EVALUATION OF ENHANCED COAGULATION FOR THE REMOVAL OF DISSOLVED ORGANIC NITROGEN AND THE CONTROL OF NITROGENOUS DISINFECTION BYPRODUCT FORMATION

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ABSTRACT

RYAN B. GUSTAFSON: Evaluation of Enhanced Coagulation for the Removal of Dissolved Organic Nitrogen and the Control of Nitrogenous Disinfection Byproduct Formation
(Under the direction of Dr. Philip C. Singer)

Enhanced coagulation is widely acknowledged as the best available conventional technology for removal of total and dissolved organic carbon (TOC/DOC) and control of regulated trihalomethane (THM4) and haloacetic acid (HAA5) disinfection byproducts (DBPs). Recent DBP toxicity research has indicated that many nitrogen-containing DBPs (N-DBPs) are more cytotoxic and genotoxic than THM4 and HAA5. The objectives of this study were to evaluate the capacity of enhanced coagulation to remove dissolved organic nitrogen (DON) and to reduce formation of dichloroacetonitrile (DCAN) and dichloroacetamide (DCAM), representative species of two important N-DBP classes. Thirteen raw drinking waters from across the U.S., encompassing the range of TOC and alkalinities within the enhanced coagulation matrix, were investigated. This thesis presents and discusses relationships between observed precursor surrogate measures, DBP formation, and results of treatment by enhanced coagulation, which demonstrate greater removal of DOC and chloroform formation potential compared to removal of DON and the selected N-DBPs.

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CHAPTER 1: INTRODCTION

Beginning in the United States in 1908, disinfection with chlorine became an increasingly widespread practice and is credited with the control of such water-borne illnesses as typhoid fever and cholera. This advancement is among the greatest public health achievements of the 20^{th} century. Stemming from the landmark findings of Johannes Rook in 1974, however, research over the past few decades has led to the realization that the chemical disinfectants vital to generating safe drinking water also react with dissolved organic matter (DOM) and inorganic species to produce undesirable, often deleterious compounds known as disinfection byproducts (DBPs). It is also well understood that among the regulated organic chlorination byproducts, there are two principal approaches for mitigation: DBP precursor removal and the use of alternative disinfectants/disinfection practices besides chlorination. While neither strategy precludes DBP formation entirely, the latter strategy introduces the associated uncertain risk of both identified and yet unknown DBPs produced by these alternative disinfectants.

Investigations into the nature of DOM and its amenability to removal comprise a significant body of research by practitioners and water quality engineers and scientists. Consideration for precursor removal is also among the principal policy inclusions of the Stage 1 Disinfectants/Disinfection Byproducts Rule. Composed of differential humic and fulvic acid content, DOM results from the decay of terrestrial and aquatic vegetative matter, and varies both spatially and temporally. While DOM characterization has advanced since

the 1970s, total organic carbon (TOC), hydrophobic organic acid (HPOA) content, and ultraviolet absorbance at 254 nm (UV_{254}) have remained among the most important surrogate measures of DOM content. Moreover, TOC and UV_{254} are the most consistently utilized and readily available parameters from which conclusions about the characteristics of DOM in source water are possible. Among other variables, the effectiveness of aluminum and ferric salt coagulants varies with source water pH, alkalinity, and the concentration and nature of DOM. Research has shown that DBP precursor removal by coagulation is more effective with high molecular weight (MW), aromatic, hydrophobic DOM while typically aliphatic, low MW, hydrophilic DOM is less amenable to coagulation. Furthermore, waters with higher relative alkalinity need greater coagulant doses or the addition of acid to achieve the same TOC removal of low alkalinity waters with the same TOC content.

After the 1970 executive reorganization consolidating all federal environmental regulatory activities into one agency, the US Public Health Service transferred drinking water regulatory responsibilities to the newly created Environmental Protection Agency (EPA). It was not until the creation of the Safe Drinking Water Act (SDWA) in 1974, however, that the EPA was recognized with federal authority to regulate drinking water quality in community water systems. Following the discovery of chloroform and other trihalomethanes (THMs) in drinking water and the related concern of its potential health effects, 1974 also marked the first of many epidemiological studies to implicate the consumption of chlorinated drinking water with cancer and other health endpoints. Correspondingly, the second amendment of the National Primary Drinking Water Regulations in 1979 was the first inclusion of DBPs in drinking water standards. Public Law 96-63 set a maximum contaminant level (MCL) of 100 μg/L for the sum of the four identified THM species as total trihalomethanes (TTHMs or

THM4) based on a running annual average of four quarterly samples. In the 38 years since Rook reported the formation of chloroform and other THMs during treatment, these byproducts have remained the principal driver and focus in DBP regulation and changes in utility practices. This period also resulted in the identification of over 600 previously unknown individual DBP species, the sum of which, when converted to chlorine equivalent units, can account for between 30 and 60 percent of the total organic halide (TOX) content of chlorinated water. This indicates that approximately 50 percent of the halide-containing byproducts and an untold non-halogenated fraction remain unidentified.

In accordance with the SDWA, the EPA later issued multi-tiered best available technology guidance for THM compliance in which utilities were recommended to consider: the use of alternative or supplemental disinfectants and oxidants including chloramines, chlorine dioxide, and ozone; changing of the point of disinfection to a location further down the treatment train; the use of powdered activated carbon for THM and THM precursor removal; and the combination of coagulation and clarification for precursor removal. Subsequently, the EPA's two-stage Disinfectants/Disinfection Byproducts Rule was promulgated in 1998 and, while simultaneously lowering the MCL for THM4 and establishing new standards for five haloacetic acids (HAA5), chlorite, and bromate, the practice of enhanced coagulation for conventional surface water treatment plants also became a formalized mandate. Enhanced coagulation is a process wherein DBP precursor removal requirements are established according to source water TOC and alkalinity. Enhanced coagulation proved an effective regulation for THM4 and HAA5 control and, in part, addresses the generation of unidentified organic halides (as well as other non-halogenated DBPs).

Enhanced coagulation is widely practiced and has served as one of the best practical means of THM and HAA mitigation and control. However, because the preponderance of research into the mitigation of DBPs in the last quarter century has focused on the interaction of chlorine and organic carbon, the associated reactions between free chlorine and the nitrogenous moiety of DOM has been largely overlooked. As a result, to date, there has been little effort to assess the removal capacity of enhanced coagulation upon dissolved organic nitrogen (DON) and to shed light on the formation and control of DBPs containing nitrogen. These compounds are frequently among those "emerging" DBPs most studied and discussed by water quality scientists and engineers, toxicologists, and industry/utility specialists because of their greater purported toxicity relative to conventional DBPs.

In an attempt to address the perceived lack of data in the literature, the principal research objectives of this study are to: (1) evaluate the effectiveness of enhanced coagulation for the removal of DON in a variety of raw drinking waters across the U.S., (2) compare DON removal and DOC removal by enhanced coagulation, (3) assess the formation potential of selected N-DBPs among different drinking water sources before and after enhanced coagulation, and (4) compare the formation of selected N-DBPs with the formation of trihalomethanes before and after treatment.

CHAPTER 2: BACKGROUND AND LITERATURE REVIEW

2.1. DISSOLVED ORGANIC MATTER

2.1.1. Origin and Composition of DOM

Dissolved organic matter is ubiquitous in surface waters and present in ground waters under the influence of surface water. DOM is composed of heterogeneous, polyfunctional macromolecular, polymeric, and colloidal-particulate aqueous biomass derived from the photosynthetic activities and breakdown of terrestrial and aquatic biota, secondary inputs of heterotrophic bacteria and fungi, products of soil dissolution and run-off (soil humus), and to a lesser extent, anthropogenic inputs such as wastewater discharge and agricultural activities (Thurman and Malcolm 1981, Huizhong et al. 2001, Dotson and Westerhoff 2009, Leenheer 2009). Other names in use for DOM that are frequently encountered include natural organic material or natural organic matter (NOM); however DOM is the chosen designation throughout this document as it refers specifically to the aqueous NOM fraction with particles up to 1 μm in diameter (Leenheer 2009). Furthermore, it is this dissolved and colloidal fraction of organic matter that is widely known to affect drinking water treatment. Such impacts of DOM range from imparting color, impeding operational process performance, and providing the substrate for reactions with disinfectants—the byproducts of which are the topic of and motivation for this research.

The concentration, composition, and chemistry of DOM vary widely, both spatially and temporally, in the natural environment. The dissolved and colloidal components in water sources depend on the source of the organic matter, temperature, ionic strength, pH, cation

composition, solubility controls imparted by surface chemistry of sediment sorbents, as well as the presence of microbiological and photolytic degradation processes (Leenheer and Croué 2003). A source water may be characterized as allochthonous or autochthonous, designations which not only imply different sources and water quality parameters, but also drive DOM composition. Authochthonous DOM is produced from cellular material and waste products of macrophytes and aquatic biota, from metabolic secretions of algae and protozoa, and from the decay of organic matter by bacteria (Crittenden et al. 2005, Leenheer 2009). Typically pedogenic in origin, DOM in an allochthonous watershed is carried into the watercourse from the land. Allochthonous DOM is subjected to removal processes and rigorous biological and chemical degradative transformations during transport. Thus, allochthonous DOM is more refractory to rapid biodegradation than autochthonous DOM (Leenheer and Croué 2003, Leenheer 2009). The trophic status of a water (e.g. dys-, eu-, meso-, oligo-trophic) is a further driver of DOM production and composition. For example, a eutrophic lake without oxygen limitations would have increased rates of DOM production and degradation, while a dystrophic lake is highly colored due to soil-derived humic DOM (Leenheer 2009, Hansen 1962).

With regard to elemental composition, on a mass basis, DOM is composed of carbon (45-60%) and oxygen (35-40%) and, to a lesser extent, hydrogen (4-5%) and nitrogen (1-2%; Thurman 1985, Crittenden et al. 2005). At the molecular level, DOM is comprised of a complex mixture of aliphatic and aromatic hydrocarbon structures with functional group attachments that include hydroxyl, amide, carboxyl, keto, and other minor functional classes (Leenheer and Croué 2003). DOM is typically present as an array of both low and high molecular weight (MW) groups that aggregate due to hydrogen bonding and polarity

induced- and polyvalent ionic interactions to form non-uniform, polymeric-like macromolecules (Leenheer and Croué 2003).

It is important to note that in addition to existing in complex mixtures of heterogeneous structures and functional groups, DOM also exists in a dynamic state. Concurrent with its precursor transport and *in situ* formation in a body of water, DOM also undergoes continuous degradation. For example, abiotic and biotic aerobic processes add oxygen and generally increase solubility with the addition of hydroxyl, carbonyl, and carboxyl groups. Conversely, anaerobic pathways add hydrogen and decrease DOM solubility (Leenheer 2009).

Finally, having addressed origins, transformation, and DOM composition at the elemental and molecular level, it is necessary to characterize the different moieties of DOM. While no two waters have the exact same DOM molecular composition, there are several common fractions that may be classified according to polarity, charge, and acid, base, or neutral properties (Leenheer and Croué 2003). It is through these common fractions that seemingly diverse bodies of water may be easily compared. Furthermore, the relative proportions of such fractions influence its behavior during treatment.

The major fractions comprising DOM are dichotomized between humic and nonhumic substances. Humic substances are defined as humic and fulvic acids and humin. Humin is not generally significant in the water column (McKnight and Aiken 1998). Humic and fulvic acids typically constitute about 50% of colloidal organic matter and DOM and can be as much 75% humic in nature (Thurman 1985, McKnight and Aiken 1998, Leenheer and Croué 2003). Together, humic and fulvic acids represent the bulk of the hydrophobic fraction, of which humic acid aggregates predominate in particulate and colloidal organic matter (Thurman 1985). Compared to humic acids, fulvic acids contain more carboxyl and hydroxyl

functional groups which dissociate in the pH range encountered in natural waters. As a result, fulvic acids are more soluble and thus more abundant in the water column than the humic acid fraction (Thurman 1985, McKnight and Aiken 1998). The nonhumics comprise the hydrophilic DOM and can be further subdivided into hydrophilic acids, bases, and neutrals, and by charge.

2.1.2. Characterization of Dissolved Organic Matter: Fundamental Techniques

While there is no direct, comprehensive measure of DOM, the use of surrogate measures and the identification of characteristic fractions are useful in describing the nature and concentration of DOM. The most common methods for characterizing DOM are the measure of total or dissolved organic carbon (TOC/DOC) content, UV absorbance at a wavelength of 254 nm (UV_{254}), and quantification of its humic content. Additional forms of characterization that have evolved over the past four decades include MW fraction analysis, fluorescence analysis, nuclear magnetic resonance (NMR) and infrared spectrometry, and among others, several forms of chromatography. TOC and UV_{254} are the most frequently measured parameters describing DOM content and reactivity in drinking water treatment applications (Archer and Singer 2006).

Carbon Analysis

The quantitative characterization of DOM content is achieved by organic carbon analysis (Leenheer 2009). The total organic carbon (TOC) content of a water sample provides the concentration of particulate-, colloidal-, and dissolved organic carbon. Dissolved organic carbon (DOC) is operationally defined as organic carbon that passes through a 0.45 µm diameter filter, and is thus a measure of the dissolved and colloidal organic matter fraction content up to 0.45 µm (Thurman 1985). The organic matter retained on the 0.45 µm filter is

the particulate organic carbon (POC) and remaining colloidal fraction, and typically represents less than 10% of the overall TOC content (Leenheer and Croué 2003).

Spectrophotometric Analysis

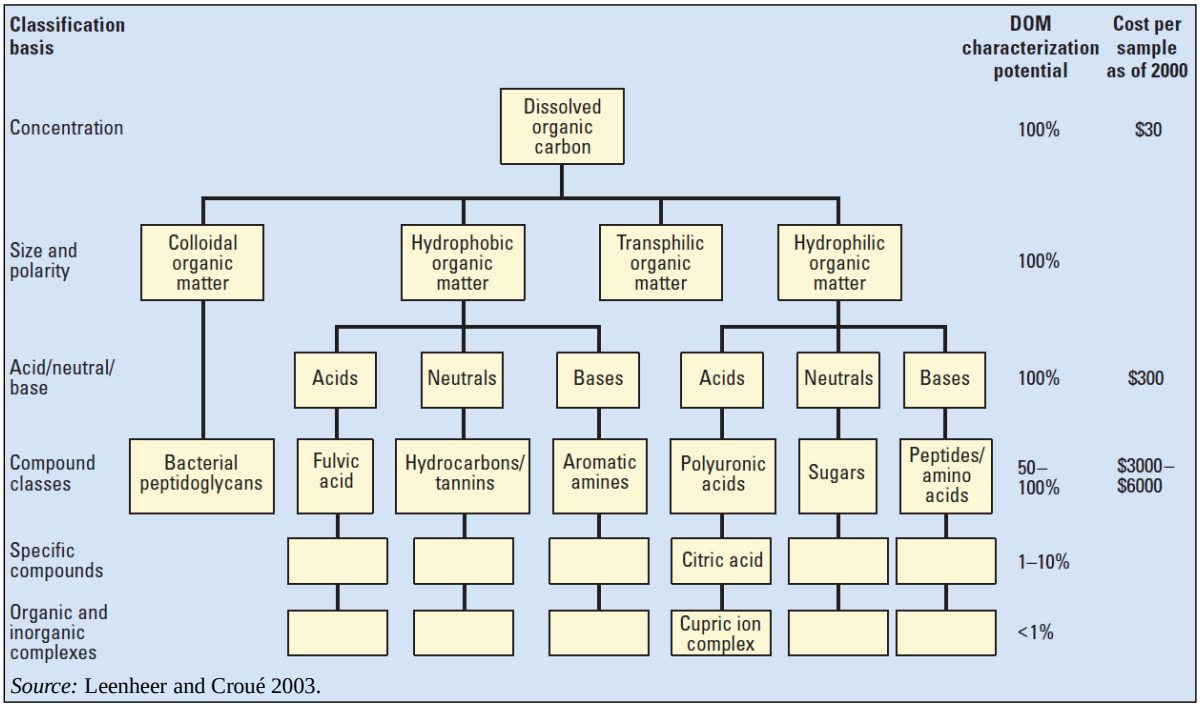
Like carbon analysis, spectrophotometric analysis is a useful means of characterizing DOM and can be used as both a rough indication of overall DOM concentration and its degree of aromaticity. UV_{254} is the most commonly used metric, and is a useful indicator of DOM reactivity (Leenheer and Croué 2003). Unlike TOC/DOC, however, UV analysis is quick, easily performed, and provides quantitative information to evaluate DBP formation potential or results of coagulation, as well as descriptive DOM measures.

DOC and UV_{254} can be used in combination to generate what is known as the Specific UV absorbance (SUVA), defined as the water sample's absorbance at 254 nm divided by its DOC concentration (Leenheer and Croué 2003). SUVA is a useful metric relaying qualitative information about DOM in a given water. Because studies have repeatedly shown that SUVA can be used to estimate the chemical nature of the DOC present, it is a key means of anticipating a water's reactivity with both coagulant and chlorine during treatment (White et al. 1997, Edwards 1997, Vrijenhoek et al. 1998, Archer and Singer 2006). The use of effective coagulation practices to mitigate DBP formation is central to DBP control strategies mandated by the USEPA (see below).

DOC Fractionation

Used in conjunction with DOC analysis, DOM can be further characterized with resin sorbents to elucidate key DOM fractions, often referred to as DOC profiling (Leenheer and Croué 2003). DOC fractionation can be used to quantitatively articulate the humic/nonhumic distribution in a relatively simple, one-step protocol with XAD-8 resin (Leenheer and Croué 2003). Depending upon research aims, more thorough characterization may be desired. Using

a comprehensive technique first developed by Leenheer (1981), Amberlite XAD-8, XAD-2, Bio-Rad AG MP-50, and Doulite A-7 resins are used in sequence to determine, respectively, (1) total hydrophobic/hydrophilic fraction, (2) hydrophobic acid, bases, and neutrals, and (3) hydrophilic acids, bases, and neutrals (Leenheer 2009). While recoveries of 90-95% have been reported for surface waters using the single XAD-8 fractionation procedure, recoveries in the multi-column array technique fell to 81% for the same surface water (Thurman and Malcolm 1981, Leenheer 2009). Subsequent modifications to the protocol of Leenheer (1981) over the last two decades, however, have improved DOM fractionation/isolation techniques such that quantitative recovery is now possible (Leenheer and Croué 2003). Figure 2.1 identifies the key fractions identified by analysis, the characterization potential, and the associated costs of such DOM characterizations.



Source: Leenheer and Croué 2003.

Figure 2.1: Capabilities of DOM fractionation, characterization potential, and cost

2.1.3. Characterization of Dissolved Organic Matter by Fluorescence Spectroscopy

Like chromophores that exist as a result of energy absorbed by molecular constituents of DOM, there are fluorescent fractions within DOM that both absorb and re-emit light energy, known as fluorophores (Hudson et al. 2007). Because the wavelength at which light is absorbed (excitation) and subsequently emitted is specific to the molecule, fluorescence may be used to characterize DOM. The advantage fluorescence offers over other forms of compositional DOM characterization is that it requires minimal sample pretreatment, uses a small sample volume, and is rapid and non-destructive (Hudson et al. 2007). Like other methods of DOM characterization, the specific form of fluorescence spectroscopy and data generated vary according to the study objectives and the intended end use of the data. Two such forms include measures of the fluorescence index (FI) and excitation emission matrix fluorescence spectroscopy (EEMS).

Fluorescence Index

The fluorescence index (FI), defined as the ratio of emission intensities at an excitation wavelength of 370 nm, has received widespread attention as a measure capable of indicating the origin of DOM as higher-plant or microbially-derived DOM (Cory and McKnight 2005). Furthermore, FI has been shown to be strongly correlated with SUVA (Jaffe et al. 2008). To a lesser extent, Jaffe and colleagues (2008) also showed correlation between FI and the DOC-total nitrogen (TN) ratio. Both of these relationships were anchored by the microbially-derived DOM region with characteristic properties of low SUVA-high FI and low C:N-high FI, respectively.

One concern with respect to FI is that it is sometimes difficult to compare FI values among different waters due to the lack of uniform definition and criteria associated with the way FI is calculated and reported. In the literature, one encounters emission intensity pairs of

450 and 500 nm and 470 and 520 nm, with an excitation wavelength of 370 nm. In an interesting study in which FI was well correlated ($R^2 > 0.95$) with the formation of several THM, HAN, and HAA species upon chlorination, Roccaro and colleagues (2008) used the former emission intensity pair, but an excitation wavelength of 320 nm was used. In addition, the method by which FI values are obtained is also not consistent in the literature. In some cases, FI is obtained from a direct scan, and in others, from the corrected EEM spectra of a sample. Furthermore, samples are diluted to avoid inner-filter effects in some cases, while in others, inner-filter corrections are applied. The concentration of DOM resulting in inner-filter interference is also not resolved in the literature (Hudson et. al. 2007).

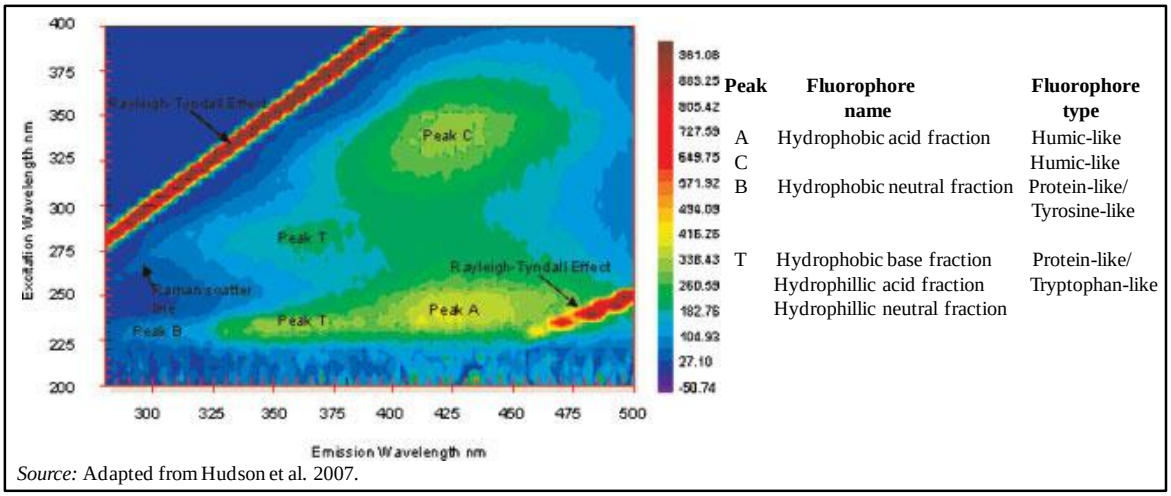
Excitation Emission Matrix Fluorescence Spectroscopy

With its first application in aquatic studies beginning in the mid-1990s, excitation emission matrix fluorescence spectroscopy (EEMS) is regarded as the state-of-the-art technique for DOM characterization and is fast becoming the standard for DOM fluorescence analysis (Hudson et al. 2007). Detailed information can be generated by synchronously scanning excitation, emission, and fluorescence intensity over a range of wavelengths, obtaining a three-dimensional spectral plot. This plot is a map of optical space known as an excitation emission matrix (EEM) or EEM spectrum (Hudson et al. 2007, Leenheer 2009). Using EEMS, one may identify both the source of DOM (terrestrial/aquatic origin) and its fractional composition by the distinctive, characteristic matrix generated (Leenheer 2009). Table 2.1 identifies the characteristic fingerprint regions of humic and amino acid fluorophores common to DOM. Furthermore, Figure 2.2 demonstrates an example EEM spectrum in which Hudson and colleagues (2007) have identified key features and corresponding regions of some DOM fluorophore components.

Table 2.1: Major component types in EEM spectra

Range of Excitation (nm)	Range of Emission (nm)	Component Type
330-350	420-480	Humic-like
250-260	380-480	Humic-like
310-320	380-420	Marine humic-like
270-280	300-320	Tyrosine-like, protein-like
270-280	320-350	Tryptophan-like, protein-like, or phenol-like

Source: Leenheer 2009.



Source: Adapted from Hudson et al. 2007.

Figure 2.2: Example EEM spectra with identified DOM fluorophores

An EEM may be further analyzed to quantitatively characterize the components within a bulk DOM sample. As Hudson and colleagues (2007) note, such means of analysis include fluorescence excitation-emission regional integration (FRI) or parallel factor analysis (PARAFAC).

2.1.4. Removal of DOM

Dissolved and colloidal organic matter interferes with several unit processes of drinking water treatment, impairs aesthetic quality of finished water, and most notably, DOM is the principal organic precursor of byproducts formed during disinfection. DOM can also bind with metal and synthetic organic chemicals, enabling the transport of these constituents through water treatment processes not optimally designed to remove DOM. Once in the

distribution system, residual DOM can also serve as a nutrient source facilitating bacterial re-growth (EPA 1999b). Hence, the removal of DOM is among critical aims of WTPs and is the focus of an extensive body of research.

The processes commonly in use today for DOM removal include coagulation/flocculation/clarification, membrane filtration, granular activated carbon adsorption, precipitative softening, and ion exchange. Advanced oxidation processes, often used in combination with other unit processes (e.g. biological filtration), are also being applied for DOM removal. The processes regarded by the USEPA as capable of achieving greater than 40% DBP precursor removal are: coagulation/flocculation/clarification in combination with filtration, particularly at slightly acidic pH; precipitative softening, particularly at high pH; GAC adsorption; and nanofiltration membrane processes (EPA 1999b).

Coagulation

Raw surface water contains inorganic and organic particulates, including clay, silt, mineral oxides, viruses, bacteria, algae, protozoan cysts and oocysts, as well as dissolved inorganic and organic matter. Particles may consist of and harbor pathogenic microorganisms, concentrate harmful organic compounds and trace metals, and reduce clarity, while DOM imparts undesirable taste and color, increases disinfectant demand and is a DBP precursor. The principal objective of coagulation is to aggregate particles and DOM so that they can be removed by downstream clarification and filtration processes. The type and dosage of coagulant is largely dependent upon a variety of water quality characteristics including temperature, pH, alkalinity, concentration and type of particulates, and concentration and characteristics of DOM. Water treatment facilities routinely monitor one or

more of the above parameters throughout the day, and often conduct jar tests on a regular basis to determine optimal coagulation conditions.

Coagulation generally utilizes either ferric salts or aluminum sulfate ($Al_2(SO_4)_3$), also referred to as alum. Alum is the most widely used coagulant for water treatment in the United States (Crittenden et al. 2005). The addition of either coagulant to water results in dissolution followed by hydration of the trivalent metal ion to form charged aquometal complexes. The aquometal complexes then pass through a series of hydrolytic reactions to form a variety of mono- and polynuclear species that are all capable of interacting with particles and DOM. Aquatic particles and DOM are predominantly negatively charged at neutral pH ranges. Thus, particles and DOM interact with the positively charged aquometal complexes and are destabilized.

Specific Considerations for DOM Removal by Coagulation

The fundamental drivers of DOM removal efficiency are coagulant type and dosage, pH, and the concentration and nature of the colloidal and dissolved organic material. As it relates to pH, the alkalinity of a water is also an important consideration. Removal of DOM by a metal salt coagulant occurs by one of two general mechanisms: (1) adsorption onto the metal hydroxide ($Al(OH)_3$ or $Fe(OH)_3$) floc and (2) the formation of insoluble metal-DOM complexes (aluminum or iron humates and fulvates), analogous to charge neutralization (Krasner and Amy 1995, Archer and Singer 2006). The charge density of humic and fulvic acid DOM components is reduced at lower pH and thus renders the humic fraction more hydrophobic and adsorbable. Correspondingly, the first mechanism is more dominant at high coagulant dosages and higher pH while the reverse is true for the second mechanism (Krasner and Amy 1995, Archer and Singer 2006).

The outcome of DOM-coagulant interaction is largely driven by the humic/nonhumic distribution of DOM. Indeed, Collins and colleagues (1986) demonstrated that higher MW DOM fractions are more amenable to removal by coagulation while fractions with the highest carboxylic acidity (highest charge density) are more difficult to remove. Reckhow and Singer (1990) noted coagulation results in preferential reduction of UV-absorbing components of DOM compared to removal of overall TOC, indicative of a greater relative decrease in aromatic content. Cumulatively, this evidence indicates coagulation preferentially removes the hydrophobic content with a greater extent of removal for the humic acid fraction than the fulvic acid fraction. Thus, waters with a dominance of nonhumic and/or low MW DOM are resistant to coagulation as a means of DOM removal.

2.2. DISINFECTION OF DRINKING WATER

Primary disinfection is a process of inactivation of microorganisms within the treatment plant, while secondary disinfection is the maintenance of a disinfectant residual in treated water during storage and throughout the distribution system. The five most common disinfectants today are free chlorine, combined chlorine (often referred to as chloramines), ozone, chlorine dioxide, and UV light (Crittenden et al. 2005).

2.2.1. Disinfection with Free Chlorine

The application of free chlorine remains the most dominant form of primary disinfection in the US. It is most commonly applied as chlorine gas, although liquid sodium hypochlorite, solid calcium hypochlorite, and other forms are still used.

Chemistry of Chlorine in Water

Hypochlorite and molecular chlorine become hypochlorous acid (HOCl) after being introduced to water as shown in Equations 2.1 and 2.2., pH governs the distribution between

hypochlorite (OCl^-), a weak disinfectant, and the strong disinfectant HOCl in accordance with Equation 2.3.

$$NaOCl + H_2O \rightarrow HOCl + OH^- + Na^+ \quad (2.1)$$

$$Cl_2(g) + H_2O \rightarrow HOCl + H^+ + Cl^- \quad (2.2)$$

$$HOCl \leftrightarrow OCl^- + H^+ \quad (2.3)$$

Free chlorine leaves a stable residual that can either be maintained in the distribution network or be converted to chloramines with the use of ammonia. The use of monochloramine has gained popularity as a means of trihalomethane (THM) control, discussed further in following sections.

2.3. DISINFECTION BYPRODUCTS

2.3.1. Discovery and Overview of DBP Formation

Rook (1974) published landmark findings in Holland that chlorine was reacting with DOM during treatment to form chloroform ($CHCl_3$) and other THMs. The results were independently confirmed in the U.S. in the findings of Bellar et al. (1974) and Symons (1975). Stemming from the work of Rook, DOM was recognized as capable of reaction with chlorine and, later, with other disinfectants/oxidants as well, to form a variety of DBPs. The dominant organic chlorination DBPs are THMs and haloacetic acids (HAAs).

At a fundamental level, chlorine reacts with DOM during treatment to generate DBPs, as shown in the following general equation modified from Singer (1993):

$$Cl_2 + DOM \rightarrow CHCl_3 + \text{Other THMs} + HAAs + \text{Other DBPs} \quad (2.4)$$

When bromide is present in a water source, it is rapidly oxidized to form hypobromous acid (HOBr), which in turn reacts with DOM. When this occurs, the products of formation in Equation 2.4 are represented by a greater abundance of mono-, di-, and tri-bromine-substituted methanes and acetic acids. This was reported by Rook (1974) for THM

formation. Iodide was later found to similarly influence THM and HAA speciation (Hua et al. 2006).

2.3.2. Health Effects

With regard to the regulated organic halides, all four THMs have been shown to be carcinogenic in animal studies, most are cytotoxic, and brominated THMs have been demonstrated to be mutagenic in studies where activation by glutathione S-transferase-theta—a common mammalian cell enzyme—was included. In general, HAAs have demonstrated evidence of cytotoxicity and genotoxicity, with the bromo-analogues being more strongly cyto- and genotoxic compared to chlorine-containing HAAs. Three of the HAA5 have shown to be positive for carcinogenicity in animal studies (Richardson et al. 2007).

2.3.3. Regulation

In 1979 the USEPA promulgated the first DBP Rule establishing a maximum contaminant level (MCL) of 100 µg/L for total trihalomethanes (THM4) for utilities serving greater than 10,000 people (EPA 1979). The regulation was based on a running annual average (RAA) of four quarterly samples taken system-wide. This rule was based on epidemiological studies that showed a slightly increased risk of bladder, colon, and rectal cancer from long-term exposure to chlorinated drinking water. This was an interim rule and was to be re-evaluated after more data on DBPs and health effects were collected.

Stage 1 Disinfectants and Disinfection Byproducts Rule

A comprehensive DBP policy tool came into existence in the form of the EPA's two-stage Disinfectants/Disinfection Byproducts (D/DBP) Rule. The 1998 Stage 1 D/DBP Rule simultaneously lowered the MCL for THM4 to 80 µg/L and established new standards for five HAAs (HAA5), chlorite, and bromate of 60 µg/L, 1.0 mg/L, and 10 µg/L, respectively.

The rule also established Maximum Contaminant Level Goals (MCLGs) for some of the DBPs and Maximum Residual Disinfectant Limits (MRDLs) and Maximum Residual Disinfectant Goals (MRDLGs) for applicable disinfectants (EPA 2001b). The limits and goals established by the rule are shown in Table 2.2.

Table 2.2: Stage 1 D/DBP regulations for disinfectant residual, THM4*, and HAA5

Disinfectant Residual	MRDLG (mg/L)	MRDL (mg/L)	Compliance Based On
Chlorine	4 (as Cl_2)	4.0 (as Cl_2)	Annual Average
Chloramine	4 (as Cl_2)	4.0 (as Cl_2)	Annual Average
Chlorine Dioxide	0.8 (as ClO_2)	0.8 (as ClO_2)	Daily Samples
Disinfection Byproducts	**MCLG (mg/L)**	**MCL (mg/L)**	**Compliance Based On**
Total trihalomethanes (TTHM)[1] - Chloroform - Bromodichloromethane - Dibromochloromethane - Bromoform	N/A N/A zero 0.06 zero	0.080	Annual Average
Haloacetic acids (five) (HAA5)[2] - Dichloroacetic acid - Trichloroacetic acid	N/A zero 0.3	0.060	Annual Average
Chlorite	0.8	1.0	Monthly Average
Bromate	zero	0.010	Annual Average

Source: EPA 2001b.

To address DBP precursor removal, the Rule also required the practice of enhanced coagulation for conventional treatment plants using surface water or ground water under the influence of surface water (EPA 2001b). The clarification process combination of coagulation, flocculation, sedimentation, and granular filtration was traditionally used to

From Table 2.2:

*THM4 is the same trihalomethane designation as TTHM which the EPA and many in the industry use but is inaccurate as more trihalomethanes (e.g. iodine-containing THM species) have been discovered.

N/A Not applicable because there are no individual MCLGs for TTHMs or HAA5.

1 Total Trihalomethanes (THM4) is the sum of the concentrations of chloroform, bromodichloromethane, dibromochloromethane, and bromoform

2 Haloacetic acids (five) is the sum of the concentrations of mono-, di-, and trichloroacetic acids and mono-, and dibromoacetic acids (EPA 2001b). The table only shows two species.

remove suspended particles. The term "enhanced coagulation" references the alteration of this process to achieve greater DOM removal, typically achieved by high dosages of metal salt coagulant and/or pH adjustment of source water (White et al. 1997, Vrijenhoek et al. 1998). Enhanced coagulation specifies DBP precursor removal requirements according to source water TOC and alkalinity in a 3x3 matrix, as shown in Table 2.3. Because coagulation is more effective at slightly acidic pH values, alkalinity is an important influence upon the

Table 2.3: Enhanced Coagulation TOC Removal Requirements

Source Water TOC [mg/L]	Source Water Alkalinity [mg/L as $CaCO_3$]		
	0 to 60	>60 to 120	>120
0 to 2.0	no action	no action	no action
>2.0 to 4.0	Element 1: 35%	Element 2: 25%	Element 3: 15%
>4.0 to 8.0	Element 4: 45%	Element 5: 35%	Element 6: 25%
>8.0	Element 7: 50%	Element 8: 40%	Element 9: 30%

Source: EPA 2001b.

process of coagulation, as noted in §2.1.4. The supplementary addition of acid to achieve a more effective coagulation pH carries with it economic burdens that may be too great for many utilities. Such considerations are reflected by the inclusion of alkalinity to the enhanced coagulation matrix, in which high alkalinity waters are allowed to achieve less TOC removal (Archer and Singer 2006). Enhanced coagulation has proved effective for mitigating THM formation at many conventional WTPs. Furthermore, by mandating a set TOC removal requirement, the EPA had also partly addressed unidentified organic halides (and presumably others not containing halides) of potential public health concern.

