formation and less for HAA formation. The opposite is true for decreased pH (Liang and Singer, 2003; Cheng, 2007; Ye *et al.*, 2009).

Chlorine may also oxidize bromide containing compounds forming hypobromous acid. Hypobromous acid has been shown to more readily react with NOM in the formation of brominated DBPs. Hypobromous acid is thought to be a better substitution agent and poorer oxidant than hypochlorous acid and therefore, generation of brominated THM and HAA species in waters with greater than 10 µg/L bromide can be much more significant than chlorinated species (Richardson *et al.*, 1999; Hua *et al.*, 2006).

Carlson *et al.* (1975) indicated that electron donating aromatic functional groups (-OH, -OR, -NH₂, -R) are more reactive in the formation of halogenated DBPs than electron accepting aromatics (-NO₂, -COOH, -COOR, -X). This is due to the groups' capacity to direct the halogens to both the *ortho* and *para* positions whereas the electron accepting functional groups orient the halogens in the *meta* position only. Placing halogens at either *ortho* or *para* positions will increase the electron density in the aromatic ring while the *meta* position will decrease it.

2.2.3 Surrogates for TTHM and HAA5 FP

Water treatment facilities cannot quickly analyze effluent for TTHM or HAA5. Generally facilities are tested by state or federal entities quarterly for Stage 2 compliance. To ensure compliance, it is necessary for facilities to estimate DBP concentration through correlation with an easily analyzed surrogate. Candidates are DOC, UV254, chlorine demand, and SUVA.

2.2.3.1 Organic Carbon

Organic carbon can be analyzed inside of 10 min with most available equipment and requires little or no preparation work. The analysis is already conducted onsite at most water treatment facilities and is therefore a good candidate as a DBP surrogate.

Several studies have been conducted to study the relationship between TOC/DOC and TTHM FP with conflicting results. Chapra and Canale (1997) found that data from four previous studies with similar experimental methods could be approximated into Eq. 2-1.

$$\text{TTHM FP} = 43.78 * \text{TOC}^{1.248} \quad \text{Eq. 2-1}$$

$$\text{TOC} = \left(\frac{\text{mg}}{\text{L}}\right), \text{TTHM FP} = \left(\frac{\mu\text{g}}{\text{L}}\right), n = 133, r^2 = 0.94$$

The data were contradictory to a study conducted by Najm et al. (1994) who found TOC correlation to be $r^2 < 0.67$ for TTHM FP. HAA5 FP was also poorly correlated.

Dissolved organic carbon has in many cases been found to be a poor surrogate for TTHM FP (Stepczuk *et al.*, 1998a; Stepczuk *et al.*, 1998b; White *et al.*, 2003) and HAA5 FP (White *et al.*, 2003).

2.2.3.2 UV254

Analyzing UV254 absorbance requires passing light through a quartz cell of water and measuring a percentage of light energy lost. The lost energy is assumed absorbed and this process takes less than 1 min with modern equipment. Again the process requires little or no preparation.

Ultraviolet absorbance arises due to unsaturated bonds in molecules or functional groups and is related to reactivity. Ultraviolet absorbance at a wavelength of 254 nm has

been found to be well correlated with TTHM FP (Singer *et al.*, 1981; Rathbun, 1996) with some studies reporting correlation coefficients between 0.93 and 0.99 (Edzwald *et al.*, 1985; Najm *et al.*, 1994; White *et al.*, 2003). Also it has been shown to have potential as a HAA5 FP surrogate (White *et al.*, 2003) but correlation coefficients are generally less than for TTHM FP (Najm *et al.*, 1994).

2.2.3.3 SUVA

Specific UV absorbance is defined as UV254/DOC and requires slightly more analysis time as both UV254 and DOC analyses are required.

The correlation with DBP FP is generally poor as not all aromatic moieties are reactive with chlorine (Fram *et al.*, 1999; Kitis *et al.*, 2001; Weishaar *et al.*, 2003; White *et al.*, 2003). This is also indicated as previously noted by the poor relationship between DOC and DBP FP. However, in some cases SUVA has been shown to be a good indicator of hydrophobic carbon with hydrophobic content being a good indicator of HAA FP (Croue *et al.*, 2000; Liang and Singer, 2003; Boyer and Singer, 2005).

2.2.3.4 Chlorine Demand

Chlorine demand is the difference between dosed chlorine and residual chlorine after a given period of time as shown in Eq. 2-2. Analysis takes less than 10 min and involves a reagent sensitive to free chlorine and a spectrometer.

$$\text{Chlorine Demand} = \text{Dosed Chlorine} - 24 \text{ hr Free Chlorine} \quad \text{Eq. 2-2}$$

Little research has been conducted regarding chlorine demand as a surrogate for DBP FP. Of the research conducted, studies are sensitive to allowed reaction time as well as water source. With reaction times on the order of a few days and water from both

reservoir and river sources, Reckhow et al. (1990) found good correlations with both TTHM FP and several halogenated acetic acids. Also, Gang (2003) found that formation of TTHM FP could be directly related to chlorine consumption by ultra filtered NOM ($R^2=.97-.99$). The relation was found to be from 30.9 to 41.9 $\mu\text{g-TTHM/mg-Cl}_2$ consumed dependant on molecular weight with the smaller molecules generating greater quantities of TTHMs. However, Edzwald et al. (1985) found correlation coefficients of 0.85 and 0.53 for river and reservoir sources respectively with reaction time fixed at 2 hr.

2.2.4 Temporal Trends in DBP Formation

Several seasonal trends such as NOM concentration, temperature, and precipitation, can be expected to affect DBP formation. Also, these variations cause operational changes in treatment plants such as chlorine dose and activated carbon use which also directly affect DBP formation.

Disinfection by-product concentrations in treated water are generally higher in the summer and fall than in the winter and spring with third quarter TTHM FP and HAA5 FP up to double that of fourth quarter (Williams *et al.*, 1998; Sohn *et al.*, 2001; Adams *et al.*, 2005; Rodriguez *et al.*, 2007). Of note, Williams et al. (1998) collected data from 35 drinking water treatment facilities with chlorine as the primary disinfectant finding a 200% increase in TTHM FP, 160% increase in DCAA, and 122% increase in TCAA from winter to summer months.

Although the cause for this increase is not entirely known, Adams et al. (2005) speculated that it is at least partially due to algal growth patterns and precipitation. Intuitively, algae blooms occur during summer months, taking advantage of greater hours of sunlight with algae and other accumulated NOM then being washed into treatment

facilities during heavier precipitation in the fall. At least in partial agreement, Chen et al. (2008) concluded that that 20%-50% of DBP FP was due to algal blooms.

Missouri Department of Natural Resources collects DBP data for all registered water distributors in Missouri. An examination of THM and HAA data shows that Boonville, MO has greatest formation of DBPs in the second quarter of each year. Figure 2-1 shows averaged DBP data from 1997 through 2010 by quarter.

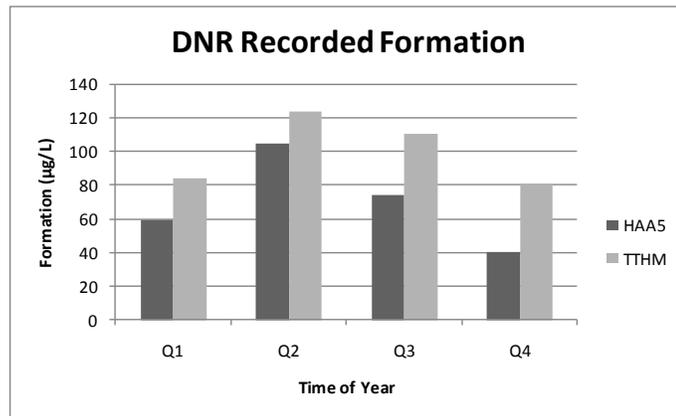


Figure 2-1 1997-2010 Quarterly Boonville, MO DNR formation data (adapted from MO DNR, 2010; Wulff, 2011)

2.3 DBP FORMATION MITIGATION

Several approaches exist to mitigate formation of DBPs in a treatment facility. Intuitively, DBPs can be removed after generation to reduce concentrations before consumption. However, in many cases it is more straightforward and therefore advantageous to generate fewer DBPs than to remove them after generation.

2.3.1 Post-disinfection

Constraints with potable water treatment facility design make it difficult and therefore uncommon to attempt to remove DBPs after generation. Although it has been shown that activated carbon (AC) will remove THMs and HAAs (Lykins *et al.*, 1988; Speth and Miltner, 1990), it is impractical to add AC to water that is entering the distribution system without the addition of new sedimentation basins. It has also been shown that biologically active carbon can remove DBPs, but it is once again impractical (Tung, 2004).

2.3.2 During Disinfection

Mitigation during disinfection refers to use of alternative disinfectants such as ozone, monochloramine, and ultraviolet irradiation. These alternatives generate less HAAs and THMs and can be as effective as chlorine in inactivating microbes (Liberti *et al.*, 2003; Muellner *et al.*, 2006; Rose *et al.*, 2007; Antonelli *et al.*, 2008; Burns *et al.*, 2008; Muñoz *et al.*, 2009). However, USEPA requires a chlorine residual in all distribution systems and consequently, ozone, and ultraviolet irradiation must be augmented with chlorine before the water enters the distribution system. In addition, with the exception of monochloramine, it is monetarily challenging for smaller municipalities to switch to alternative disinfectants as major facility modifications are required. Monochloramine requires little modifications and is therefore being used more frequently to meet required EPA chlorine residuals.

2.3.3 Pre-disinfection

Enhanced coagulation and adsorption of NOM before disinfection are common techniques to reduce DBP formation. Enhanced coagulation involves the testing of several coagulant doses and chemicals at a particular pH in order to find which combination is most effective at reducing DBP formation. Activated carbon, other adsorbents, and ion exchangers can be added to the water before the coagulation process also in an attempt to remove a large portion of NOM.

Adsorption, most generally, is the adhesion of dissolved molecules to a surface. Adsorption occurs in most instances due to surface energy. In a material, inner molecules are surrounded by similar molecules, thus satisfying their bonding requirements. However, the molecules at the edges or surfaces are not wholly surrounded and therefore have unsatisfied bonding requirements. This can cause other materials, such as NOM, with similarly unsatisfied bonding requirements to bond or adsorb.

2.3.3.1 Activated Carbon

Activated carbon is of particular interest as it has been oxidized to generate an extremely porous structure and therefore high surface area that is beneficial for adsorption. Wei et al. (2008) found that HPI was the major component of aquatic DOC (50%) with HPO-A (30%) contributing. Also, that DOC removal of up to 39% could be obtained with granular AC treatment ($3.3 \mu\text{g C m}^{-2}$ @ 1 hr and pH 7.8). HPI and HPO-A fractions were shown to be the main TTHM FP precursors, accounting for 80% of TTHM FP. While a reduction of 56% TTHM FP was found following AC treatment, a reduction of 71% and 38% TTHM FP for HPO-A and HPI fractions were found individually. This implies that AC, while being effective at removing portions of TTHM FP and DOC, is more effective at removing HPO than HPI fractions.

Modified AC has also been of recent interest. A study in 2009 (Klimenko *et al.*, 2009) concluded that oxidation of AC by hydrogen peroxide decreases the adsorption efficiency of AC. However, this decrease of absorption efficacy was compensated by the catalytic effect of hydrogen peroxide oxidation of the fulvic acids. Therefore, AC and H₂O₂ synergistically react with more fulvic acids than just AC. Unfortunately, fulvic acids have been shown to be less chlorine reactive, and therefore less DBP producing than humic acids (Zhang *et al.*, 2009). It is possible that fulvic-like acids contained in the HPI fraction would respond similarly with combined hydrogen peroxide and AC treatment, but little conclusive research has been conducted.

2.3.3.2 Carbon Nanotubes

Carbon nanotubes (CNT) are different from AC in that AC has varying oxidation states and functional groups formed at the adsorption sites during the oxidation process while CNT has globally conjugated unsaturated carbons in three dimensional arrays. This provides for adsorption sites along the surface of a cylindrical structure rather than in micropores of different sizes as is found in AC.

Carbon Nanotubes have been shown to preferentially adsorb the more chlorine reactive high molecular weight humic acids over fulvic acids. In AC, smaller molecules are preferentially adsorbed because they can reach small and large pores, where as in CNT, large molecules are adsorbed more readily due to their higher adsorption strength (Hyung and Kim, 2008). Regardless of NOM type (bulk, fulvic, or humic), when adsorption isotherms were conducted after adsorption to CNT, aromatic carbon content showed the strongest relationship. Adsorption capacity has been shown to double (from 30 to 60 $\mu\text{g C m}^{-2}$ @ 144 hr and pH 7) when aromatic group content increased from 30% to 60% (Hyung and Kim, 2008). This was consistent with findings that aromatic group

content is related directly to chlorine reactivity, more specifically, generation of DBPs (Wu, 1998). Although adsorption capacity is highly dependent on pH and ionic strength in the water, it is unlikely that control will be had over pH or ionic strength in an application.

2.3.3.3 High Clay Content Soils

Conventionally, research conducted regarding adsorption has been performed to determine ability of high clay content soil to retain NOM for agricultural purposes. Previous studies on sorption of NOM to soils have primarily been conducted at lower pH (3-5) to model subsurface soils (Gu *et al.*, 1994; Meier *et al.*, 1999). As pH decreases, adsorption capacity of clay generally increases as the oxides contained in the clay are usually deprotonated at higher pH (Tipping, 1981).