Stage 2 Disinfectants and Disinfection Byproducts Rule

The Stage 2 D/DBP Rule added no new compounds and made no changes to MCLs or MCLGs. However, it addressed concerns that the public was not adequately protected by the manner in which HAAs and THMs were monitored and reported with a system-wide running

annual average (RAA). While DBP mitigation at the WTP remains the most critical element of limiting DBP formation, it had long been argued that elevated exposure to DBPs could still be taking place, especially in far reaches of the distribution system. The system-wide RAA inaccurately reflects exposure for the entire distribution system when known variations in water age and other characteristics are considered. To generate more equitable public health protection, the Stage 2 D/DBP Rule requires utilities to perform an evaluation of the distribution system to identify locations with high DBP concentrations to be used in subsequent compliance monitoring. The MCLs thus would be calculated for each monitoring location, generating not a system-wide RAA but a locational running annual average (LRAA, EPA 2005b).

2.3.4. DBP Science

Occurrence of DBPs in US Drinking Waters

In addition to the presently regulated DBPs, the Information Collection Rule (ICR) marked an important benchmark as an industry-wide study of the occurrence of several DBPs, many of which had not been included in previous occurrence studies. DBPs monitored in the ICR survey, in addition to the THMs and HAAs, included four haloacetonitriles (HANs), two haloketones, trichloronitromethane (chloropicrin), trichloroacetaldehyde (chloral hydrate), cyanogen chloride, and 12 aldehydes (Krasner et. al 2006). Among the principal findings of the ICR, it was found that, on average, THM4 and HAA5 accounted for about 60% of the measured total organic halide (TOX) concentration among surface water facilities. The other organic halides (HANs, haloketones, chloral hydrate, and chloropicrin) accounted for about 7% (EPA 2005a). This disparity between TOX and the organic halide content of the measured DBPs indicated that a third of the halogenated DBPs formed were as of yet unidentified.

Following the ICR, the EPA's Office of Water initiated an effort to prioritize the greater than 500 DBPs reported in the literature on the basis of predicted adverse health impacts. This prioritization brought together a multidisciplinary panel of experts from the Office of Water and the Office of Prevention, Pesticides, and Toxics Substances to conduct an "in-depth mechanism-based, structural activity relationship analysis, supplemented by an extensive literature search for genotoxicity and other data […] to rank the carcinogenic potential of these DBPs" (Weinberg and Krasner 2002). Accordingly, additional occurrence studies have been performed over the last decade targeting the high priority DBPs identified in the EPA analysis, DBPs shown to occur at bench scale or in limited full-scale surveys, select DBPs resulting from alternative disinfectants, as well as the conventional and regulated DBPs. Table 2.4 identifies many of the high priority and other DBPs that were included in nationwide occurrence studies by Weinberg and Krasner (2002) and Krasner et al. (2006).

Table 2.4: Priority DBPs monitored in nationwide occurrence study

halomethanes		
chloromethane	dichloroiodomethane	bromodiiodomethane[b]
bromomethane (methyl bromide)[a]	bromochloroiodomethane	triiodomethane (iodoform)[b]
bromochloromethane	dibromoiodomethane[b]	carbon tetrachloride
dibromomethane	chlorodiiodomethane[b]	tribromochloromethane
haloacids		
3,3-dichloropropenoic acid		
haloacetonitriles		
chloroacetonitrile	bromodichloroacetonitrile	tribromoacetonitrile
bromoacetonitrile	dibromochloroacetonitrile	
haloacetates		
bromochloromethyl acetate		
haloketones		
chloropropanone	1-bromo-1,1-dichloropropanone	1,1,3,3-tetrabromopropanone[b]
1,3-dichloropropanone	1,1,3,3-tetrachloropropanone	1,1,1,3,3-pentachloropropanone[c]
1,1-dibromopropanone	1,1,1,3-tetrachloropropanone	hexachloropropanone[c]
1,1,3-trichloropropanone		
haloaldehydes		
chloroacetaldehyde	bromochloroacetaldehyde[b]	tribromoacetaldehyde[b]
dichloroacetaldehyde		
halonitromethanes		
chloronitromethane[b]	bromochloronitromethane[b]	dibromochloronitromethane[b]
bromonitromethane	dibromonitromethane	tribromonitromethane (bromopicrin)[b]
dichloronitromethane[b]	bromodichloronitromethane[b]	
haloamides		
monochloroacetamide[b]	dichloroacetamide	trichloroacetamide[b]
monobromoacetamide[b]	dibromoacetamide[b]	
halogenated furanones		
3-chloro-4-(dichloromethyl)-5-hydroxy-2(*5H*)-furanone (MX)	3-chloro-4-(bromochloromethyl)-5-hydroxy-2(*5H*)-furanone (BMX-1)	
3-chloro-4-(dichloromethyl)-2-(*5H*)-furanone (red-MX)	3-chloro-4-(dibromomethyl)-5-hydroxy-2(*5H*)-furanone (BMX-2)	
(*E*)-2-chloro-3-(dichloromethyl)butenedioic acid (ox-MX)	3-bromo-4-(dibromomethyl)-5-hydroxy-2(*5H*)-furanone (BMX-3)	
(*E*)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (EMX)	(*E*)-2-chloro-3-(bromochloromethyl)-4-oxobutenoic acid (BEMX-1)[b]	
(*Z*)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid (ZMX)[g]	(*E*)-2-chloro-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-2)[b]	
2,3-dichloro-4-oxobutenoic acid (mucochloric acid) (MCA) (ring and open forms)	(*E*)-2-bromo-3-(dibromomethyl)-4-oxobutenoic acid (BEMX-3)[b]	
VOCs[d] and miscellaneous DBPs		
1,1,1,2-tetrabromo-2-chloroethane[e]	methyl-*tert*-butyl ether[a]	benzyl chloride
1,1,2,2-tetrabromo-2-chloroethane[b]		
carbonyls		
2-hexenal	cyanoformaldehyde	6-hydroxy-2-hexanone[f]
5-keto-1-hexanal[f]	methylethyl ketone[f]	dimethylglyoxal

Source: Krasner et al. 2006

The results of these studies indicate that, in addition to the conventional DBPs, the high priority DBPs can and do occur in WTPs across the nation. Additionally, Weinberg and Krasner (2002) found several of these new DBPs at levels higher than previously encountered. New bromo- and iodo-analogues of both conventional DBPs as well as emerging DBPs of concern were identified, including bromonitromethanes, brominated

furanones, and iodo-THMs and iodoacids (Weinberg and Krasner 2002, Krasner et al. 2006). The studies also disproved the widely accepted hypothesis that mitigation of THM4 or HAA5 with alternative disinfectants would in turn be effective for controlling other potentially harmful, halogenated DBPs.

2.3.5. Precursors: Reactivity of DOM with Chlorine

The water quality parameters known to influence chlorination by-product formation include temperature, pH, bromide and iodide concentration, and the concentration and nature of DOM. Disinfection by-product formation potential (DBPFP) is favored with increasing temperature and DOM concentration (Archer and Singer 2006). In the analysis of DOM surrogate parameters, Najm et al. (1994) showed THM4 and HAA5 formation increased with both TOC and UV_{254}, with better correlation obtained for UV than TOC for both species. TOX formation potential (TOXFP), which encompasses the entire halogenated DBP content, was shown to increase with increasing SUVA (Archer and Singer 2006). These observations indicate that DBPFP is strongly influenced by the degree of aromaticity of DOM.

The formation and speciation of DBPs is further influenced by the different structural components and functional groups within DOM and, at its most basic level, the humic/nonhumic distribution of DOM. In general, research has shown that upon chlorination, the hydrophobic acid fraction of DOM results in greater formation of THM4 and HAA9 than the trans- and hydrophilic acid (collectively referred to as nonhumic) fractions (Liang and Singer 2003). The impact of the hydrophilic acid fractions, however, is not negligible. Collins et al. (1986) noted that utilities along the Colorado River had difficulty reducing THM4 formation despite efforts to improve coagulation and clarification. Further analysis indicated that this was due to the relative abundance of hydrophilic DOM in this source water, accounting for nearly 2/3 of the TOC and greater than half of the THM formation

potential (Collins et al. 1986). Furthermore, research indicates that there is preferential formation of THMs over HAAs as the pH and the hydrophilic fraction increase (Liang and Singer 2003).

In the chlorination of operationally defined precursor isolates differentiated by both hydrophobicity and MW, Hua and Reckhow (2007) found that MW distribution by itself provided no significant trends compared to DBPFP. Their study suggested a general trend in THM and HAA formation potential is evident for fractions separated by hydrophobicity and, further, that hydrophobic and high MW DOM is the major precursor fraction in the formation of unknown TOX. Additionally, hydrophilic and low MW DOM was shown to play a significant role in the formation di-halo acetic acids and THMs. This fraction also appears to be highly reactive with bromine and iodine (Hua and Reckhow 2007).

In a more specific analysis of the DBPFP of DOM surrogates at the compound level, Bond and colleagues (2009) exposed 21 different classes of precursors to excess chlorine. Represented compounds included phenolic, carboxylic acid, carbohydrate, amino acid, amide, and furan structures ranging from MW 1701 (tannic acid) to MW 60 (acetic acid). The compounds also represented the spectrum of operationally defined fractions based upon relative hydrophobicity in which some compounds represented more than one fraction. The results of this analysis largely confirmed that while DOM surrogate compounds may have similar physical properties, the action of compound-specific DBP formation varies widely. Indeed, kinetic and mechanistic studies of organic matter oxidation and halogenation have shown functional class to be a strong driver of reaction pathway (Deborde and von Gunten 2008).

In the analysis by Bond et al. (2009), chlorine substitution was the only compound-specific parameter with a strong correlation to DBPFP. While they did find correlations among the formation of different DBP classes, the authors found no apparent link between chlorine demand and DBPFP. This suggests that oxidation reactions, rather than chlorine addition/substitution (halogenations), are the dominant pathway in chlorine consumption, which has been proposed by other researchers under different reaction conditions (e.g. Zhang and Minear 2006). In contrast, study of the chlorine incorporation into fulvic acid reported by Reckhow and Singer (1990) indicated halogenation to be the dominant pathway, with 25-29% Cl_2 incorporation over a 72-hour contact time. This observation is likely different than those of Bond et al. (2009) and Zhang and Minear (2006) due to different contact times, poor representation of the selected compounds as surrogates of bulk fulvic acid, and/or low Cl_2/DOC ratios of chlorination conditions.

As noted throughout this document, THMs and HAAs represent a fraction of the myriad of identified and unidentified DBPs formed during chlorination. Table 2.5 shows the association between compound classes and formation of DBPs beyond that of regulated species alone.

Table 2.5: Associations of DBPs and Major chemical classes of DOM

	Class of chemical compounds				
Class of disinfection by-products	Humic species	Carbohydrates	Amino acids	Proteins	Carboxylic acids
Trihalomethanes (THM)	Primary source	Not known, probably minor	Minor *	Important *	Secondary source†
Haloacetic acids (HAA)	Primary source	Not known, probably minor	Not known, probably insignificant	Not known, may be significant	Secondary source
Chlorophenols	Primary source	Insignificant	Insignificant	Insignificant	Insignificant
MX	Primary source‡	Not known, probably insignificant	Not known, probably insignificant	Not known, probably insignificant	Insignificant
Haloketones	Primary source	Not known, may be significant	Not known, probably insignificant	Not known, may be significant	Insignificant
Chloral hydrate	Primary source	Not known, probably insignificant	Not known, probably insignificant	Not known, probably insignificant	Insignificant
Haloacetonitriles	Important	Not known, probably insignificant	Important	Important	Insignificant
Trihalonitromethane	Important	Not known, probably insignificant	Important	Important	Insignificant
Cyanogen halide	Important	Not known, probably insignificant	Important	Important	Insignificant
Aldehydes	Primary source §	Not known, may be significant	Not known, probably insignificant	Important	Not known, probably minor
Contribution to the pool of DBP precursors	Predominant (80-90%)	Little known, probably <5%	Important (5-10%)	Important (5-10%)	Probably 5-10%

Source: Croué et al. 1999.

* some amino acids produce THMs (Larson and Weber 1994) but their concentration is much smaller than that of humic species

† β-hydroxy and β-keto acids have been shown to produce THMs upon chlorination (Larson and Weber 1994)

‡ Xu et al. 1997, DeMarini et al. 1995, Smeds et al. 1997, Conrad and Huck 1996

§ Paode et al. 1997

It should be noted that, in the face of DOM heterogeneity, variable treatment techniques, and other water quality influences, the inclusion of the greater than 600 individual DBP species

identified poses a daunting challenge to the water quality field. The use of DOM surrogates, DBP reference compounds, TOX, and targeted analysis of those DBPs deemed to be of highest priority serves as a means of navigating this challenge. Furthermore, humic substances are among the best studied component of DOM and have proven to be the predominant fraction of DBPs precursors in countless analyses. However, the more recent realization that N-DBPs are among the most toxic DBPs, has led some researchers to suggest that an important precursor moiety has been overlooked.

2.4. DISSOLVED ORGANIC NITROGEN

The preponderance of research into the mitigation of DBPs in the last quarter century has focused on the interaction of chlorine and dissolved organic carbon, while the associated reactions between free chlorine and the nitrogenous moiety of DOM have been largely overlooked. N-DBPs have been found to be more geno- and cytotoxic than currently regulated DBPs (Muellner et al. 2007, Plewa et al. 2008). Furthermore, while nitrogen fate and occurrence has been studied in the natural environment for several decades, its behavior in drinking water treatment contexts is poorly characterized. As a result, there has been little effort, to date, to assess the removal capacity of enhanced coagulation for dissolved organic nitrogen (DON) or as a means of N-DBP control.

2.4.1. Occurrence of DON

On a mass ratio, nitrogen comprises 0.5 to 10% of DOM. Total dissolved nitrogen (TDN) includes organic and inorganic forms of nitrogen, and in pristine watersheds, DON is often the dominant form of TDN. Due to agricultural runoff and other human impacts, DON represents only a fraction of the TDN in many waters (Westerhoff and Mash 2002). Concerns about elevated levels of both inorganic and organic nitrogen have arisen due to growing population centers and increasing centralization of wastewater treatment facilities, the inputs

of which can constitute sizeable contributions to downstream drinking water sources (Dotson and Westerhoff 2009). Analysis of US Geological Survey data show a median DON concentration of 0.37 mg/L and, in a sampling campaign of 28 WTPs, raw water average DON concentration was 0.19 mg/L (Lee and Westerhoff 2006).

The ratio of DOC to DON has been used as a parameter for characterizing DOM and is purported to be an important indicator of the source of the DOM. Autochthonous DOM sources are associated with low DOC/DON ratios, whereas higher ratios are representative of allochthonous DOM sources (Westerhoff and Mash 2002). Linkages between FI and DOC/TN (total nitrogen) ratios have been reported (Jaffé et al. 2008) and are relevant in many waters not impacted by human activity. Both DON and DOC/DON have been correlated with different peak intensities of EEMs and, overall, in a 28-utility survey, EEMs were better correlated with DON content than proposed UV/Vis spectroscopy measures (Lee et al. 2006). SUVA, which is in general a more robust DOM surrogate, has been shown to decrease with decreasing DOC/DON ratios (Westerhoff and Mash 2002).

Each fraction of DOM discussed earlier in this chapter has a characteristic DOC/DON ratio and, thus, the relative abundance of one fraction or another in a water source can have pronounced influences upon the overall DON content. In general, neutral and base DOM fractions tend to be nitrogen-rich relative to hydrophobic acid fractions which are nitrogen-poor. Polar acid (hydrophilic) fractions as well as colloidal organic matter also tend to be nitrogen enriched. At the compound class level, amino acids are thought to comprise as much as 35% of DON (Thurman 1985). These constituents are present in effluents from wastewater treatment facilities and as soluble microbial products (SMPs) from aquatic biota. Amino acids are present in both free and combined forms and can also be incorporated into larger

DOM molecules (Westerhoff and Mash 2002). SMPs also contain low MW and macromolecular sources of DON. Furthermore, positive correlations are observable between DON and algal productivity, with high algal populations in eutrophic lakes resulting in 0.7-1.2 mg/L DON (Westerhoff and Mash 2002).

2.4.2. Drinking Water Treatment Implications of DON

Removal by Coagulation

Studies of DOM coagulation have traditionally focused upon removal of UV_{254}, DOC/TOC, and operationally defined fractions of DOM, while characterization of DON removal by coagulation has only recently received attention. The greatest fractions of DOM removed by coagulation are hydrophobic organic acids which generally contain little DON. More polar acidic fractions, however, are nitrogen enriched and are removed with similar efficiency as the hydrophobic fractions (Westerhoff and Mash 2002). Colloidal organic matter also typically contains appreciable amounts of DON and is readily removed during coagulation. However, in general, the predominant DON fractions, i.e. the bases and neutrals, are poorly removed by coagulation (Westerhoff and Mash 2002).

Results of a full-scale WTP survey of DON removal by Lee and colleagues (2006) showed that 20% of DON was removed during coagulation, compared to 29% removal of DOC. Utilities that employed coagulant aids achieved 23% removal of DON, compared to 9% DON removal for those that used metal-salt coagulant alone (Lee et al. 2006). In a follow-up jar test study to further investigate the role of cationic polymer coagulant aids, better removal was confirmed with use of a coagulant aid (Lee and Westerhoff 2006).

Fractional analysis by MW has shown that the distribution of DON is comparable to that of DOC and that both DON and DOC are poorly removed in the <1000 dalton size range (Lee et al. 2006). A later study by Dotson and Westerhoff (2009) showed that DOC and

DON removal were quite comparable among 16 WTPs sampled during summer months. Total amino acid (AA) removal exceeded the removal of free AAs, 65.2% and 25.4%, respectively, and coagulation was shown to be the most significant unit process for removal of total AAs (Dotson and Westerhoff 2009). AAs accounted for 15% of DON on average in their study, but have been reported to be as high as 35% of DON in lakes, and 20% to >75% during run-off events in different soil types (Dotson and Westerhoff 2009). No studies were found to have investigated DON removal specifically in the context of enhanced coagulation.

Disinfection and N-DBP formation

With respect to chlorination and DBP formation, DON, and specifically AAs, have been shown to exert a chlorine demand and result in the undesirable formation of organic chloramines. Organic chloramines pose challenges to accurate residual measurement and are poor drinking water disinfectants (Westerhoff and Mash 2009). In the chlorination and chloramination of DOM isolates characterized by DOC/DON, dichlororacetonile (DCAN), chloropicrin, and N-nitrosodimethylamine (NDMA) were formed, although NDMA was not detectable in chlorinated samples (Lee et al. 2007). Although correlations were not particularly strong, N-DBP formation generally decreased with increasing DOC/DON ratio and DCAN was formed at the highest levels.

The results reported in the latter investigation were somewhat surprising. While DCAN was most abundant during both chlorination and chloramination, chloramination resulted in DCAN levels five times as great compared to free chlorine (Lee et al. 2007). The authors suggested that inorganic nitrogen from monochloramine may result in elevated DCAN formation; this in line with one of two formation pathways thought to control DCAN formation, both of which are proposed to operate simultaneously during chloramination (Shah and Mitch 2011). However, in an analysis by Mitch et al. (2009), DCAN formation

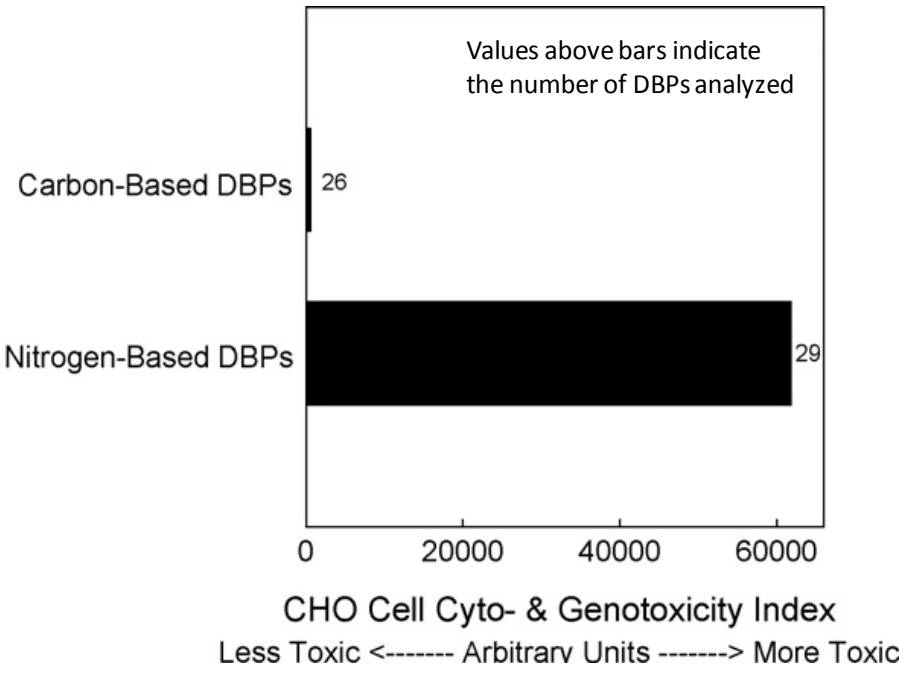
was predominantly higher with free chlorine than with monochloramine. Thus, the findings reported by Lee et al. (2007) may not by typical and are likely rooted in the reaction conditions specific to their study, with reaction duration and free chlorine residual being particularly important. This is because DCAN can undergo base-catalyzed hydrolysis to form other products including dichloroacetamide and dihaloacetic acids (Reckhow 2002).

Chlorination and chloramination of DOM isolates reported by Chu et al. (2010) resulted in the formation of haloacetamide (HAM) species, including dichloro- and trichloro-acetamide (DCAM and TCAM, respectively). Analysis of precursor fractions in this study indicated that hydrophobicity and DOC/DON ratio influenced DCAM formation levels. Curiously, between two similarly hydrophilic fractions, DCAM formation was higher in the fraction with higher DOC/DON. The authors suggest that the characteristics of DON, rather than the amount of DON, influenced the yield of DCAM (Chu et al. 2010).

Furthermore, chlorination of DON surrogates and of AAs resulted in formation of DCAN, THMs and HAAs. In general, AAs have a low THM yield but demonstrate high TOXFP, and have been proposed to alter the distribution of THMs and HAAs (Westerhoff and Mash 2002). While formed at much lower levels than THMs, N-DBPs such as haloacetonitriles (HANs), halonitromethanes (HNMs), NDMA, and HAMs are among the most toxic DBPs discovered in drinking water (Muellner et al. 2007, Plewa et al. 2008).

Health Concerns

Nitrogenous DBPs are noteworthy due to their frequent occurrence ranging from low-ng/L to µg/L levels and, as shown in Figure 2.3, comprise a considerably toxic category. Furthermore, N-DBPs have been listed as research priorities by the EPA (Muellner et al. 2007). This class includes many unregulated and emerging DBPs including NDMA and related compounds, HANs, HNMs, and HAMs. While some HANs and HNMs were



Source: Richardson et al. 2007.

Figure 2.3: Toxicity of N-DBPs relative to carbon-based DBPs

identified relatively early in the timeline of DBP research, others including HAMs, have only recently been identified (Richardson et al. 2007).

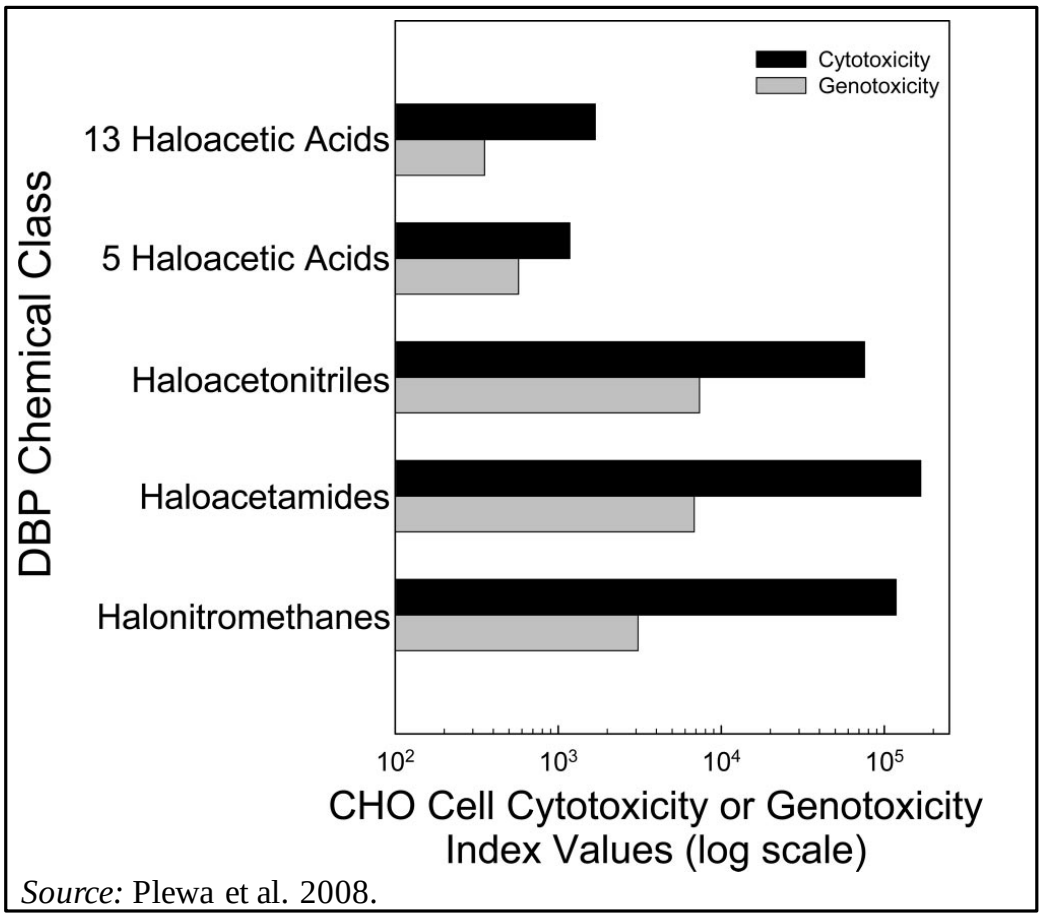
The original group of haloacetonitriles—chloro-, bromo-, dibromo-, and trichloroacetonitrile (CAN, BCAN, DBAN, and TCAN) collectively referred to as HAN4 are the most commonly measured HANs and were found in a variety of occurrence surveys and in the USEPA Information Collection Rule database. The ICR database indicated that HAN4 were formed at WTPs using chlorine, chloramines, chlorine dioxide, and ozone and levels ranged from <0.5 to 41 µg/L, with a median of 2.7 µg/L. In later surveys, the list of HANs has grown to include bromo-, bromodichloro-, dibromochloro-, tribromo-acetonitrile (DCAN, BDCAN, DBCAN, and TBAN, respectively) and 3-bromopropanenitrile (Muellner et al. 2007). HAN4 have been shown to be mutagenic in bacterial assays and as direct-acting genotoxicants in Chinese hamster ovary cells (CHO), in which brominated, di- and trihalogenated HANs were more genotoxic. In a comprehensive study of seven HANs by

Muellner and colleagues (2007) which included iodoacetonitrile (IAN), CHO cell chronic cytotoxicities ranged from 2.8 μM (DBAN) to 0.16 mM (TCAN) with a descending rank order of DBAN > IAN ≈ BAN > BCAN > DCAN > CAN > TCAN. The study also identified an acute genotoxic potency range from 37 μM (IAN) to 2.7 mM (DCAN) in which the rank order was IAN > BAN ≈ DBAN > BCAN > CAN > TCAN > DCAN. The latter genotoxic potency rank order was in good agreement with structure-activity analysis, and the study confirmed that HANs represent a more toxic class of DBPs than the regulated C-DBPs (Muellner et al. 2007, Richardson et al. 2007).

Haloacetamides comprise yet another N-DBP class that has shown more cyto- and genotoxicity than their regulated C-DBP counterparts. For example, Plewa and colleagues (2008) performed an analysis of 13 HAMs identical in study design to their 2007 analysis of HANs by Muellner et al. (2007). In the HAM study, they found all species to be cytotoxic and 12 of 13 species to be genotoxic, with more cyto- and genotoxic potency related to increasing iodo- and bromo- substitution. As a class, the authors determined HAMs were 142 times more cytotoxic than HAA5 and two times and 1.4 times more cytotoxic than HANs and HNMs, respectively. With regard to genotoxic potency, HAMs as a class were 12 and 2.2 times more genotoxic than HAA5 and HNMs, respectively (Plewa et al. 2008).

Although shown to be weakly mutagenic in bacterial assays, the group of nine HNMs were found to be potent genotoxicants in mammalian cells. In a comparative quantitative analysis, the rank order of genotoxicity was dibromo- > bromodichloro- > tribromo- > trichloro- > bromo- > dibromochloro- > bromochloro- > dichloro- > chloro-nitromethane, again indicating that bromine substituted and mixed bromo-chloro-nitromethanes were more genotoxic than chlorinated nitromethanes alone (Richardson et al. 2007). Figure 2.4 shows

the cyto- and genotoxicity of HAN, HAM, and HNM classes, relative to regulated and other HAAs.



Source: Plewa et al. 2008.

Figure 2.4: Toxicity of some important N-DBP classes relative to HAAs

In summary, unregulated and emerging classes of DBPs, particularly iodo- and bromo-substituted compounds and N-DBPs, are, in general, more toxic than the 11 DBPs currently regulated. Furthermore, relative to disinfection with chlorine, many of the disinfection alternatives sought to mitigate formation of the regulated constituents result in elevated formation of some of these more toxic DBPs. As the toxicological and epidemiological data expands for these and other classes of DBPs not included among the regulated DBP species, it is likely that new regulations will evolve to further address the formation and control of DBPs beyond those presently regulated.

CHAPTER 3: MATERIALS AND METHODS

3.1. GENERAL APPROACH

Raw waters from drinking water utilities using surface sources were sought to populate elements of the enhanced coagulation matrix according to TOC and alkalinity (see Chapter 2, Table 2.6). Waters were requested such that the study would represent good geographic distribution across the US, samples from both lake/reservoir and river sources, and seasonal variation. It was the intention that each element would be represented by two waters, but due to constraints, this aim was later modified such that selected waters encompassed the range of TOCs and alkalinities encountered in the matrix.

Upon receipt of each water, TOC/TN, DOC/TDN, UV_{254}, pH, alkalinity, and turbidity were measured and a jar test was performed with alum to determine the optimal coagulant dose for turbidity and TOC removal. Following the satisfaction of pre-defined coagulation removal criteria, 6-8 L of raw water were coagulated in 2 L vessels with the determined alum dose and combined to generate a uniform bulk sample for all subsequent analyses. Chlorine demand studies were performed on raw and treated waters. After chlorination of raw and treated waters according to Uniform Formation Conditions as described by Summers et al. (1996), THM4 and selected N-DBPs were analyzed to establish DBP formation potentials. For comparison to raw water characteristics, coagulated samples were analyzed for TOC/TN, DOC/TDN, UV_{254}, pH, and turbidity. Each raw and treated water was also analyzed for humic content (HPOA) using XAD-8 resin, fluorescence index (FI), and inorganic nitrogen

concentration to calculate DON content. The schematic in Figure 3.1 provides an overview of the study framework.

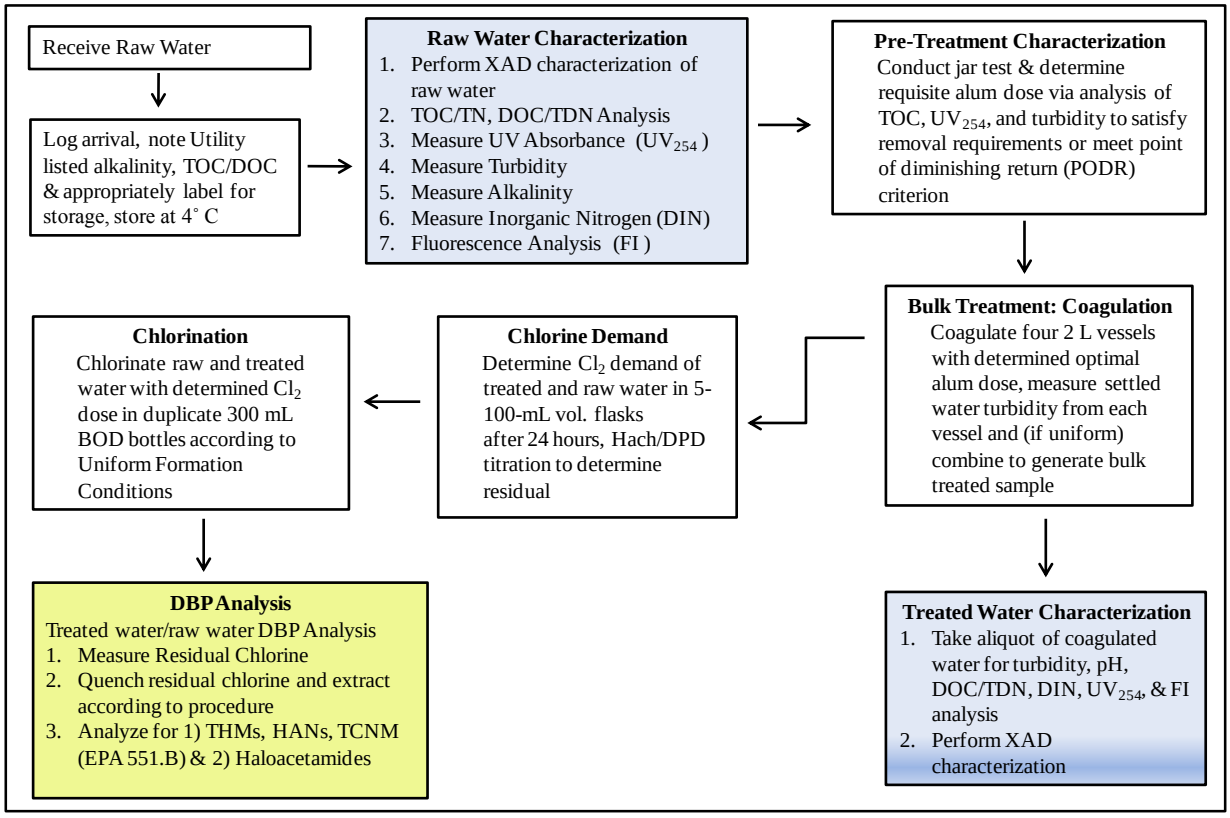


Figure 3.1: General experimental approach

3.2. EXPERIMENTAL PROCEDURES

3.2.1. Laboratory-Grade Water

Water from one of two sources was used for the make-up of aqueous reagents, the cleaning of glassware, and the utilization of water for any other purpose. In-house deionized water (DIW) was produced from tap water by a combination of reverse osmosis, GAC filtration, mixed-bed resin deionization, and UV oxidation. Unless noted otherwise, tap water or DIW was used only for glassware cleaning and rinses prior to acid-bath and/or final rinses with high-quality deionized, organic-free water, respectively. Deionized organic-free water, referred to henceforth as laboratory-grade water (LGW), was generated in the laboratory by

passing in-house DIW through a Dracor (Durham, NC) treatment system which consisted of a 1.0 μm pre-filter, 0.5 ft^3 of activated carbon, and two mixed-bed deionizer resins. The Dracor system components were exchanged with new, recharged components twice a year.

3.2.2. Glassware and Reagents

All glassware, scoopula, volumetric pipette tips (if re-used), or other laboratory equipment was thoroughly cleaned prior to use according to the following laboratory protocol:

(1) overnight bath in tap water containing ~10% Alconox detergent (White Plains, NY)
(2) three tap water rinses
(3) 1-2 rinses with LGW or DIW
(4) overnight bath in 10% nitric acid (HNO_3)
(5) 3-5 rinses with LGW, and
(6) inverted or placed in an oven to dry.

In the case of glassware known to be clean and/or to be used repeatedly during a day, a rinse with 10 or 20% HNO_3 for volumetric and non-volumetric glassware, respectively, followed by five rinses with LGW, and oven-drying was typical. For dilute aqueous mixtures, drying was not necessary, and likewise, acid-rinse was often omitted according to end-use. In all cases, chlorine-demand-free glassware (see below) was omitted from acid-bath or acid-rinse once it had been made chlorine-demand-free. Acid baths were changed out approximately every six months, wherein concentrated HNO_3 (Fisher Scientific, Fairlawn, NJ), was added to the previously determined volumes of LGW in three respective Nalgene vessels, such that the final concentration was 10% HNO_3 by volume. If not identified specifically, all reagents were ACS-grade or higher.

Steps 4-6 were omitted for volumetric glassware due to concerns about changing their calibrated volume. Likewise, carboys/cubitainers and other especially large containers, and

metallic equipment, were not subjected to the acid bath. In place, a rinse with 10 or 20% HNO_3 as described previously, followed by 5 rinses with LGW and, if necessary to de-water, a final methanol (Fisher Scientific, Fairlawn, NJ) rinse and inversion.

For DBP analysis, high-purity, HPLC-grade methanol (Fisher Scientific, Fairlawn, NJ) or MS-grade methanol (Mallinckrodt Baker, Phillipsburg, NJ) was utilized for de-watering. If the glassware was put into use immediately, this de-watering step was often followed by two rinses with make-up solvent methyl-t-butyl ether (MtBE; EDM Chemicals Inc., Gibbstown, NJ).

Vials for TOC analysis, because of their frequent use and small size relative to most glassware in use, had a separate bath to avoid breakage or any potential cross-contamination. After the acid bath, TOC vials were rinsed five or more times with LGW and placed in the oven overnight to dry. Clear 60-mL glass sample vials (EP Scientific, Miami, OK) for DBP analysis were treated in like manner as other glassware, but as with the 20-mL TOC vials, were rinsed copiously in all steps with LGW and placed in an oven to dry. Caps for these sample vials and any other plastic caps were treated according to standard protocol but were not subjected to the oven for drying, and were inverted and placed in a hood overnight or longer.

Chlorine demand-free glassware was prepared by submerging glassware overnight in a bath containing 200-500 mg/L (as Cl_2) sodium hypochlorite prepared from 4-6% stock sodium hypochlorite (Fisher Scientific, Fairlawn, NJ) and LGW. The glassware was then rinsed 3-5 times with LGW and air-dried. This glassware was only used for the chlorination experiments. Chlorine demand-free glassware was cleaned between experiments by rinsing three or more times with LGW since it no longer had a chlorine demand. The following

chlorine demand-free glassware was prepared: 100-mL volumetric flasks and glass stoppers, 300-mL BOD bottles and glass stoppers, and beakers (50- and 100-mL).

3.2.3. Sample Collection, Handling and Care

With the exception of Lake Michie (Durham, NC) raw water that was obtained by the author in person at the water treatment plant (WTP), raw water samples were obtained directly from the selected utilities by overnight shipping with Federal Express (FedEx). Utility personnel were first notified by the author of an outgoing cooler shipment from the laboratory which contained instructions and a prepaid FedEx shipping label for return to UNC, blue ice to be frozen at the WTP prior to return shipment, and two LDPE carboys (cubitainer; EP Scientific, Miami, OK). Cubitainers were cleaned as described previously in §3.2.2 and labeled prior to shipment. Other relevant instructions included:

(1) rinsing the containers twice prior to filling
(2) taking raw influent water prior to the addition of any treatment chemicals
(3) listing the date and time of sample collection, and if possible, the most current TOC and alkalinity data
(4) after adding the frozen blue ice, samples, information sheet, placing the prepaid return shipping label in the sleeve affixed to the cooler top, and taping the cooler for return shipment.

Upon return of the coolers to UNC, containers were checked for leaks and placed in a cold room for dark storage at 4°C until processing or further analysis. Except for aliquots taken for treatment or analysis, all samples were maintained in a cold room or laboratory refrigerator.

In order to obtain representative, homogenous aliquots of sample raw water, containers were thoroughly agitated prior to pouring or siphoning any water for treatment or analysis. If aliquots were taken by siphon, the clean polyurethane tubing was placed in the upper half of

the container to avoid obtaining a disproportionate amount of large, aggregated or otherwise rapidly-settling particles. Aliquots taken were often removed from cold storage and placed in dark storage within the laboratory to bring them to ambient temperature before treatment. In some cases, sample containers were placed in a shallow bath of warm water to accelerate their return to room temperature. The containers were removed from the bath before the water temperature increased above ambient room temperature (20°C).

3.2.4. Preliminary Jar-Testing with Alum

Preliminary coagulation jar-test experiments were conducted with aluminum sulfate ($Al_2(SO_4)3{\cdot}12\text{-}14H_2O$), (alum; Fisher Scientific, Fair Lawn, NJ). A 2,500 mg/L alum dosing solution was prepared by weighing the appropriate amount of alum using an Ohaus AR2140 analytical balance (Ohaus Corp., Pine Brook, NJ) and adding the alum to a 1-L or 0.5-L volumetric flask which was filled with LGW. A magnetic stir bar was used to agitate the alum stock solution for 15 minutes to ensure complete dissolution. Alum was delivered by 1-10 mL variable-volume micropipette (Socorex Isba S.A., Lausanne, Switzerland). Six different alum doses were chosen based on raw water characteristics. Five hundred milliliters of homogenous sample was added to each 600-mL glass beaker with a sampling port positioned 3 in. below the top of the beaker. The beakers were then rapid-mixed two at a time for one minute with a magnetic stir bar and stir plate before being stirred using a Phipps and Bird (Richmond, VA) six-paddle stirrer together for 10-15 seconds at 100 RPM for uniformity and then for 20 minutes at 35 rpm. The rectangular stainless steel paddles were 2x1inches.

After 20 minutes of slow mixing, the paddle was lifted out of the jar and the sample was allowed to settle undisturbed for 30 minutes. Following 30 minutes of quiescent settling, the supernatant was withdrawn from the beaker through the sample port into labeled duplicate

40-mL vials, a labeled TOC vial and a labeled amber bottle. The first 10-20 mL of sample was always discarded. Each dosed sample, as well as the raw water sample, was then analyzed for turbidity, TOC/TN, and UV_{254}.

3.2.5. Bulk Coagulation of Raw Water

The criteria for choosing an appropriate alum dose for bulk coagulation were based primarily on turbidity removal and TOC removal, but UV_{254} absorbance was also considered. For coagulation, the Stage 1 and Stage 2 enhanced coagulation requirements define PODR as the point at which a 10 mg/L increase in the alum dose results in less than 0.3 mg/L of TOC removal (EPA 1999b). The alum dose chosen had to result in a settled water turbidity below 2 NTU and be at or near the PODR. In addition, the dose selected for bulk treatment was often at or near the UV_{254} absorbance and turbidity minima. If such conditions did not appear to be met in any of the first six doses, additional alum doses were selected as necessary.

Once the requisite alum dose was established, raw water was coagulated in bulk to generate enough coagulated water to perform chlorination experiments, with 2-3 L remaining for analytical characterization. The bulk coagulation experiments were identical to the preliminary coagulation experiments in mixing rate, flocculation duration, and settling time, except that rather than using 600-mL beakers, larger (2-L) vessels were used and mixed with 3x1 in. paddles. To generate 6 L of treated water, four 2-L square jars (Phipps and Bird Inc., Richmond, VA) fitted with a sampling port located 4 in. below the fill line were necessary. Experience showed that a 10% increase of the requisite alum dose for the bulk treatment over that determined from the jar test resulted in treated water more representative of TOC, turbidity, and UV_{254} obtained during the preliminary jar-testing. This is likely due to the different shape of the vessel or the 3:1 rather than 2:1 proportionality of the stirring paddles used in bulk treatment compared to the smaller beakers. Also, due to the larger volume of

raw water, alum stock solutions were typically 5-10 g/L such that the same 1-10 mL variable-volume micropipette could be employed. Alum stock solutions were prepared daily. After settling, the treated samples were withdrawn from each vessel through the sampling port and combined for homogeneity and subsequent TOC, UV_{254} absorbance, and turbidity analysis. The remainder of the sample was set aside for chlorination and residual DOC characterization and DON analysis.

3.2.6. Chlorine Demand and Chlorination under Uniform Formation Conditions

Raw and treated waters were chlorinated in a manner consistent with Uniform Formation Conditions (UFC), as described by Summers et al. (1996), with solutions generated from a 4-6% sodium hypochlorite stock solution (NaOCl; Fisher Scientific, Fair Lawn, NJ). A 250-mL working solution was generated with 4-8 mL stock NaOCl in LGW using a chlorine demand-free (see § 3.2.2) volumetric flask. This working solution was standardized according to Standard Method 4500-Cl-B (APHA et al. 1998), in which stock solution strength is determined by titration with 0.1 N standard sodium thiosulfate (Fisher Scientific, Fair Lawn, NJ). A 200-mL dosing solution was then generated in a chlorine demand-free volumetric flask, after addition of pH 6.7 borate buffer in a 4-5:1 volume ratio with the chlorine working solution and LGW. The targeted strength of the dosing solution was determined according to the anticipated range of required doses. The Cl_2 dosing solution was applied to either 100-mL volumetric flasks (chlorine demand studies) or headspace-free 300-mL BOD bottles (DBP formation potential experiments) with a 1-10 mL variable volume micropipette. For very low chlorine doses, a 0.1-1 mL Fisherbrand Finnpipette was used (Fisher Scientific, Fair Lawn, NJ). The dosing solution strength was verified by triplicate DPD titration according to Standard Method 4500-Cl-F (APHA et al. 1998). The volume of NaOCl dosing solution

necessary to achieve the desired doses was calculated according to make-up in either 100- or 300-mL vessels containing raw and treated waters buffered with 0.2 mL or 0.6 mL pH 8 borate buffer, respectively. Flasks and BOD bottles were filled to ~85% of capacity with sample before buffer or chlorine dosing solution addition, then inverted three times, filled to capacity with sample, and again inverted 5-7 times. As noted previously, chlorine demand studies were performed with labeled, 100-mL chlorine demand-free volumetric flasks and were filled to the meniscus. DBP formation potential experiments utilized labeled, chlorine demand-free, 300-mL BOD flasks. After final pH adjustment to 8 ± 0.2 with 0.1 N HCl or 0.1 N NaOH, the chlorination flasks were filled to absolute capacity to render the samples headspace-free once the glass stopper was in place.

Chlorine demand studies and DBP formation potential experiments, as per UFC requirements, were incubated for 24 ± 1 hours, in a dark, 20°C constant temperature room. Following the incubation period, the chlorine residual was determined using DPD titration as described previously or with a Hach (Loveland, CO) free chlorine test kit and colorimeter. Experience showed that the test kit consistently generated values within 5% of those obtained by DPD titration. The Hach kit was preferable as it required substantially less volume of sample, generated less glassware, and was quicker overall. In order to determine the appropriate chlorine dose for chlorination experiments and DBP analysis, preliminary Cl_2 demand studies were carried out. Chlorine demand studies were concluded after measuring chlorine residual among the three or four different doses and charting dose and residual to determine a dose producing a free residual of 1.0 ± 0.4 mg/L as Cl_2. This was the dose selected for the DBP formation potential experiments. In a few isolated cases, especially with

waters known or believed to contain relatively high amounts of either DON or ammonia (NH_3/NH_4^+), additional chlorine demand studies with higher doses were required.

At the conclusion of the incubation period for DBP formation potential experiments, the sample bottle was inverted 5 times before filling to capacity two labeled 60-mL vials containing 10-15 mg of ACS-grade granular ammonium sulfate ($(NH_4)_2SO_4$; Mallinckrodt Baker, Phillipsburg NJ) to quench residual free chlorine. The headspace-free 60-mL vials were sealed tightly with PTFE-lined screw caps and stored in a refrigerator at 4°C for subsequent DBP analysis. Analysis of residual free chlorine was performed with sample remaining in the BOD bottle using a Hach free chlorine DPD test kit.

3.3. ANALYTICAL METHODS

3.3.1. Turbidity

Turbidity was measured with a Hach 18900 ratio turbidimeter (Hach Company, Loveland, CO). Before use, the turbidimeter was checked with a set of solid turbidity standards (Gelex Turbidity Standard, Hach Company, Loveland, CO), and verified with an aqueous turbidity standard every 6 months. Prior to extracting a sample for turbidity measurement, the sample was gently shaken to ensure a representative aliquot.

3.3.2. Alkalinity

Alkalinity was measured by standard sulfuric acid (H_2SO_4) titration in the presence of bromcresol green–methyl red alcoholic indicator solution (LabChem Inc., Pittsburgh PA) in the manner described under Standard Method 2320 (APHA et al. 1998). Following the addition of six drops of indicator to 50-mL of raw water in a 100-mL beaker, 0.02 N standard H_2SO_4 (Fisher Scientific, Fair Lawn NJ) was added drop-wise while stirring with a magnetic stirrer until the sample turned from green to the pink endpoint. The alkalinity titration was performed in duplicate unless there was more than a 5% relative percent difference (RPD)

between the two analyses, in which case a third titration was performed. The alkalinity reported was the average of the measured values.

3.3.3. pH

pH was measured using an Accumet AB-15 electronic pH meter with an Accumet electrode (Fisher Scientific, Fair Lawn NJ). The meter was calibrated daily using pH 4, 7, and 10 buffer solutions (Fisher Scientific, Fair Lawn NJ). The electrode was refilled with saturated potassium chloride solution (Fisher Scientific, Fair Lawn NJ) whenever the fluid level fell below half full. All buffers and samples were stirred either with a magnetic stirrer or by manually moving the electrode through the sample to ensure a stable and accurate pH measurement.

3.3.4. UV-Visible Absorbance

Unless otherwise noted, ultraviolet(UV)/visible(Vis) absorbance measurements were performed using a dual beam Hitachi U-2000 spectrophotometer (Hitachi Instruments Inc., Danbury, CT) and 1-cm quartz cells. Before measurement, the instrument was turned on and, according to laboratory instrument protocol, reference values were input from the A/D calibration menu. Subsequently, a wavelength scan was performed with sample cells absent. After warming up for a minimum of 30 minutes, the desired wavelength was input and the instrument was zeroed using LGW in both sample and reference cells, wiped with a tissue after each handling. Between each measurement, the sample cell was rinsed 2-3 times with LGW, and once with a small volume of sample before being returned to the sample compartment. The UV/Vis absorbance was reported once a stable reading was obtained, except during instances in which there was oscillation in the final absorbance value, in which case the mid-point was recorded. Following every analysis, the sample cell was refilled with LGW and any drift from zero was recorded. This drift was rarely encountered above 0.5-1%

of the measured absorbances. For analyses over 30 min in duration, the reference cell was either removed and set aside to cool, or between non-consecutive analyses, the instrument was auto-zeroed after each cuvette was refilled with LGW. Periodically, sample cells were left overnight in LGW to prevent the likelihood of scale formation after periods of intense use.

Ultraviolet Absorbance at 254 nm

Following Standard Method 5910 (APHA et al. 1998), water samples were characterized by UV_{254} absorbance. Prior to analysis, all samples were filtered through either pre-rinsed 0.45 μm membrane filters (Pall Corporation, Ann Arbor, MI) or with PVDF or PTFE syringe filters (Whatman, Inc., Piscataway NJ; Fisher Scientific, Fair Lawn NJ, respectively). A filtered sample was then taken for UV analysis using a 1-cm path length quartz cuvette. The cuvette was rinsed twice with LGW and then twice with filtered sample prior to measuring UV absorbance at 254 nm.

3.3.5. Organic Carbon and Total Dissolved Nitrogen Analysis

Measurements of organic carbon and total- and dissolved nitrogen (TN and TDN), respectively, were made on a Shimadzu TOC 5000 Analyzer with Total Nitrogen Module (TNM-1) and an ASI 5000 autosampler (Shimadzu Corporation, Atlanta, GA). The instrument measures non-purgeable organic carbon according to the High Temperature Combustion Method (APHA et al. 1998) in which organic carbon is converted to CO_2 and quantified by a nondispersive infrared detector. In sequence with TOC analysis, the nitrogen module accomplishes analysis of TN by high temperature combustion and subsequent oxidation in an oxygen-rich combustion tube with platinum catalyst at high temperature. Bound nitrogen is converted to nitrogen monoxide (NO), further oxidized to nitrogen dioxide (NO_2) and quantified by a chemiluminescence detector as NO_2^* descends from its excited

state. Measurement of DOC and TDN was obtained in the same manner as TOC/TN, except the sample was first passed through a pre-rinsed 0.45 μm membrane filter, as for UV_{254} analysis, to remove particulate material.

A stock standard solution of organic carbon was prepared by dissolving 2.125 g of ACS-grade potassium hydrogen phthalate (Fisher Scientific, Fair Lawn, NJ) into 1 L of LGW to yield a resulting concentration of 1,000 mg/L as C. Likewise, a 1,000 mg-N/L TN stock standard solution was prepared by adding 7.219 g potassium nitrate (KNO_3; Fisher Scientific, Fair Lawn NJ) to a 1-L volumetric flask and filling to the meniscus with LGW. Each stock standard solution was re-made every 2 months and mixed thoroughly prior to use. From the respective stock solutions, a combined 100 mg C/L and 100 mg-N /L working solution (primary standard) was prepared by quantitative delivery of each solution into a 100-mL volumetric flask. Prior to filling the flask, 2.5 mL of 2 N HCl were added with a 0-5 mL glass pipette to preserve the solution for up to 7 days. Both the stock and working solutions were stored at 4°C.

On the day of analysis, four calibration standards were made from the working solution: 0, 0.5, 5, 10 mg/L for TOC/DOC and 0, 0.05, 0.5, 5 mg/L calibration standards for TDN. Calibration standards and samples were transferred to 20-mL TOC vials, acidified with 6-8 drops of 2 N HCl, covered with parafilm, and placed on the autosampler tray. The first 2-3 vials contained LGW, followed by the calibration standards, 1-2 rinse vials containing LGW, a 2 mg/L check standard (not included in the calibration), and the samples of interest. After every 4-6 samples, a check standard and rinse were analyzed to verify the calibration, collect a measure of variance, and verify instrument performance and accuracy. At the end of the analysis, 5 and 10 mg/L check standards and 2-3 blank vials were analyzed to verify that the

instrument maintained calibration throughout the run. Prior to injection, each sample was sparged by the instrument for five minutes with zero-grade air (National Welders Supply Co., Durham, NC) to remove inorganic carbon before analysis. Reported values for each sample represent the average of three injections made by the instrument.

3.3.6. Inorganic Nitrogen

A number of different approaches were sought to quantify dissolved inorganic nitrogen (DIN), such that dissolved organic nitrogen (DON) could be determined. Dissolved organic nitrogen, as noted in Chapter 2, is calculated as TDN – DIN, where DIN is the sum of nitrite/nitrate (NO_2^-/NO_3^-) and ammonia (NH_3/NH_4^+). Due to poor reproducibility, the use of Hach rapid methods and the removal of DIN by dialysis pretreatment were ultimately abandoned in place of standard methods.

Nitrite/Nitrate

Nitrite and nitrate were measured in combination by cadmium reduction of NO_3^- and colorimetric analysis of NO_2^- according to Standard Method 4500-E (APHA et al. 1998). In this method, NO_3^- is reduced to NO_2^- by passing the sample through a column of cadmium granules coated with copper sulfate. After passing through the column, NO_2^- is then determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye that is measured colorimetrically with a standard curve. Two identical cadmium reduction columns were used in parallel to expedite the procedure. Using the potassium nitrate primary standard described above for TN (§3.3.5.), secondary standards were made by quantitative delivery of 1.25, 2.5, 6.25, and 10 mL and diluting to 100 mL with LGW to generate concentrations of 0.05, 0.1, 0.25, and 0.4 mg/L NO_3^- as N, respectively. The secondary standards were passed through the cadmium reduction columns and then used to generate a standard curve for each column

employed, with LGW as the blank. Sulfanilamide solution was generated by adding 5 g sulfanilamide to a mixture of 50 mL concentrated HCl and 300 mL LGW and diluting to a final volume of 500 mL with LGW. The naphthyl ethylenediamine solution consisted of 0.5 g N-(1-naphthyl)-ethylenediamine dihydrochloride dissolved in 500 mL LGW.

Using raw water TDN measurements to estimate NO_3^- concentration, raw and treated samples were diluted to ensure they would fall within the calibration range. Five mL of buffer solution was added to 50 mL of each standard and sample before introduction to either of the cadmium reduction columns. The buffer solution consisted of 100 g ammonium chloride (NH_4Cl), 20 g sodium tetraborate, and 1 g disodium dihydrate EDTA dissolved in 1 L LGW. Before introduction of any sample or standard, 50 mL of buffered LGW was passed through the duplicate columns, at a flow rate of 6 mL/min, using a Masterflex pump. Between standards, 10 mL of buffered LGW was passed through the columns to prevent carry-over from the previous run. After discarding the first 10-15 mL of each standard, three 5 mL aliquots of column effluent were collected approximately 2-3 minutes apart. Samples were passed through the column in like manner, with two 5-mL aliquots taken for analysis. While preparing the column for the next standard or sample with LGW and buffer, 100 µL sulfanilamide solution was added to each 5 mL aliquot and mixed. After 5 min, 100 µL naphthyl ethylenediamine solution was added for colorimetric analysis no more than 2 h later. Colorimetric analysis was performed at 543 nm with LGW in the reference cell. If the absorbance obtained was greater than 1.2, the solution was diluted by one half with LGW and re-measured. The absorbance measurements for the nitrate standards were used to generate a standard curve for each column. The column-specific standard curves were used to convert absorbance measurements of the samples to their NO_3^- and NO_2^- concentration. The

extinction coefficient was used with the equation of the standard curve and then multiplied by the dilution factor to generate the NO_2^- concentration. The concentrations reported are the sum of both NO_3^- and NO_2^- and represent the average of the two sample aliquots.

Ammonia/Ammonium

Duplicate raw and treated water samples were analyzed according to Standard Method 4500-NH_3 F (APHA et al. 1998). In this method, a blue compound, indophenol, is formed by the reaction of ammonia, hypochlorite, and phenol, as catalyzed by sodium nitroprusside. Phenol solution was made by dissolving 5.0 g phenol into 95% ethyl alcohol. Sodium nitroprusside reagent was generated by adding 0.25 g $Na_2[Fe(CN)_5NO]\cdot 2H_2O$ to 50 mL LGW. Oxidizing solution was made by adding 25 mL stock NaOCl to 100 mL of alkaline reagent, consisting of 25 g sodium citrate and 1.25 g NaOH dissolved into 125 mL LGW. To a 5-mL sample volume, 0.2 mL phenol solution was added and the solution was mixed. This was followed by 0.2 mL nitroprusside, mixing, and then 0.5 mL oxidizing solution, after which the sample was mixed and capped. After a reaction period of 1 hour, the NH_3/NH_4^+ content of the samples was determined colorimetrically at 640 nm in a 1-cm cell with a standard curve. The standard curve was developed as follows. Stock standard NH_4^+ solution was generated by adding 0.4279 g NH_4Cl to 1 L LGW. From the stock solution, a primary standard solution was made by adding 5 mL to 500 mL LGW, resulting in 0.08 µmol NH_4^+ as N. Secondary standards were then made by adding 1, 2, 4, 8, and 12 mL of primary standard to 100 mL LGW, resulting in 0.8, 1.6, 3.2, 6.4, and 9.6 µM NH_4^+ as N standards, respectively. Using LGW as the blank, a standard curve was made from the secondary standards after reagent addition, reaction, and analysis as described.

3.3.7. Dissolved Organic Nitrogen

As noted previously, DON was determined by subtracting DIN from TDN. After determining the concentration of NO_2^-/NO_3^- (as N) and NH_3/NH_4^+ (as N) of the raw and treated waters as described above, DON (mg/L as N) was calculated as follows:

$$DON = TDN - NO_2^-/NO_3^- - NH_3/NH_4^+ \quad \text{(Equation 3.1).}$$

As discussed in Chapter 4, waters impacted by high DIN concentration relative to TDN are subject to more uncertainty in the concentration of DON reported.

3.3.8. Residual Chlorine

The free chlorine residual from UFC chlorination experiments was measured with a Hach Pocket Colorimeter (Hach Company, Loveland CO) and DPD reagent. Prior to each use, the colorimeter was zeroed using sample prior to adding reagent. The range of the instrument was 0 to 2.2 mg/L as Cl_2.

3.3.9. Dissolved Organic Matter Characterization by XAD-8 Fractionation

Dissolved organic matter was characterized by its relative proportion of hydrophilic and hydrophobic organic acid content using an XAD fractionation procedure similar to that described by Thurman and Malcolm (1981) and Aiken et al. (1992), with the principal modifications being those described by Boyer (2004). An approximate 1.3-L aliquot of each raw and coagulated water was filtered through a 0.45 µm membrane filter (Pall Corporation, Ann Arbor, MI) previously rinsed with 1 L LGW and a small volume of sample. For especially turbid raw waters, it was necessary to use pre-rinsed 2 µm and 0.7 µm glass fiber filters in series to remove particulate material and render the sample fit for the final 0.45 µm filter. Each sample was then acidified to a pH of 1.8-1.9 using concentrated HCl to protonate functional groups within the DOM. The sample was then preserved by storage at 4˚C in a 1-L amber glass bottle for later characterization and analysis.

The fractionation procedure was performed using a Masterflex pump (Cole-Parmer, Vernon Hills, IL), and one of two identical Kontes 30-cm glass columns (Kimble Chase, Vineland, NJ) with an internal diameter of 7 mm. The columns contained ~12-15 cm^3 of Amberlite XAD-8 resin (Rohm and Haas, Philadelphia, PA) bordered by a 5-10 mm section of acid-washed glass wool to prevent resin loss during fractionation or reverse-flow. The resin was cleaned and conditioned with 3-5 bed volumes of 0.1 N NaOH and 0.1 N HCl in three alternating cycles of each solution. Because the top 30-50% of the resin bed length would discolor after sample passage (indicative of DOM adsorbed to resin), two reverse-flow solution cycles were used to clean the resin following sample fractionation. While fluidizing the bed in the process, experience showed that this reverse-flow step more rapidly eluted the hydrophobic retentate and facilitated a cleaner, more uniform bed volume for subsequent fractionations. The bed was then re-packed by returning to down-flow operation for 1-2 pre-conditioning cycles at a high flow rate (12-15 mL/min). After packing, the resin bed was inspected for any bubbles or cavities and the flow was adjusted to ~4 mL/min for the conditioning cycles as described above. Prior to sample introduction, the bed was inspected for any significant discoloration and the ~4 mL/min flow rate was verified.

Filtered and acidified, each raw and coagulated water was passed through the XAD-8 column to quantify the humic/nonhumic distribution. The first 3-4 bed volumes of sample effluent were discarded to obtain a representative characterization free from any residual cleaning/conditioning solution. To prevent the columns from running dry, a simple power adapter with timer function was used to turn off the pump after 3.8 hours if it was not being directly monitored. Once the entire sample volume had been passed through the column, 100-200 mL was retained in a labeled amber glass bottle for subsequent analysis of DOC.

The hydrophobic acid moiety is retained by the XAD-8 resin, while the effluent DOC consists of the hydrophilic and transphilic (nonhumic) fraction. Thus, the difference in DOC between the column effluent and influent represents the HPOA fraction of the DOM, expressed as the characteristic %HPOA as follows:

$$\%HPOA = \frac{DOC_{influent\ water} - DOC_{effluent}}{DOC_{influent\ water}} \times 100 \qquad \text{(Equation 3.2).}$$

3.3.10. Excitation-Emission Fluorescence Spectroscopy

Raw and coagulated waters were filtered through pre-rinsed 0.45 μm PVDF or PTFE syringe filters prior to analysis, and placed in a 1-cm quartz cuvette. The absorbance spectrum of each sample over wavelengths from 200 nm to 700 nm (in increments of 2 nm) was measured using a Hewlett Packard Model 8452A diode array spectrophotometer (Hewlett Packard Co., Cary, NC). For the first batch of samples, a Fluoromax-4 fluorometer (Horiba Jobin Yvon, Inc., Edison, NJ) equipped with a xenon lamp and photomultiplier tube detector was used to generate excitation-emission fluorescence spectra (EEMs). For the second batch of samples, a Fluorolog FL3-2iHR with CCD detector (Horiba Jobin Yvon, Inc., Edison, NJ) was used in the FI scan mode. Using the parameters described by Cory et al. (2010), water samples were excited across wavelengths of 240 to 450 nm in increments of 5 nm, and fluorescence emissions were measured at 320 to 500 nm in increments of 2 nm. The slit width for both excitation and emission was 5 nm.

All processing of EEMs data was done in Matlab (v 7.7) following the procedures of Cory et al. (2010) in which the absorbance spectrum of each sample was used to remove potential interference in the EEMs due to the inner-filter effect caused by strongly absorbing carbon in the sample (Mobed et al. 1996). Blank EEMs of LGW were then subtracted from the sample EEMs to minimize Rayleigh and Raman scattering peaks, after checking to verify that there

was no detectable fluorescence in the LGW EEMs. All EEMs were corrected for instrument-specific response using excitation correction factors generated with rhodamine (DeRose et al. 2007) and manufacturer-generated emissions correction factors. EEMs were normalized to the area of the Raman peak in the blank EEMs at an excitation wavelength of 350 nm; thus EEM intensities are reported as Raman Units (Stedmon and Bro 2008). The fluorescence index (FI; McKnight et al. 2001) was calculated from each EEMs as the ratio of the emission intensity at 470 nm to that at 520 nm at an excitation wavelength of 370 nm (Cory et al. 2010). Because of the different characteristics of fluorophores found in terrestrially- and microbially-derived fulvic acids, the FI offers insight into the nature and origin of the DOC in the water. FI values less than 1.30 indicate terrestrial carbon, while values greater than 1.45 reflect microbially-derived carbon (Cory et al. 2010, McKnight et al. 2001).

3.3.11. Analysis of Selected DBPs

Liquid-Liquid Extraction

Following chlorination and quenching of the samples as indicated in §3.2.6, DBPs were separated via liquid-liquid extraction similar to Standard Method 6332 (AHPA, 1998). While the method indicates that quenched samples can be extracted up to two weeks later, due to concerns of degradation among select DBP species, samples underwent extraction immediately after residual chlorine analysis. A 30-mL aliquot was taken from each 60-mL volume of quenched sample for duplicate extraction and the excess quenched sample was used to rinse a 50-mL graduated cylinder between sample processing. To prevent volatilization of target compounds, the 30-mL sample volume was measured by carefully pouring down the side of a 50-mL graduated cylinder and transferred in like manner into a 60-mL extraction vial with PTFE-lined screw cap.

After each sample had been transferred to duplicate extraction vials, 5-6 drops of 0.2 N H_2SO_4 were added to each vial to lower the pH to 2-3, then 3 mL of MtBE/internal standard extraction solvent (described below) was added using a repipetter and the vials were re-capped. Approximately 4 g sodium sulfate (Na_2SO_4) was added to the extraction vial before re-capping and the sample was immediately mixed for one minute using a vortex mixer. To remove moisture, the Na_2SO_4 was baked for 24 hours prior to use. This procedure was repeated for each extraction vial. After the samples had separated for at least five minutes and a distinct organic layer was visible, a Pasteur pipette was used to withdraw the supernatant composed of internal standard and target analytes dissolved in the MtBE solvent. Using a fresh Pasteur pipette for each sample, the organic extract was carefully divided among two sets of labeled, duplicate 1.5 mL amber GC vials containing 500 µL glass inserts. Each GC vial was capped with a PTFE-faced cap and sealed with a crimping tool. All remaining solvent was extracted into a labeled GC vial and all vials were placed in a freezer until analysis. Calibration standards (see below) were extracted in an analogous manner.

Internal and Calibration Standards

According to the method, 1,2 dibromopropane (Sigma Aldrich, St. Louis, MO) was used as the internal standard. The extracting solvent (MtBE) was prepared by adding the internal standard to Omnisolv High Purity MtBE (EDM Chemicals Inc., Gibbstown NJ). A stock solution of the internal standard was prepared by adding 10 µL of the 2000 µg/mL 1,2 dibromopropane neat standard to MtBE in a 5-mL volumetric flask. A primary dilution of the stock solution was made by diluting 125 µL in a 5-mL volumetric flask. Finally, the extracting solvent was prepared by diluting 250 µL of the primary dilution into a 500-mL volumetric flask with MtBE. Extracting solvent was prepared fresh on the day of extraction and was placed in a 1-L amber glass jar fitted with a repipetter to facilitate dispensing of the

solution. All internal standard solutions were stored in amber glass vials in a freezer when not in use.

For GC-analysis of DBPs, because haloacetamides (HAMs) require a different temperature program than THMs and other halogenated volatile (halovolatile) DBPs, two separate sets of calibration standards were generated. The THM/halovolatile calibration standards were prepared from primary dilutions of 2000 μg/mL neat standard of both the EPA THM Calibration Standard Mixture and the EPA 551B Halogenated Volatiles Standard Mixture (Supelco, Inc., Bellefonte, PA). The two standard mixtures contain chloroform, bromoform, bromodichloro- and dibromochloromethane (THM4), and bromochloro-, dibromo-, dichloro- and trichloroacetonitrile (HAN4), trichloronitromethane (chloropicrin), 1,1-dichloro-2-propanone, and 1,1,1-trichloroacetone, respectively. Two primary standard solutions of each mixture were prepared by adding 100 μL and 20 μL of 2,000 μg/mL neat standard to 2-mL volumetric flasks and filling with MtBE. Both the stock and primary standard solutions were stored in amber vials in a freezer when not in use. Except for the two highest calibration levels, which required neat standard, the resulting 100- and 20 μg/mL THM and halovolatile primary standard solutions were used to prepare six calibration standards. To generate the calibration standards, 100-mL volumetric flasks containing ~90 mL LGW were placed in a fume hood and appropriate volumes of each standard were injected below the water surface using a gas-tight syringe. The flasks were then filled to the mark with LGW, and re-capped to be extracted as described previously. Using LGW as a blank, a typical standard curve contained 9 calibration standards ranging from of 0-400 μg/L and 0-100 μg/L for THMs and halovolatiles, respectively.

As liquid neat standards are not commercially available, dichloroacetamide (DCAM) and trichloroacetamide (TCAM) stock solutions were generated by quantitative transfer of 0.01 g ACS-grade solid standard (Sigma Aldrich, St. Louis, MO) to 5-mL volumetric flasks and filled to the miniscus with MtBE. Two primary standard solutions were then generated by adding 100 µL and 20 µL of each stock solution to 2-mL volumetric flasks containing MtBE. The combined HAMs standards were then used to generate eight calibration standards ranging from 0.4 to 50 µg/L in the manner described for THM/halovolatile standards. The calibration standards and LGW blank were extracted as described previously. The DBP species analyzed in this study and calibration ranges are presented in Table 3.1. Because samples were analyzed in two batches, separate calibration curves were prepared for each batch. Each batch had a calibration range tailored to the levels of DBPs anticipated for samples within that batch.

Table 3.1: DBPs selected for analysis and batch calibration range

General Class	DBP Analyte	Formula/ Abbreviation	Group Abbreviation	Batch #1 Calibration Range (µg/L)		Batch #2 Calibration Range (µg/L)	
				Low	High	Low	High
Trihalo-methanes	Chloroform	$CHCl_3$	THM4	1	500	1	400
	Bromodichloromethane	$BrCl_2CH$					
	Dibromochloromethane	Br_2ClCH					
	Bromoform	$CHBr_3$					
N-DBPs	Dichloroacetonitrile	DCAN	Haloacetonitrile (HAN)	1	100	0.5	100
	Bromochloroacetonitrile	BCAN					
	Dibromoacetonitrile	DBAN					
	Trichloroacetonitrile	TCAN					
	Dichloroacetamide	DCAM	Haloacetamide (HAM)	1	50	0.4	50
	Trichloroacetamide	TCAM					
	Trichloronitromethane	TCNM	TCNM	1	100	0.5	100
Other C-DBPs	1,1-Dichloro-2-propanone	11DCP	N/A	1	100	0.5	100
	1,1,1-Trichloroacetone	111TCP					

Gas Chromatographic Analysis

Standards and samples were analyzed on a Hewlett Packard Model 5890A Series II gas chromatograph (GC) with electron capture detection (Hewlett Packard Co., Cary, NC). Table 3.2 shows the characteristics of the instrument and the temperature program used for THM/volatile DBP analysis, while Table 3.3 indicates the conditions for analysis of HAMs. According to laboratory protocol, hexane and hexachlorobenzene instrument performance standards preceded analysis of standards and samples. Blanks of MtBE and the extraction solvent composed of MtBE and internal standard were placed at the beginning of each sample sequence, followed by the complete set of calibration standards and the unknown samples.

For each water of interest, duplicate extracts were analyzed to provide quality assurance. Vials containing calibration check standards and MtBE blanks were placed intermittently between groups of the unknown samples to monitor the instrument for drift. Chromatograms were analyzed by integrating the peak areas of each of the DBP species as well as the internal standard. The resulting peak areas were normalized by the area of the internal standard, and converted to concentrations using the calibration curves. Illustrative chromatograms for THM/halovolatiles and HAMs are shown in Appendix Figures A-1 and A-2. Calibration curves for $CHCl_3$, DCAN, and DCAM are presented in Appendix Figures A-3, A-4, and A-5, respectively.