Regarding kaolinite, a clay with high aluminum oxide content, Meier *et al.* (1999) have found sorption of 80 to 100 $\mu\text{g C m}^{-2}$ @ 24 hr and pH 4 while Kahle *et al.* (2004) found 9 to 44 $\mu\text{g C m}^{-2}$ sorption @ 24 hr and pH 7. This is consistent with expected decrease in adsorption capacity due to higher pH. However, even at low pH (4), it has been shown that if both aluminum and iron oxides were removed from clay soils, up to 94% decrease in adsorption was obtained (Kaiser and Zech, 2000). Although these findings are contradictory, it can be assumed that the oxides contained in the soil play a part in adsorption at all pH ranges.

Goethite, a mineral found in clay soils is iron oxyhydroxide ($\text{Fe}^{3+}\text{O}(\text{OH})$) and has a great capacity for NOM adsorption (300 $\mu\text{g C m}^{-2}$ @ 24 hr and pH 4) (Meier *et al.*, 1999). This is likely due to its capability for ligand exchange between carboxylic and phenolic groups of the NOM and the hydroxyl groups of the iron oxide (James *et al.*, 2007; Genz *et al.*, 2008). Sorption onto goethite also decreases the average molecular

weight of a solution indicating that higher molecular weight, more humic molecules have been adsorbed (Meier *et al.*, 1999; James *et al.*, 2007). Removal of the iron and aluminum containing oxides in a soil has been shown to reduce the adsorption capacity of HPO material more than HPI (Kaiser and Zech, 2000) and, therefore, it can be inferred that the oxides sites preferentially adsorb hydrophobic fractions of the NOM present. Finally, it can be concluded that goethite has similar characteristics to AC in respect to preferential adsorption of highly aromatic, high molecular weight, hydrophobic molecules.

2.3.3.4 Iron Oxide

The high capacity for natural oxides such as goethite to adsorb NOM has generated interest in iron oxide. Genz *et al.* (2008) studied granular ferric hydroxide (GFH) for NOM removal. Granular ferric hydroxide is frequently used for arsenic removal and is applied in numerous European waterworks. It is similar to goethite and is predominately akaganeite, a poorly crystallized iron oxide. Granular ferric hydroxide was found to have potential for adsorption of DOC (36 to $107 \mu\text{g C m}^{-2}$ @ 72 hr and pH between 7 and 8). In particular, larger, more polar, more UV-active fulvic acids are preferentially adsorbed. The study also showed that adsorption was strongly dependent on pH, pointing again to ligand exchange as a primary mechanism.

A similar study found that pure iron oxide in the form of hematite removes 330 and $180 \mu\text{g C / m}^2$ @ 18 hr and pH of 4.1 and 6.5 , respectively. It was also noted that phosphate and sulfate have a severe negative impact on adsorption (Gu *et al.*, 1994).

Yujung *et al.* (1997) studied iron oxide from an application perspective. Olivine was coated with approximately 5% by weight iron oxide and used as filter media. Five percent was achieved only after several coatings eliciting a need for a more efficient

process. A 57% reduction in DOC was found after being passed through the filter media with contact time of only 10 min. However, it was discovered that adsorption efficiency decreases sharply with time and media would need to be regenerated once every few days assuming influent DOC is 3-5 mg/L. The coated media can be regenerated to near full adsorption capacity with NaOH, however, repeated backwashing also degrades adsorption capacity past 10 regenerations.

2.3.3.5 MIEX®

Anion exchange resins have been shown to remove large quantities of NOM from natural waters (Anderson and Maier, 1979; Bolto *et al.*, 2002; Singer and Bilyk, 2002; Boyer and Singer, 2005; Humbert *et al.*, 2005). Generally, an anion exchange resin exchanges a chloride ion from a quarternary ammonium functional group for an organic anion. Adsorption is typically avoided if possible as it decreases the resins ability to be regenerated by brine.

MIEX® (magnetic ion exchange) is relatively new, being produced commercially first in 1999, and has two properties that separate it from previously available anion exchange resins. First, it is smaller (2-5 times) than traditional resins with a mean particle diameter of 180 µm (Boyer and Singer, 2005). MIEX® also contains enough iron oxide to render it magnetic which aids in agglomeration and therefore settling of the material. This rapid sedimentation is critical as the material is intended to be regenerated and reused. Similar to other ion exchangers, MIEX® is a macroporous, strong base, polyacrylic resin with quarternary amine functional groups.

When MIEX® is used without coagulation, UV254 reductions of 50%-85% and DOC reductions of 40%-75% have been reported (Cook *et al.*, 2001; Hamm and Bourke, 2001; Pelekani *et al.*, 2001). Trihalomethane and HAA formation is also reduced with

declination in the ranges of 30%-85% for THM (Hamm and Bourke, 2001; Singer and Bilyk, 2002) and 50-68% for HAA formation (Boyer and Singer, 2005).

MIEX® has been shown to preferentially remove high SUVA DOM. Thirty to seventy five percent was reported in HPO matter removal compared to TPI matter with 20%-75% removal. This high SUVA DOM is HPO in nature and generated greater amounts of HAAs (Boyer and Singer, 2005).

MIEX® has also been shown to remove large amounts of bromide from waters (Singer and Bilyk, 2002; Boyer and Singer, 2005). However, when alkalinity approaches 100 mg/L, as little as 15% bromide removal was evident. As much as 94% was possible with alkalinity of 20 mg/L. Little bromide reduction was possible with coagulation alone (Singer and Bilyk, 2002; Boyer and Singer, 2005).

3 IRON IMPREGNATED AC FOR DBP FP REDUCTION

3.1 INTRODUCTION

Natural organic matter is present in all natural ground and surface waters. Natural organic matter is derived from decomposing plant and animal matter and is considered non-toxic. However, when combined with free chlorine in a water treatment facility, potentially carcinogenic DBPs form as the result of a halogen substitution for one or more hydrogen atoms (Eschenbrenner, 1945; Eschenbrenner and Miller, 1946; Dunnick *et al.*, 1985; National Toxicology Program, 1987; Bull *et al.*, 1990; Dunnick and Melnick, 1993; McGeehin, 1993; King and Marrett, 1996; Hildesheim *et al.*, 1998; Cantor *et al.*, 1999). Recently, USEPA has placed restrictions on THM and HAA levels in distributed waters (U.S. EPA, 2006). Removal of NOM by adsorption before reaction with chlorine is currently a cost effective method of reducing DBP levels in treated water.

A great deal of adsorption research has been conducted on soils with high iron oxide content (Tipping, 1981; Gu *et al.*, 1994; Yujung *et al.*, 1997; James *et al.*, 2007). It has been shown that goethite, a naturally occurring iron oxide, has a capacity for NOM removal of $300 \mu\text{g C m}^{-2}$ after 24 hrs (Meier *et al.*, 1999). This is likely due to ligand exchange between the carboxylic and phenolic groups of the NOM and the hydroxyl groups of the iron oxide (James *et al.*, 2007; Genz *et al.*, 2008). It has also been reported that removal of oxides from a soil reduces the capacity for adsorption of NOM (Kaiser and Zech, 2000) but little or no research has been completed regarding the DBP FP of the

removed NOM. Therefore, an adsorption study regarding DBP FP reduction with iron oxides was of interest.

3.2 MATERIALS AND METHODS

3.2.1 Sampling

Raw water was collected in May 18, 2010 from the City of Boonville's water treatment facility. A submerged intake in the Missouri River just north of the City of Boonville pumps water up to the facility. A grab sample was collected from a pressurized inlet to the facility's first sedimentation basin. The sample was then transferred immediately to the Missouri Water Resources' research lab where it was stored at 3°C for the duration of the study. The intent was not to study only Boonville's treatment process, but to study DBP forming surface water in general and therefore, raw water was used rather than water sampled directly before AC addition in the treatment train.

3.2.2 Activated Carbon

Hydrodarco® B (Norit Americas Inc., Marshall, TX) was obtained onsite from the City of Boonville water treatment plant. During the time of this study, Boonville used Hydrodarco® as a form of DBP reduction on a seasonal basis. Aqua Nuchar® was obtained from Meadwestvaco, Richmond, VA. Carbon nanotubes were acquired from Nanotech Port Co., Shenzhen, China. Iron impregnated activated carbon (Fe-AC) was obtained as Darco 20-50 (Norit Americas Inc.) and subsequently prepared by Zhimang

Gu (University of Missouri) for related research (Gu *et al.*, 2005). A summary of the material's properties from the manufacturers is given in Table 3-1. It should be noted that the properties listed are for Darco 20-50 and therefore may not accurately represent the material after iron impregnation.

Table 3-1 Properties of carbons used as treatment materials in 24 hr adsorption study

Material	Particle Size	Surface Area (m ² /g)	Iodine Number (mg/g)
Hyrdodarco B	90% <45 μm		>500
Aqua Nuchar	90% <45 μm	1200-1600	>900
CNT	1-100 nm		
Fe-AC	.3-.8 mm	650	625

3.2.3 Carbon Treatment

300 ml bottles containing different doses of AC (20, 40, 60, 80 mg/L) were filled with 250 ml of raw water. Doses were not chosen to represent Boonville's facility but to investigate NOM removal at high doses of AC and to investigate potential removal by new adsorptive materials. The minimum amount of agitation to keep the AC suspended was found to be 225 rpm and therefore bottles were shaken at 225 rpm for 24 ± 1 hrs. Water was then immediately filtered using a 0.45 μm filter and stored at 3°C pending analysis.

3.2.4 TOC/DOC Analysis

After filtration, non-purgeable organic carbon (DOC) was analyzed using a Shimadzu Total Organic Carbon Analyzer (Shimadzu Corp., Atlanta, GA) with an ASI

auto-sampler. Acidification was conducted using 2M hydrochloric acid obtained from Fisher Scientific, Fair Lawn, NJ as 36M and subsequently diluted.

3.2.5 UV254 Analysis

Filtered water was transferred to a 1 cm³ cuvette via pipette. Absorbance at a wavelength of 254 nm was measured 10 times using a Varian CARY50Conc UV-visible light spectrophotometer and averaged.

3.2.6 Chlorination

Chlorination was completed in accordance with Summers et. al (1996). A sodium hypochlorite dosing solution (about 2,000 mg/L) was made from 13% active chlorine (sodium hypochlorite) stock solution and buffered at pH 8 with 0.01M KH₂PO₄.

The dosing solution's concentration was then measured 3 times and averaged to ensure accuracy. Approximately 50 ml filtered water was transferred to 125 ml amber incubation bottles and buffered with borate solution. An appropriate amount of sodium hypochlorite dosing solution was added and the bottle was capped and inverted twice. The bottle was filled with borate buffered filtered water and capped ensuring no head space. The bottles were then stored in the dark for 24 hrs. Chlorine residual was then measured using a Hach DR/2400 spectrophotometer after which chlorine was quenched with 4.4 mg NH₄Cl dissolved in deionized water (DI).

3.2.7 THM Analysis

A gas chromatograph (Varian, Model 3800) / mass spectrometer (GC/MS) (Varian, Saturn 3800) equipped with a Tekmar 3000 purge and trap concentrator was used for the determination of THM concentrations. This process was similar to the Standard Method for the Examination of Water and Wastewater 6200 B and US EPA Method 524.

3.2.8 HAA Analysis

For the determination of HAA concentrations, a method involving liquid/liquid extraction and derivatization similar to Standard Method for Examination of Water and Wastewater 6521 and US EPA Method 552.2 was used. At an acidic pH, methyl tertiary-butyl ether (MTBE) was used to extract non-dissociated acidic compounds. Sodium sulfate was added to increase extraction efficiency as a salting agent. A 10% v/v solution of sulfuric acid and methanol was added to produce methyl ester derivatives that could be separated chromatographically (Varian, Model 3800).

3.2.9 Calculations

Chlorine demand was calculated using Eq. 2-2. Percent reduction was calculated with respect to filtered only water and is represented in Eq. 3-1.

$$\text{Percent Reduction} = \frac{(F-S)}{F} \times 100 \quad \text{Eq. 3-1}$$

$$F = \text{Value for Filtered Water} \left(\frac{\text{mg}}{\text{L}}, \frac{1}{\text{m}}, \frac{\text{L}}{\text{mg} * \text{m}}, \frac{\mu\text{g}}{\text{L}} \right)$$

$$S = \text{Value for Treated Sample} \left(\frac{\text{mg}}{\text{L}}, \frac{1}{\text{m}}, \frac{\text{L}}{\text{mg} * \text{m}}, \frac{\mu\text{g}}{\text{L}} \right)$$

3.3 RESULTS AND DISCUSSION

3.3.1 Characteristics of Filtered Water

After sample collection and filtration but before chlorination, UV254 and DOC were measured. After chlorination, THM and HAA were measured and reported as TTHM FP and HAA5 FP. A summary of the filtered water's characteristics is shown in Table 3-2. The water was characterized with high DOC, high UV254, and elevated DBP FP levels typical of mid spring.