Table 3.2: Gas chromatograph conditions for THM4, HANs, and TCNM

Injector:	
Syringe Size	10 µL
Injection Volume	2 µL
Injector Temperature	117 ˚C
Solvents:	
Wash Solvent	MtBE
Pre-Injection Washes	3
Post-Injector Washes	2
Pumps	3
Oven and Column:	
Equilibration Time	3 min
Maximum Temperature	300 ˚C
Carrier Gas	Helium
Flow Rate	1 mL/min
Pressure	11.3 psi
Column	Zebron ZB-1
Column Dimensions	30.0 m, 0.25 mm diameter, 1.00 µm film thickness
Split Flow	1 mL/min
Temperature Program:	
Initial temperature 35 ˚C held for 22 minutes before (1) increasing 10 ˚C/min to 145 ˚C for two minutes, (2) increase 20 ˚C/min to 225 ˚C for ten minutes, and (3) increase 20 ˚C/min to 260 ˚C for five minutes; 55.75 min total run time.	
Detector:	
Type	ECD
Temperature	290 ˚C

Table 3.3: Gas chromatograph conditions for HAMs

Injector:	
Syringe Size	10 µL
Injection Volume	2 µL
Injector Temperature	180 ˚C
Solvents:	
Wash Solvent	MtBE
Pre-Injection Washes	3
Post-Injector Washes	2
Pumps	3
Oven and Column:	
Equilibration Time	3 min
Maximum Temperature	300 ˚C
Carrier Gas	Helium
Flow Rate	1 mL/min
Pressure	11.3 psi
Column	Zebron ZB-1
Column Dimensions	30.0 m, 0.25 mm diameter, 1.00 µm film thickness
Split Flow	1 mL/min
Temperature Program:	
Initial temperature 37 ˚C held for one minute before (1) increasing 5 ˚C/min to 110 ˚C for 10 minutes, (2) increase 5 ˚C/min to 250 ˚C for one minute; 54.6 min total run time.	
Detector:	
Type	ECD
Temperature	300 ˚C

3.3.12. DBP Data Validation

As noted previously, each sample of raw and treated water was chlorinated in duplicate from which duplicate extracts were made. Thus, for each DBP analyte, four values were obtained for each raw and treated water sample. The reported concentration was the average of the four values after verifying that the relative percent difference (RPD) did not exceed

5% for THM4 or 10% for the other analytes. In cases where the RPD exceeded the limits, it was necessary to determine which value accounted for the difference and omit that value from the average.

CHAPTER 4: RESULTS AND DISCUSSION

4.1. RAW DRINKING WATER SELECTION

Thirteen waters were selected from across the U.S., encompassing the range of alkalinities and TOC values within the enhanced coagulation matrix. Table 4.1 identifies the waters collected and their placement within the 3x3 matrix. While the original intent was to

Table 4.1: Selected raw drinking waters within the enhanced coagulation matrix*

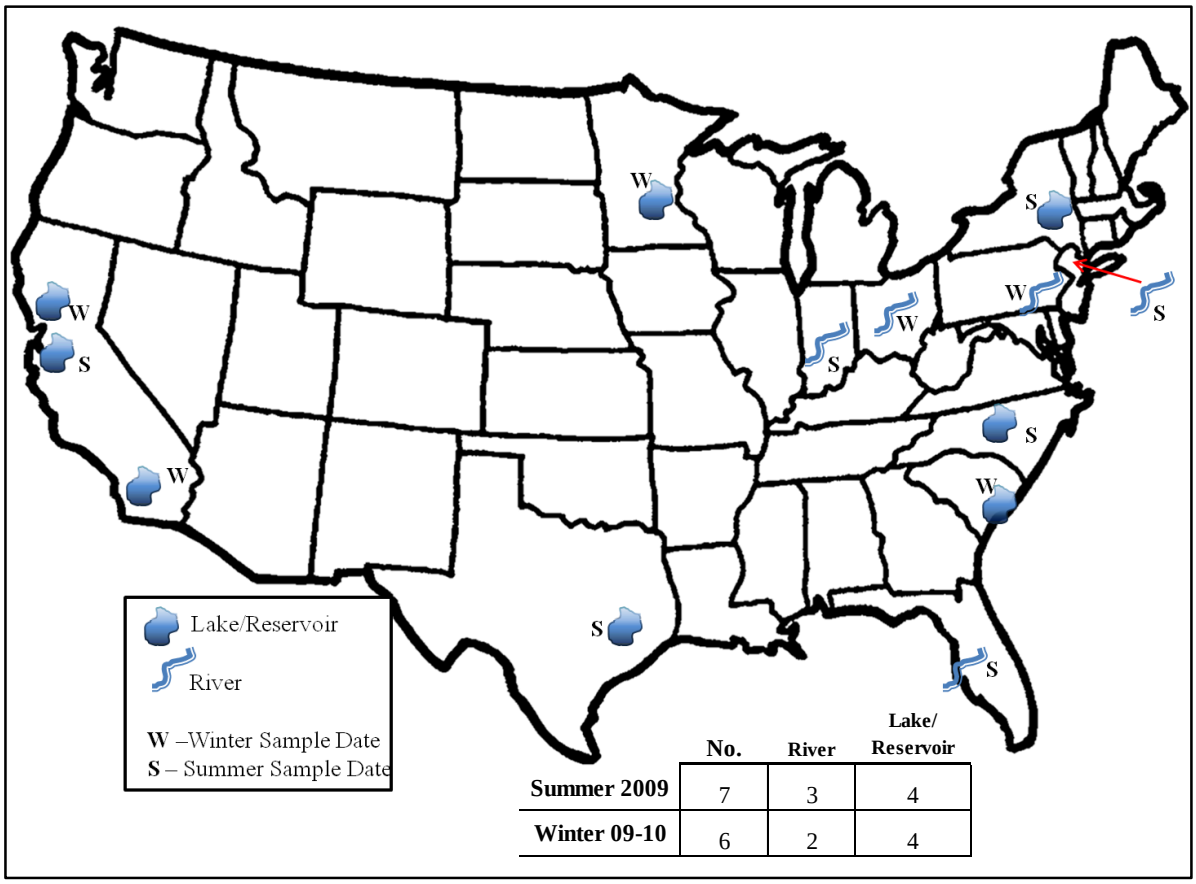
Raw Water TOC (mg/L as C)	Raw Water Alkalinity (mg/L as $CaCO_3$)		
	0 to 60	>60 to 120	>120
0 to ≤2.0	Schuylkill River, Philadelphia PA		
>2.0 to ≤4.0		Passaic River, Totowa NJ Croton Reservoir, Valhalla NY	White River, Indianapolis IN
>4.0 to ≤8.0	Lake Michie, Durham NC Bushy Park Reservoir, Charleston SC	Upper San Leandro Reservoir, Oakland CA; Scioto River, Columbus OH	Otay Reservoir, San Diego CA Vadnais Lake, St. Paul MN
>8.0	Lake Houston, Houston TX Hillsborough River, Tampa FL		Lake Campbell, San Francisco CA

*The grayed boxes are not part of the enhanced coagulation matrix as such TOC ranges require no removal action but are shown to demonstrate the position of the Schuylkill River sample.

select two waters representative of each element of the 3x3 matrix, due to timing constraints and logistics, this aim was not met. Moreover, because of the dynamic nature of water sources induced by aquatic and terrestrial biota, precipitation, seasonal, or other influences, not every element within the matrix was populated. In some cases, between dates of communication with the utility and actual sample collection, changes to the characteristic

TOC or alkalinity altered the placement of the water from an intended element to a neighboring position in the matrix. Additionally, marginal discrepancies between the values reported by the utility and those measured in-house upon receipt placed some waters outside the intended element. In all, 13 waters with a wide range of properties were examined.

Water samples were collected in the summer of 2009 and winter of 2009/2010. Seven waters were obtained during summer sampling dates and six were obtained during winter sampling dates. Additionally, five waters were from river sources and eight originated from impoundments. Figure 4.1 illustrates the geographic distribution and sampling period of the waters examined.



	No.	River	Lake/ Reservoir
Summer 2009	7	3	4
Winter 09-10	6	2	4

Figure 4.1: Approximate geographic location and sampling period of selected raw drinking waters

4.2. RAW WATER CHARACTERISTICS

Table 4.2 presents the water characteristics of interest for the 13 waters obtained for this study. As shown in Table 4.2, the range of TOC values was 1.7-11.4 mg/L, with specific UV absorbance (SUVA) ranging from 1.62 to 4.07 L/mg-m. The humic content of the waters, as reflected by percent HPOA, ranged from 33 to 57%, while the fluorescence index (FI) ranged from 1.29 to 1.55. The range of DON concentration was 0.09 to 0.86 mg/L as N. As noted previously, despite the limitations indicated with respect to the number of raw waters examined and their respective placement within the enhanced coagulation matrix, the entire range of TOC and alkalinity values of the matrix was represented in this study.

Table 4.2: Raw Water Characteristics

Water	Turb-idity (NTU)	Alkalinity (mg/L as $CaCO_3$)	TOC (mg/L as C)	DOC (mg/L as C)	UV_{254} (1/cm)	SUVA (L/mg-m)	% HPOA	FI	TDN (mg/L as N)	DON (mg/L as N)
Schuylkill River, PA	28.2	28	1.7	2.0	0.045	2.28	33.7	1.51	1.07	0.09
Croton Reservoir, NY	0.6	65	2.6	2.5	0.064	2.57	34.5	1.44	0.58	0.09
White River, IN	12.9	170	3.8	3.3	0.067	2.01	32.8	1.51	1.10	0.13
Passaic River, NJ	5.0	72	3.9	3.8	0.112	2.96	45.7	1.48	1.87	0.24
Upper San Leandro Reservoir, CA	1.3	119	4.1	4.1	0.102	2.49	37.4	1.44	0.41	0.15
Otay Reservoir, CA	1.2	151	4.6	4.2	0.069	1.62	33.4	1.54	0.49	0.33
Lake Michie, NC	5.6	23	5.5	5.5	0.175	3.21	49.0	1.40	0.57	0.22
Bushy Park Reservoir, SC	1.6	32	6.3	6.2	0.254	4.07	55.3	1.41	0.34	0.23
Vadnais Lake, MN	0.7	158	7.1	7.1	0.171	2.41	40.1	1.52	0.81	0.20
Scioto River, OH	68.6	121	7.2	7.1	0.274	3.87	39.7	1.55	6.27	0.86
Lake Houston, TX	15.6	46	8.3	8.7	0.314	3.37	52.2	1.31	0.74	0.14
Lake Campbell, CA	24.4	150	8.3	8.3	0.260	3.12	32.5	1.53	0.91	0.35
Hillsborough River*, FL	1.0	54	11.4	11.4	0.466	4.07	56.7	1.29	0.56	0.28

*Hillsborough River was diluted 1:1 with LGW to render it more representative of waters nationwide and waters within the enhanced coagulation matrix. The values shown are after dilution.

4.2.1. Humic Content and Surrogate Parameters

Figures 4.2 and 4.3 demonstrate the relationship between humic content and spectroscopic analysis among the thirteen waters, showing %HPOA compared to both SUVA and FI, respectively. SUVA, recall, is the UV absorbance at 254 nm (UV_{254}) normalized by DOC concentration, wherein one would anticipate an increasing proportion of hydrophobic DOM with increasing SUVA. The results shown in Figure 4.2 are consistent with this expectation.

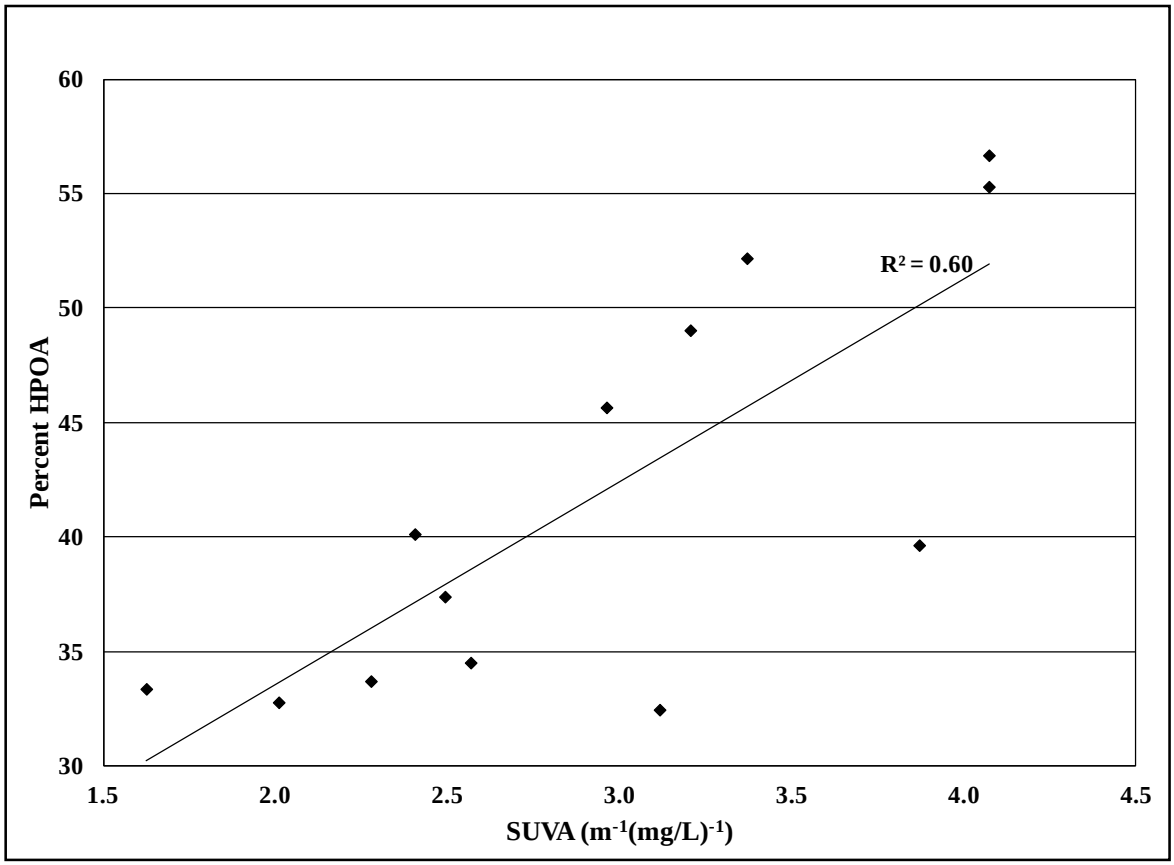


Figure 4.2: Relationship between humic content and specific UV absorbance

Waters with a higher relative proportion of hydrophobic DOC and a higher SUVA have been demonstrated to be more amenable to coagulation by ferric or aluminum salts and have demonstrated a greater DBP formation potential compared to waters with greater relative proportions of hydrophilic DOM (Croué et al. 1999, Liang and Singer 2003).

Similarly, FI values approaching 1.20 are closely associated with a preponderance of humic content due to the fluororophore-abundant nature of aromatic, phenolic, and conjugated double bonds found within hydrophobic DOM components (Jaffé et al. 2008). Figure 4.3 demonstrates the relationship between FI and %HPOA content, which does not

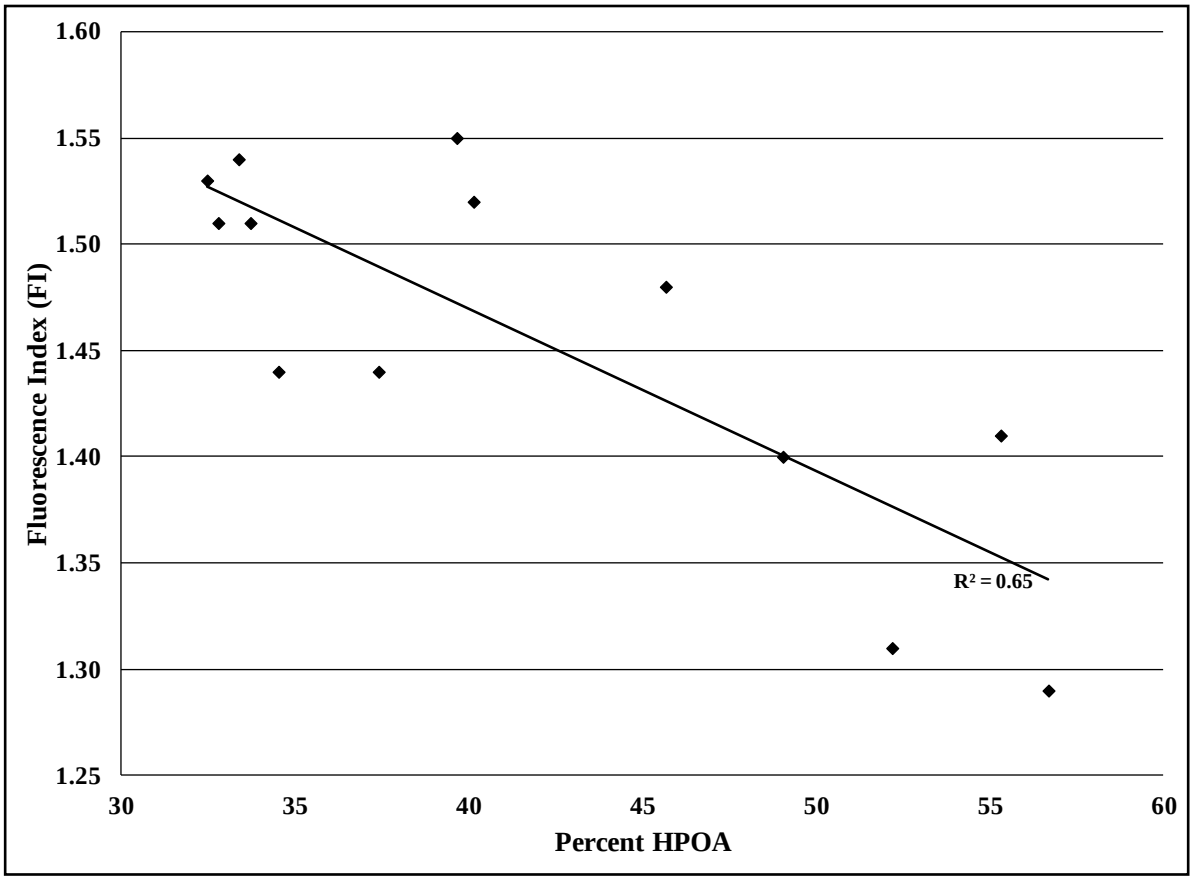


Figure 4.3: Comparison of fluorescence index and raw water humic content

appear to have been demonstrated previously in the literature. The results indicate that an increase in humic content, as reflected by percent HPOA, is met with a corresponding decrease in FI, as expected.

A direct comparison of FI and SUVA is shown in Figure 4.4 in which FI decreases as SUVA increases, as expected. The relationship appears to vary somewhat with season among the raw waters examined in this study, although there are a limited number of samples for

each season. Without seasonal consideration, Jaffé et al. (2008) demonstrated a similar trend to that shown in Figure 4.4 with a much larger set of waters.

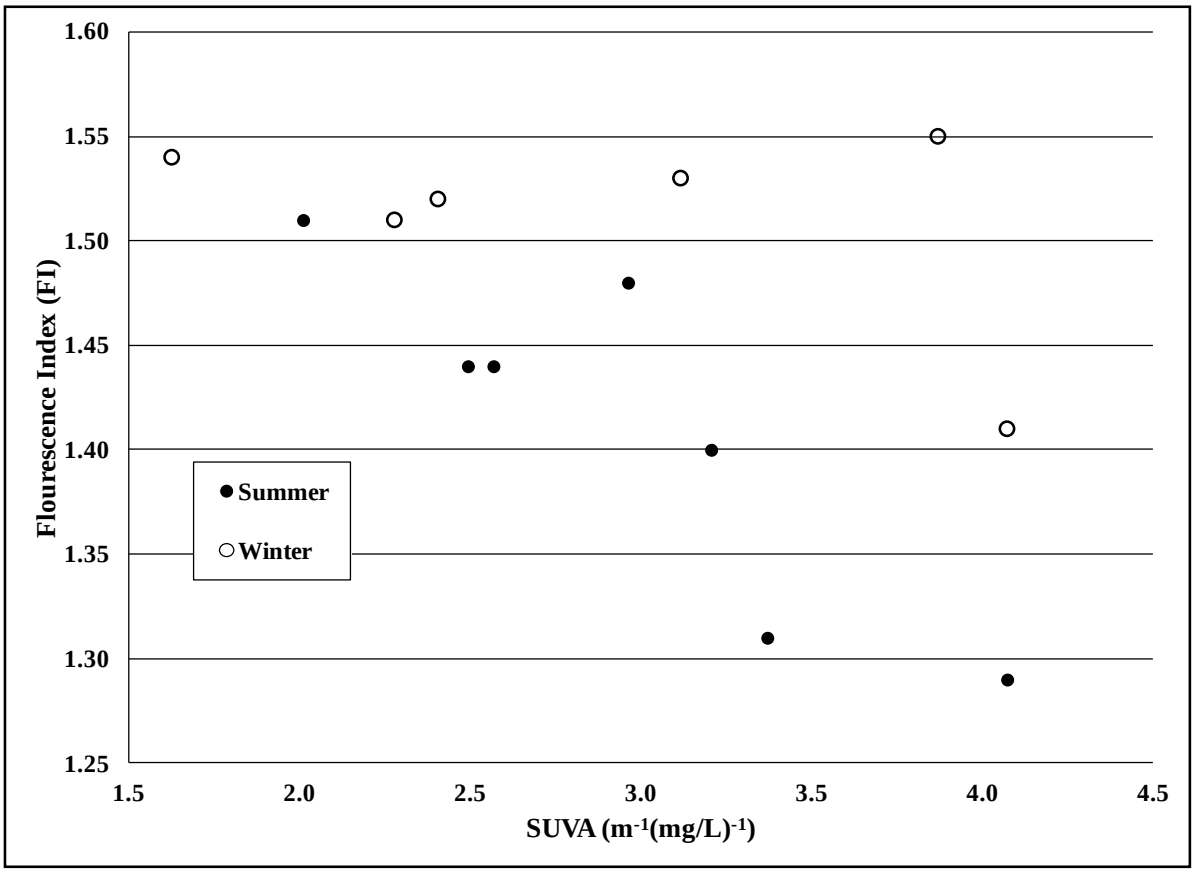


Figure 4.4: Relationship between raw water fluorescence index and specific UV absorbance

4.2.2. Dissolved Organic Nitrogen

Treatment of DON Data

Dissolved organic nitrogen, as discussed in detail in Chapter 3, is not measured directly but ascertained by three separate measurements (total dissolved nitrogen, nitrate/nitrite, and ammonia). While the reported DON concentration is calculated as the difference between TDN and the latter three DIN species, the accuracy of the DON concentration is limited due to the propagation of uncertainty (analytical variance) introduced independently by each of the other measurements. The accuracy of the calculated DON value is influenced by the

relative proportion of DIN and DON, often characterized by the ratio of DIN to TDN. While DON concentration may be comparable to that of DIN in pristine watersheds, DON represents a lower percentage of TDN in human-impacted watersheds (Lee and Westerhoff 2005). Waters with high DIN/TDN ratios are especially problematic in attempts to quantify the concentration of DON. A recent pretreatment method has been developed by Lee and Westerhoff (2005) to improve the accuracy of measuring DON in which the authors suggest dialysis of waters in which DIN/TDN are greater than 0.6. Unfortunately, as noted in Chapter 3, attempts to include dialysis pretreatment were unsuccesful in this study.

Because raw waters were chosen according to DOC and alkalinity and not according to DON concentration (or more importantly the DIN/TDN ratio), any discussion of DON data reported in this study carries with it an important consideration of the analytical challenges posed by DON as described above. In this study, raw water DIN/TDN ratios exceeded 0.8 for two impoundments and four rivers sampled. Accordingly, for any correlation or finding involving DON to be meaningful in this study, it was necessary to focus on waters not impacted by such high DIN/TDN ratios and their corresponding uncertainties. Employing only raw waters in which the DIN/TDN was less than 0.6, as recommended by Lee and Westerhoff (2005), would have excluded all but three waters in this study. In an effort to retain the results from a majority of the waters tested but also to improve accuracy associated with the DON values, a DIN/TDN ratio of 0.75 was used to distinguish between "reliable" DON values and uncertain values. In this manner, data from the seven raw waters in which DON concentration was at least 25% of TDN by mass are distinguished from those samples with a higher raw water DIN/TDN ratio. Thus, when DON findings are

incorporated into figures or discussed, the data is restricted to those seven waters in which raw water DIN/TDN was less than 0.75.

To identify the impact of this DIN/TDN criterion on DON concentration range and distribution, Figure 4.5 shows box and whisker plots of raw DON concentrations among all waters (left) and among waters having DIN/TDN ratios less than 0.75 (right). For each box, from bottom to top, the values identified are minimum, median, average, and maximum concentrations while horizontal box lines indicate 25th percentile, 50th percentile (median), and 75th percentile, respectively. One will note from Figure 4.5 that omitting six waters with

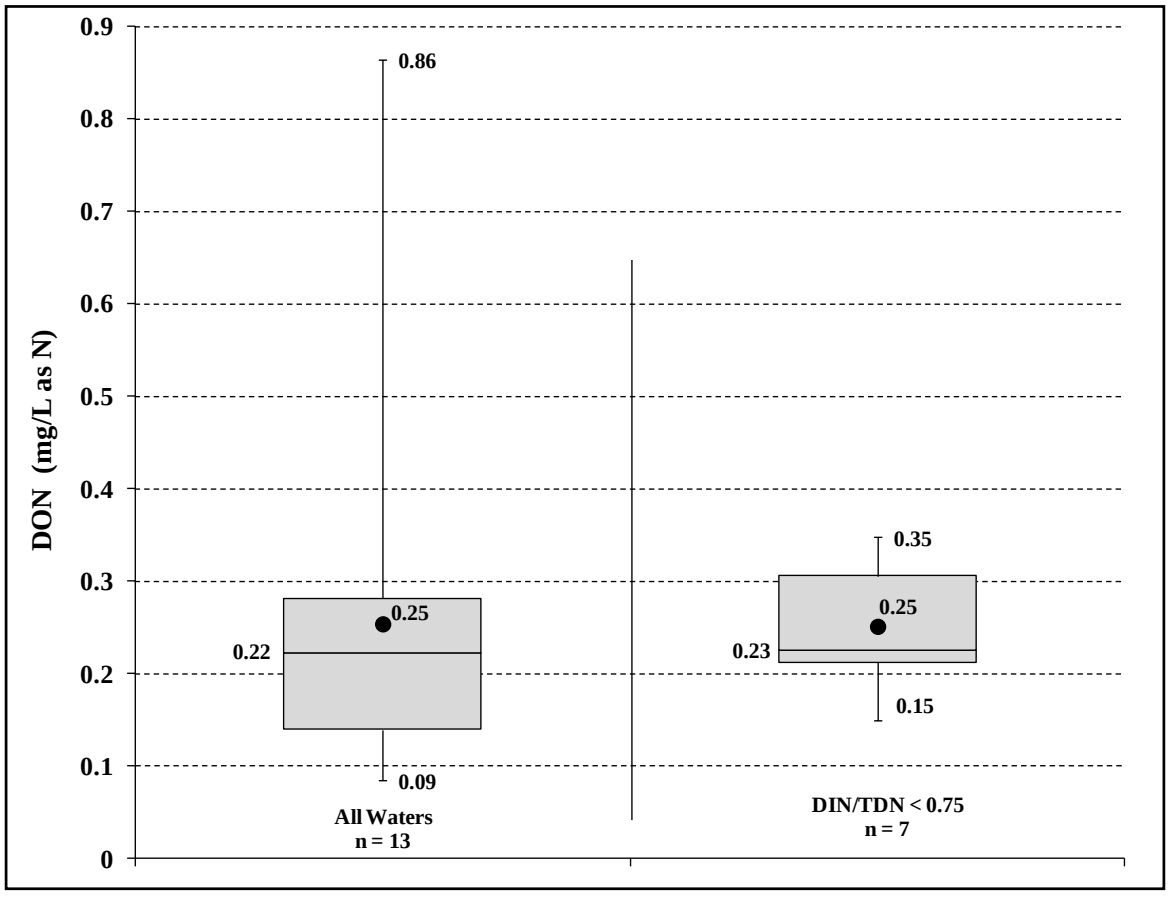


Figure 4.5: Range and distribution of raw water DON concentration before and after application of DIN/TDN criterion

a DIN/TDN ratio greater than 0.75 had little impact on average concentrations, but did alter the range and distribution considerably.

Raw Water DON Occurrence and Relationships with Other Parameters

The average DON concentration of raw waters sampled in this study was 0.25 mg/L. Using U.S. Geologic Survey water quality data from over 15,000 sources in which DON was detected, Westerhoff and Mash (2002) reported an average surface water DON concentration of 0.37 mg/L. In another study of 28 water treatment facilities, the average raw water DON concentration was 0.186 mg/L (Lee et al. 2006). Concentrating on 16 water treatment facilities influenced by algal activity or wastewater discharge, Dotson and Westerhoff (2009) reported an average raw water DON concentration of 0.29 mg/L. The average raw water DON concentration reported in this study is in good agreement with these other studies.

As shown in Figure 4.6., raw water DON occurrence tended to increase in relationship to DOC although there is a great deal of scatter and the data are limited. As noted in Chapter 2, just as organic carbon is distributed among hydrophobic and hydrophilic acid, neutral, and base fractions within bulk DOM, organic N content is not restricted to one DOM fraction. Proportionally, however, nonhumic fractions are typically nitrogen enriched and generally represent the dominant DON fraction within bulk DOM (Westerhoff and Mash 2002). In the waters characterized in this study, no apparent relationship was evident between raw water DON occurrence and nonhumic DOC (see Appendix B-1).

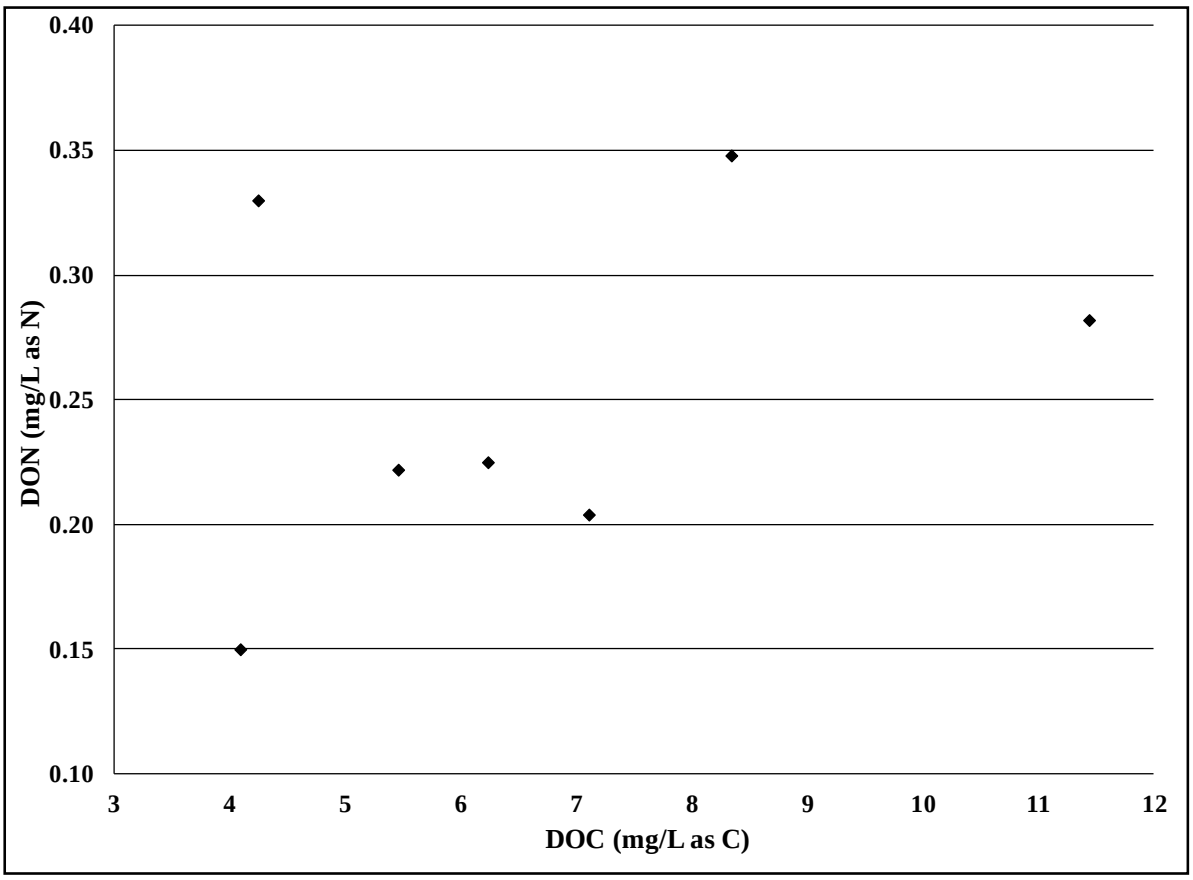


Figure 4.6: Comparison of raw water dissolved organic carbon content and dissolved organic nitrogen content

While SUVA, FI, and percent HPOA content are useful descriptors of the chemical nature of DOM, the shift of focus to include DON in water research has led researchers to establish parameters that also incorporate organic nitrogen content. Measures of the carbon-to-nitrogen ratio have been presented alongside other commonplace drinking water variables and have been suggested both as a means of DOM characterization and as being noteworthy in DBP formation studies (Westerhoff and Mash 2002). Because DON occurence is typically associated with hydrophilic DOM, the ratio of dissolved organic carbon to dissolved organic nitrogen (DOC/DON) would be expected to increase with increasing humic character. Accordingly, one would anticipate a direct relationship between the DOC/DON ratios with both SUVA and percent HPOA, and an inverse relationship with FI.

The relationship between raw water DOC/DON ratio and percent HPOA is shown in Figure 4.7.

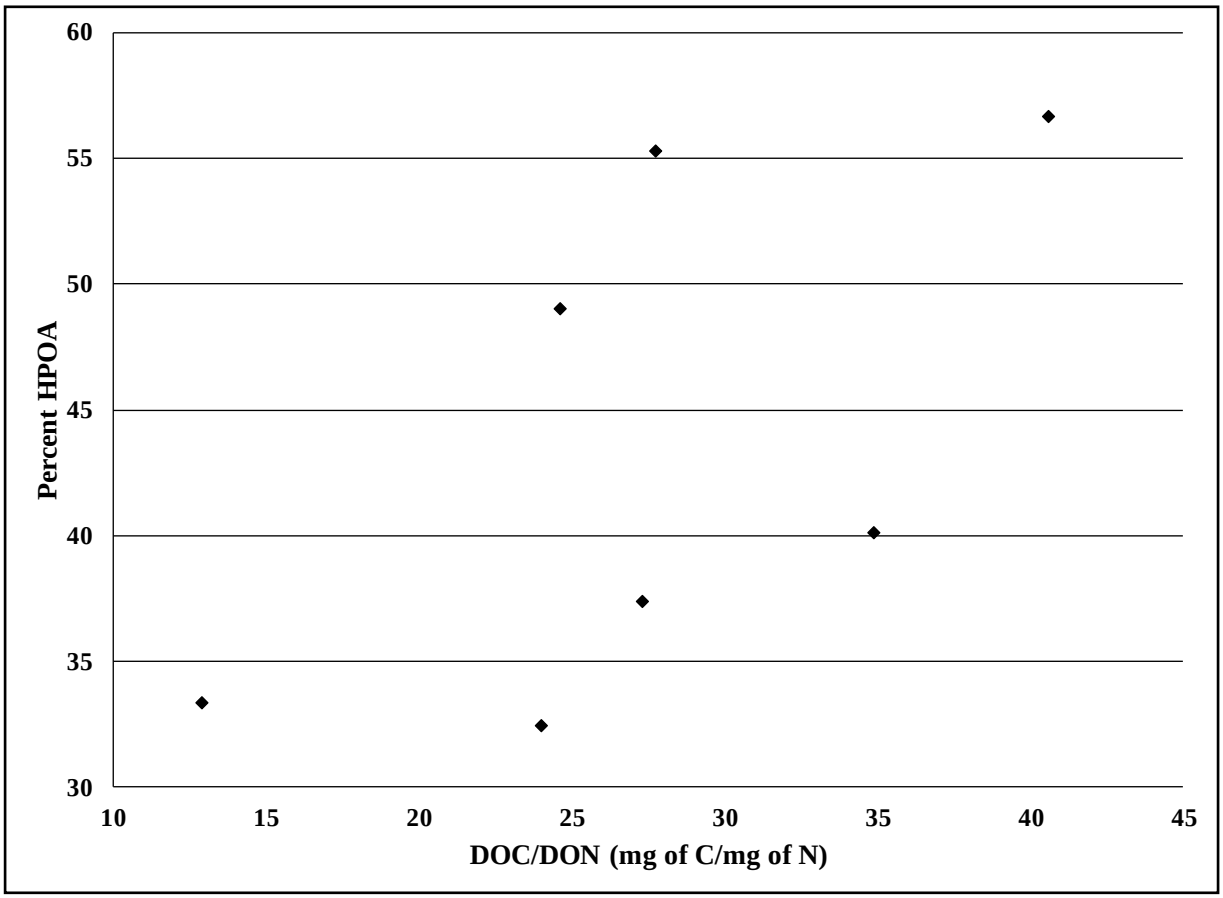


Figure 4.7: Correlation between humic content and the ratio of dissolved organic carbon to dissolved organic nitrogen

Figure 4.7 shows a general trend in which percent HPOA tends to increase as organic nitrogen content decreases relative to organic carbon. Raw water SUVA and FI are compared to the DOC/DON ratios in Appendix Figures B-2 and B-3, respectively. As with percent HPOA, SUVA increases with increasing DOC/DON ratio, while the reverse is true for FI. Jaffé et al. (2008) showed a similar relationship between FI and the ratio of DOC-to-TDN as that shown in Appendix Figure B-3. Total dissolved nitrogen, however, is a less useful surrogate for organic nitrogen because it includes inorganic nitrogen which often dominates over organic nitrogen in many aquatic systems.