Table 3-2 Filtered Boonville, MO River (May 18, 2010) water characteristics

DOC (mg/L)	UV254 (1/m)	SUVA	TTHM FP (µg/L)	HAA5 FP (µg/L)	pH
5.32	18.41	3.54	240	83	8

3.3.2 DOC, UV254, and SUVA

Dissolved organic carbon reduction was least when Fe-AC was used as a sorbent with only 16% reduction at the highest dose of 80 mg/L. Aqua Nuchar® removed the largest quantity of DOC with up to 50% reduction at a dose of 100 mg/L (Figure 3-1 and

Figure 3-2). This indicates that both iodine adsorption and surface area are possible indicators of DOC sorption.

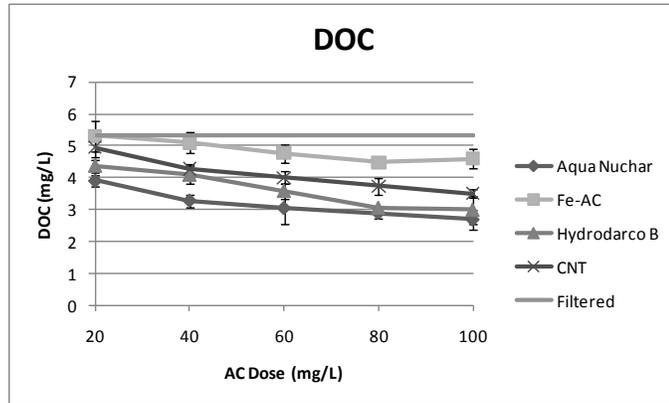


Figure 3-1 DOC of Boonville, MO River water after 24 hr adsorption by several activated carbons

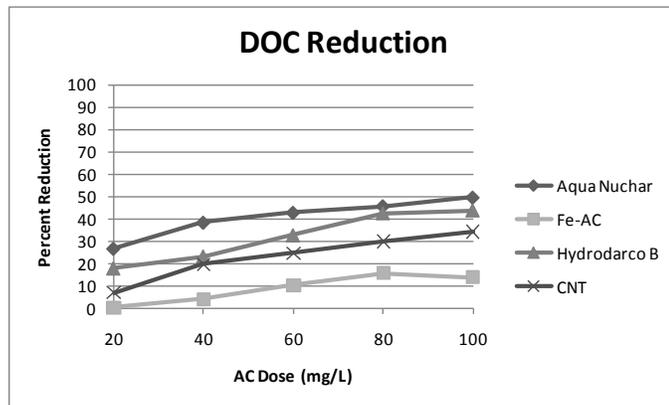


Figure 3-2 DOC of Boonville, MO River water percent reduction by adsorption on several activated carbons

Fe-AC reduced UV254 absorbance the least with decreases in UV254 only at doses of 60 (7%) and 80 mg/L (12%) and increases at other doses. Aqua Nuchar® again decreased UV254 absorbance more than the other materials with a maximum decrease of 55% (Figure 3-3 and Figure 3-4). Again, surface area and iodine adsorption number are possible indicators of a material's affinity for UV254 reduction.

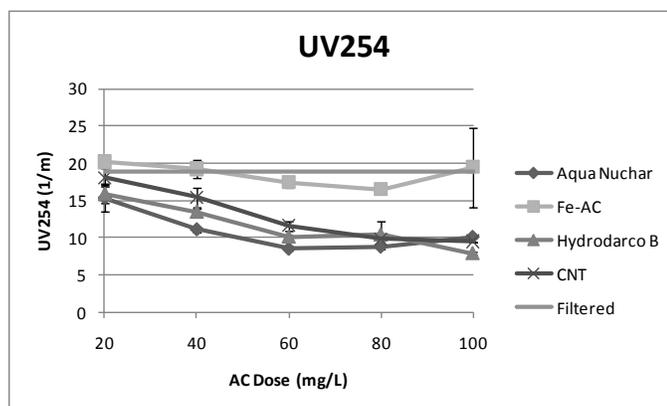


Figure 3-3 UV254 of Boonville, MO River water after 24 hr adsorption of NOM by several activated carbons

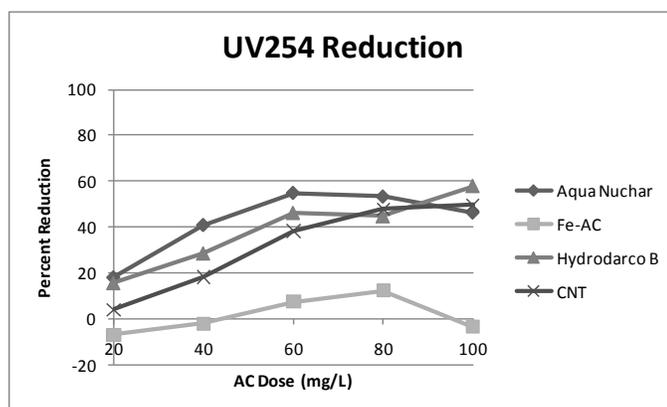


Figure 3-4 UV254 of Boonville, MO River water percent reduction by adsorption of NOM on several activated carbons

There was little correlation between AC dose and SUVA (Figure 3-5). This is likely a representation of poor HPI NOM removal as SUVA is a representation of more aromatic, HPO structures in NOM (Croue *et al.*, 1999; Liang and Singer, 2003).

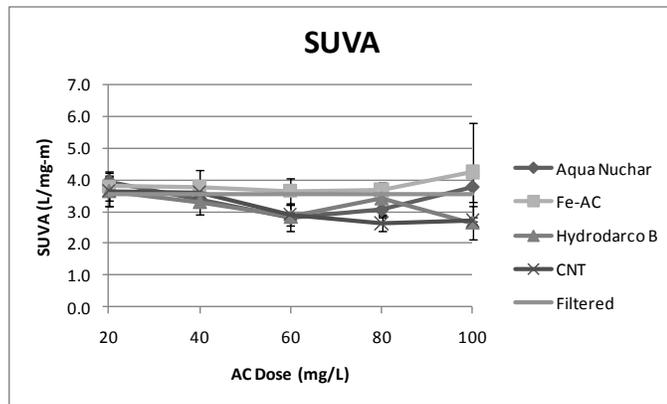


Figure 3-5 SUVA of Boonville, MO River water after 24 hr adsorption of NOM by several activated carbons

3.3.3 TTHM FP

EPA has set a maximum contaminant level of 80 $\mu\text{g/L}$ for TTHM. Filtered water TTHM FP was 240 $\mu\text{g/L}$. Reduction of TTHM FP to an acceptable level was achieved in only one case by Aqua Nuchar® at a dose of 80 mg/L. TTHM FP levels are shown in Figure 3-6 and percent reduction is shown in Figure 3-7. Although the EPA limit was only achieved in one case, TTHM FP was decreased by all ACs. Again, Fe-AC performed worse than other common carbons, attaining only a maximum of 31% reduction. Aqua Nuchar® again had greatest reductions, indicating that DOC and UV254 were indicators of TTHM FP.

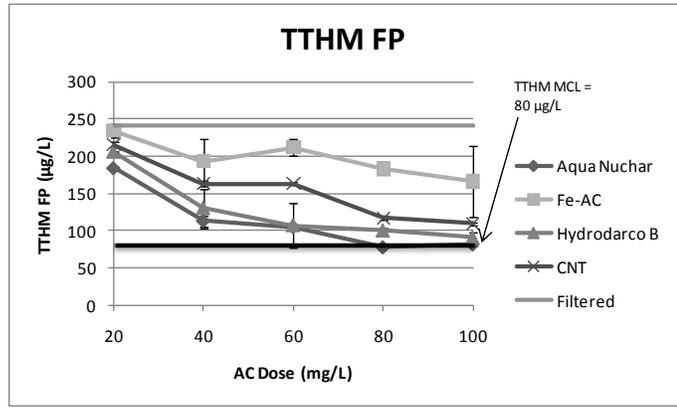


Figure 3-6 TTHM FP of chlorinated Boonville, MO River water after 24 hr adsorption of NOM by several activated carbons

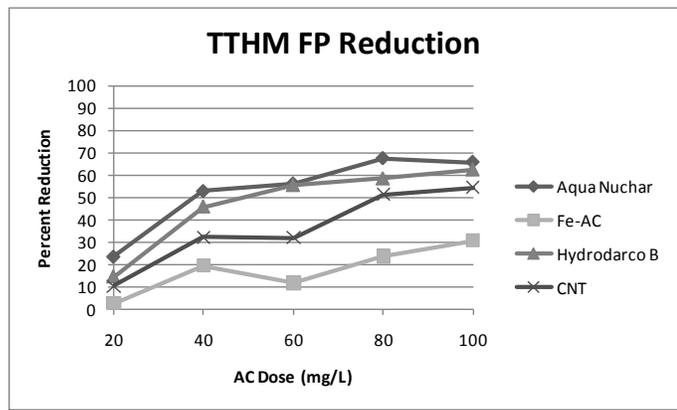


Figure 3-7 TTHM FP of chlorinated Boonville, MO River water percent reduction by adsorption of NOM on several activated carbons

As shown in Figure 3-8, percentage TTHM from brominated species (BDCM, CDBM, Bromoform) increased with increasing doses of AC. This is an indication of little or no adsorption of bromide with the AC used. Fe-AC and CNT had less pronounced increases in percentage of TTHM brominated, not because they reduced TTHM and brominated THM, but because they reduced neither to a great extent.

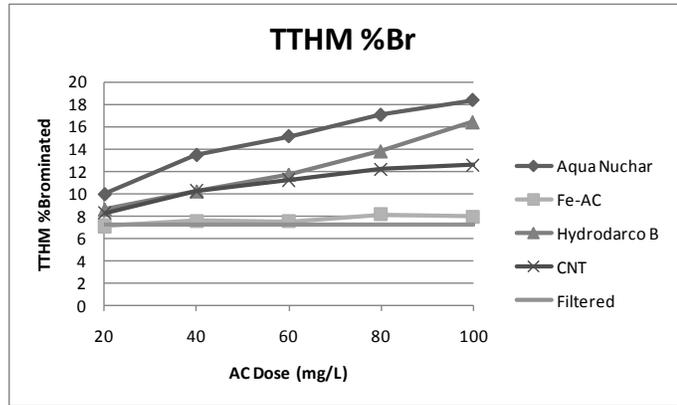


Figure 3-8 Percent TTHM from brominated species resulting from reactions with NOM in Boonville, MO River water after 24 adsorption on several activated carbons

3.3.4 HAA FP

EPA has set a regulatory limit on HAA5 at 60 µg/L. Filtered water contained HAA5 FP of 75 µg/L. Concentrations below the EPA maximum contaminant level were achieved by Aqua Nuchar®, Hydrodarco®, and CNT at AC doses of 60 mg/L and greater. Fe-AC treated water did not contain less than 62 µg/L HAA FP for any dosage. Lower doses of Fe-AC had HAA formations exceeding those of the filtered water average. Formation potential is shown in Figure 3-9 and Figure 3-10.

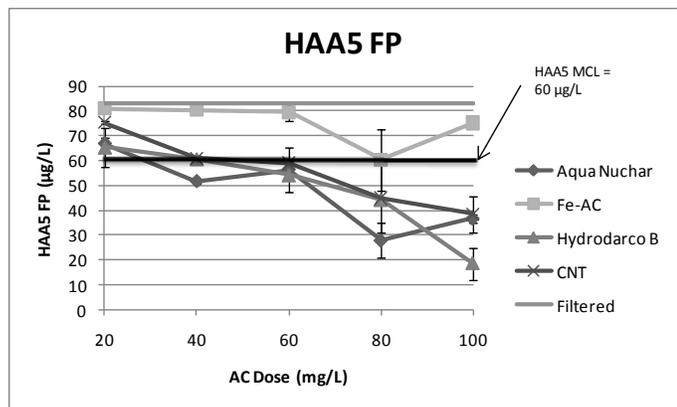


Figure 3-9 HAA FP of chlorinated Boonville, MO River water after 24 hr adsorption of NOM by several activated carbons

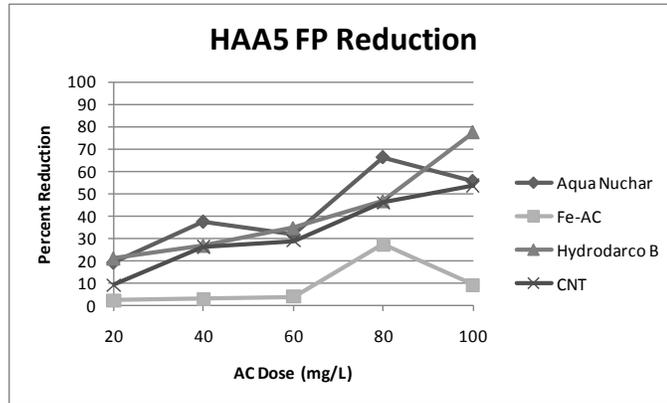


Figure 3-10 HAA5 FP of chlorinated Boonville, MO River water percent reduction by adsorption of NOM on several activated carbons

3.3.5 DBP Surrogate Parameters

3.3.5.1 DOC

Dissolved organic carbon represents the quantity of NOM contained in the water. However, not all NOM is reactive with chlorine. Figure 3-11 shows that TTHM formation could be predicted by DOC concentration with an $R^2=0.74$. HAA5 formation could not be predicted as accurately with DOC, having an $R^2=0.63$. For use as a surrogate, these correlations are likely not great enough.

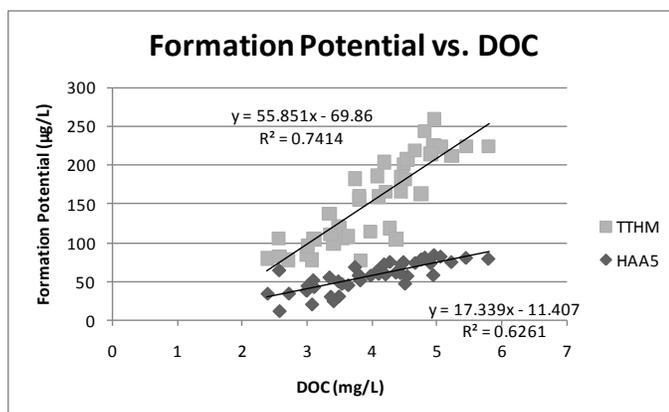


Figure 3-11 Formation potential vs. DOC of Boonville, MO River water after 24 hr adsorption of NOM on activated carbons

3.3.5.2 UV254

With the exception of Fe-AC samples, UV254 was a good indicator of TTHM FP. Results are shown in Figure 3-12. Due to the poor correlation directly resulting from Fe-AC inconsistencies, it has been removed from the data set used to generate Figure 3-13. Haloacetic acids were predicted poorly by UV254. UV254 is an indication of more HPO, aromatic molecules in water and therefore, waters with a highly reactive HPI NOM content will have poor correlation between UV254 and formation potential.

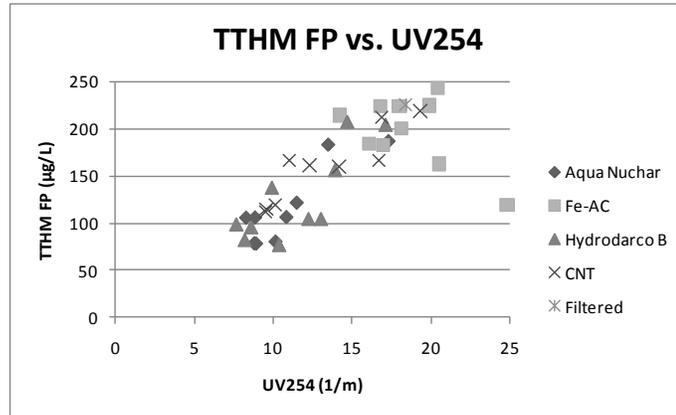


Figure 3-12 TTHM FP vs. UV254 of Boonville, MO River water after 24 hr adsorption on specified materials

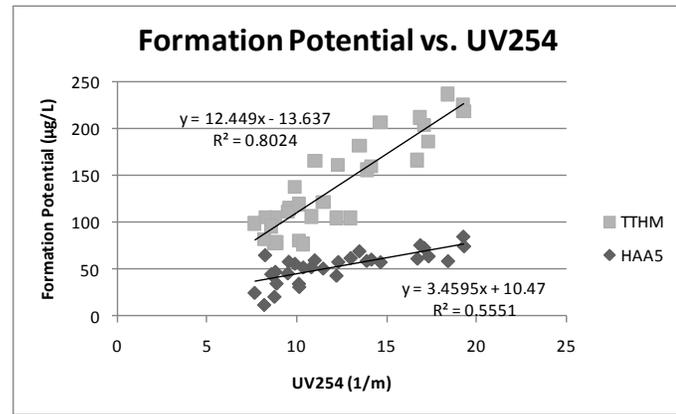


Figure 3-13 Formation potential vs. UV254 of Boonville, MO River water excluding Fe-AC data

3.3.5.3 SUVA

SUVA was a poor indicator of TTHM and HAA5 FP as shown in Figure 3-14. Removing Fe-AC from the data set did not make a great difference in the model although it was again the most poorly correlated. Again, as HPO NOM tends to absorb more ultraviolet light than HPI, UV254 and therefore SUVA is a representation of HPO content and will in turn tend to have poor correlations with formation if a large fraction of formation is derived from reactions with HPI content.

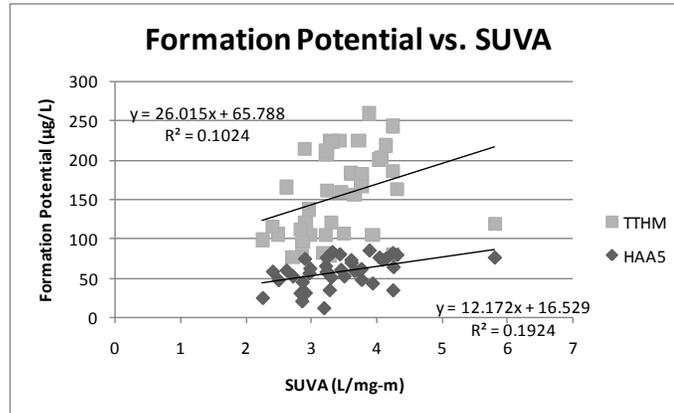


Figure 3-14 Formation potential vs. SUVA of Boonville, MO River water after 24 hr adsorption of NOM on activated carbons

3.3.5.4 Chlorine Demand

After chlorination, free chlorine was measured in order to assure 1 ± 0.4 mg/L free chlorine residual (Summers *et al.*, 1996). The difference between the amount of chlorine added and the final free chlorine before quenching is identified as chlorine demand (Eq. 2-2). Figure 3-15 shows that chlorine demand was closely related to TTHM FP. Chlorine demand was less accurate at predicting HAA5 FP. Although chlorine demand is closely related to formation, it is not likely that the correlation is great enough to be used as a surrogate on site.

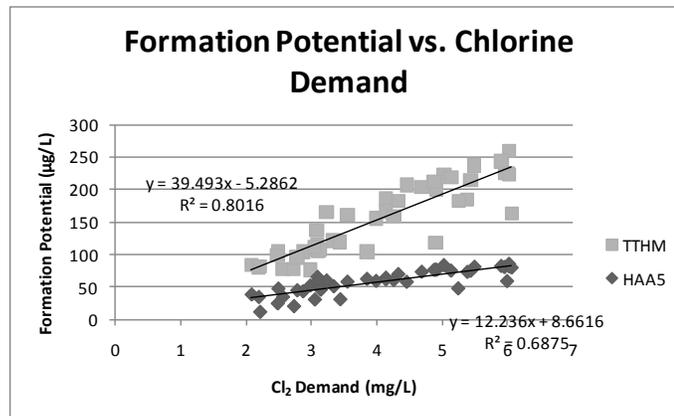


Figure 3-15 Formation potential vs. chlorine demand of Boonville, MO River water after 24 adsorption of NOM on activated carbons

3.4 CONCLUSIONS

Aqua Nuchar® removed the greatest amount of THM and HAA precursors, and was therefore used for further studies. Fe-AC removed the least DBP precursors possibly due to Fe blockage of meso and macro pores on the AC surface. Fe-AC and CNT were used to assess possible new materials for DBP FP removal. As removal by these materials was poor compared to common AC, they were not studied further.

Iodine adsorption number and surface area were indicators of DOC sorption and UV254 reduction. UV254 was the most accurate predictor of TTHM and HAA5 FP which confirms that aromatic moieties contribute greatly to DBP formation. Chlorine demand was also an indicator of TTHM and HAA5 FP. Chlorine demand and UV254 did not predict HAA5 FP as well as TTHM FP.

4 REMOVAL OF DPB FP IN A BENCH SCALE WATER TREATMENT FACILITY

4.1 INTRODUCTION

The study was conducted to determine if the previous 24 hr adsorption study was representative of adsorption that may occur in a treatment facility. Aqua Nuchar® as well as Hydrodarco® were selected as activated carbons with potential for NOM removal. In addition, given the hypothesis formed in section 3.4, that iodine adsorption number is related to NOM adsorption and therefore reduced DBP FP, Hawkins Sabre Series® AC was introduced to the sample set. With data supporting NOM sorption by phyllosilicates (Kaiser and Zech, 2000; Kahle *et al.*, 2004), greensand was tested for potential DBP FP reduction. Activated carbons have a greater specific surface area when compared with greensand and therefore greensand was used at an elevated dosage. MIEX® was included in this study as a comparison of NOM removal by adsorption and removal through ion exchange.

4.2 MATERIALS AND METHODS

4.2.1 Sampling

A grab sample was obtained August 25, 2010 from Boonville's pressurized raw Missouri River water inlet. The sample was stored at 3°C for a less than two weeks prior to treatment and analysis.

4.2.2 Treatment Materials

Hydrodarco® B (Norit Americas Inc., Marshall, TX) was obtained onsite from the City of Boonville, MO water treatment plant. At the time of sampling the City of Boonville used Hydrodarco® as a form of DBP reduction on a seasonal basis. Aqua Nuchar® was obtained from Meadwestvaco, Richmond, VA. MIEX® resin was acquired from Orica Watercare, Watkins, CO. Prior to treatment, resin was loaded with natural NOM and regenerated with brine solution. Hawkins Sabre Series® (CR325AA-10) was acquired onsite from the City of Marceline, MO water treatment facility. A summary of the materials' properties is given in Table 4-1.

Table 4-1 Properties of commercially available activated carbons and greensand used as treatment materials in Boonville, MO River water

Material	Particle Size	Surface Area (m ² /g)	Iodine Number (mg/g)
Hyrdodarco B	90% <45 µm		>500
Aqua Nuchar	90% <45 µm	1200-1600	>900
Hawkins Sabre Series®	90% <45 µm		>1000
Greensand	~0.5 mm		

4.2.3 Treatment

1 L of raw, unfiltered water was mixed in square 2 L containers with an appropriate quantity of treatment material using a gang stirrer. For samples being treated with activated carbon, 20 and 60 mg/L doses were used. MIEX® samples were dosed with 2 or 6 mL/L. Doses were again not chosen to represent Boonville's facility, but to investigate NOM removal at high doses of treatment materials. Contact with treatment materials was intended to model a treatment facility and therefore a 30 min rapid mix (100 rpm) followed by a 30 min sedimentation period (15 rpm) were used. Water was not coagulated. Water was then filtered to 0.45 µm in an attempt to model a theoretical treatment facility's process train (sedimentation, coagulation, activated carbon treatment, sedimentation, filtration, disinfection).

4.2.4 DOC Analysis

After filtration, non-purgeable organic carbon was analyzed using a Shimadzu Total Organic Carbon Analyzer (Shimadzu Corp., Atlanta, GA) with an ASI auto-sampler. Acidification was conducted using 2M hydrochloric acid obtained from Fisher Scientific, Fair Lawn, NJ.

4.2.5 UV254 Analysis

Filtered water was transferred to a 1 cm³ cuvette via pipette. Absorbance was measured at a wavelength of 254 nm 10 times using a Varian CARY50Conc UV-visible light spectrophotometer and averaged.

4.2.6 Chlorination

The filtered samples were chlorinated similarly to section 3.2.6 and in accordance with Summers et al. (1996) to contain 1 mg/L free chlorine after 24 hrs. Free chlorine was then quenched with NH_4Cl to prevent further DBP generation.

4.2.7 THM Analysis

A gas chromatograph (Varian, Model 3800) / mass spectrometer (GC/MS) (Varian, Saturn 3800) equipped with a Tekmar 3000 purge and trap concentrator was used for determination of THM concentrations. This process was similar to the Standard Method for the Examination of Water and Wastewater 6200 B and US EPA Method 524.

4.2.8 Calculations

Chlorine demand was calculated using Eq. 2-2. Percent reduction was calculated with respect to filtered only water and is represented in Eq. 3-1.

4.3 RESULTS AND DISCUSSION

Percent reductions are shown in Figure 4-1 and will be discussed in the following sections. MIEX® typically reduced DOC, UV254, SUVA, and TTHM FP the greatest with Hawkins Sabre Series® also performing well at elevated doses.

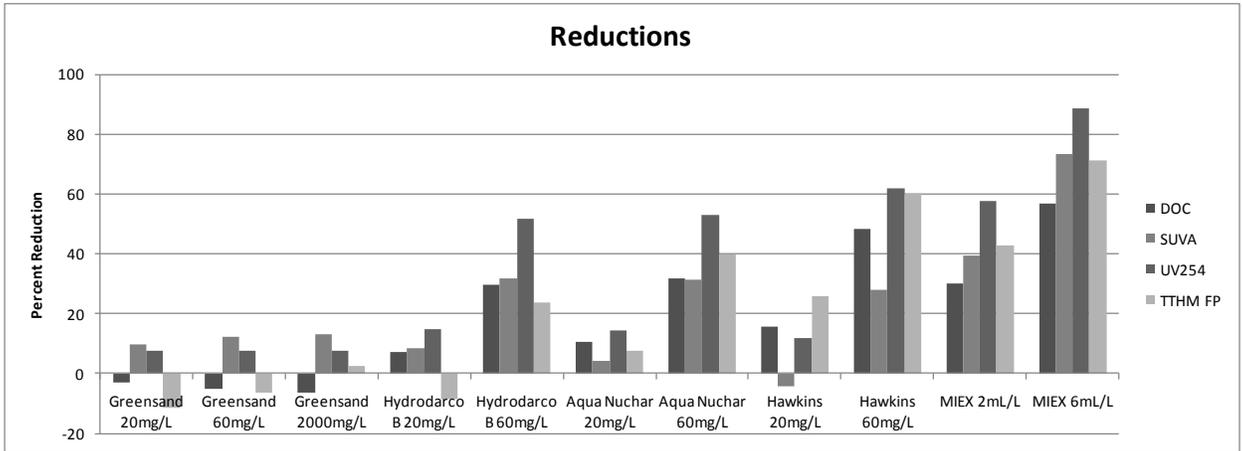


Figure 4-1 Boonville, MO River DOC, UV254, SUVA, and TTHM FP percent reductions after greensand, activated carbon, or MIEX® treatment

4.3.1 Characteristics of Filtered Water

Total trihalomethane formation potential of the water after filtration was still above the EPA regulatory limit of 80 µg/L. The water was again high in DOC, SUVA, and TTHM FP. This was expected due to the aforementioned temporal trends in DBP formation (Sec 2.2.4) and the sampling date.