4.3. RESULTS OF TREATMENT BY ENHANCED COAGULATION

4.3.1. Removal of DOC and UV-Absorbing Substances

As indicated in Chapter 3, each raw water was coagulated in bulk after jar-testing was used to determine the requisite alum dose to meet either the prescribed TOC removal criteria in the Stage 1 and 2 D/DBP rules, or the point of diminishing returns (PODR). Table 4.3 summarizes the alum dosages used and the treated water characteristics. The percentage reduction in DBP formation potential is discussed in § 4.5.

As has been previously demonstrated by a number of investigators (e.g. Weishaar et al. 2003, Archer and Singer 2006), coagulation resulted in a preferential removal of UV-absorbing, aromatic DOM relative to overall organic carbon. This is explored further among the 13 waters studied in the relationship between the removal of UV_{254} and DOC (Figure 4.8) and in the relationship between DOC removal and raw water SUVA (Figure 4.9).

Table 4.3: Treated Water Characteristics after Enhanced Coagulation

Water	Alum Dose (mg/L)	pH	Turb-idity (NTU)	TOC (mg/L as C)	DOC (mg/L as C)	UV_{254} (1/cm)	SUVA ($m^{-1}(mg/L)^{-1}$)	% HPOA	FI	TDN (mg/L as N)	DON (mg/L as N)
Schuylkill River, PA	30	7.4	0.1	1.0	1.0	0.016	1.67	34.7	1.72	0.99	0.05
Croton Reservoir, NY	20	7.8	0.5	2.1	1.8	0.045	2.42	26.4	1.58	0.58	0.04
White River, IN	35	7.7	1.4	3.1	2.5	0.053	2.15	35.0	1.70	1.12	ND
Passaic River, NJ	30	7.6	0.9	3.2	2.5	0.077	3.10	43.6	1.64	1.73	0.13
Upper San Leandro Reservoir, CA	40	8.1	0.7	3.3	2.4	0.069	2.93	9.0	1.62	0.40	0.16
Otay Reservoir, CA	35	8.1	0.5	4.1	4.1	0.057	1.40	35.3	1.58	0.40	0.27
Lake Michie, NC	35	7.1	1.6	3.1	2.9	0.079	2.68	46.4	1.62	0.51	0.13
Bushy Park Reservoir, SC	55	7.2	0.6	2.7	2.4	0.049	2.08	1.7	1.66	0.31	0.20
Vadnais Lake, MN	90	8.0	0.5	4.6	4.3	0.092	2.14	35.4	1.68	0.72	0.15
Scioto River, OH	80	7.5	1.3	4.4	3.8	0.102	2.66	34.8	1.66	5.77	0.29
Lake Houston, TX	60	7.5	2.0	4.3	3.9	0.126	3.20	43.0	1.60	0.68	0.29
Lake Campbell, CA	85	7.5	1.2	4.7	4.1	0.109	2.69	38.7	1.67	0.76	0.27
Hillsborough River, FL	80	7.1	1.8	5.1	4.0	0.134	3.37	53.9	1.59	0.41	0.06

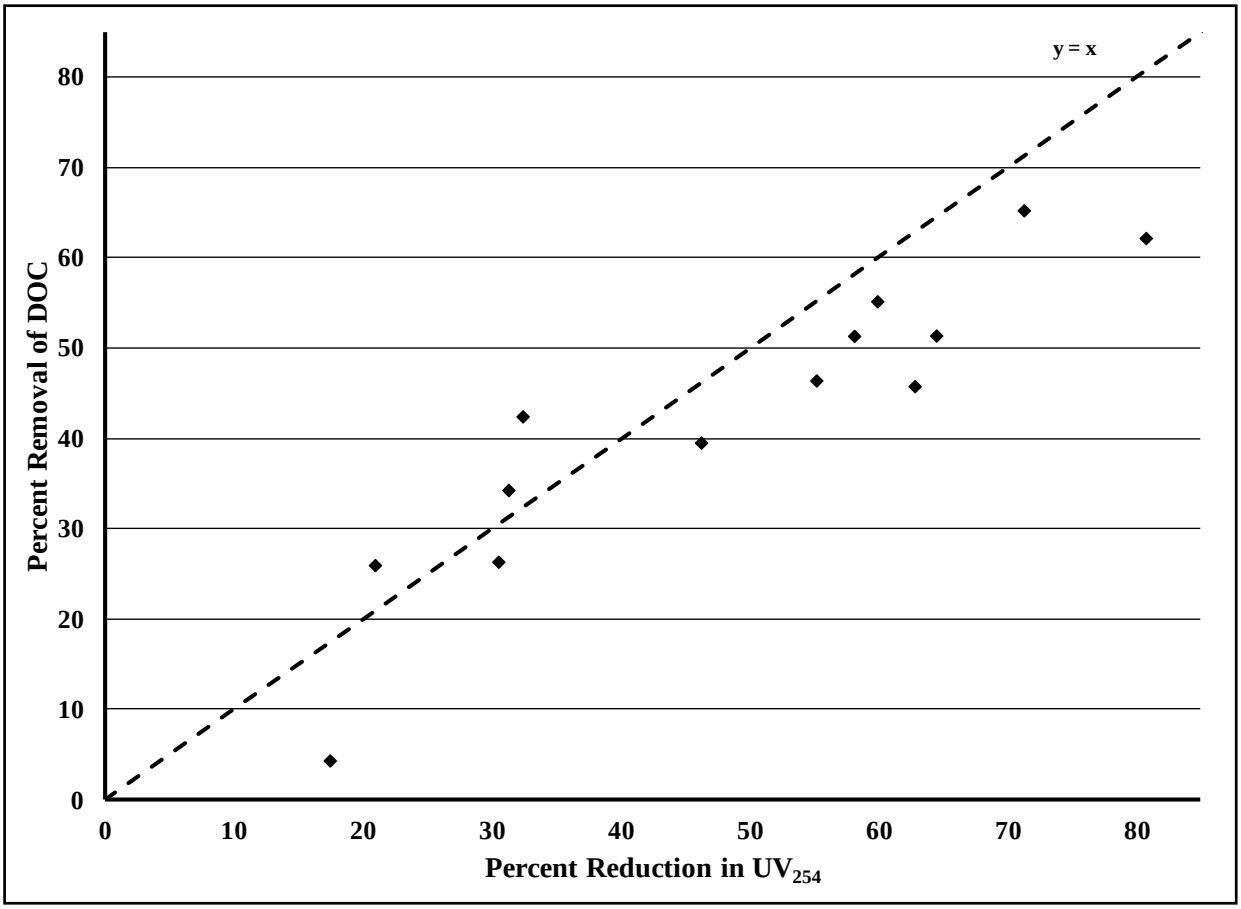


Figure 4.8: Removal of UV-absorbing components of DOM relative to overall DOC removal

One will note that the preponderance of data points lie to the right of the 1:1 line which represents equivalent removal of both UV_{254} and DOC in Figure 4.8, indicating that UV-absorbing substances are removed preferentially compared to overall DOC. Due to the preferential removal of aromatic DOM, SUVA and %HPOA tend to decrease after coagulation while FI tends to increase relative to the corresponding values in the raw water (compare values in Tables 4.2 and 4.3). Figures comparing both SUVA and FI before and after coagulation are available in the Appendix Figures C-1 and C-2.

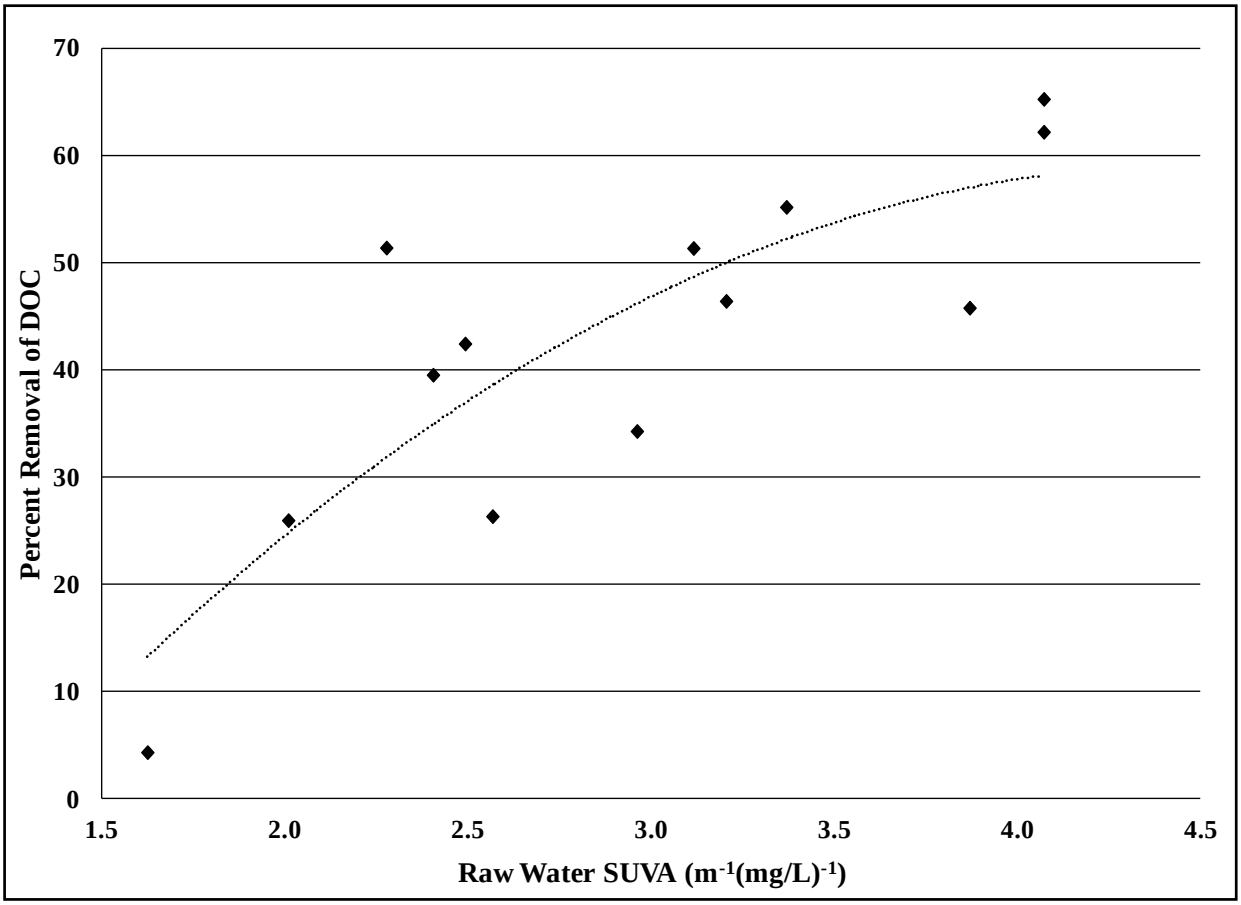


Figure 4.9: Demonstration of improved DOC removal with increasing raw water SUVA

Figure 4.9 displays the impact of raw water SUVA upon DOC removal by enhanced coagulation. Consistent with trends identified by several researchers (e.g. White et al.1997, Archer and Singer 2006), the figure indicates that the removal of DOC by coagulation increases with raw water SUVA. This demonstrates that coagulation is generally more effective for waters that are humic in nature, reflected by a high raw water SUVA.

4.3.2. Removal of DON by Enhanced Coagulation

Because the behavior of UV_{254} and DOC is well understood in the context of coagulation, DON removal is discussed relative to these parameters. For those waters in which DON values were assumed to be accurate (DIN/TDN<0.75), enhanced coagulation generally resulted in less removal of DON than DOC (see Figure 4.10). Among seven waters with

reliable DON concentrations, average removal of DOC was 45%, compared to an average removal of 28% for DON. Figure 4.10 shows the removal of DON relative to DOC in which the 1:1 line represents equivalent removal of both. While the removal of DON by enhanced coagulation is characterized by a wide range (0-80%), the majority of

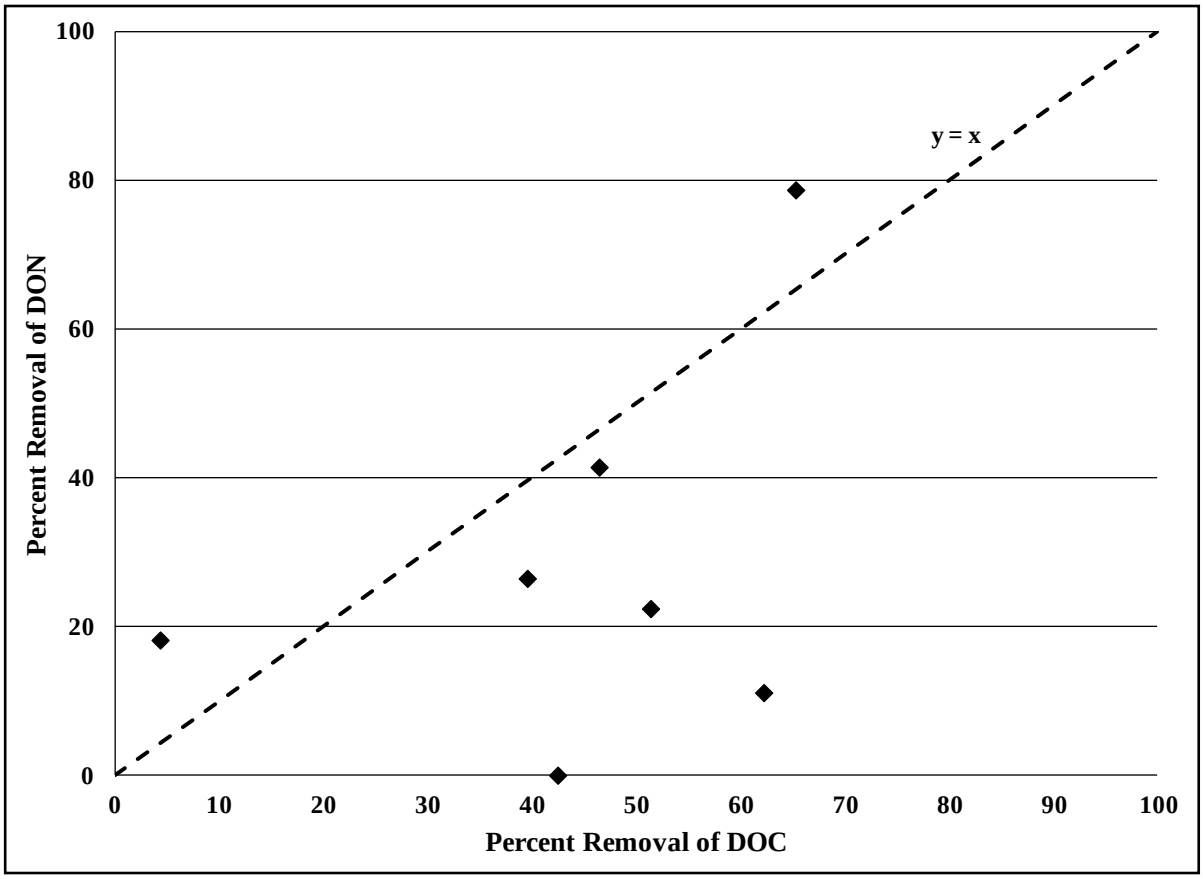


Figure 4.10: Comparison of dissolved organic nitrogen removal and dissolved organic carbon removal after enhanced coagulation

findings fall below the 1:1 line, indicating that DOC removal tended to exceed DON removal. No decrease in DON concentration was observed for the Upper San Leandro Reservoir sample after treatment despite 42% DOC removal.

The finding that enhanced coagulation resulted in greater DOC removal than DON removal was anticipated from the literature. While there are only a handful of investigations that have examined DON removal during water treatment, and fewer still that employed real

waters as opposed to synthetic waters containing model DON compounds, the general conclusion is that DON is less effectively removed by coagulation relative to DOC. Studies that have concentrated on the fate of bulk DON rather than model compounds during water treatment include the work of Lee et al. (2006), Lee and Westerhoff (2006), and Mitch et al. (2009). In a study that concentrated on coagulation, Lee and Westerhoff (2006) reported the results of coagulation jar-tests of three raw waters with DON and DOC concentrations ranging from 0.25-0.35 mg/L as N and 3.9-6.5 mg/L as C, respectively. While the authors reported DON removal ranges from 5 to 40% over a range of alum and cationic polymer doses, DON removal was slightly lower (5-15%) than DOC removal and never exceeded DOC removal. This is in agreement with the results depicted in Figure 4.10 which demonstrate that, for most waters, the nitrogenous moiety of DOM does not appear to be as amenable to removal by coagulation as the carbonaceous fraction.

Enhanced coagulation resulted in greater removal of DON than of DOC in two waters, as shown in Figure 4.10. For a water of low to moderate DOC, with a low SUVA and a sizable concentration of DON, the conditions may be such that DON removal could exceed that of DOC. Otay Reservoir water is a high alkalinity water that fits that description, with a low SUVA of 1.62 L/mg-m and an appreciable DON concentration of 0.33 mg/L as N. DON and DOC removal were 18% and 4%, respectively. The low removal of DOC (and UV_{254}) is consistent with expectations for low SUVA waters (e.g. Edzwald et al. 1985, Liang and Singer 2003). Furthermore, similar findings have been reported by Westerhoff and Mash (2002) for two conventional water treatment plants in the Southwestern U.S. using low alum doses to treat low SUVA, high alkalinity sources.

The other water in which DON removal exceeded DOC removal was Hillsborough River, with 78% removal of DON and 65% removal of DOC. Hillsborough River water is opposite in nature to Otay Reservoir water. As noted in Table 4.2, after 1:1 dilution with LGW the Hillsborough River sample had a SUVA of 4.07 L/mg-m, a DOC concentration of 11.5 mg/L, and a DON concentration of 0.28 mg/L. The high percent removal of DOC is consistent with expectations for a high SUVA, highly colored water (Edzwald et al. 1985, White et al. 1997). The finding that DON removal was comparable to, and slightly exceeded DOC removal implies that this water was likely enriched in proteinaceous DON components which have been shown to be removed with similar efficiencies as hydrophobic acid fractions in some waters (Westerhoff and Mash 2002). Dotson and Westerhoff (2009) also showed some DON components are effectively removed by coagulation, often exceeding bulk DOC removal.

Dissolved organic nitrogen, like DOC, consists of a variety of compounds that exhibit a range of characteristics such as polarity, size, structure, and hydrophobicity that render different fractions of DON more or less amenable to coagulation. While a recent, comprehensive DON fractionation method has been proposed by Leenheer et al. (2007) for application in N-DBP research, the use of similar DON fractionation procedures has not been reported in the context of coagulation. However, some investigators have included coagulation of DON fractions in their studies, but in lesser detail. Lee et al. (2006) observed that the molecular weight distribution of DON paralleled that of DOC and that higher-molecular-weight fractions of both DON and DOC were preferentially removed by coagulation. Additionally, Westerhoff and Mash (2002) noted that polar acidic fractions were removed during coagulation with similar efficiency as hydrophobic acid fractions. Because

these polar acidic fractions tend to be nitrogen enriched, this implies a DON fraction that is readily amenable to coagulation. Furthermore, in a nationwide sampling campaign, Dotson and Westerhoff (2009) showed that total amino acid removal exceeded bulk DOC removal, and coagulation removed the largest mass of total amino acids compared to other unit processes. Total amino acids, the authors note, may comprise up to 35% of DON (Dotson and Westerhoff 2009).

While the breakdown of DON into specific fractions was beyond the scope of this study, the removal of DON by enhanced coagulation can be compared to raw water humic content, as shown in Figure 4.11. (A similar figure comparing DON removal and raw water SUVA is

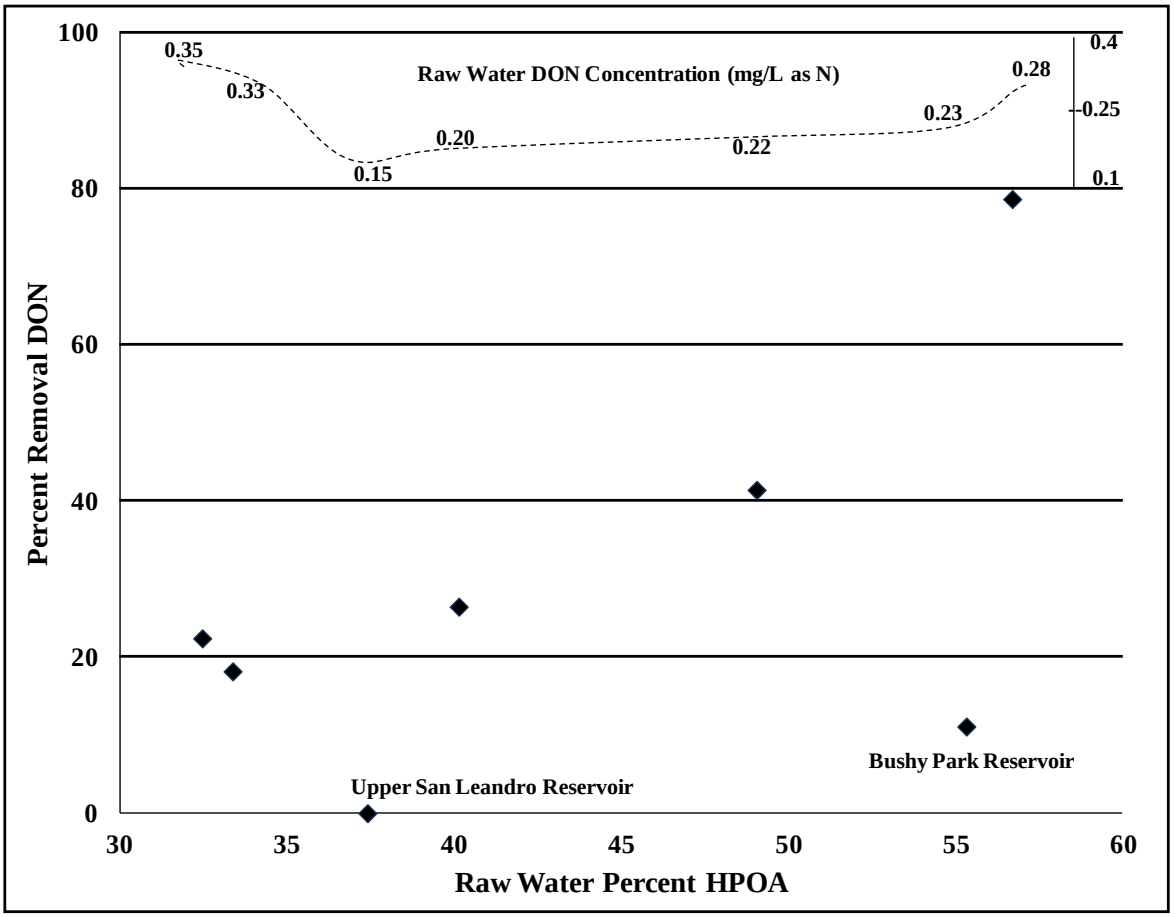


Figure 4.11: Comparison of raw water humic content to percent removal of dissolved organic nitrogen and raw water DON concentration (top)

presented in Appendix Figure C-3). Also included within the figure is a representation of raw

water DON concentrations relative to percent HPOA. Figure 4.11 indicates that the removal of bulk DON varies considerably between different water sources and suggests that DON removal by enhanced coagulation (with alum) is largely dictated by the relative proportion of specific DON fractions amenable to coagulation. There appears to be an association between humic DOC content and DON removal among five of the waters in which the removal of DON increased with an increasing proportion of HPOA. As shown at the top of Figure 4.11, no relationship is evident between raw water DON concentrations and percent HPOA. This is surprising because, as noted previously, DON is generally thought to be most abundant in nonhumic fractions of DOM. The fractional distribution of DON between humic and nonhumic materials is likely to be highly watershed-specific as the processes influencing DON occurrence include seasonal variation, DOM source (i.e. autochthonous or allochthonous), and trophic status, among others (Westerhoff and Mash 2002, Lee et al. 2006). In general, the findings in Figure 4.11 highlight the need for more comprehensive coagulation studies of DON fractions.

4.4. RAW WATER DBP FORMATION

In chlorinated samples of raw and treated waters, only chloroform ($CHCl_3$), bromodichloromethane ($BrCl_2CH$), and two N-DBPs of interest, dichloroacetonitrile (DCAN) and dichloroacetamide (DCAM) were consistently observed at levels above the reportable detection limits. Table 4.4 contains the formation potential data for $CHCl_3$, DCAN, and DCAM. Chloroform was included as a reference DBP because of its well established formation as a chlorination DBP and the long history of research regarding its presence in chlorinated drinking water. Because waters with low bromide concentrations were selected for this study, $CHCl_3$ represented at least 85% of THM4, on a molar basis, in all samples except Otay Reservoir (29%). Based upon proportionally higher formation of

Table 4.4: DBP Formation Potential Data

Water	Raw				Treated			
	Cl_2 Consumed (mg/L)	$CHCl_3$ Formation (µg/L)	DCAN Formation (µg/L)	DCAM Formation (µg/L)	Cl_2 Consumed (mg/L)	$CHCl_3$ Formation (µg/L)	DCAN Formation (µg/L)	DCAM Formation (µg/L)
Schuylkill River, PA	2.56	88.1	2.46	4.24	0.78	12.4	0.58	1.98
Croton Reservoir, NY	2.11	107	7.60	3.44	1.54	60.2	4.42	3.36
White River, IN	7.12	180	15.7	14.7	3.29	92.5	9.59	5.44
Passaic River, NJ	3.89	211	13.6	5.94	3.37	118	10.8	4.65
Upper San Leandro Reservoir, CA	3.38	174	12.7	5.57	3.09	110	9.90	4.26
Otay Reservoir, CA	2.83	32.2	1.64	2.36	2.75	16.0	1.20	0.602
Lake Mitchie, NC	5.06	337	17.5	6.99	2.87	145	9.51	3.50
Bushy Park Reservoir, SC	8.08	*406*[+]	14.0	17.7	2.71	69.4	3.78	6.38
Vadnais Lake, MN	5.54	261	13.6	1.79	3.66	111	9.70	2.18
Scioto River, OH	10.80	381	25.7	5.01	5.73	142	14.5	12.08
Lake Houston, TX	9.29	*559*	30.0	10.0	4.56	202	15.7	5.13
Lake Campbell, CA	10.08	*471*	23.2	3.97	4.93	165	13.5	5.82
Hillsborough River, FL	14.8	*1074*	42.4	16.4	5.16	300	19.1	7.70

[+]Values outside calibration range appear in italics.

brominated-DBPs, it appears that Otay Reservoir water did contain a substantial bromide concentration.

4.4.1. Chloroform Formation

Under uniform formation conditions, raw water $CHCl_3$ formation ranged from 32.2 to 1070 µg/L. Chloroform formation was found to be strongly correlated with UV_{254} (R^2=0.92) and raw water DOC (R^2=0.82), as demonstrated in Figures 4.12 and 4.13, respectively. As

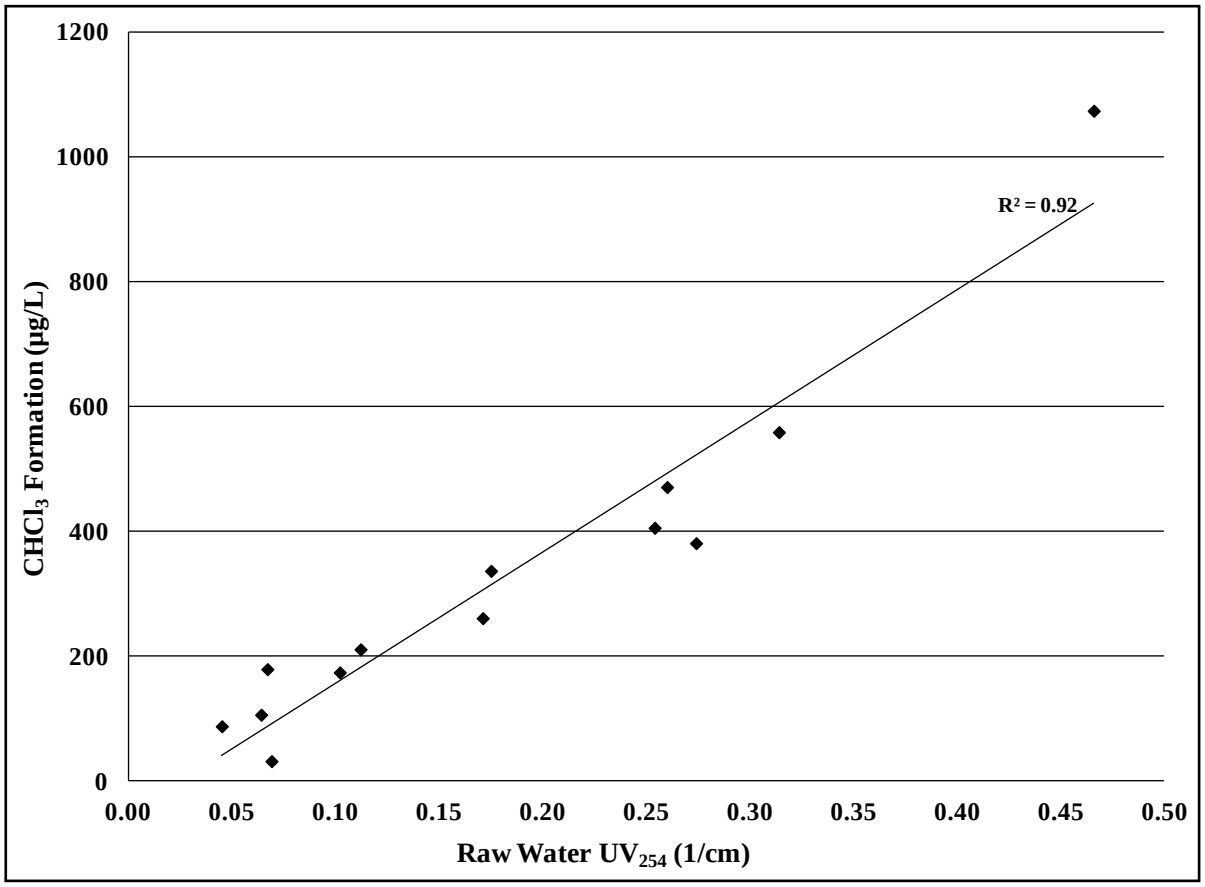


Figure 4.12: Relationship between raw water UV_{254} absorbance and chloroform formation

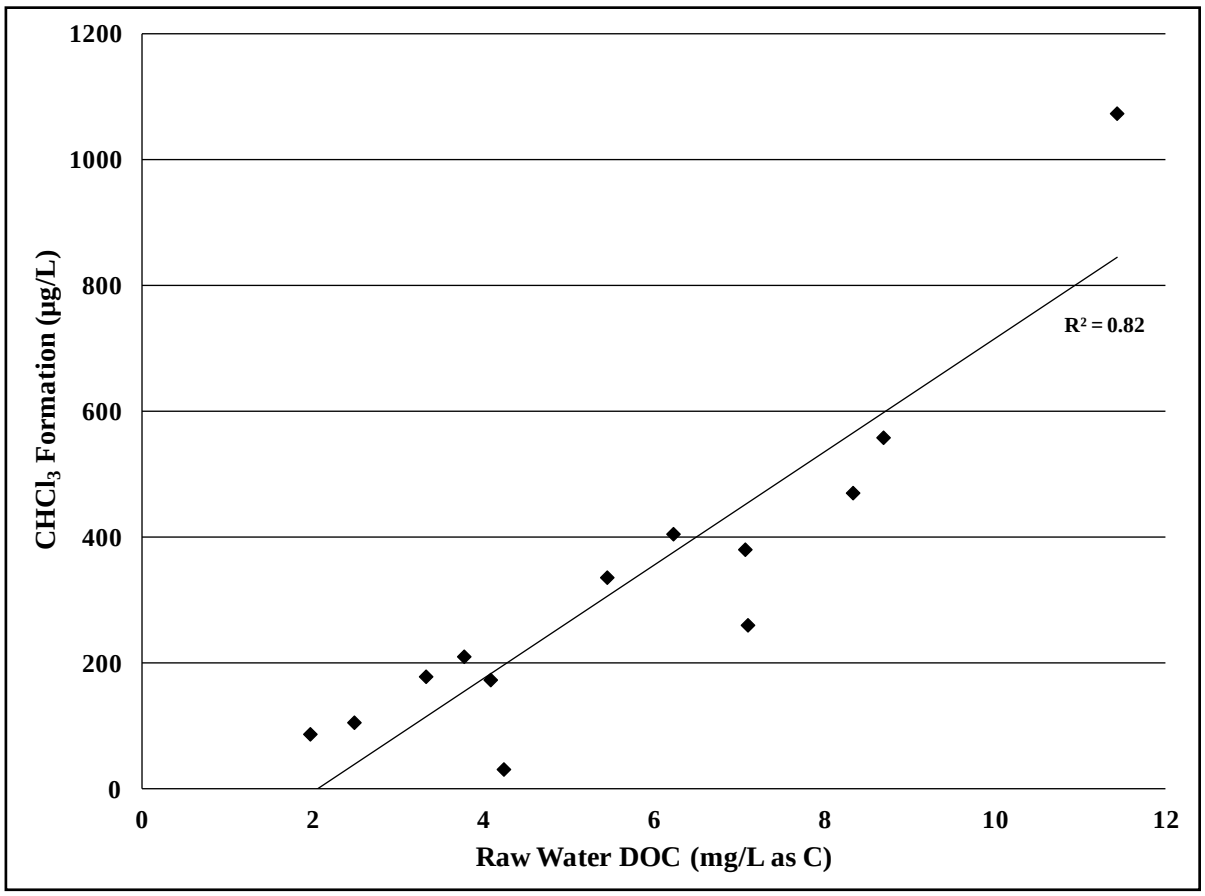


Figure 4.13: Formation of chloroform compared to raw water dissolved organic carbon content

shown in Figure 4.14, normalized $CHCl_3$ formation (i.e. µg $CHCl_3$/mg DOC) was also directly proportional to SUVA (R^2=0.66). Likely due to a high bromide concentration, normalized $CHCl_3$ formation of Otay Reservoir water was only 7.6 µg/mg DOC, while normalized $CHCl_3$ formation of the other waters ranged from 36.6 to 93.9 µg/mg DOC, with an average of 52.3 µg/mg DOC. This compares well with a THM4 average specific yield of 52.2 µg/mg DOC reported by Reckhow and Singer (1990) in which $CHCl_3$ accounted for 93-99% of THM4.