Table 4-2 Filtered Boonville, MO River (Aug. 25, 2010) water characteristics

DOC (mg/L)	UV254 (1/m)	SUVA (L/mg*m)	TTHM FP (µg/L)	pH
4.83	15	3	232	8

4.3.2 DOC, UV254 and SUVA

A slight increase (3%-6%) in DOC was found when greensand was used to treat the water. Again, Aqua Nuchar® performed slightly better than Hydrodarco® for both doses used. However, Hawkins Sabre Series® outperformed both with a performance

increase over Aqua Nuchar® by 5% at a dose of 20 mg/L and 16% at a dose of 60 mg/L. MIEX® decreased DOC the greatest with reduction up to 57%. Dissolved organic carbon is shown in Figure 4-2 with percent reductions shown in Figure 4-1.

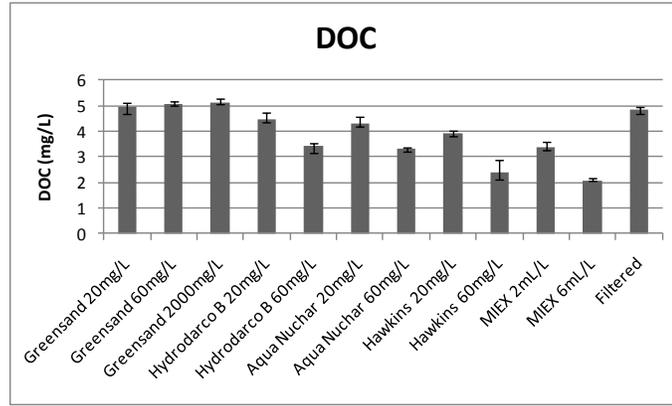


Figure 4-2 DOC of Boonville, MO River water after greensand, activated carbon, or MIEX® treatment

Despite an increase in DOC, greensand showed a slight decrease in UV254, confirming that phyllosilicates do have affinity for adsorption of NOM containing unsaturated bonds. However, little difference in UV254 reduction between doses of 20 mg/L and 2000 mg/L indicates that greensand may be extremely selective in its sorption. Hydrodarco®, Aqua Nuchar® and Hawkins were similar in performance with Hawkins reductions being only slightly greater. UV254 similarities in conjunction with DOC variations for Hawkins and Aqua Nuchar® AC indicate that some of the adsorbed DOC may have been nonaromatic carbon.

Hawkins AC performance increase agrees with Section 3.3.2 regarding iodine adsorption number and surface area as an indicator of UV254 and DOC reduction. MIEX® reduced SUVA the greatest (74%). Figure 4-3 shows UV254 results with percent reduction in Figure 4-1. Figure 4-4 shows SUVA results with percent reduction

again in Figure 4-1. The reduction in both SUVA and UV254 by activated carbons and MIEX® indicates the removal of highly aromatic, HPO NOM. However, UV254 and SUVA give little indication of HPI NOM content.

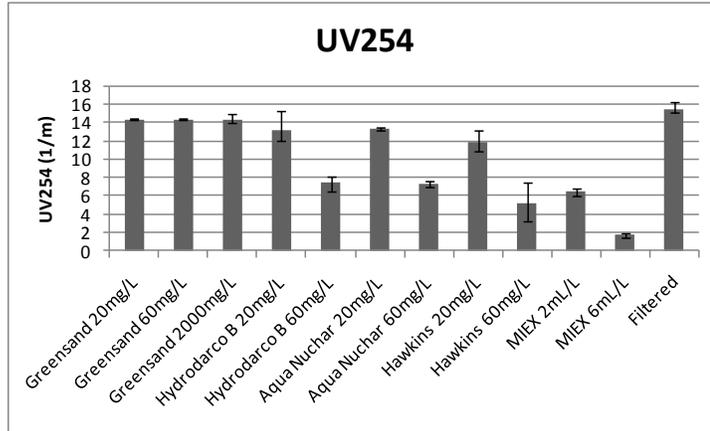


Figure 4-3 UV254 of Boonville, MO River water after greensand, activated carbon, or MIEX® treatment

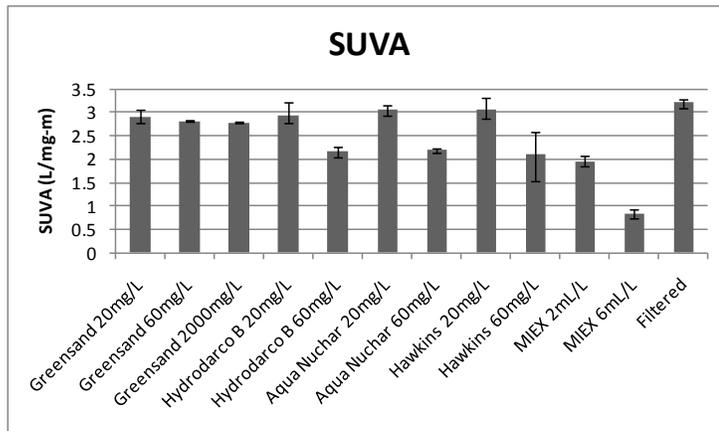


Figure 4-4 SUVA of Boonville, MO River water after greensand, activated carbon, or MIEX® treatment

4.3.3 TTHM FP

At 20 mg/L for both greensand and Hydrodarco® and at 60 mg/L for greensand, a slight increase in TTHM FP was found. Greensand showed little decrease in TTHM FP at a dose of 2000 mg/L. It was expected that greensand would not perform well at normal doses as it has low surface area and it was hypothesized that a considerable increase in dose would allow the material to adsorb greater quantities of NOM and possibly reduce TTHM FP to a greater extent. This was not the case. MIEX® reduced TTHM FP by 43% and 71% at doses of 2 and 6 mL/L. Formation potential results are shown in Figure 4-5 and percent reduction comparisons are shown in Figure 4-1.

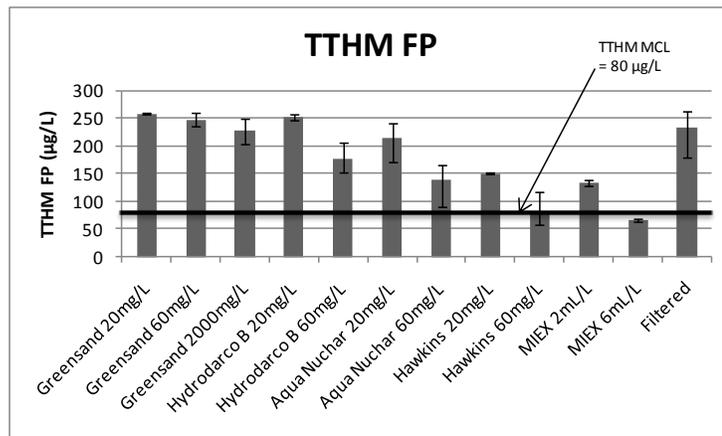


Figure 4-5 TTHM FP of chlorinated Boonville, MO River water after greensand, activated carbon, or MIEX® treatment

Regarding speciation, MIEX® had the highest removal of both chloroform and brominated THMs. Aqua Nuchar®, Hawkins AC, and MIEX® all tended to shift the speciation towards greater amounts of brominated THMs and removed larger quantities of chloroform precursors. The filtered water (control) only formed 47 µg/L of brominated THMs while MIEX® treated water reduced this to 38 and 27 µg/L at doses of 2 and 6 mL/L respectively. Hawkins AC also reduced brominated THMs by 27% at a

dose of 60 mg/L. The reduction of brominated THMs indicates bromide removal with MIEX® and agrees with literature (Singer and Bilyk, 2002; Boyer and Singer, 2005). Speciation is shown in Figure 4-6 and Figure 4-7.

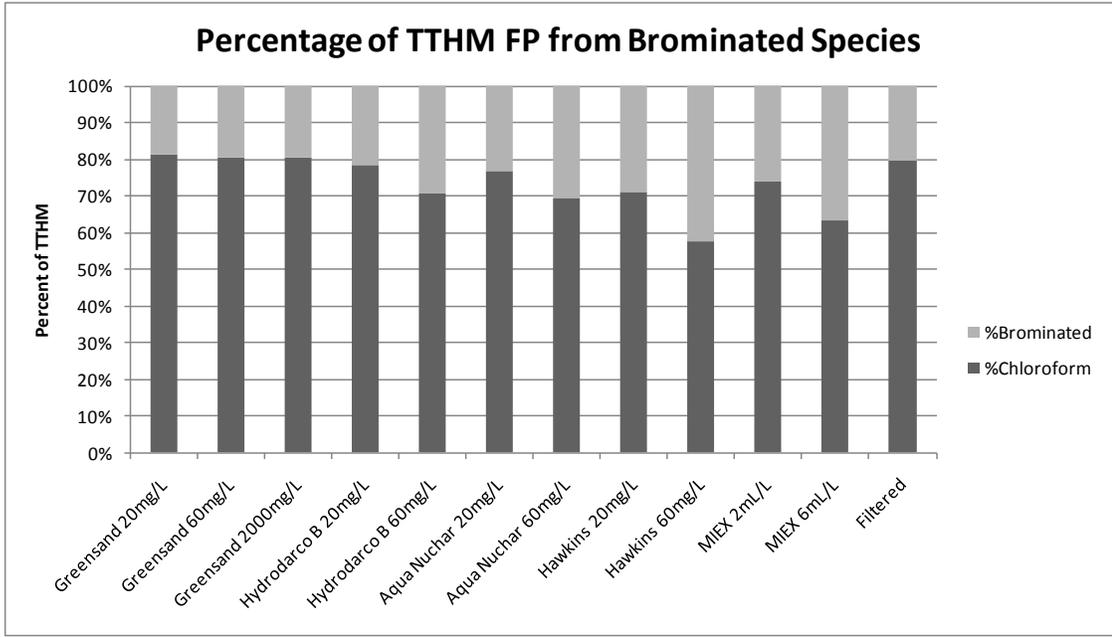


Figure 4-6 Percent of TTHM FP of Boonville, MO River water from chlorinated and brominated THM species after greensand, activated carbon, or MIEX® treatment

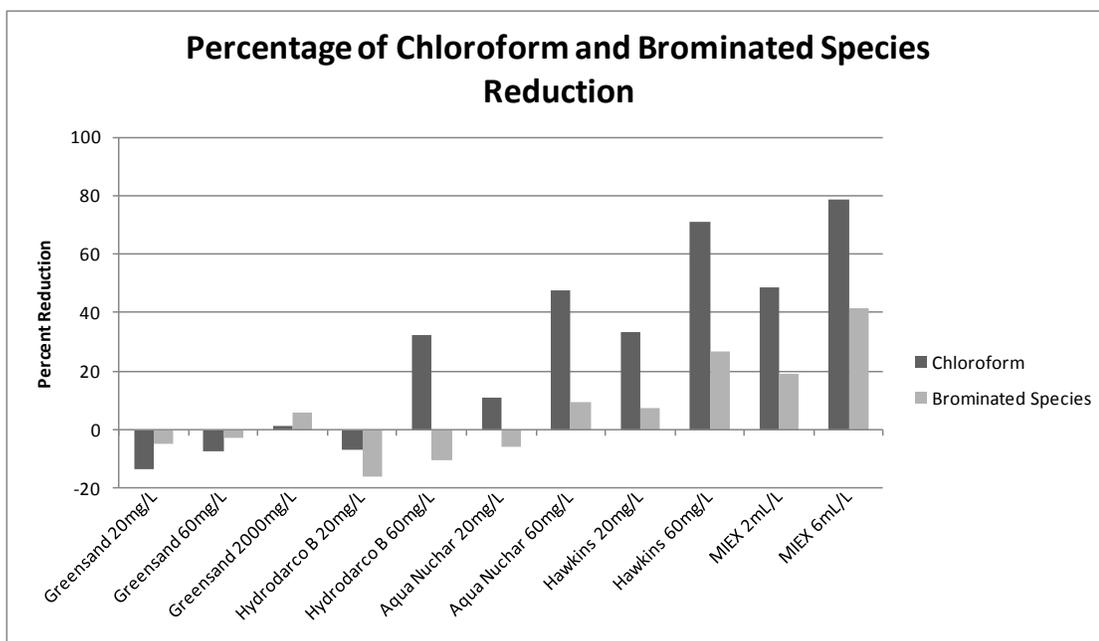


Figure 4-7 Percent reduction of chlorinated and brominated THM species resulting from reactions with Boonville, MO River NOM after treatment with greensand, activated carbon, or MIEX®

4.3.4 DBP Surrogate Parameters Post Treatment

4.3.4.1 DOC

Dissolved organic carbon reductions closely mirrored TTHM FP. Approximately 8% of DOC removal was non-THM producing for Hawkins AC and MIEX®. The relationship was not as clear for Aqua Nuchar® but it does appear that the majority of DOC removed was THM forming in nature. The association between Hydrodarco® and DOC reduction was unclear due to an increase in TTHM FP in the 20 mg/L dose. Correlation is shown in Figure 4-8. Slope of the linear fit was within 6% of results found in Section 3.3.5.1.

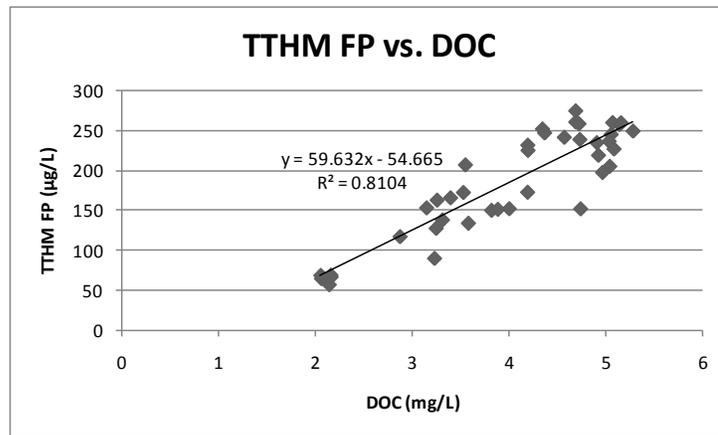


Figure 4-8 TTHM FP vs. DOC of Boonville, MO River water after greensand, activated carbon, or MIEX® treatment

4.3.4.2 UV254

Correlation between UV254 and TTHM FP reduction for all ACs studies was minimal. UV254 reduction was always higher than TTHM FP reduction but to different extents. This indicates that although MIEX®, Hydrodarco®, Hawkins Sabre Series®, and Aqua Nuchar® all reduced TTHM FP, the mechanism was through different NOM fraction removal. MIEX® removed more aromatic THM forming NOM than the activated carbons. Correlation is shown in Figure 4-9. Slope of the fit is within 7% of Section 3.3.5.2 and suggests a consistent formation of TTHM with regard to aromatic moieties from Boonville water and implies that UV254 may have potential as a TTHM surrogate.

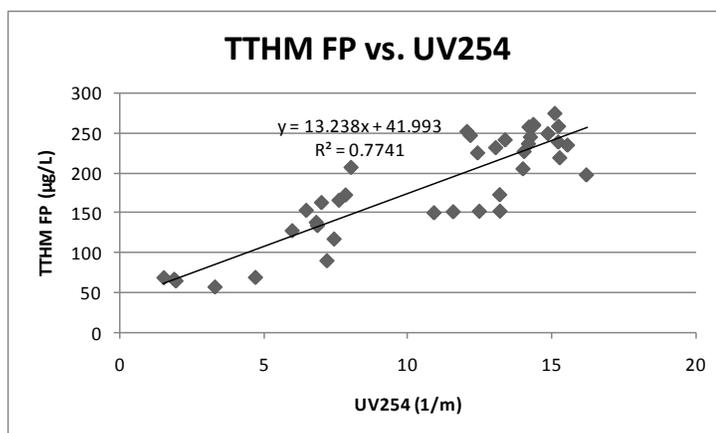


Figure 4-9 TTHM FP vs. UV254 of Boonville, MO River water after greensand, activated carbon or MIEX® treatment

MIEX® and Hawkins AC TTHM FP reductions were particularly well correlated with UV254 as shown in Figure 4-10. This indicates possible similarities in removal of UV254 absorbing DOC.

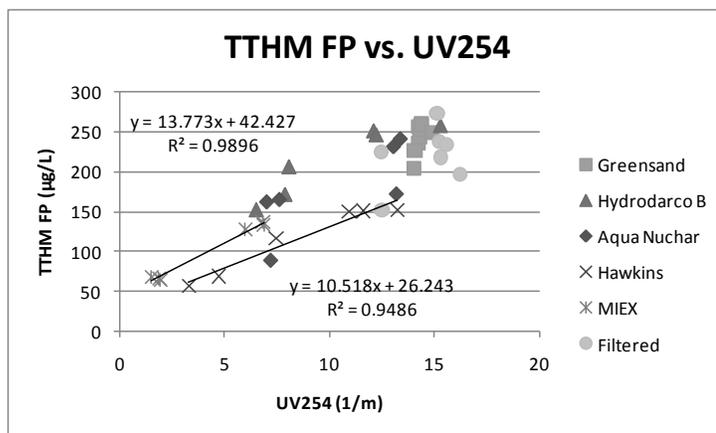


Figure 4-10 TTHM FP vs. UV254 of Boonville, MO River water for specific materials

4.3.4.3 SUVA

Specific UV254 reductions closely mirrored TTHM FP for MIEX® and Hawkins AC. For other materials, SUVA reduction was not well correlated with TTHM FP reduction. Results are shown in Figure 4-11. MIEX® and Hawkins AC relations are

shown in Figure 4-12. The correlation again shows the potential for similarities in MIEX® and Hawkins AC removal of highly aromatic molecules.

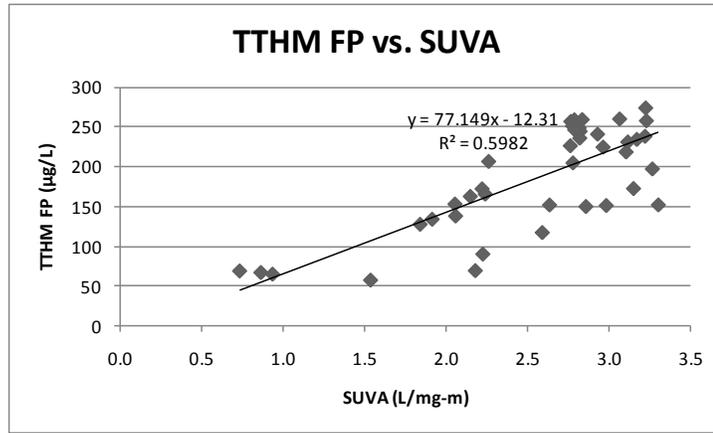


Figure 4-11 TTHM FP vs. SUVA of Boonville, MO river water after treatment with greensand, activated carbon or MIEX®

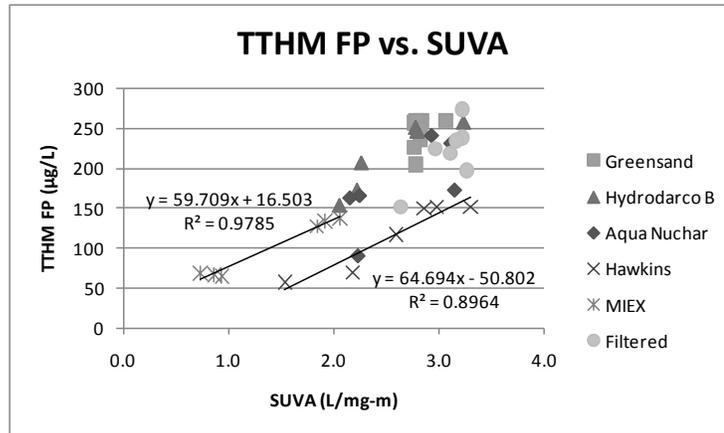


Figure 4-12 TTHM FP vs. SUVA of Boonville, MO River water for specific materials

4.3.4.4 Chlorine Demand

Total THM FP was less predictable with chlorine demand when compared to Section 3.3.5 ($R^2=0.801$). However, it is notable that the slope of the linear fit is within 3% of the previous study (Section 3.3.5= $39.49x$). Chlorine demand is shown in Figure

4-13. As correlation is inconsistent temporally, it is an unlikely candidate as a DBP surrogate.

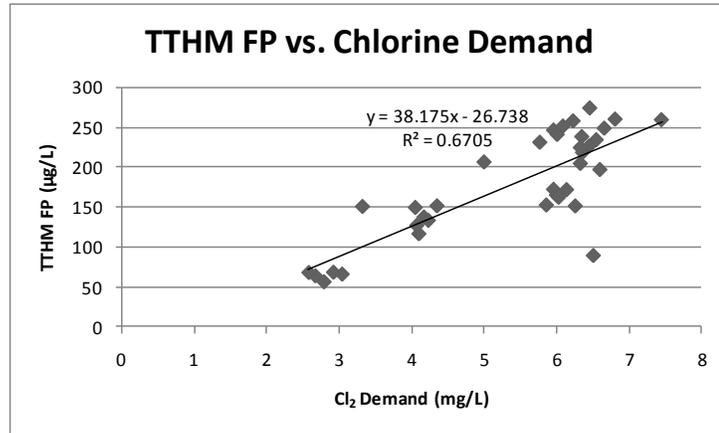


Figure 4-13 TTHM FP vs. chlorine demand of Boonville, MO River water after greensand, activated carbon, or MIEX® treatment

4.4 CONCLUSIONS

Greensand was an unlikely candidate for THM precursor removal. This was possibly due to reduced surface area and therefore reduced adsorption sites for NOM. Reduction of SUVA was not a good indicator for TTHM FP reduction for Aqua Nuchar® and Hydrodarco® but correlated well for Hawkins AC as well as MIEX®. Hawkins AC reduced SUVA more than it reduced TTHM FP while Aqua Nuchar® reduced TTHM FP more than it reduced SUVA. Activated carbons, although similar in structure and makeup, performed considerably different from one another and different from MIEX®, which reduced SUVA and TTHM FP equally. Reductions in brominated species were found, but, in general, they were reduced less than chloroform. This was again expected as bromide is difficult to remove from water.

Chlorine demand and UV254 had the greatest correlation with TTHM FP. Specific surface area and iodine adsorption number were confirmed to be good indicators of TTHM reduction potential.

5 NOM FRACTIONATION

5.1 INTRODUCTION

Natural organic matter is an extremely complex heterogeneous material made up of hydrophilic acids, humic substances, proteins, lipids, carboxylic acids, polysaccharides, amino acids, and hydrocarbons (Wei *et al.*, 2008). Given the diverse nature of NOM and therefore complicated removal processes, there is interest in fractionation and subsequent analysis of DBP precursors. Generally, more aromatic, more hydrophobic matter is removed through ion exchange and adsorption (Tipping, 1981; Gu *et al.*, 1994; Humbert *et al.*, 2005; Hyung and Kim, 2008; Wei *et al.*, 2008). In order to provide more efficient treatment, it is important to know which fraction of NOM creates DBPs.

Hawkins AC was selected as an activated carbon as it had the greatest potential for DBP FP reduction based on a Section 4.3.3. MIEX® was selected as an ion exchange resin due to its previously demonstrated capacity for brominated species reduction and affinity for NOM sorption.

5.2 MATERIALS AND METHODS

5.2.1 Sampling

Raw water was grab sampled from Boonville, MO water treatment facility's pressurized inlet on October 22, 2010. Water was transferred immediately to a refrigerator at the University of Missouri and stored at 3°C. All glassware used was detergent cleaned, DI rinsed, chlorinated for 24 hrs, DI rinsed again, and air dried at 300°C before use.

5.2.2 Treatment Materials

Hawkins Sabre Series® (CR325AA-10) AC was obtained onsite from the City of Marceline, MO water treatment facility. MIEX® was obtained from Orica Watercare, Watkins, CO. MIEX® resin was loaded with NOM and regenerated with brine before use. Hawkins AC was used as a virgin material.

5.2.3 Treatment

Within 2 weeks of sampling, 1 L of raw, unfiltered water was mixed in square 2 L containers with an appropriate quantity of treatment material using a gang stirrer. An attempt was made (based on previous initial results) to match DOC removal from MIEX® and Hawkins AC so THM/HAA species removal could be directly compared. The appropriate doses were selected to be 5 mL/L and 60mg/L for settled MIEX® resin and Hawkins AC, respectively.

Treatment was intended to model a treatment facility and therefore a 30 min rapid mix (100 rpm) followed by a 30 min sedimentation period (15 rpm) was used. Water was then filtered to 0.45 μm , again in an attempt to model a treatment facility filtration system.

5.2.4 XAD Fractionation

Amberlite XAD4 and Supelite DAX8 resins were obtained from Fisher Scientific, Fair Lawn, NJ. Columns were prepared with virgin resin. Resin was rinsed in 0.1M NaOH for 24 hrs 5 successive times with fines being decanted daily. Dissolved organic carbon of the resins fell from above 100 mg/L to ~10 mg/L. Resin was then washed in methanol 3 times for 24 hrs and stored in methanol until used. The resins were rinsed 3 times with DI water using a decantation method in a beaker before being packed into respective columns as a methanol/DI slurry. In accordance with the hydrophilic/hydrophobic breakthrough described in Leenheer (1981), a 15ml column of resin was used. Care was taken not to expose the resins to the air during packing to avoid channeling in the columns. The top and bottom of the columns were packed with glass fiber to avoid movement and resuspension of the resin. After the columns were packed, they were rinsed of methanol with DI water until DOC was below 2 mg/L. Columns were allowed to sit overnight, saturated with DI water. Directly before sample application, columns were rinsed successively with ~125 ml of 0.1M NaOH followed by ~125 ml 0.1M H₂SO₄ to remove material that may have adsorbed while packing and rinsing the columns. Also, DOC was checked and confirmed to be less than 0.2 mg/L during final NaOH and H₂SO₄ rinses to ensure the columns were not leaching foreign organics.