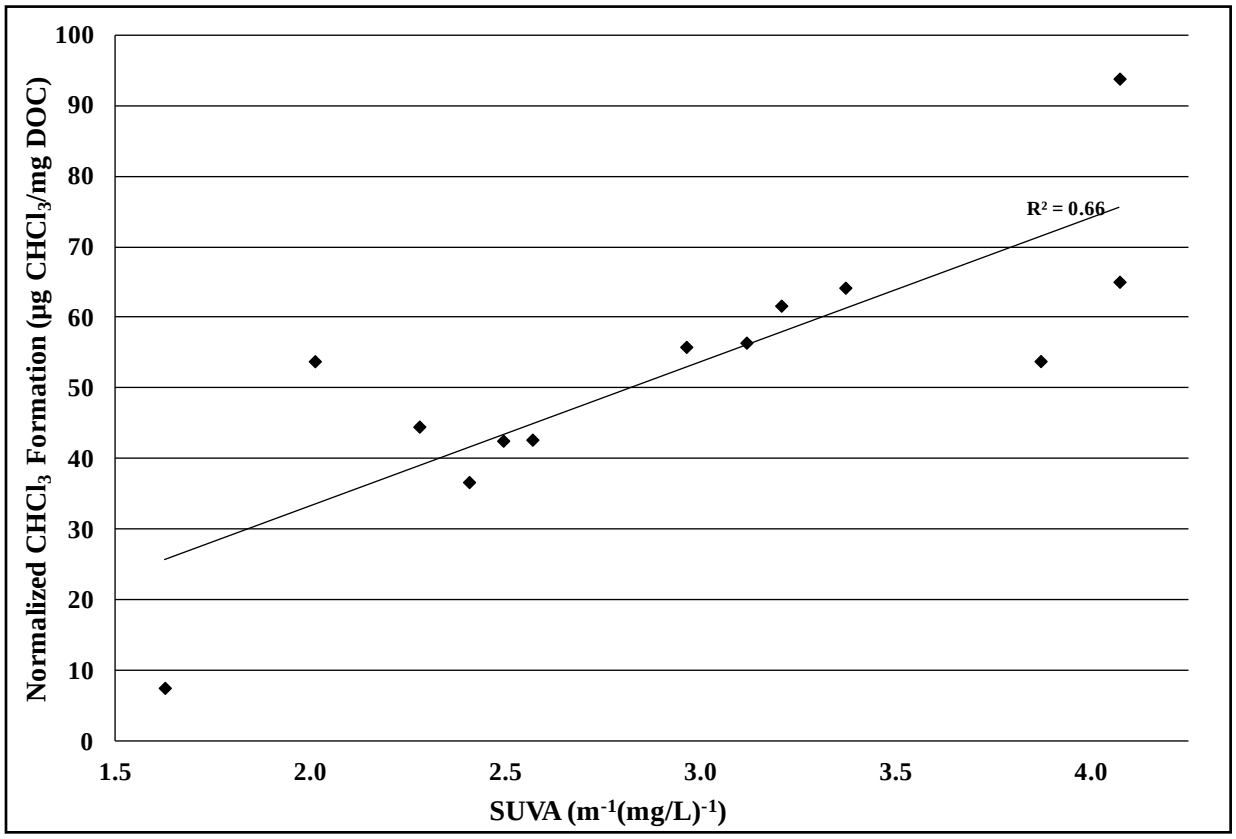


Figure 4.14: Normalized chloroform formation per unit organic carbon relative to raw water SUVA

For the waters examined in this study, Figures 4.12 and 4.13 indicate that absolute $CHCl_3$ formation correlates well with UV_{254} and DOC, suggesting these are good surrogates for $CHCl_3$ formation potential. Normalized $CHCl_3$ formation also increases with SUVA, as demonstrated in Figure 4.14. These relationships are in agreement with the literature (e.g. Edzwald et al. 1985, Reckhow et al. 1990, Archer and Singer 2006). Normalized $CHCl_3$ formation was also directly proportional to %HPOA (R^2=0.52), and inversely proportional to FI (R^2=0.49). These relationships are displayed in the Appendix (Figures B-4 and B-5). The increase in normalized $CHCl_3$ formation with SUVA and %HPOA and the reverse relationship with FI indicates that hydrophobic DOC is more reactive to form $CHCl_3$ than the hydrophilic/transphilic (nonhumic) DOC fraction. The waters examined in this study adhere to the same general trends identified in previous studies (e.g. Edzwald et al. 1985, Najm et al.

1994, Liang and Singer 2003) and serve as a representative basis for comparison with the targeted N-DBP species. With regard to seasonal trends, average specific yield (normalized formation) of $CHCl_3$ was 44.1 µg/mg DOC for waters obtained during winter months, compared to an average of 59.3 µg/mg DOC for summer raw water samples.

4.4.2. N-DBP Formation

The quantification of a variety of N-DBP species relevant to the chlorination of raw water was among the principal objectives of this research. Chlorinated water samples were analyzed for the following seven N-DBP species: bromochloro-, dibromo-, dichloro- and trichloroacetonitrile, trichloronitromethane (chloropicrin), and dichloro- and trichloroacetamide. Only dichloroacetonile (DCAN) and dichloroacetamide (DCAM) were consistently observed above reportable detection limits. Chloropicrin was detected in fewer than half of the raw waters examined, while bromochloroacetonitrile (BCAN) was only detected in the Otay Reservoir water sample. Hence, the latter two species were not included in this analysis. Only findings for DCAN and DCAM are discussed in the remainder of this chapter. DCAN and DCAM have been reported to be the most commonly occurring species of their respective classes (Krasner et al. 2006, Chu et al 2010). Furthermore, both HANs and HAMs have been identified as being considerably more cyto- and genotoxic than currently regulated THM and HAA species (Plewa at al. 2008).

Dichloroacetonitrile

Raw water DCAN formation ranged from 1.6 to 42.4 µg/L and, as demonstrated in Figure 4.15, closely followed the formation of $CHCl_3$. On a molar basis, the ratio of DCAN

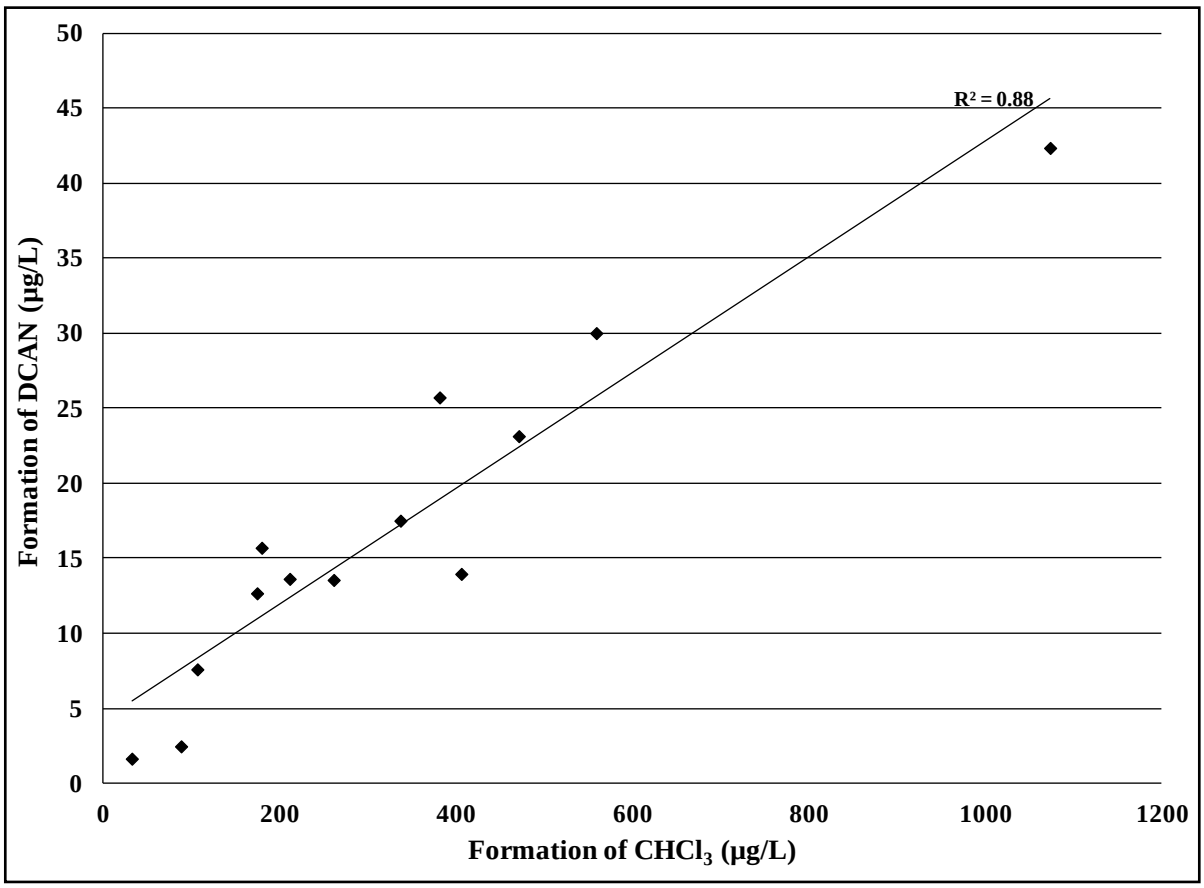


Figure 4.15: Correlation between raw water chloroform formation and dichloroacetonitrile formation

formation to $CHCl_3$ formation ranged from 0.030 to 0.095 and was 0.06 on average. While the relationship described between DCAN and $CHCl_3$ in Figure 4.15 suggests that DCAN and $CHCl_3$ share common precursors, a general trend was observed in which the DCAN/$CHCl_3$ formation ratio decreased with increasing percent HPOA (see Appendix Figure B-6). This implies that relative to $CHCl_3$, the nonhumic precursor fraction generates proportionally greater levels of DCAN compared to hydrophobic precursor constituents. As it relates to DCAN mitigation strategies employing coagulation (see §4.5.2), it can thus be expected that reduction in DCAN formation will be generally less than that of $CHCl_3$ and particularly so in waters that are nonhumic in nature because humic materials are more readily removed by coagulation than hydrophilic materials.

Figure 4.16 shows the formation of DCAN relative to raw water DOC content. With the exception of the identified Otay water which was omitted from the regression, raw water

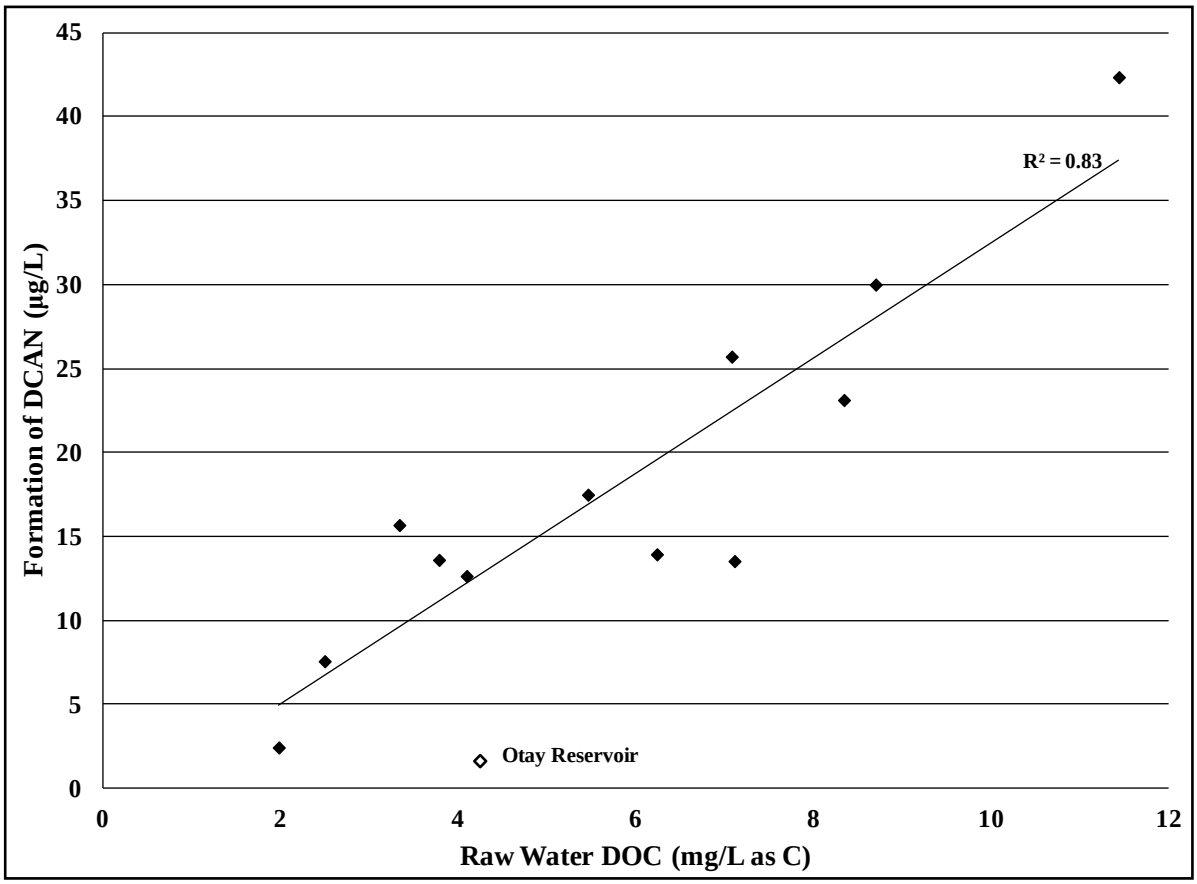


Figure 4.16: Comparison of raw water dissolved organic carbon content and formation of dichloroacetonitrile

formation of DCAN was well correlated with DOC concentration and, like $CHCl_3$, with UV_{254} absorbance (R^2=0.85, Appendix Figure B-7). Due presumably to a high bromide concentration, normalized DCAN formation was only 0.4 µg/mg DOC in the Otay Reservoir sample and the formation of BCAN was 2.8 times greater than DCAN formation on a molar basis. Excluding this sample, specific DCAN yield ranged from 1.2 to 4.7 µg/mg DOC, and was 2.9 µg DCAN/mg DOC on average. As observed with the formation of $CHCl_3$, samples obtained during the summer had greater average specific DCAN yield (3.6 µg/mg) compared to winter samples (2.0 µg/mg).

The normalized DCAN formations observed in this study are higher than those typically reported in the literature. However, due to its chemical instability and its potential for decomposition into other components, DCAN yield is sensitive to reaction conditions, and particularly to reaction time (Chu et al. 2010). Reckhow and Singer (1990) reported an average specific yield of 1.1 µg/mg DOC after a 72h reaction period.

The formation of DCAN is shown relative to raw water DON content in Figure 4.17. Omitting the Otay Reservoir sample, five waters constitute a trend in which DCAN formation

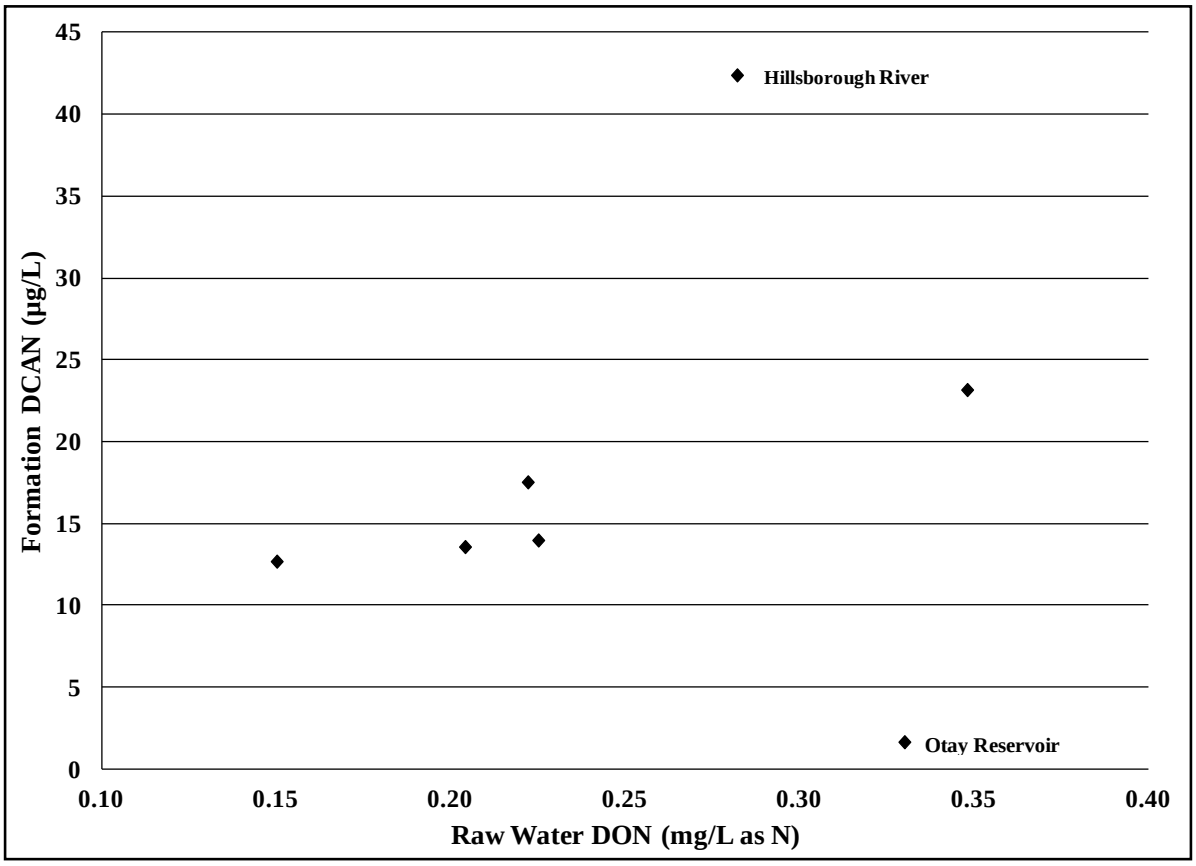


Figure 4.17: Formation of dichloroacetonitrile compared to raw water dissolved organic nitrogen content

increased with increasing DON content. As shown in Figure 4.17, the Hillsborough River sample also did not adhere to the trend indicated. Including the latter water with the other five samples, a weak linear relationship was observed (R^2=0.35). In the absence of both Otay

Reservoir and Hillsborough River samples, however, the correlation is surprisingly strong (R^2=0.87). Unlike Otay Reservoir, exclusion of Hillsborough River is not easily justified. While the DCAN formation potential of Hillsborough River water was disproportionately high relative to its DON content, this was not observed in relation to DOC (or UV_{254}), or relative to $CHCl_3$ formation, as indicated previously. Figure 4.17 seems to suggest that while DON may be indicative of DCAN formation potential in many cases, for waters like the Hillsborough River sample, it may poorly reflect DCAN formation potential.

The wide range in DCAN formation that is depicted in Figure 4.17 illustrates a key concept. Depending on the characteristics of a particular water, the reactive portion of DON resulting in DCAN formation may be representative of only a fraction of the total DON present. In chlorination studies of aquatic humic extracts from 10 different waters, DCAN formation potential was strongly correlated to organic N content, but the same was not observed for fulvic extracts (Reckhow et al. 1990). In more recent studies summarized by Mitch and colleagues (2009), detailed DOM isolate characterization from water sources enriched in DON showed HAN formation to be greatest among hydrophilic base and colloid fractions. Six of the seven water sources employed in the latter reference were wastewater effluents or bacterial/algal cultures and thus not generally representative of most raw drinking water sources. One source Mitch et al. (2009) considered to be algal-enriched, Saguaro Lake (AZ), was more typical of the raw waters utilized in this study, and in particular, of the sources sampled during the summer months. Formation of HANs from DOM isolates of Saguaro Lake indicated that both the hydrophilic acid plus neutral fraction and the protein hydrophobic neutral fraction generated considerable amounts of HAN on a per carbon basis, despite having C: N ratios of 14.5 and 8.0, respectively. Rank order of

HAN formation from the Saguaro Lake DOM isolates was hydrophilic bases (26 nmol/mg DOC) > hydrophilic acids plus neutrals ≈ protein hydrophobic neutrals (17 nmol/mg DOC) > colloids (14 nmol/mg DOC) (Mitch et al. 2009). Haloacetonitriles have been shown to be formed by chlorination of free amino acids, heterocyclic nitrogen in nucleic acids, proteinaceous materials, and combined amino acids bound to humic matter (as cited in Lee et al. 2007). Moreover, Lee et al. (2007) reported that, in their own studies, there was a significant, positive correlation with both proteinaceous and proteinaceous/aromatic DOM content and DCAN formation. In the context of whole water studies, however, just as certain types and fractions of DOC are associated with the formation of different DBPs, it appears based on both Figure 4.17 and literature references that measures of DON content alone may be too general to account for the formation of specific N-DBPs.

Dichloroacetamide

The raw water formation of DCAM ranged from 1.8 to 17.7 µg/L and generally formed at lower levels than observed for DCAN formation. As shown beginning with the relationship between formation of $CHCl_3$ and DCAM formation in Figure 4.18, the correlations involving the formation of DCAM are not as strong compared to similar relationships shown for DCAN formation (Figures 4.15-4.17).

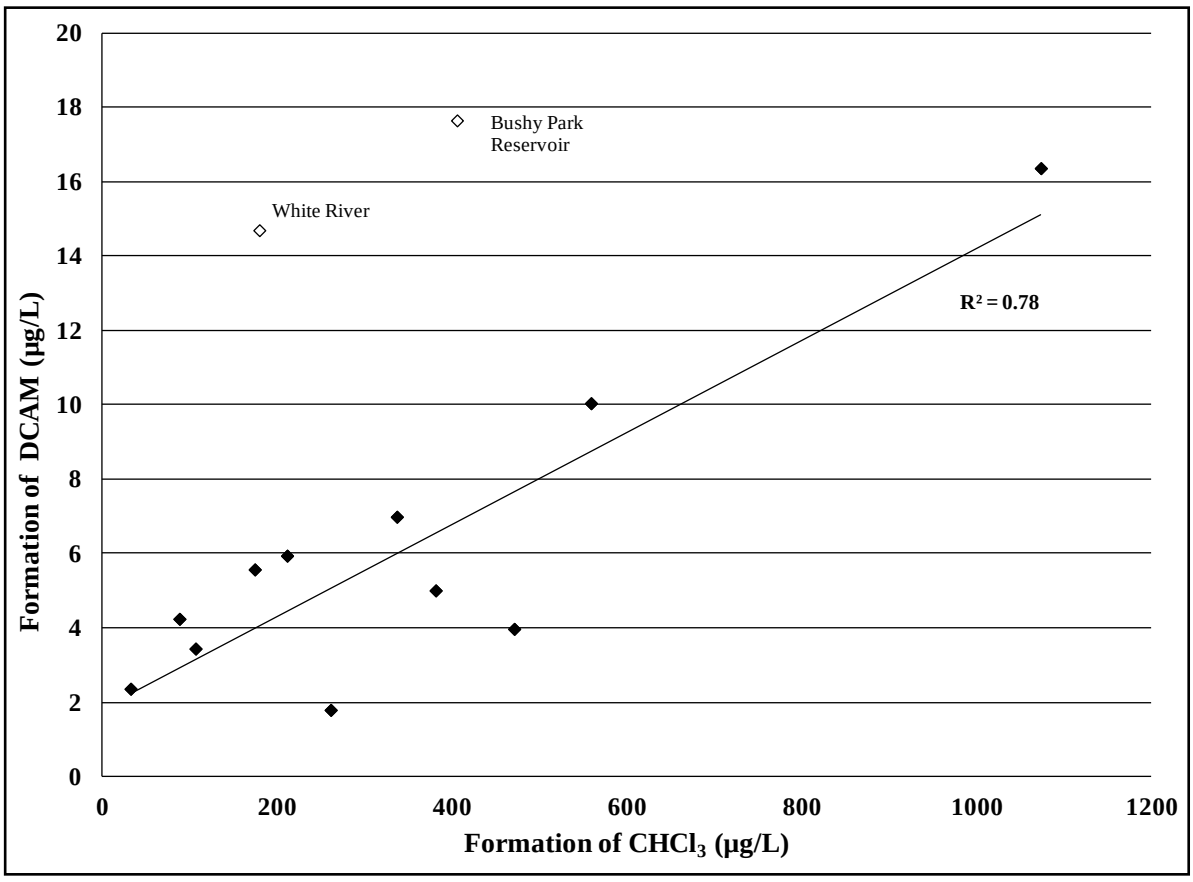


Figure 4.18: Relationship between chloroform formation and raw water formation of dichloroacetamide

In general, raw water DCAM formation was well correlated with the formation of $CHCl_3$ among most water samples (R^2=0.78). To demonstrate the trend more readily, the two identified waters were omitted from the regression in Figure 4.18. The formation of DCAM in the omitted waters, White River and Bushy Park Reservoir, were 14.7 and 17.7 µg/L, respectively. These two waters are discussed in further detail after presentation of the other relationships.

As shown in Figure 4.19, raw water DCAM formation was not well correlated with DOC concentration (R^2=0.44). The 11 waters included in the regression in Figure 4.19 constitute a weak general trend in which DCAM formation potential increased with increasing DOC concentration. While DOC may be an appropriate surrogate parameter for DCAN formation

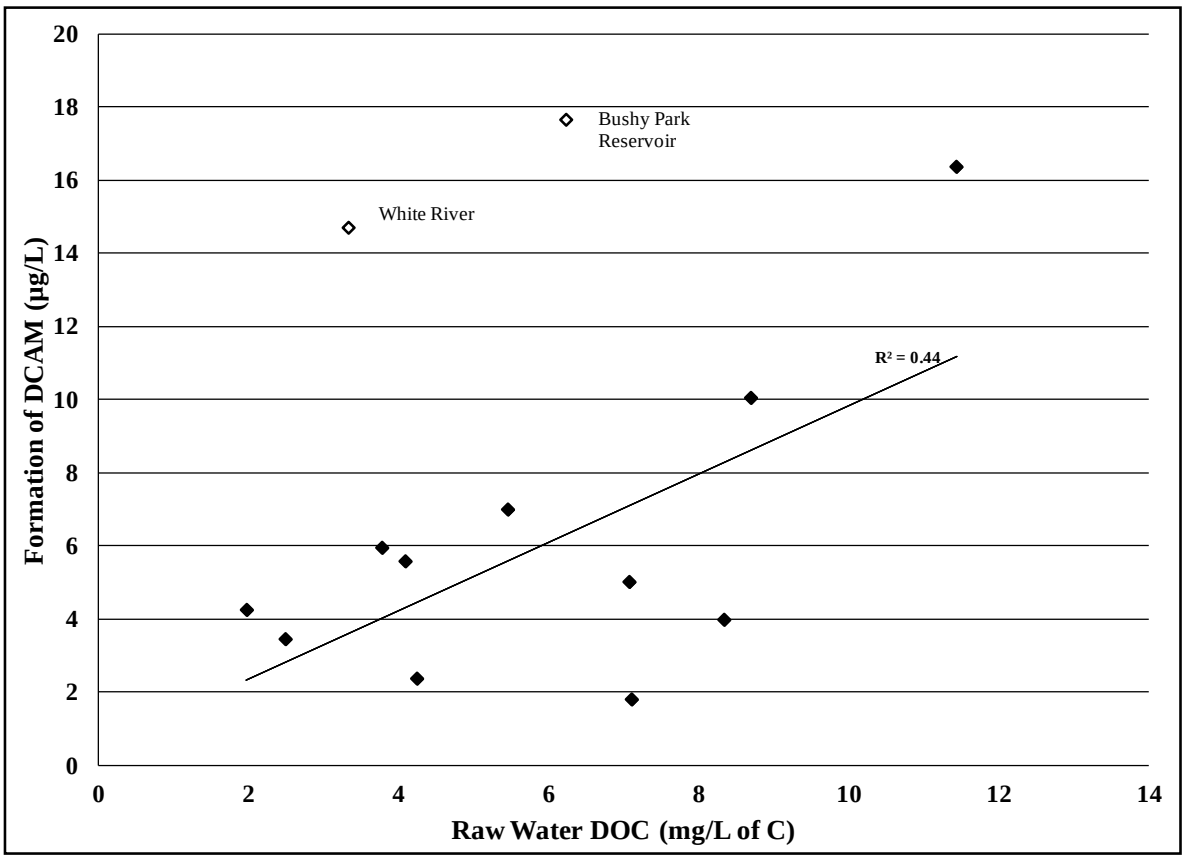


Figure 4.19: Comparison of dichloroacetamide formation and dissolved organic carbon content

potential, as suggested by Figure 4.16, the relationship between DCAM formation and DOC content is not well defined in Figure 4.19.

Anomalous waters aside, DCAM formation was considerably different for several samples in which DOC concentration was similar. This suggests that certain DOM fractions are responsible for elevated levels of DCAM formation and, in general, these fractions appear to be poorly represented by measures of bulk DOC. This notion is further supported by findings that DCAM formation was better correlated with UV_{254} (R^2=0.63, see Appendix Figure B-8), percent HPOA (R^2=0.74, not shown), and FI (R^2=0.75, not shown) than with DOC. As these other surrogates reflect reactivity and structure of DOC, rather than overall DOC itself, this implies that the nature of the DOC (and not the absolute quantity of DOC) may control DCAM formation.

Normalized with respect to DOC, DCAM specific yield was 1.5 µg/mg DOC on average and ranged from 0.3 to 4.4 µg/mg DOC. The same seasonal variation in $CHCl_3$ and DCAN formation was observed for DCAM formation. Normalized DCAM formation was greatest among water samples taken during summer months, with an average of 1.8 µg DCAM/mg DOC, compared to an average of 1.2 µg/mg DOC for winter samples. Again omitted as outliers, Bushy Park Reservoir and White River exhibited DCAM yields of 2.8 and 4.4 µg/mg DOC, respectively. In the absence of these, the average specific yield was 1.1 µg/mg DOC, and summer and winter averages were 1.4 and 0.84 µg/mg DOC, respectively.

The other relevant precursor measured, DON, did not exhibit any correlation with DCAM formation, as shown in Figure 4.20. The lack of a relationship further suggests that the

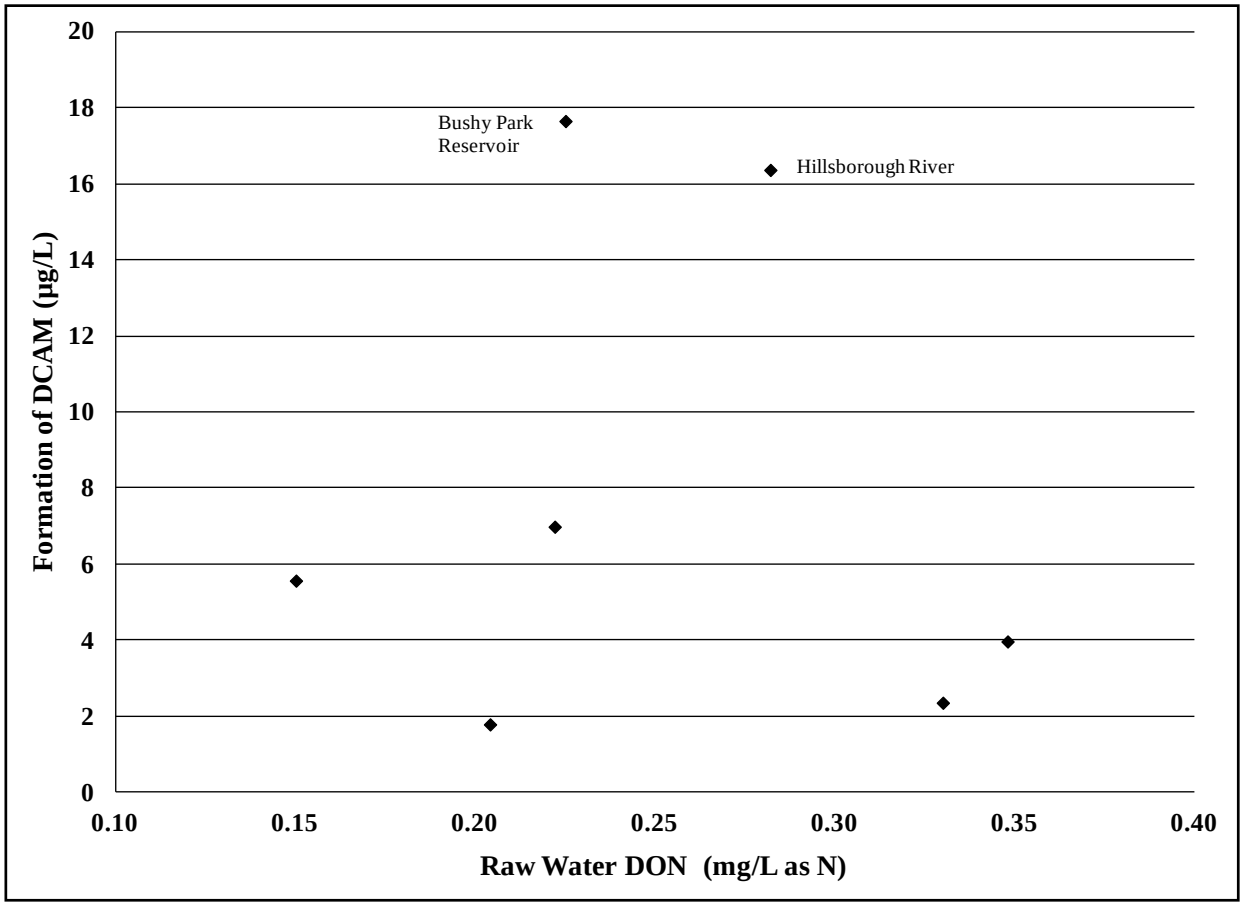


Figure 4.20: Dichloroacetamide formation relative to raw water dissolved organic nitrogen content

formation of DCAM is a result of one or more sub-fractions that, to a greater extent than was observed for DCAN (Figure 4.17), appear to be poorly accounted for by bulk DON content. While there are few studies in the literature to quantitatively evaluate precursors of DCAM, the recent work of Chu et al. (2010a) supports this finding. Over an 8-month campaign, Chu and colleagues (2010a) chlorinated and chloraminated samples from a Chinese lake in which dichloro- and trichloroacetamide (TCAM) formation was monitored. While TCAM was rarely above the detection limit, DCAM was observed in all samples and formation was greatest during summer months. Furthermore, the authors used a water sample taken during a period of peak DCAM formation to characterize the formation potential of six DOM isolates. Among the chlorinated DOM isolates, the authors reported that DCAM formation was highest among the hydrophilic acid fraction, followed by the hydrophilic bases, and to a much smaller extent the hydrophobic acid fraction, with yields of 1.5, 0.60, and 0.12 nmol DCAM per mg DOC, respectively. Of note, the authors indicated that despite having less DON content, the DCAM formation potential of hydrophilic acids was more than double that of hydrophilic bases. Interestingly, the weighted sum of DCAM yields from the six fractions (0.4 nmol/mg DOC) only accounted for 60% of raw water DCAM formation (0.67 nmol/mg DOC). While the authors suggested that this may be due to a combination of factors, they noted that a potentially important DCAM precursor, colloidal organic matter, was not recovered in the fractionation procedure employed (Chu et al. 2010b).

The formation of DCAM is compared to DCAN formation in Figure 4.21. As observed in the relationship between the formation of $CHCl_3$ and DCAM, White River and Bushy Park Reservoir samples did not adhere to the general trend in which the DCAM formation tracked formation of DCAN. With the exception of the two waters noted, Figure 4.21 demonstrates a

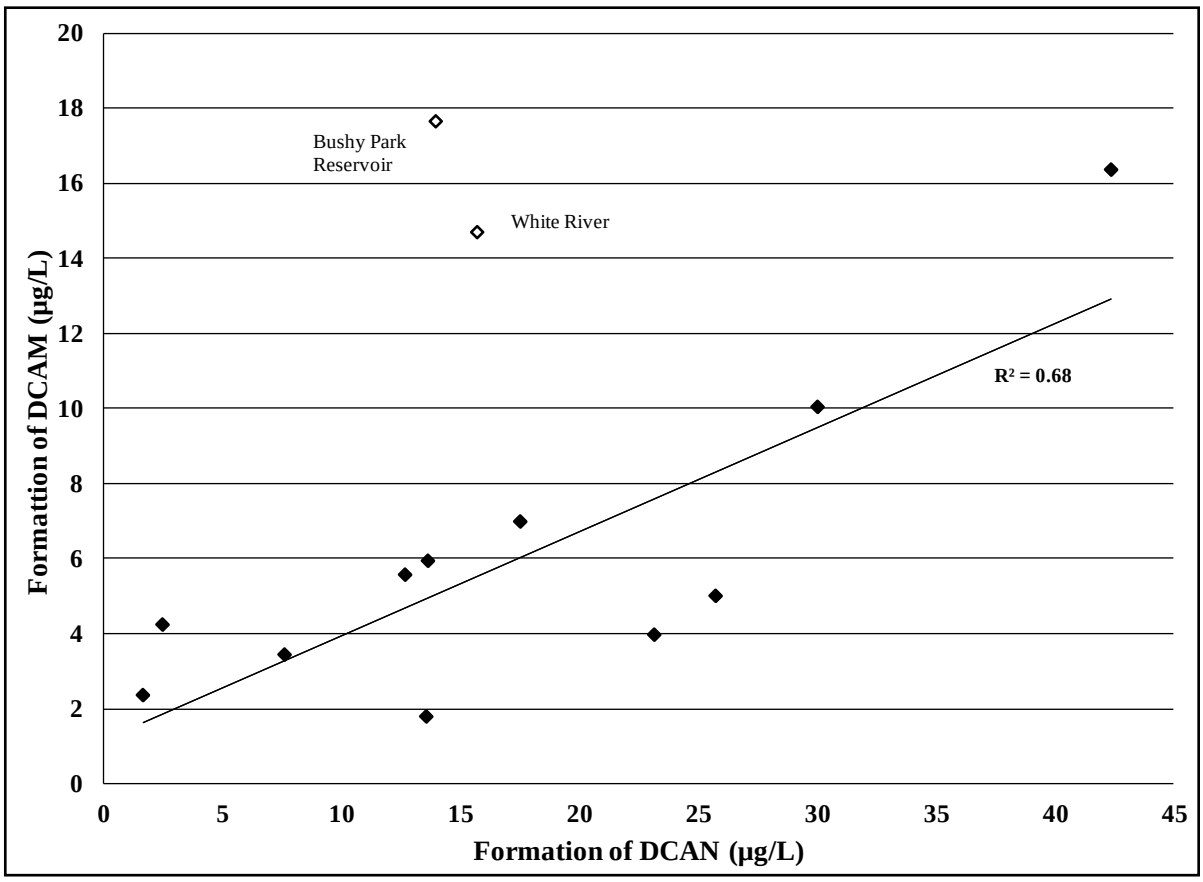


Figure 4.21: Comparison of raw water dichloroacetamide and dichloroacetonitrile formation

good correlation between DCAM and DCAN formation. As shown, most waters formed more DCAN than DCAM. The average ratio was 2.8 µg DCAN/µg DCAM.

As noted in Figures 4.18-4.21, Bushy Park Reservoir and White River samples exhibited high DCAM formation relative to the norm. As these waters are quite disparate in nature, there is no obvious reason to suggest why enhanced DCAM formation was observed in these two samples. White River is characteristically hydrophilic with low DOC (3.3 mg/L), SUVA (2.01 L/mg-m), and HPOA (33%). White River was also in the midst of a significant diatom bloom when the sample was taken. Bushy Park Reservoir, however, is predominately humic in nature, with a high DOC (6.2 mg/L), high SUVA (4.07 L/mg-m), and high HPOA content (55%). The DON concentration of the latter water was 0.23 mg/L as N, while, the White River sample was abundant in inorganic nitrogen constituents (DIN/TDN=0.88). Therefore,

the reported DON concentration of 0.13 mg/L as N in this source is highly uncertain and makes the comparison of DON content in these samples difficult. Because of the diatom bloom present when sampled, White River may have had a DON concentration substantially higher than the reported value. Sources in the literature indicate that algal-dominated sources of DOM are typified by low C/N ratios and low aromatic C content. Additionally, algae are considered primary producers of amino acids during growth and succession and constitute sources of extracellular organic material predominantly comprised of N-enriched aliphatic compounds and colloidal aminosugars (Westerhoff and Mash 2002). By whatever cause, both White River and Bushy Park Reservoir samples appear to have contained DON fractional components that are precursors of DCAM and are present at levels resulting in enhanced formation of DCAM.

4.5. MITIGATION OF DBP FORMATION BY ENHANCED COAGULATION

A principal objective of this study was to evaluate the effect of enhanced coagulation for the removal of N-DBP precursors for a variety of raw waters representing the range of elements in the enhanced coagulation matrix. As noted previously, uniform chlorination conditions were utilized to characterize the formation of $CHCl_3$, DCAN, and DCAM between the raw and coagulated waters. Because enhanced coagulation is an accepted and widely practiced means of THM control, the reduction in $CHCl_3$ formation was used as a reference for reduction of the N-DBP species of interest. Table 4.5 summarizes the percentage reduction results of DBP surrogates and the corresponding reduction in formation of the DBP species of concern.

Table 4.5: Percent Reduction of DBP Surrogates and DBP Formation Potential by Enhanced Coagulation

Water	TOC	DOC	UV_{254}	DON*	$CHCl_3$	DCAN	DCAM
Schuylkill River, PA	43.0	51.4	64.4	41.5*	85.9	76.3	53.5
Croton Reservoir, NY	18.5	26.4	30.5	52.9*	43.5	41.9	2.3
White River, IN	17.3	26.0	20.9	100*	48.5	39.0	63.0
Passaic River, NJ	17.5	34.3	31.3	46.3*	44.3	20.5	21.8
Upper San Leandro Reservoir, CA	19.1	42.5	32.4	0.0	37.1	21.8	23.6
Otay Reservoir, CA	10.0	4.3	17.4	18.2	50.4	26.9	74.5
Lake Michie, NC	42.7	46.4	55.1	41.4	57.1	45.7	49.9
Bushy Park Reservoir, SC	57.0	62.2	80.7	11.1	82.9	73.0	63.9
Vadnais Lake, MN	36.2	39.5	46.2	26.5	57.6	28.5	0.0
Scioto River, OH	38.4	45.8	62.8	66.4*	62.8	43.7	0.0
Lake Houston, TX	48.7	55.2	59.9	0*	63.8	47.8	48.9
Lake Campbell, CA	42.9	51.4	58.1	22.4	64.9	41.9	0.0
Hillsborough River, FL	55.5	65.3	71.2	78.7	72.0	54.9	53.0

***Reduction of DON for waters in which DIN/TDN exceeded 0.75 appear with *notation**

Independent of alkalinity and pH, humic content and other forms of compositional heterogeneity that are known to affect coagulation considerably, the following averages are shown only to help convey the general results at the most basic level—particularly in relation to the fate of DON, DCAN, and DCAM—and to generate further questions about such relationships. Indeed, the enhanced coagulation matrix exists because the same outcome cannot be expected of coagulation in widely varying sources. Enhanced coagulation resulted

in average removals of 42% and 49% for DOC and UV_{254}, respectively. Average DON removal was 28% for waters assumed to have reliable DON measurement accuracy (waters with DIN/TDN<0.75) compared to 45% removal of DOC for those same waters. Enhanced coagulation achieved average reductions of 59%, 43%, and 35% in the formation of $CHCl_3$, DCAN, and DCAM, respectively.

4.5.1. Reduction in Chloroform Formation

The reduction in $CHCl_3$ formation achieved by enhanced coagulation ranged from 37 to 86%. The reduction of chloroform formation correlated most strongly with the reduction in UV_{254} absorbance (R^2=0.74), as shown in Figure 4.22. This is consistent with expectations

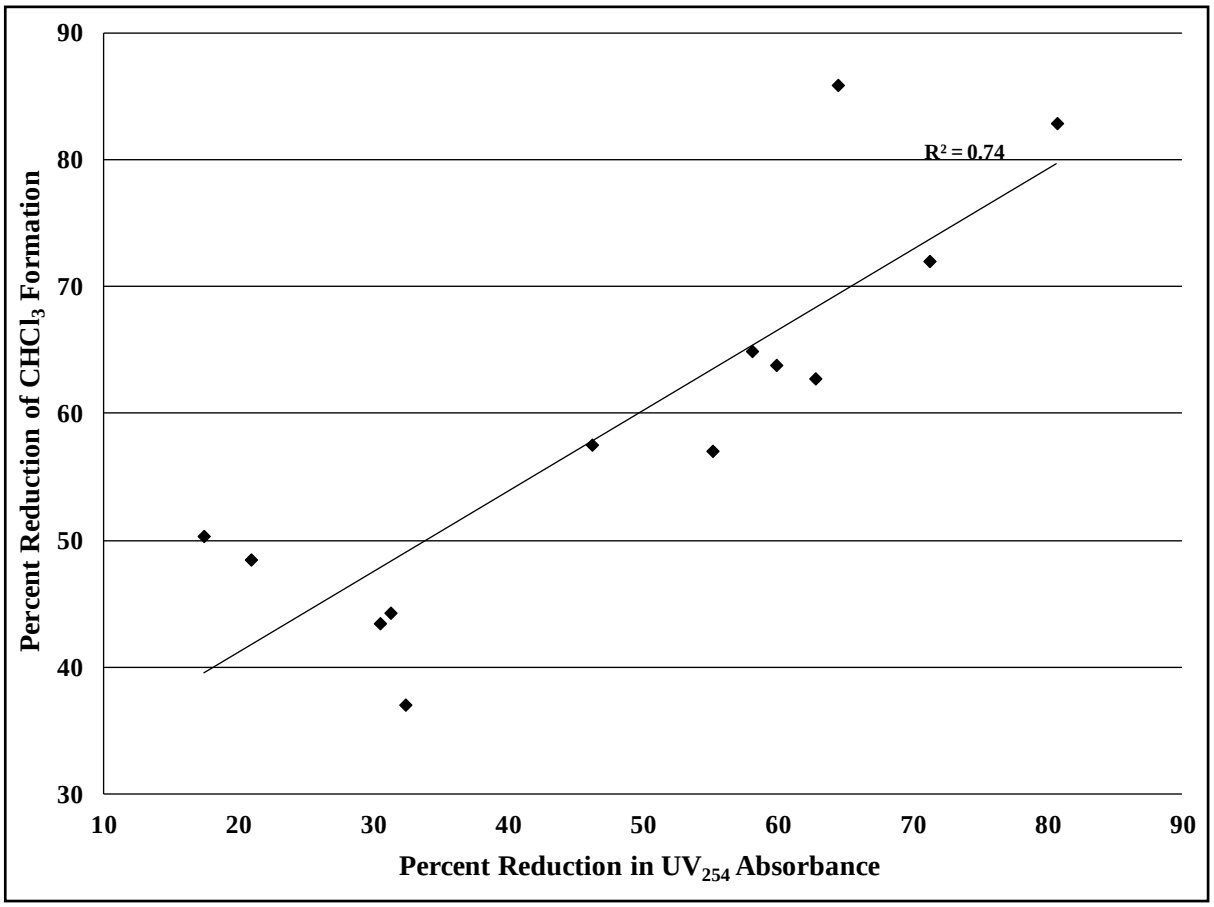


Figure 4.22: Correlation between the reduction of chloroform formation and the removal of UV-absorbing precursors by enhanced coagulation

based on previous investigations (e.g. Edzwald et. al. 1985, Croué et al. 1999, Weishaar et al.

2003). The reduction in $CHCl_3$ formation correlated less strongly with DOC removal (R^2=0.45; see Appendix Figure C-4) than was observed for UV_{254} removal. Consistent with the results for DOC removal (Figure 4.9), reduction in $CHCl_3$ formation improved with increasing raw water SUVA (see Appendix C-5). These relationships are in agreement with the findings of several investigators (Hubel and Edzwald 1987, White et al. 1997, Edwards 1997, Vrijenhoek et al. 1998, Archer and Singer 2006).

4.5.2. Mitigation of N-DBP Formation

As suggested previously in relation to some outlier water samples, this study employed whole waters which also contain particulate and some colloid sources of organic N which are likely to contribute to the formation of N-DBPs. Particulate and colloidal organic N larger than 0.45 µm would not have been captured by the measures of DON used in this research (N analyses used filtered samples), and the contribution of these fractions to the formation of DCAN and DCAM was not differentiated from formation from the dissolved fractions. This is a possible contribution to the scatter observed in raw water DCAN and DCAM formation when compared to surrogates which are based on dissolved characteristics (e.g. DOC, DON, UV_{254}, SUVA, FI, and percent HPOA). Moreover, the reduction of DCAN and DCAM formation potential resulting from removal of particulate and colloid constituents was also not distinguished from removal of other N-DBP precursor fractions. Particulate and colloid sources of DCAN and DCAM may be minor in most waters and, as it relates to DBP control, these fractions may also be negligible if they are indeed well-removed during treatment. However, these fractions were not characterized in this study.

As with the trends in raw water DBP formation, the reduction of DCAN formation followed that of $CHCl_3$ formation, as shown in Figure 4.23. The reductions in formation of $CHCl_3$ and DCAN as a result of enhanced coagulation with alum are well correlated

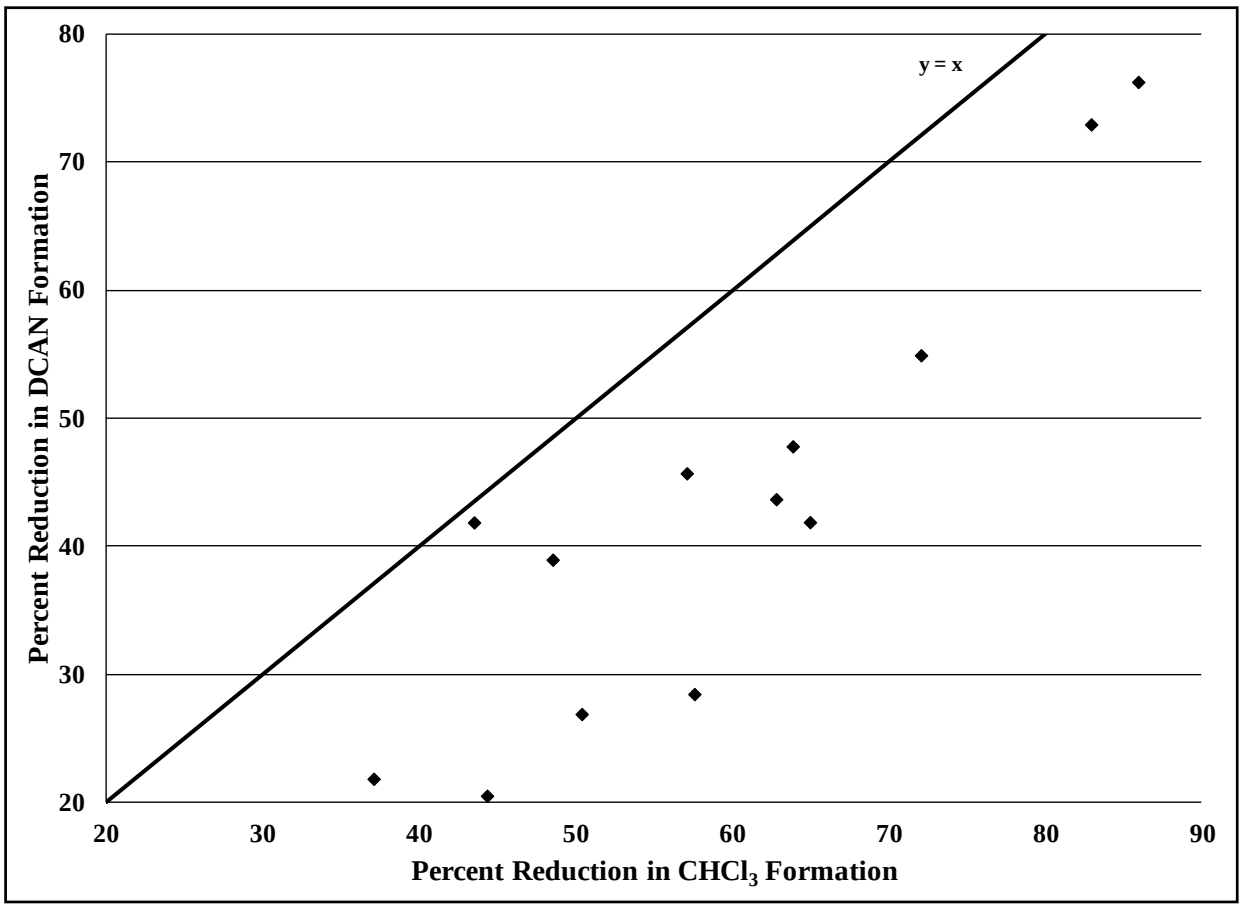


Figure 4.23: Preferential mitigation of chloroform formation relative to dichloroacetonitrile formation after enhanced coagulation

(R^2=0.81) in these samples. The figure demonstrates that while the percent reduction in DCAN formation increased with percent reduction in $CHCl_3$ formation, the reduction in $CHCl_3$ formation potential exceeded that of DCAN formation potential in all cases. This is indicated by the position of the data to the right of the 1:1 line in Figure 4.23. The reduction in DCAN formation ranged from 21 to 76% and, on average, was 16% less than that observed for reduction in $CHCl_3$ formation.

The relationship depicted in Figure 4.23 suggests that, while sharing common precursors or having precursors similar in nature, coagulation can be generally anticipated to result in greater chloroform precursor removal than DCAN precursor removal. This expectation was noted following Figure 4.15, wherein the apparent relationship between the DCAN-to-$CHCl_3$

formation ratio and humic content (refer to Figure B-6 in Appendix) is described. Both the results suggested by Figure 4.23 and the relationship identified in Appendix B-6 are supported by findings that a significant proportion of DCAN precursors are hydrophilic in nature. Coagulation would not be expected to remove these nonhumic DCAN precursor fractions as effectively as THM precursors which have been shown to be generally more hydrophobic in nature (Shah and Mitch 2011). Examples of DCAN precursor characterization include an evaluation of HAN formation in a variety of DOM isolates reported by Mitch et al. (2009) and a recent review of N-DBP formation pathways conducted by Shah and Mitch (2011). The relationship between DOM characteristics and reduction in N-DBP formation by coagulation is considered in further detail below (see Figures 4.27 and 4.28).

Reduction in DCAN formation is shown relative to both reduction of UV_{254} absorbance and removal of DOC in Appendix Figures C-6 and C-7. While these relationships are not as strong as those shown for reduction in $CHCl_3$ formation, in general, reduction of UV_{254} absorbance and removal of DOC showed moderate (R^2=0.59) and weak (R^2=0.34) correlation with reduction in DCAN formation, respectively. With regard to DON, it was expected that the removal of DON by coagulation would not share a relationship with reduction in DCAN formation because raw water DCAN formation potential was not well correlated with DON content (see Figure 4.17). Furthermore, even for waters similar in nature, a wide range in the removal of DON by enhanced coagulation was observed (see Figures 4.10 and 4.11). Surprisingly, the reduction of DCAN formation potential by coagulation was found to be correlated with removal of DON , as shown in Figure 4.24. With the exception of Bushy Park Reservoir water, the reduction in DCAN formation was directly

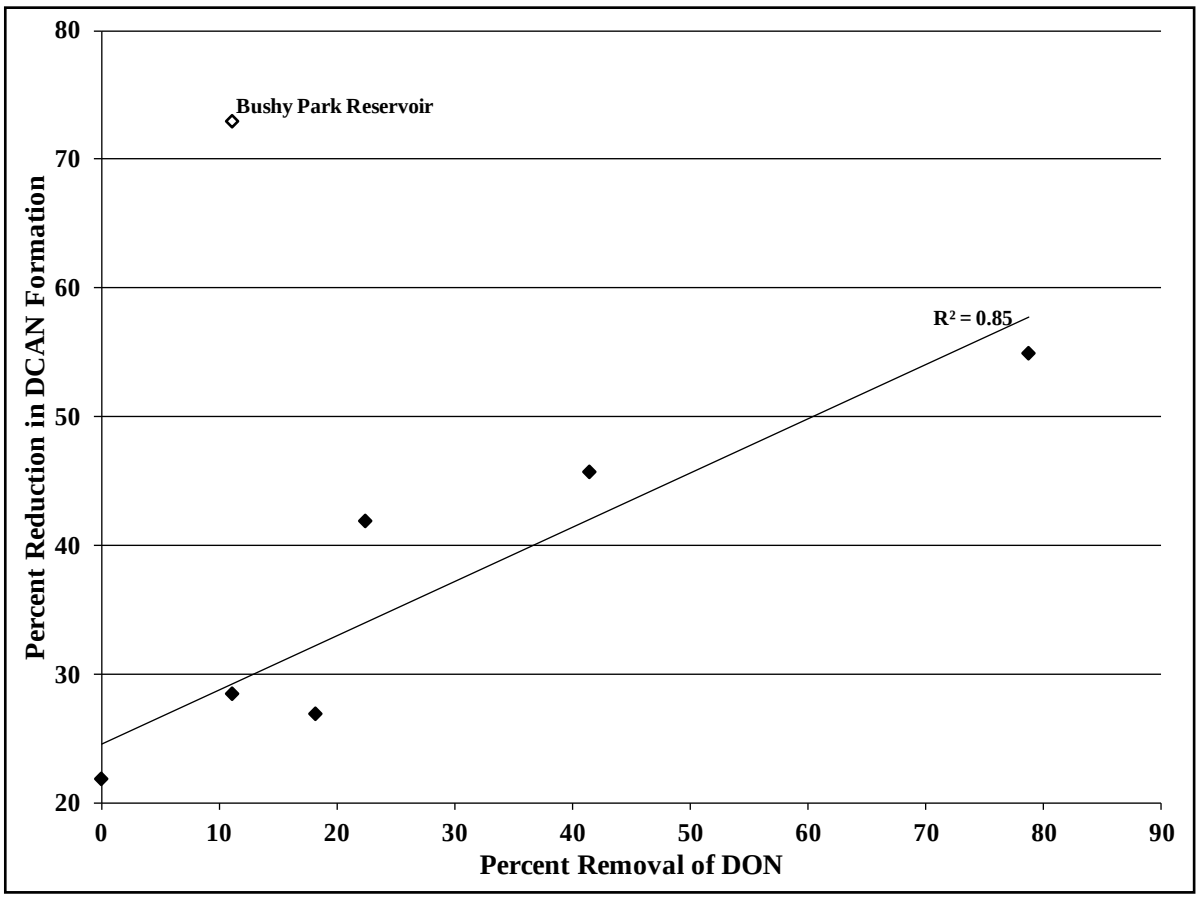


Figure 4.24: Reduction of dichloroacetonitrile formation potential compared to the removal of dissolved organic nitrogen

proportional to the removal of DON. Omitting this sample, which had above average reduction in formation of all three DBP species monitored, the relationship between reduction in DCAN formation and DON removal is quite robust (R^2=0.85). The rationale for the high DCAN reduction observed in Bushy Park Reservoir may be explained by a predominance of amino acids relative to other fractions of DON less abundant in DCAN formation potential. Comprising 15-35% of DON in lakes and rivers, amino acids have been reported to form DCAN and have been shown to be amenable to removal by coagulation (Westerhoff and Mash 2002, Mitch el al. 2009, Dotson et al. 2010).

As shown in Figure 4.25, the reduction in DCAM formation was generally less than the reduction in $CHCl_3$ formation. With the exception of White River and Otay Reservoir

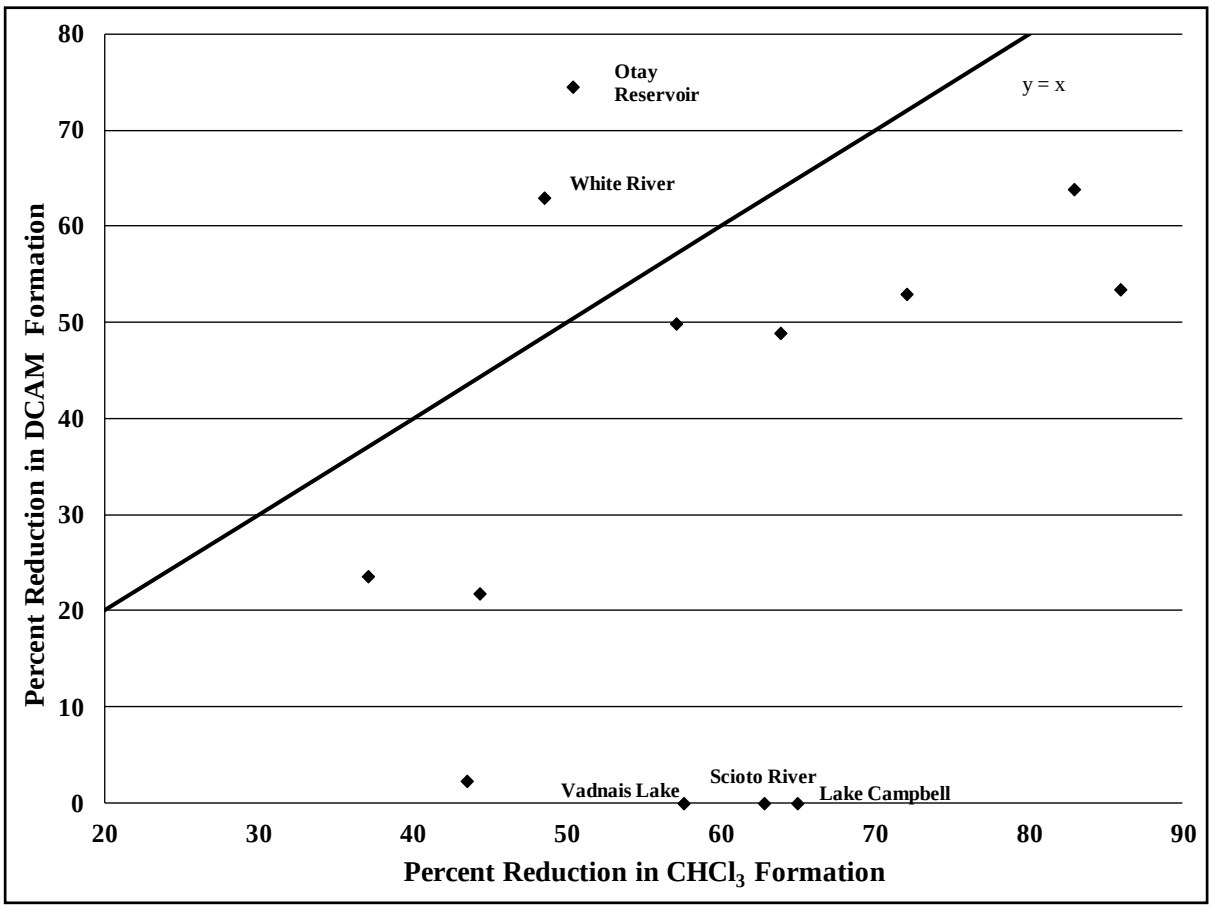


Figure 4.25: Impact of enhanced coagulation upon formation potentials of dichloroacetamide and chloroform

samples, in which the reduction in DCAM formation was greater than the corresponding reduction of $CHCl_3$ formation, the 11 other waters fall below the 1:1 line indicating equivalent reduction in formation potential of both DCAM and $CHCl_3$. While seven waters appear to constitute a weak trend in which coagulation resulted in proportional removal of DCAM and $CHCl_3$ precursors, there is a wide distribution in the observed reduction of DCAM formation potential. The figure is further confounded by four waters that exhibited little to no reduction in DCAM formation due to coagulation. The reduction in DCAM formation ranged from 2.3% to 75%.

As noted, the reduction in DCAM formation exceeded that of $CHCl_3$ for Otay Reservoir water and White River water. The latter sample was addressed in §4.4.4 and was noted as

being characteristically hydrophilic in nature, with an enhanced DCAM yield relative to both the average among all waters and relative to its own raw water formation of chloroform and DCAN, and its raw water DOC content (Figures 4.18, 4.21, and 4.19, respectively). While Otay Reservoir may be largely disregarded with respect to DCAM formation trends for reasons associated with its presumably high bromide content as noted in §4.4.4, both samples of White River and Otay Reservoir water appear to have had considerable colloid content as suggested by the difference between raw water TOC and DOC concentrations in these waters (see Table 4.2). This fraction, that was likely to have been very well removed by coagulation, constituted 7.5% and 12% of raw water TOC (by mass) in Otay Reservoir and White River samples, respectively. Colloids have generally been shown to be enriched in DON and are important precursors of DCAN (Lee et al. 2007, Mitch et al. 2009). As Chu and colleagues (2010b) note, colloids have not been investigated as precursors of DCAM.

The reduction in DCAM formation as a result of coagulation is compared to reduction in DCAN formation in Figure 4.26. Because raw water DCAN formation was observed to be well correlated with DOC whereas DCAM was not (see Figures 4.16 and 4.19, respectively), it was anticipated that the reduction in DCAN formation as a result of enhanced coagulation would generally exceed that of DCAM formation. This was not necessarily the case, however, as shown in Figure 4.26. While little or no net reduction in DCAM formation was observed in four waters, the reduction in DCAM formation was about equal to the reduction observed for DCAN formation in six waters and exceeded DCAN reduction in two waters. This finding may suggest that some waters evaluated here contained constituents which appear to have been both amenable to coagulation and precursors common to DCAN and DCAM. Unlike the reduction in DCAN formation (see Figure 4.24), however, the removal of

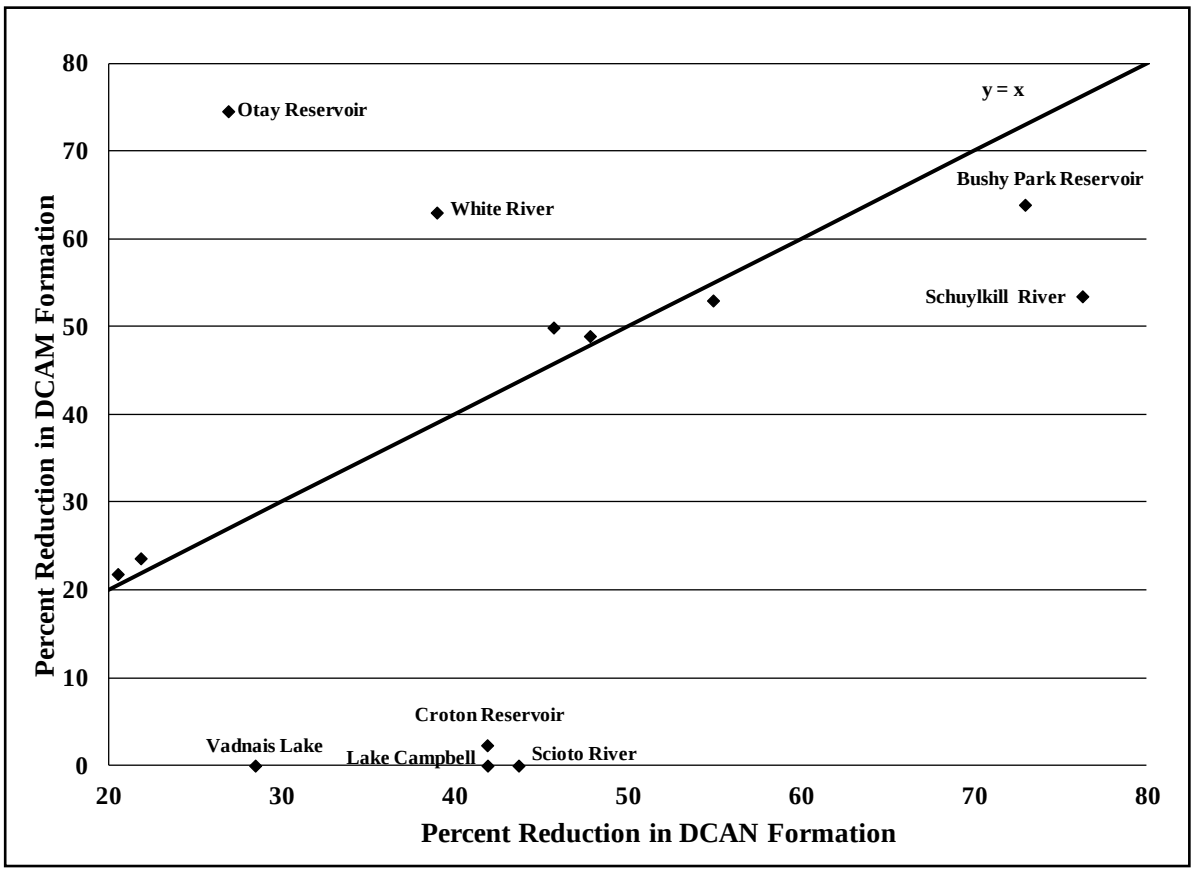


Figure 4.26: Reduction of dichloroacetamide relative to dichloroacetonitrile by enhanced coagulation

DON by enhanced coagulation did not appear to share any relationship with reduction in DCAM formation (see Figure C-8 in Appendix).

4.6. ADDITIONAL CONSIDERATIONS

Among the waters evaluated in this study, the reduction in formation of both DCAN and DCAM achieved by enhanced coagulation was predominantly less than that achieved for $CHCl_3$ (refer to Figures 4.23 and 4.25). This outcome was anticipated for DCAN based upon findings reported in other studies (e.g. Lee et al. 2007, Mitch et al. 2009, Shah and Mitch 2011). Findings reported by Chu et al. (2010a) comprise the bulk of the literature available for DCAM formation. Thus, not only has formation of DCAM not been well documented in the literature, this study is the first of its kind to evaluate DCAM control (as well as DCAN control) with enhanced coagulation. Because (1) the nonhumic fraction is generally not

removed well by coagulation, and (2) compared to THMs, DCAN and DCAM have a greater relative proportion of nonhumic precursors, enhanced coagulation would be expected to be a less effective control strategy than has been observed for THMs. To examine this hypothesis more thoroughly, raw water nonhumic content is shown in relation to DOC removal and reductions in CHCl3, DCAN, and DCAM formation in Figures 4.27-4.30.

The removal of DOC by enhanced coagulation was observed to decrease in relation to increasing nonhumic content, as shown in Figure 4.27. The left side of the figure shows that,

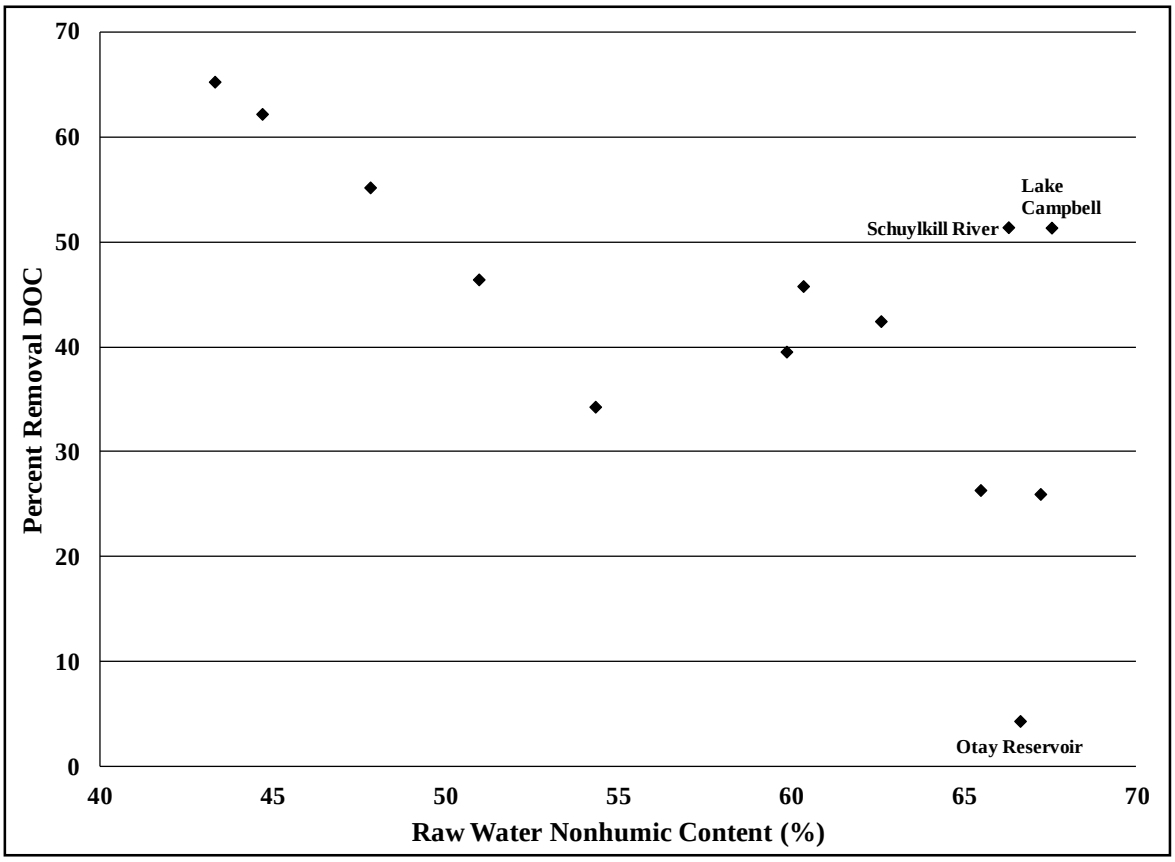


Figure 4.27: Effect of raw water nonhumic content upon DOC removal by enhanced coagulation

for five waters in which HPOA is the dominant organic carbon fraction, the removal of DOC exhibited a strong linear relationship with humic content. The removal percentages show more variability for waters with greater proportions of nonhumic material. Despite good correlation between raw water DOC content and formation of $CHCl_3$ and DCAN (Figures

4.13 and 4.16, respectively), Figure 4.27 further clarifies why reductions in DBP formation did not correlate well with DOC removal following treatment by enhanced coagulation.