After acid/base rinsing, the columns were loaded with filtered or treated and filtered water that had been adjusted to pH 2 with 2M H₂SO₄. All samples were fractionated in triplicate. Water was allowed to gravity flow at a rate of 6-15 bed volumes per hour first through the column packed with DAX8 to adsorb strongly HPO NOM and then through the column packed with XAD4 to adsorb weakly HPO NOM. The strongly HPO fraction will be referred to henceforth as simply the HPO fraction while the weakly HPO will be referred to as transphilic (TPI). The hydrophilic (HPI) NOM fraction passes the columns. Both HPO and TPI were back flush eluted individually at 5 bed volumes per hour with approximately 10 bed volumes of 0.1M NaOH. The eluate from the backflush was collected and diluted with Millipore water, then adjusted to natural pH with 2M and 0.1M H₂SO₄. The HPI fraction was first analyzed for DOC before being adjusted to natural pH.

5.2.5 DOC Analysis

Immediately after fractionation, non-purgeable organic carbon was analyzed using a Shimadzu Total Organic Carbon Analyzer (Shimadzu Corp., Atlanta, GA) with an ASI auto-sampler. Acidification was required only if the sample was from the HPO or TPI fractions and was conducted using 2M hydrochloric acid obtained from Fisher Scientific, Fair Lawn, NJ.

In an effort to exceed the instrument's lowest level of detection, both HPO and TPI samples were analyzed at double concentration meaning that they were only diluted back to half original sample volume. Results were then divided by two. As HPI samples require no dilution due to the procedure, it was required that these be analyzed at normal concentrations. In general, concentrations of all analytes are to be compared with the

same fraction of other samples and not across fractions. In other words, HPO and TPI concentrations are to be compared only with another sample's HPO or TPI concentration, as the analysis methods are consistent, but not with HPI concentrations.

In previous backwash processes, it was important to use NaOH that had been exposed to the air as little as possible in all the required steps if the sample was to be analyzed for DOC due to the hygroscopic properties of NaOH and dissatisfactory purging of inorganic carbon by the instrument.

5.2.6 UV254 Analysis

Fractionated water was transferred to a 1 cm³ cuvette via pipette. Absorbance was measured at a wavelength of 254 nm 10 times using a Varian CARY50Conc UV-visible light spectrophotometer and averaged.

5.2.7 Chlorination

Chlorination was completed in accordance with Summers et. al (1996). A sodium hypochlorite dosing solution (about 2,000 mg/L) was made from 13% active chlorine (sodium hypochlorite) stock solution and buffered at pH 8 with 0.01M KH₂PO₄.

An appropriate amount of sodium hypochlorite dosing solution to generate 1 ±0.4 mg/L free chlorine was added and the bottle was capped and inverted ten times. The reactions were performed in headspace free amber colored glass bottles during a 24 hr period in the absence of light. Chlorine was quenched with 4.4 mg NH₄Cl in DI water.

5.2.8 THM Analysis

A gas chromatograph (Varian, Model 3800) / mass spectrometer (GC/MS) (Varian, Saturn 3800) equipped with a Tekmar 3000 purge and trap concentrator was used for determination of THM concentrations. This process was similar to the Standard Method for the Examination of Water and Wastewater 6200 B and US EPA Method 524.

5.2.9 HAA Analysis

For determination of HAA concentration, a method involving liquid/liquid extraction and derivatization similar to Standard Method for Examination of Water and Wastewater 6521 and US EPA Method 552.2 was used. At an acidic pH, methyl tertiary-butyl ether (MTBE) was used to extract non-dissociated acidic compounds. Sodium sulfate was added to increase extraction efficiency as a salting agent. A 10% v/v solution of sulfuric acid with methanol was added to produce methyl ester derivatives that could be separated chromatographically (Varian, Model 3800).

5.2.10 Calculations

Chlorine demand was calculated using Eq. 2-2. Percent reduction was calculated with respect to filtered only water and is represented in Eq. 3-1.

5.3 RESULTS AND DISCUSSION

5.3.1 Dissolved Organic Carbon

To ensure full recovery of organics, DOC was compared before and after fractionation. Recovery is shown in Table 5-1.

Table 5-1 Boonville, MO River water DOC recoveries from XAD4 and DAX8 resins

	DOC (mg/L)	% Recovery
Hawkins Sabre Series	1.4	133
HPO	0.6	40
TPI	0.5	32
HPI	0.8	60
MIEX	1.4	124
HPO	0.6	45
TPI	0.4	28
HPI	0.7	51
Filtered	3.0	120
HPO	1.4	46
TPI	0.9	29
HPI	1.3	45
Raw	3.4	

Recovery was higher than anticipated, at times in excess of 130%, considering recovery has generally been between 80% and 97% (Leenheer, 1981; Thurman and Malcolm, 1981). This is likely due to the aforementioned poor purging of inorganic (CO₂) carbon. After acidification, the sample was purged with pressurized air, containing CO₂ and therefore the sample likely contained ambient CO₂ concentrations. It was found that even with calibration curves completed with this method, it was not possible to attain DOC concentrations below 0.18 mg/L.

Dissolved organic carbon results agree with previous research and highlight the considerable percentage of HPI and TPI NOM that has been often disregarded as a DBP precursor (Bolto *et al.*, 2002; Wei *et al.*, 2009; Zhang *et al.*, 2009). Of the 3.6 mg/L DOC recovered, approximately 2.2 mg/L (>61%) was contained in the TPI and HPI fractions.

Unfractionated organic carbon reduction was similar for both MIEX® and Hawkins AC. This is important so that other analytes can be compared directly. Hawkins AC DOC reduction was 57.1% while MIEX® was 57.8% as can be seen in Figure 5-1.

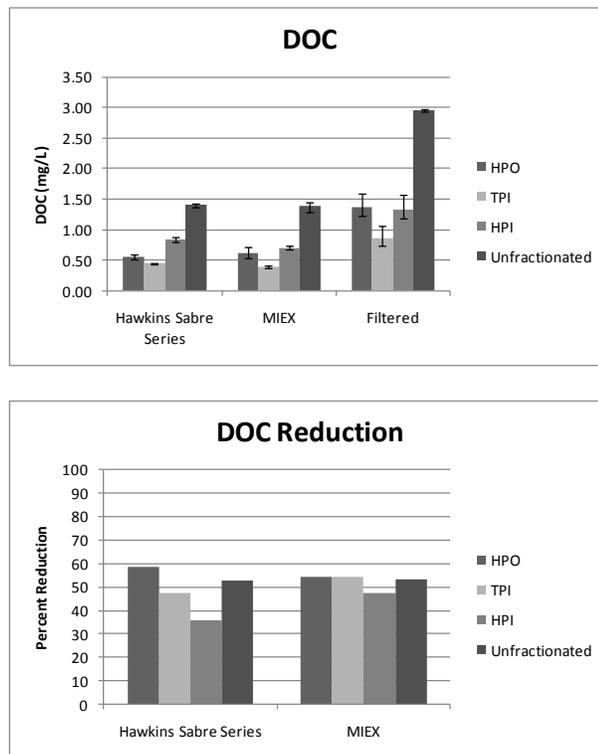


Figure 5-1 Fractionated DOC of Boonville, MO River water after treatment with activated carbon or MIEX®

Also of note, at these doses, Hawkins AC removed similar quantities of HPO material as MIEX®, 59% and 54%, respectively, while MIEX® removed more HPI and

TPI material than AC. This is in support of previous literature that concludes that AC, primarily kinetically governed by adsorption, removes less HPI material, or material that is inherently attracted to polar water molecules (Wei *et al.*, 2009). MIEX® removed all fractions similarly.

5.3.2 TTHM and HAA FP

Figure 5-2 shows DBP formations. MIEX® and Hawkins AC have similar reductions in formation potential in the HPO fraction indicating similar removal of HPO precursors. The greatest difference between treatment efficacies was a 29% difference in reduction of TTHM FP in the HPI fraction (Hawkins AC, 21%; MIEX®, 50%) shown in Figure 5-3. MIEX® has been shown previously to reduce HPI DOC (Boyer and Singer, 2005) but it had not been previously shown that this DOC reduction directly translates to a reduction in TTHM formed from the HPI fraction.

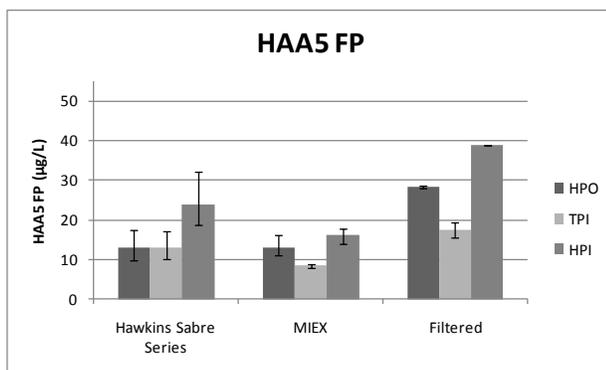
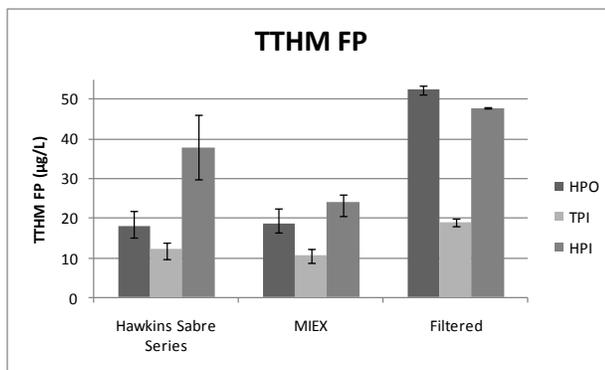


Figure 5-2 Disinfection by-product formation potentials resulting from reactions with fractionated NOM in chlorinated Boonville, MO River water after treatment with activated carbon or MIEX®

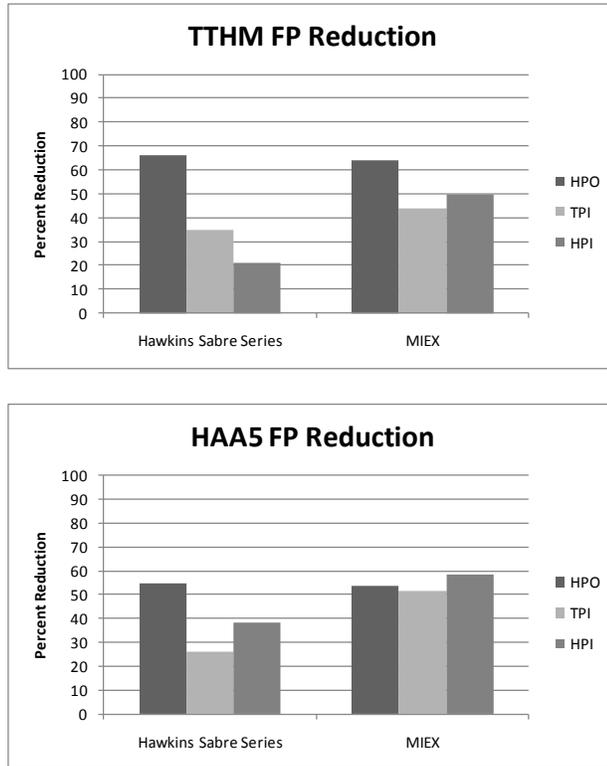


Figure 5-3 Disinfection by-product formation potential reductions resulting from reduced reactions with fractionated NOM in chlorinated Boonville, MO River water

Total THM FP was 68.0 and 53.5 $\mu\text{g/L}$ after Hawkins AC and MIEX® treatments, respectively. Of this 14.5 $\mu\text{g/L}$ difference, 11% (1.7 $\mu\text{g/L}$) was derived from THM produced from reactions with TPI material and 89% (13.7 $\mu\text{g/L}$) from HPI. Less than 1% was from differences in reductions of THM resulting from reactions with HPO NOM. It was expected that MIEX®'s high reduction of DBPs in literature was due to its greater NOM reduction at low doses. When NOM reduction was normalized to AC, it was expected that MIEX® would remove similar quantities of precursors and therefore reduce DBP FP similarly. Instead it was found that while MIEX® removes the same quantity of HPO NOM and only a slightly greater amount of HPI and TPI NOM, it reduced the formation potentials of these fractions to a greater extent.

Reductions in HAA5 FP from MIEX® were also pronounced. Formation from the TPI and HPI fractions was reduced 26% and 20% greater, respectively, after MIEX® treatment than with Hawkins AC. MIEX® showed little preference for hydrophobicity of HAA5 precursors while Hawkins AC again preferred HPO precursors.

Total HAA5 FP was 49.6 and 37.7 µg/L after Hawkins AC and MIEX ® treatments respectively. Of this 11.9 µg/L difference, 37.5% (4.5 µg/L) was provided by the difference in reactions with TPI material and 64% (7.7 µg/L) by HPI. Haloacetic acid forming reactions with HPO NOM increased with MIEX® although not to a great enough extent to warrant discussion other than to clarify the aforementioned greater than 100% reductions. With similar reductions in total DOC, it was again expected that reductions in HAA5 FP would be similar for treatment materials. This was incorrect as MIEX® targeted HAA5 forming organics while Hawkins AC appeared to partially adsorb nonreactive NOM.

Much of the unexpected reductions in formation potential with little reduction in corresponding NOM are explained by poor correlation between HPI/TPI DOC and formation potential as shown in Figure 5-4. This was particularly evident in THM forming HPI and TPI material. Data were used from all waters; MIEX® treated, Hawkins AC treated, and filtered only.

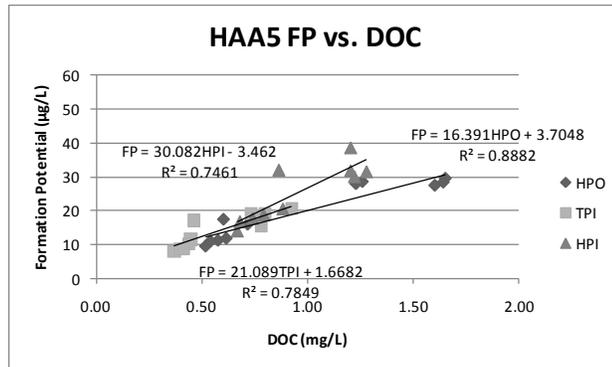
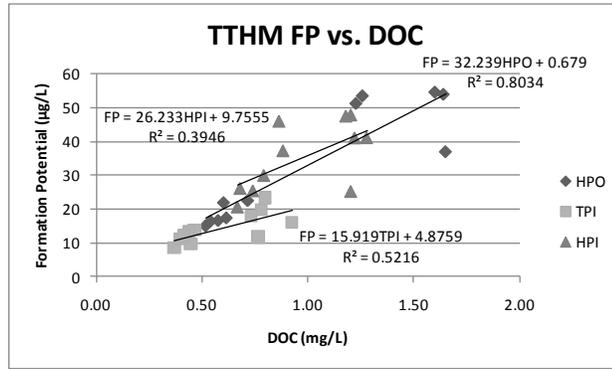


Figure 5-4 Formation potential resulting from NOM fractions vs. DOC in fractions of Boonville, MO River water

Figure 5-5 shows brominated species from reactions with specific NOM fractions. As expected, the HPI fraction has the greatest quantity of brominated THM. Due to the affinity of polar water molecules for ionic species such as bromide, adsorption by nonionic resins is low and therefore, bromide passes the columns almost entirely.

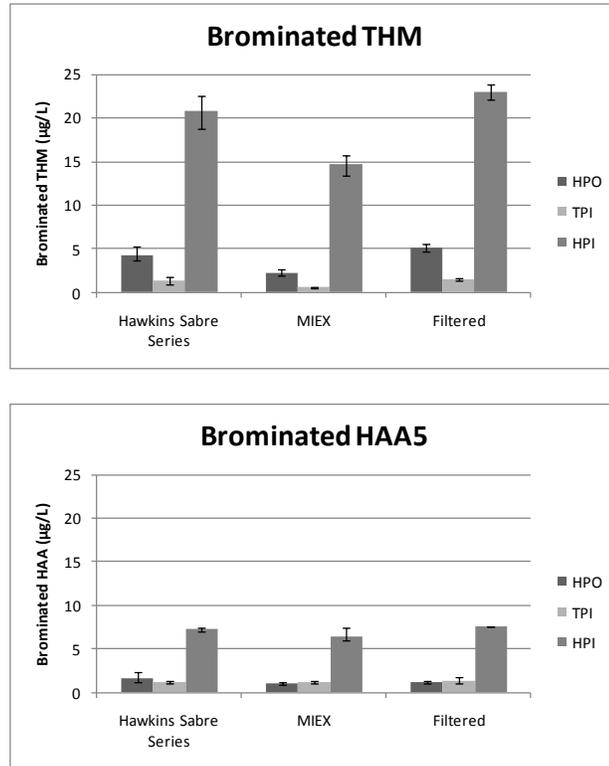


Figure 5-5 Brominated DBPs resulting from reactions with NOM fractions in chlorinated Boonville, MO River water

MIEX® also appeared to remove a portion of brominated THM precursors and Hawkins AC removed little or no bromide based on formation of brominated THMs. Literature cited has generally been concerned with removal of bromide (Singer and Bilyk, 2002; Humbert *et al.*, 2005) with little data regarding brominated DBP FP and therefore comparisons are difficult to make. However, considering Humbert *et al.* (2005) found 45% reduction of bromide at a decreased MIEX® dose (4 mL/L), reduction of brominated DBPs was less than anticipated.

5.3.3 UV254 and SUVA

MIEX® and Hawkins AC removed approximately 76% of HPO UV254 absorbing NOM. As they also removed similar amounts of HPO DOC, this is a good indication of a HPO DOC and UV254 correlation that was expected given the more aromatic nature of HPO NOM. MIEX® and Hawkins AC reduced the HPI fraction's UV absorbance similarly (~45%). MIEX® reduced the TPI fraction absorbance 27% greater than Hawkins AC. UV254 and reductions can be seen in Figure 5-6.

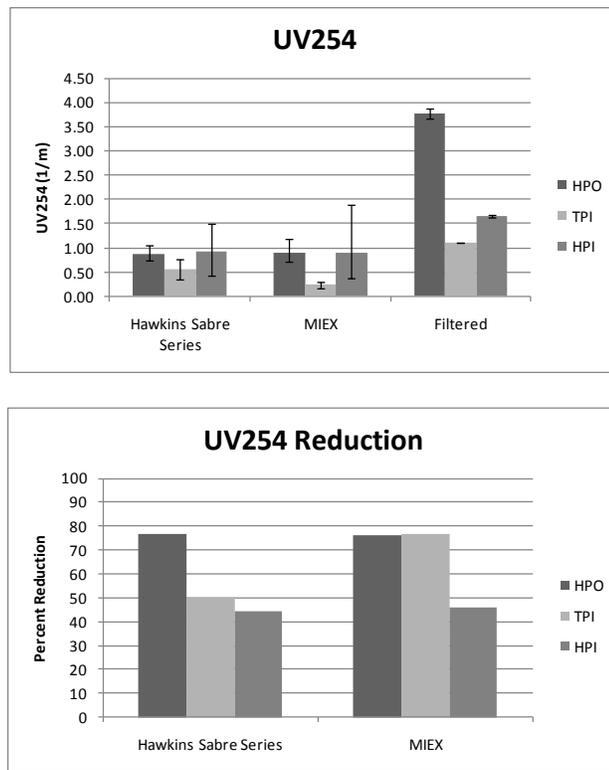


Figure 5-6 UV254 absorbance in fractionated water after activated carbon or MIEX® treatment

Again, correlation between formation potential and UV254 of the HPI fraction was low as shown in Figure 5-7. This is consistent with previous literature cited (Bolto *et al.*, 2002; Wei *et al.*, 2009; Zhang *et al.*, 2009) and generates uncertainty in the

commonly used approach of UV254 as a surrogate for DBP FP by many treatment facility operators. This is particularly the case in waters with high HPI NOM content or where sampling for UV254 is after MIEX® or AC treatment. Data used are again from all waters; MIEX® treated, Hawkins AC treated, and filtered only.

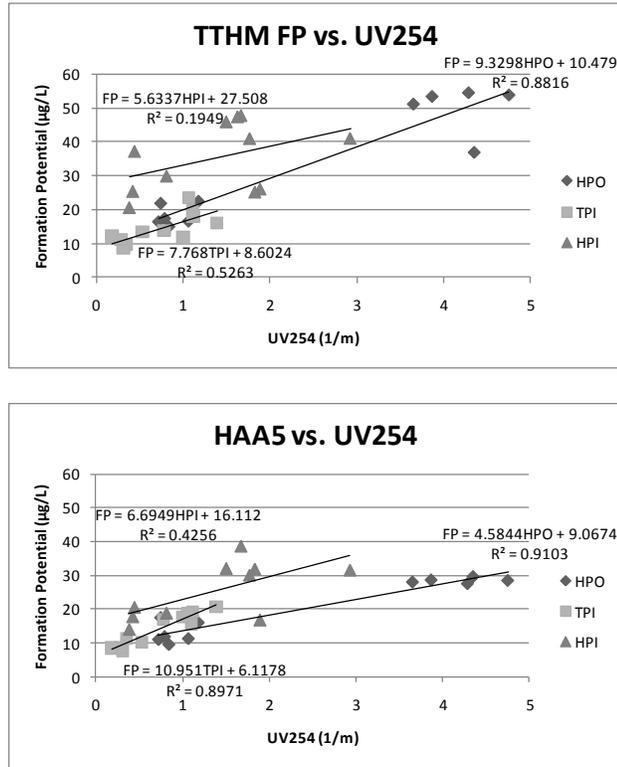


Figure 5-7 Formation potential derived from reactions with NOM fractions vs. UV254 in Boonville, MO River water

Specific UV absorbance compounds error from both DOC and UV254 measurements and therefore had greater percent error. In all cases, the HPO fraction had the highest SUVA, indicating a highly aromatic structure of HPO DOC. MIEX® removed a portion of SUVA from the TPI fraction. Results can be seen in Figure 5-8.

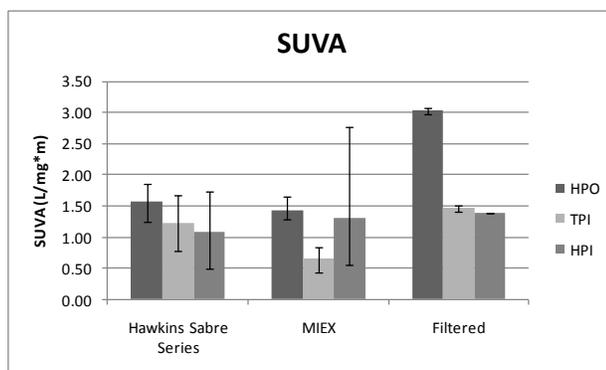


Figure 5-8 SUVA of Boonville, MO River water by NOM fraction after activated carbon and MIEX® treatment

5.4 CONCLUSIONS

When bulk DOC reductions were the same, Hawkins AC and MIEX® performed differently as DBP treatments. MIEX® and Hawkins AC reduced DOC, UV254, SUVA, TTHM FP and HAA5 FP in the HPO fraction similarly. This was expected as HPO material is inherently easily adsorbed onto AC. MIEX® reduced the DOC in the HPI fraction slightly greater than Hawkins AC, but reduced TTHM FP and HAA5 FP to a greater extent. This demonstrates the preferential affinity of MIEX® not only for HPI material but specifically for DBP forming HPI material. Much of the resin's superior DBP FP reduction over Hawkins AC was due to its greater removal of HPI and TPI precursors, not bulk NOM.

Brominated DBPs were found for the most part in the HPI fraction. This was expected due to the difficulty of removing a bromide ion from highly polar water molecules. MIEX® reduced brominated DBP formations greater than Hawkins AC but to a lesser extent than anticipated.

6 RECOMMENDATIONS AND OPPORTUNITIES FOR FUTURE RESEARCH

All studies were conducted without regard for coagulation processes that are used in Boonville and around the world. All results and conclusions should be confirmed at bench scale with the aid of coagulation/flocculation before significant changes in a treatment process are planned.

A change in the AC used for treatment is generally not considered significant and therefore it is recommended that Boonville, MO water treatment facility discontinue use of Hydrodarco® and begin use of Hawkins Sabre Series®. Although carbon doses were not selected with regard to Boonville, MO, Hawkins AC reduced DBP FP to a greater extent than the currently used Hydrodarco® at all doses and will therefore likely reduce DBP FP at Boonville. This is also one of the simplest means of confirming that results translate to a full scale system with coagulation.

Bromide reduction should be investigated as some brominated species reduction could be found from both Hawkins AC and MIEX®. These studies should be conducted at Boonville during a period when brominated DBP species formation is above 90 µg/L or conducted at a different site altogether. Also, brominated HAA formation should be investigated more thoroughly.

Although SUVA has been shown to be a good indicator of DBP FP in past studies, it is not accurate in these studies. This is likely due to the incorporation of AC and MIEX® treated samples (HPI and TPI DOC reduction without UV254 reduction) in the correlation studies. Therefore, SUVA should not be used as an indicator of change in

DBP FP before and after treatment but only for an initial analysis of formation potential of raw water if at all.

In addition, SUVA is thought to be a measure of reactivity of DOC. This assumes that most of the DOC that generates DBPs is aromatic and HPO in nature. The lack of good correlation can be explained at least partially by the great contribution of TPI and HPI DOC to DBP FP.

Furthermore, as UV254 and SUVA are often used as predictors of DBP FP, it should be noted that this is highly dependent on treatment process and seasonality. As DOC diminishes in the fall and winter, UV254 becomes extremely low as error in SUVA measurement becomes large. However, this is generally not a concern for Boonville and several other treatment facilities as they are in compliance by a considerable amount for these seasons.

Of great importance regarding UV254 is the method of treatment used by the facility. Accuracy as a predictor of DBP FP is reduced for similar reasons as SUVA in that UV254 absorption is a measure of aromatic, unsaturated bonds. The compounds containing these bonds are largely HPO in nature and therefore the correlation between UV254 and DBP FP is weak when HPI and TPI fractions of DOC are large, specifically after treatment with an AC.

Finally, iodine adsorption number is somewhat indicative of DOC adsorption and DBP FP reduction. A study with several ACs should be conducted and the usefulness of this parameter assessed using several different source waters containing many types of NOM.

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