Figure 4.28 illustrates a general trend in which the reduction in chloroform formation potential decreased in relation to increasing raw water nonhumic content. With the exception

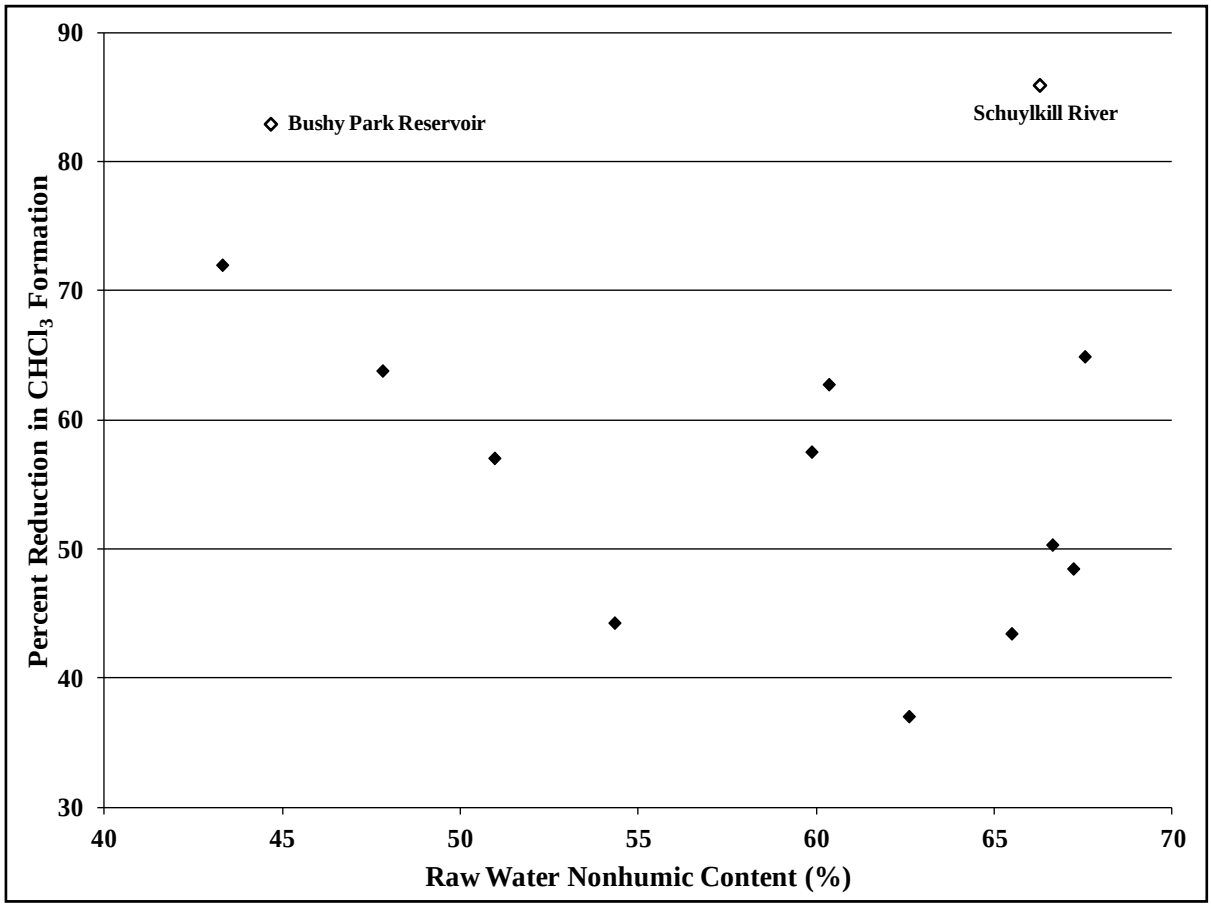


Figure 4.28: Relationship between nonhumic content and reduction in chloroform formation

of Bushy Park Reservoir water, observed reductions in formation appear to be very similar to DOC removal among waters with high HPOA content. The two identified waters share similarly high reduction in formation despite very different proportions of humic and nonhumic DOM. In relation to nonhumic content, the reduction in DCAN formation by enhanced coagulation demonstrates a wide distribution, as shown in Figure 4.29, and tracked less well with humic content compared to removal of DOC or reduction in

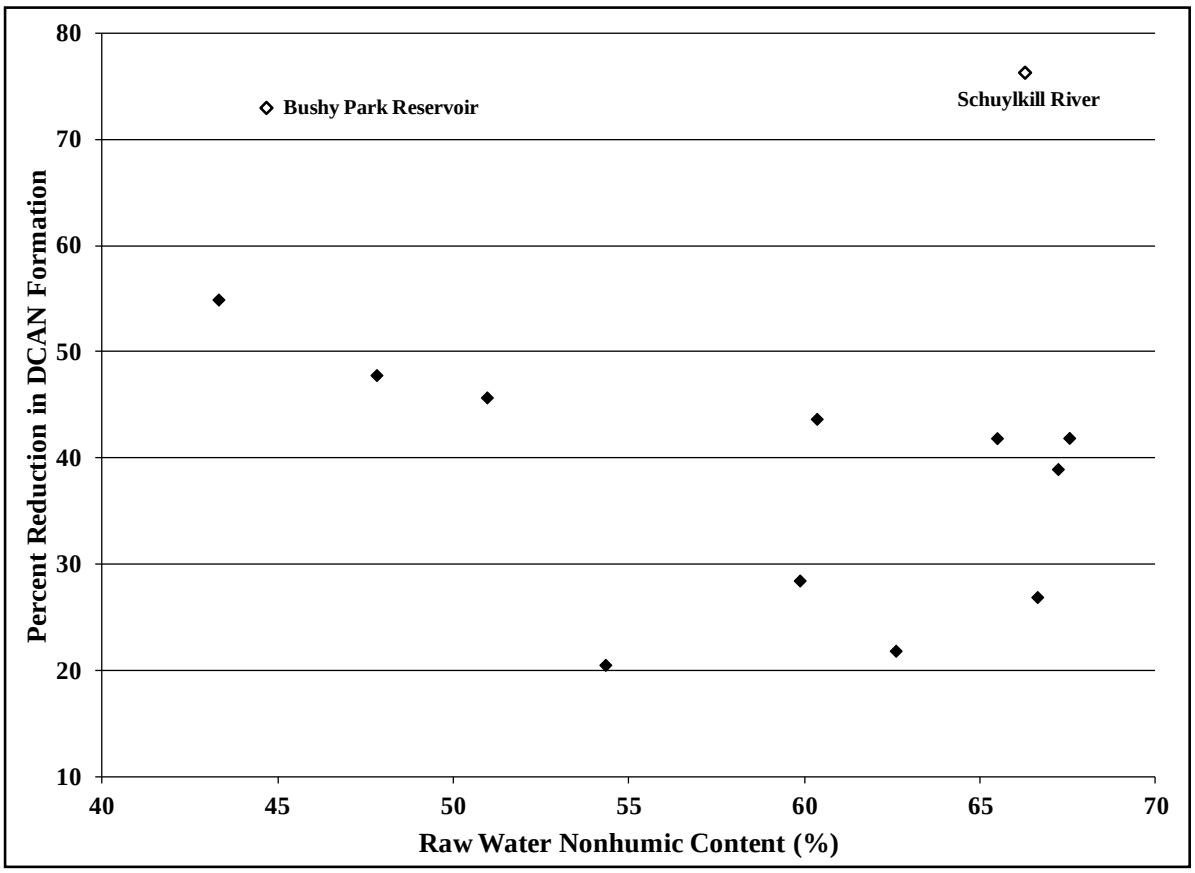


Figure 4.29: Comparison of nonhumic content and reduction in formation of dichloroacetonitrile

$CHCl_3$ formation. Save for the two waters identified as outliers, a trend is suggested in which the reduction in DCAN formation potential generally decreased relative to increasing nonhumic content. However, for the seven waters containing 60-70% nonhumic DOC, the reduction in DCAN formation differed by 10-20%. This suggests that some nonhumic waters still contain DCAN precursors that, to varying degrees, are amenable to coagulation. While the trend is markedly similar to that depicted in Figure 4.28, note that the bulk of the data points are positioned between 20 and 50% reduction in DCAN formation, compared to 40-70% reduction in formation of $CHCl_3$.

A similar relationship between the reduction in DCAM formation and raw water nonhumic content is suggested in Figure 4.30. When the three waters identified are omitted,

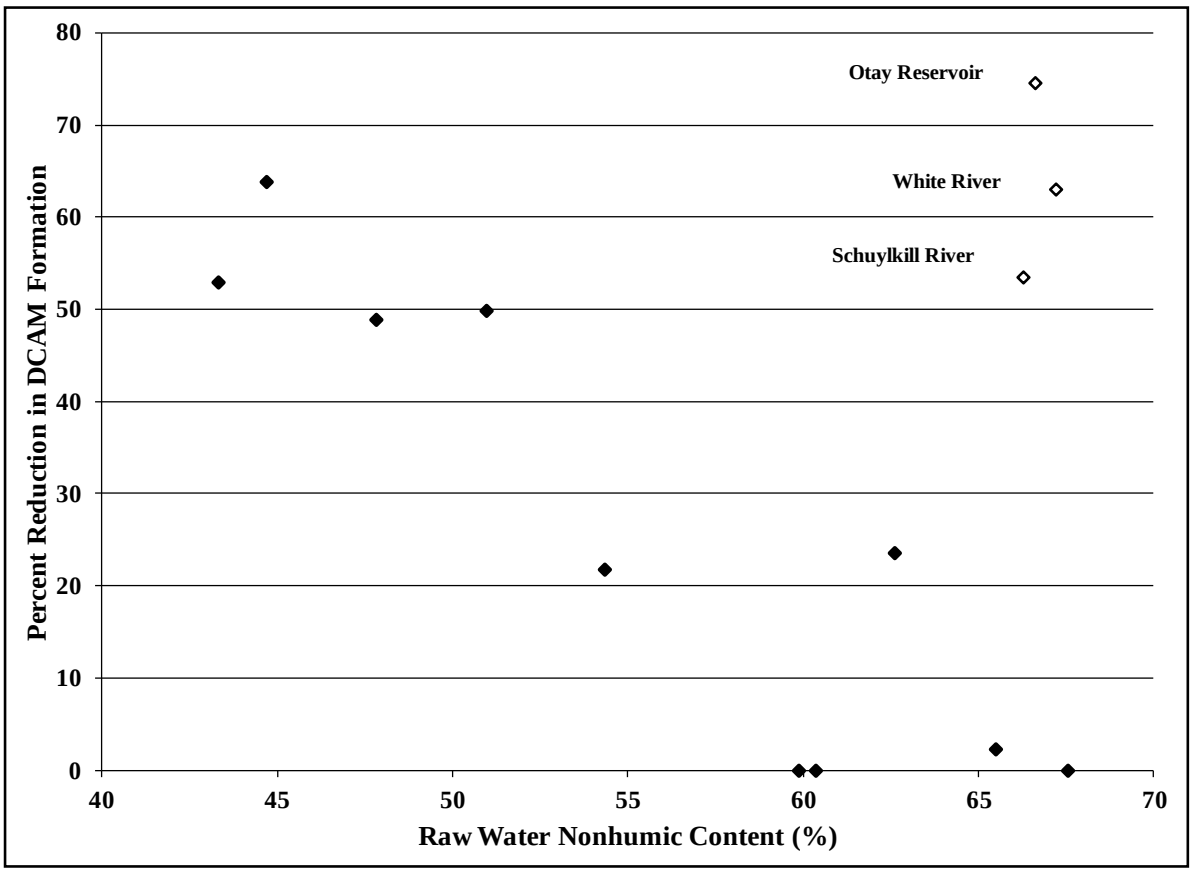


Figure 4.30: Correlation between nonhumic content and reduction in dichloroacetamide formation

a clear trend is evident. While the outliers contradict a general trend in which reduction in DCAM formation potential decreased with increasing nonhumic DOC content, they also serve to highlight the variability of DCAM precursor removal observed in this study.

Collectively, Figures 4.27-4.30 show that, for the five waters in which HPOA is the dominant organic carbon fraction, removal of DOC and DBP precursor tracked humic content exceptionally well. For the other waters which have greater nonhumic character, removal of the four parameters exhibits appreciable scatter. This heterogeneity in removal is a consequence of the relative proportions of hydrophilic and transphilic DOM in these waters, and the degree to which these fractions are amenable to removal by coagulation. The trends identified in Figures 4.29 and 4.30 suggest that, relative to THM control, enhanced

coagulation may prove less effective in controlling the formation of DCAN and ineffective for control of DCAM formation in waters dominated by nonhumic organic carbon.

4.7. IMPLICATIONS

Based upon the waters characterized in this study, the results indicate that application of the existing enhanced coagulation framework will generally reduce formation of DCAN and DCAM at levels proportional to TOC removal. Reductions in DCAN formation were observed to be better than achieved for TOC removal for nine waters, and 95% of that achieved for TOC removal in 12 of the 13 waters examined. Reductions in DCAM formation were 95% or better than achieved for TOC reduction for nine waters. However, no appreciable reduction was observed for the other four waters investigated. The observed difference between reductions in DCAN and chloroform formation potential ranged from 1.6-30% (16% on average); nine of the 13 waters examined had DCAN reductions within 80% of the corresponding chloroform reduction. While reduction in DCAM formation was greater than that of chloroform in two samples, seven waters had reductions in DCAM formation within 80% of the corresponding chloroform reduction.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1. CONCLUSIONS

The practice of enhanced coagulation was evaluated for its capacity to remove DON and to reduce the formation of two nitrogenous DBPs, DCAN and DCAM, in 13 raw drinking waters. The waters selected represent the range of alkalinities and TOC values within the enhanced coagulation matrix, geographic diversity, and were sampled in either winter or summer from both rivers and impoundments. This work indicates that enhanced coagulation with alum results in less removal of DON than DOC and results in greater reduction in formation of $CHCl_3$ compared to either DCAN or DCAM. The specific findings of this study are as follows:

- With the exception of one water with enhanced DCAN formation, raw water DCAN formation demonstrated a strong relationship with DON concentration for waters with reliable DON measurement accuracy. The formation of DCAM appeared to be independent of DON concentration.
- While the strength of the findings is somewhat hindered due to limitations associated with DON analysis and the number of samples analyzed, DON removal by enhanced coagulation was found to vary considerably between sources and was generally less than that achieved for DOC. Removal of DON appeared to increase with increasing raw water HPOA content in five of the seven waters with reliable DON

measurements. The reduction in DBP formation potential due to enhanced coagulation was greatest for $CHCl_3$, followed by DCAN, and DCAM. Reduction in DCAN formation was well correlated with reduction in $CHCl_3$ formation. Reduction in DCAN formation was also correlated with DON removal in six of seven waters.

- Reduction of DCAM formation potential was not well correlated with reduction of $CHCl_3$ or DCAN formation potential or with removal of precursor surrogates (i.e. DOC, UV_{254}, DON).
- While the reduction in $CHCl_3$ formation by enhanced coagulation was predominantly greater than bulk DOC removal, the same was generally not true for reduction in DCAN and DCAM formation. This indicates that, relative to chloroform precursors and bulk DOC, some precursors of DCAN and DCAM especially, are often not well removed by enhanced coagulation. These findings are consistent with recent research suggesting that these N-DBPs have a greater proportion of nonhumic precursors compared to THMs (Shah and Mitch 2011, Chu et al. 2010).

5.1.1. Additional Findings: Raw Water

Raw water DON occurrence tended to increase with increasing DOC. The raw water DOC-to-DON ratio increased with humic content (HPOA) and SUVA, and was inversely proportional to FI. The raw water formation of $CHCl_3$ was found to be well correlated with UV_{254} and DOC, as has been demonstrated in previous research. Specific $CHCl_3$ yields tended to increase with raw water SUVA and humic content, relationships also observed for specific DCAN yields. Average specific yields of all monitored species were observed to be highest among samples obtained during summer months.

Raw water formation of DCAN was found to be directly proportional to $CHCl_3$ formation, and with respect to relationship strength, DCAN formation demonstrated the following order:

$CHCl_3$ formation > UV_{254} > DOC > DCAM formation. The formation of DCAN generally exceeded raw water DCAM formation. The formation of DCAM was less well correlated with $CHCl_3$ formation, UV_{254} absorbance, and DOC than was observed for raw water DCAN formation.

5.1.2. Additional Findings: Treatment by Enhanced Coagulation

Consistent with the findings of other researchers, enhanced coagulation resulted in greater removal of UV-absorbing material relative to bulk DOC. The removal of DOC was found to increase with raw water SUVA. Both SUVA and %HPOA tended to decrease following coagulation while FI tended to increase after treatment, again consistent with findings by others that humic material is more amenable to coagulation by alum than nonhumic moieties of DOM. Reduction of DBP formation potential tended to improve with increasing raw water humic content (e.g. SUVA, HPOA), although such trends were less pronounced for DCAM formation. Reduction in DCAN formation demonstrated moderate and weak relationships with UV_{254} reduction and DOC removal, respectively.

5.2. RECOMMENDATIONS

There are several opportunities for additional study that would help to further characterize (1) the removal of DON by enhanced coagulation, and (2) the role of enhanced coagulation to control N-DBP formation. The principal limitation underlying this study was the uncertainty resulting from the DON analysis method employed. Accordingly, it would be useful to recreate this study with improved methods of DON measurement, such as dialysis pretreatment as described by Lee and Westerhoff (2005). Alternately, raw waters not impacted by a high relative concentration of inorganic nitrogen could be selected. Improving accuracy of DON measurement and/or selecting waters not impacted by DIN would strengthen the conclusions of this study.

Furthermore, it would be interesting to employ methods to characterize the nature of the bulk DON, both in relationship to DON removal and N-DBP formation. Available means of characterization include DON fractionation as described by Leenheer and colleagues (2007), and expanded fluorescence study, such as parallel factor (PARAFAC) analysis. Differentiation of bulk DON into hydrophilic and hydrophobic acid, neutral, and base fractions could identify fraction-specific removal efficiency and reactivity to form DCAN, DCAM, and other N-DBPs. An example of such a study was reported by Chu et al. (2010) in which formation of DCAM from different precursor fractions was evaluated. Alternately, PARAFAC or other non-destructive fluorescence techniques may offer further insight of DON functional groups, coagulation outcome, and N-DBP reactivity.

Finally, it would also be interesting to evaluate DON removal by iron salt coagulants in place of alum. This would allow comparison of DON removal by iron salts to removal by alum and other coagulants reported in the literature (e.g. Lee and Westerhoff 2006).

While this study has suggested some seasonal variation in relationship to raw water characteristics and DBP formation, DON characterization was limited to seven waters with reliable measurement accuracy. This sample size was too small to render any meaningful conclusions about seasonal impacts of DON occurrence and removal. Thus, there is opportunity to evaluate DON occurrence and removal by coagulation, as well as DBP formation, both among autochthonous and allochthonous sources of DOM and between different seasons. This study has indicated that DCAN and chloroform share some precursors that are similar in nature based upon surrogate measures and comparison of formation potential, but it appears that both DCAN and DCAM have proportionally more nonhumic precursors than THMs. Overall analysis of enhanced coagulation data seems to suggest that

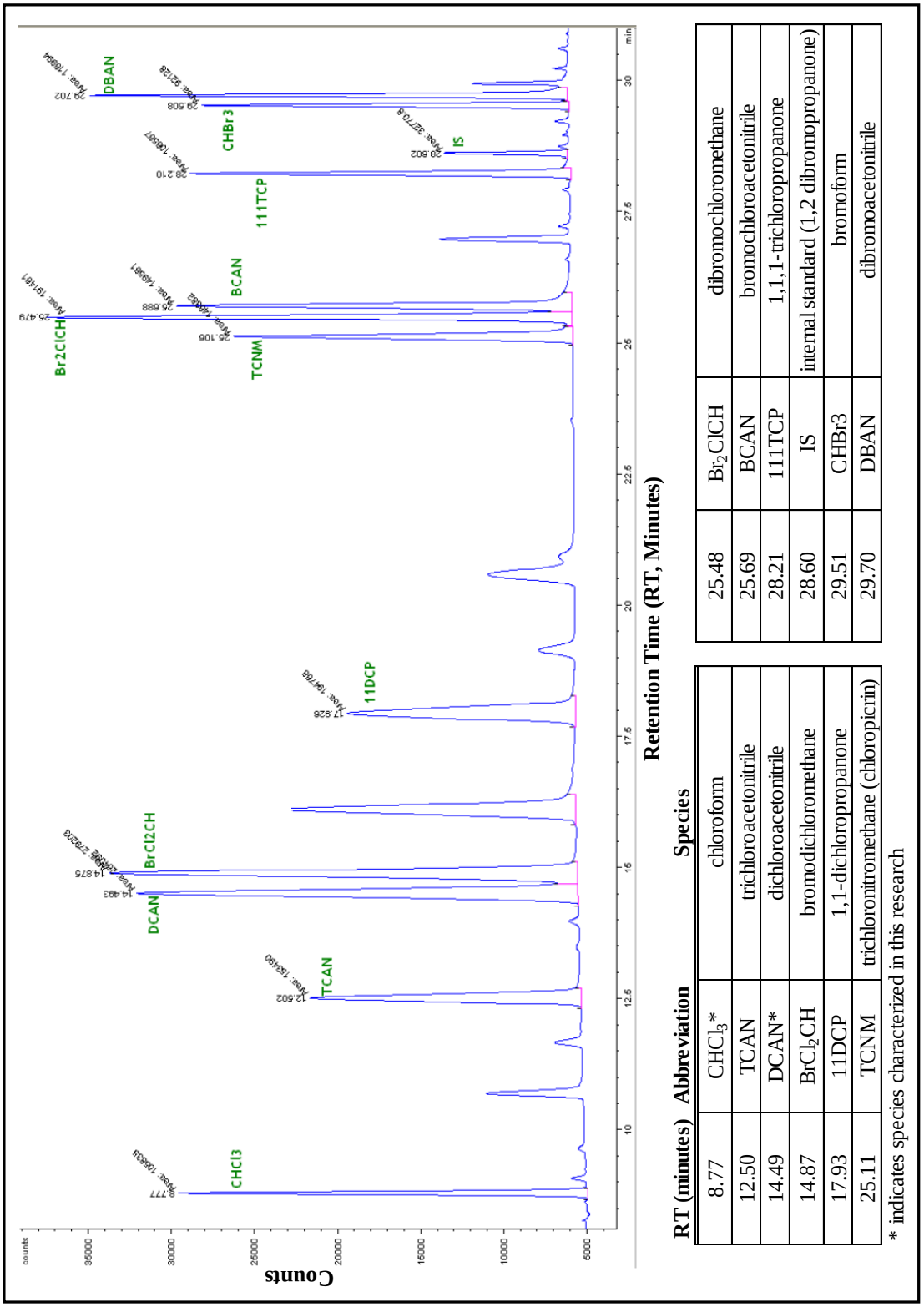
better DON removal and greater reduction in N-DBP formation potential is experienced for humic raw waters. This implies that enhanced coagulation may be an ineffective control strategy for haloacetonitriles and haloacetamides for particularly nonhumic drinking water sources employing free chlorine disinfection. Because this could have important implications if regulation is expanded to include these N-DBP species, further research is needed to evaluate additional nonhumic water sources in order to characterize the removal of nonhumic precursor fractions of HANs and HAMs.

With regard to N-DBP formation, the use of more sensitive instrumentation could expand the analysis to include more N-DBPs of interest. While DCAN and DCAM formation typically dominate N-DBP formation and are both toxicologically important, there are other HANs and HAMs of interest, as well as chloro-/bromo- nitromethanes, cyanogen halides, and nitrosamines that were not quanitied by the GC-ECD analytical method employed in this research. The use of liquid chromotography could expand detection to the sub-µg and ng/L levels necessary to quantify many of these other N-DBPs. Furthermore, to more completely reflect utility practice, it would also be interesting to monitor the formation and relative speciation of N-DBPs when monochloramine is employed as the terminal disinfectant rather than free chlorine.

In the course of this research, it became evident that colloidal organic matter has not been evaluated as a precursor of DCAM. This needs to be addressed in future research as well.

Finally, this study targeted low bromide waters for evaluation. To more fully understand N-DBP formation, waters with higher bromide levels should be incorporated in future investigations.

APPENDIX A: ILLUSTRATIVE CHROMATOGRAMS AND CALIBRATION CURVES FOR DBP ANALYSIS

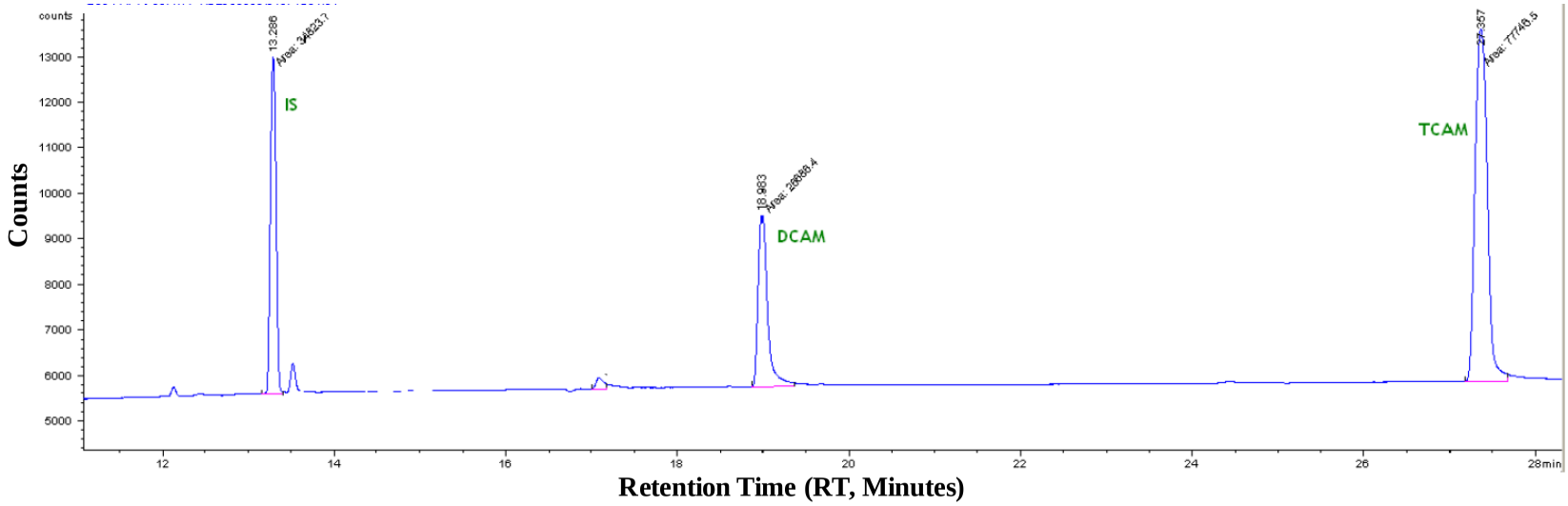


RT (minutes)	Abbreviation	Species
8.77	$CHCl_3$*	chloroform
12.50	TCAN	trichloroacetonitrile
14.49	DCAN*	dichloroacetonitrile
14.87	$BrCl_2CH$	bromodichloromethane
17.93	11DCP	1,1-dichloropropanone
25.11	TCNM	trichloronitromethane (chloropicrin)

25.48	Br_2ClCH	dibromochloromethane
25.69	BCAN	bromochloroacetonitrile
28.21	111TCP	1,1,1-trichloropropanone
28.60	IS	internal standard (1,2 dibromopropanone)
29.51	$CHBr_3$	bromoform
29.70	DBAN	dibromoacetonitrile

* indicates species characterized in this research

Figure A-1: Illustrative halovolatile calibration standard chromatogram



RT (minutes)	Abbreviation	Species
13.4	IS	internal standard (1,2 dibromopropanone)
19.0	DCAM*	dichloroacetamide
27.4	TCAM	trichloroacetamide

* indicates species characterized in this research

Figure A-2: Illustrative haloacetamide calibration standard chromatogram

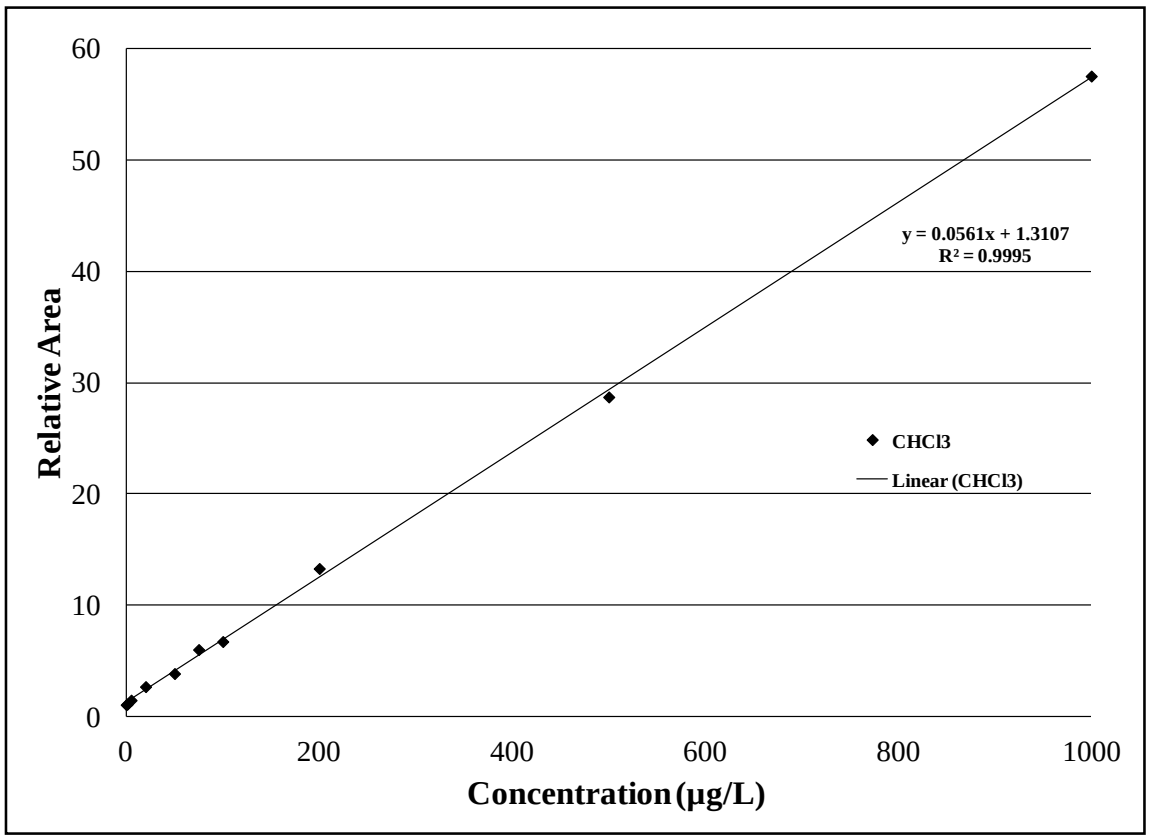


Figure A-3: Illustrative calibration curve for chloroform

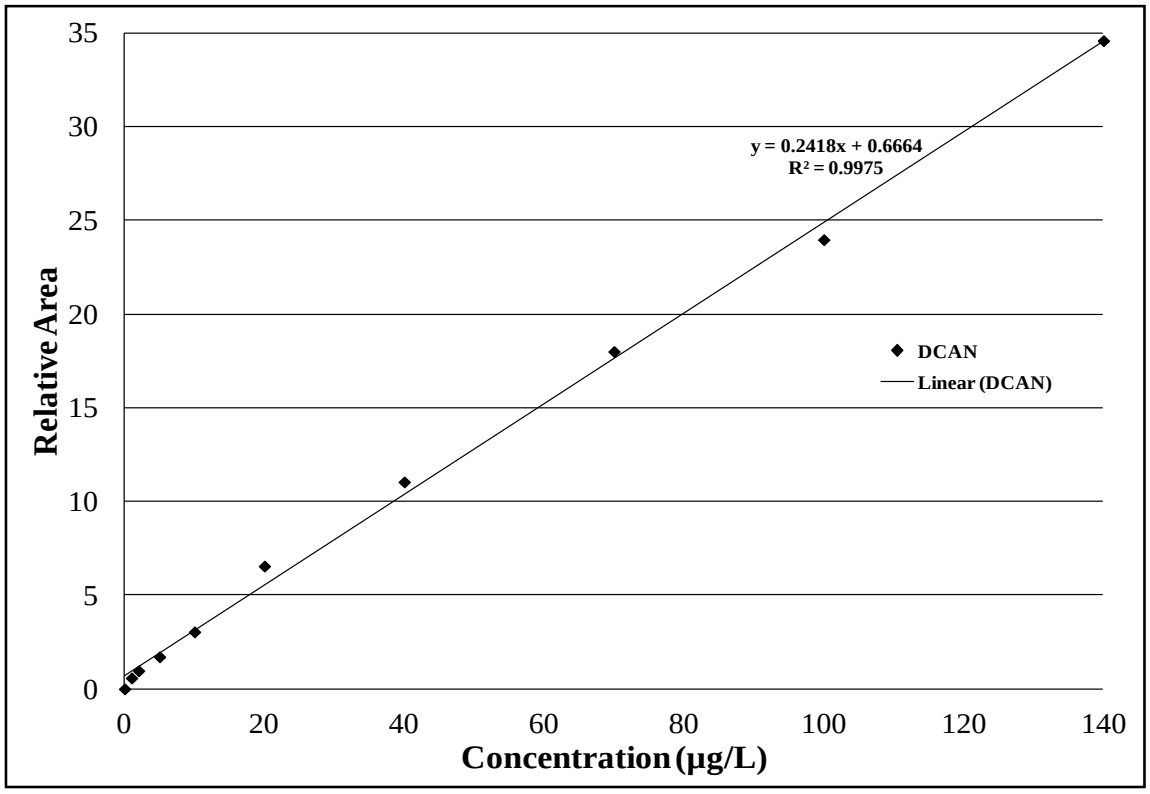


Figure A-4: Illustrative calibration curve for dichloroacetonitrile

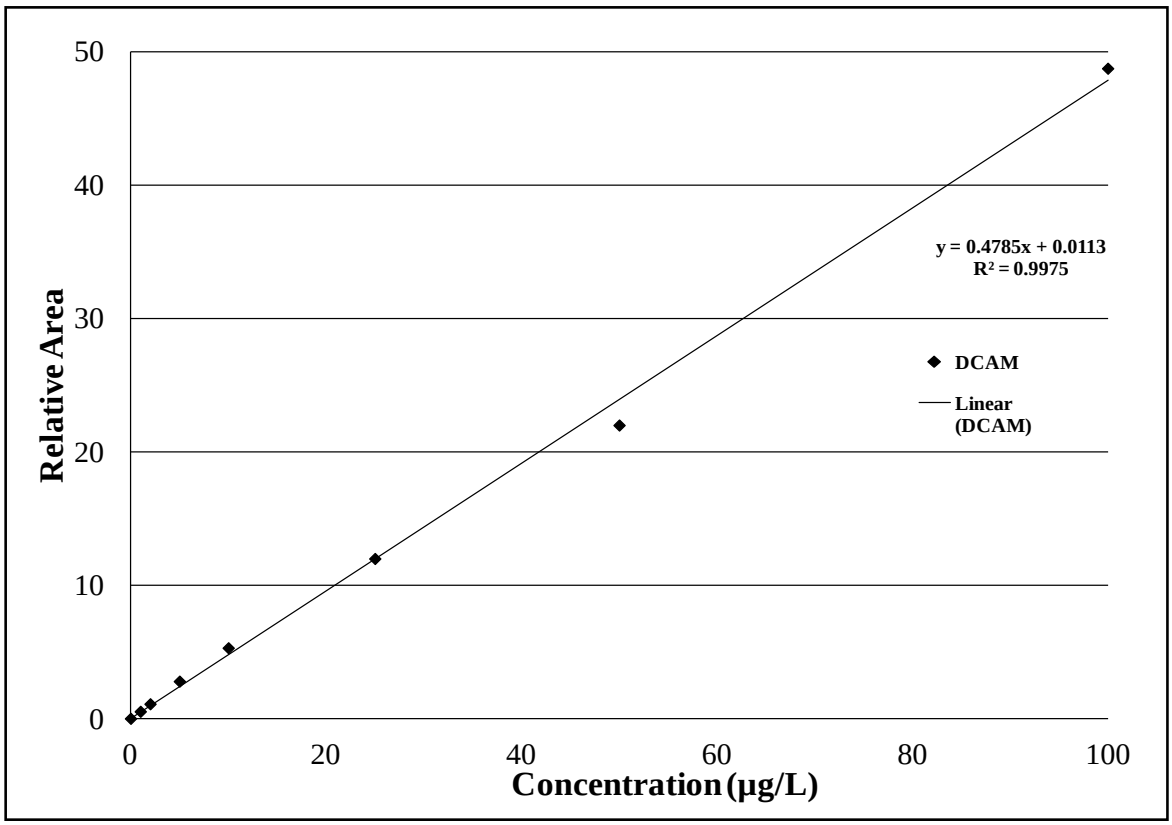


Figure A-5: Illustrative calibration curve for dichloroacetamide

APPENDIX B: SUPPLEMENTARY RAW WATER FINDINGS

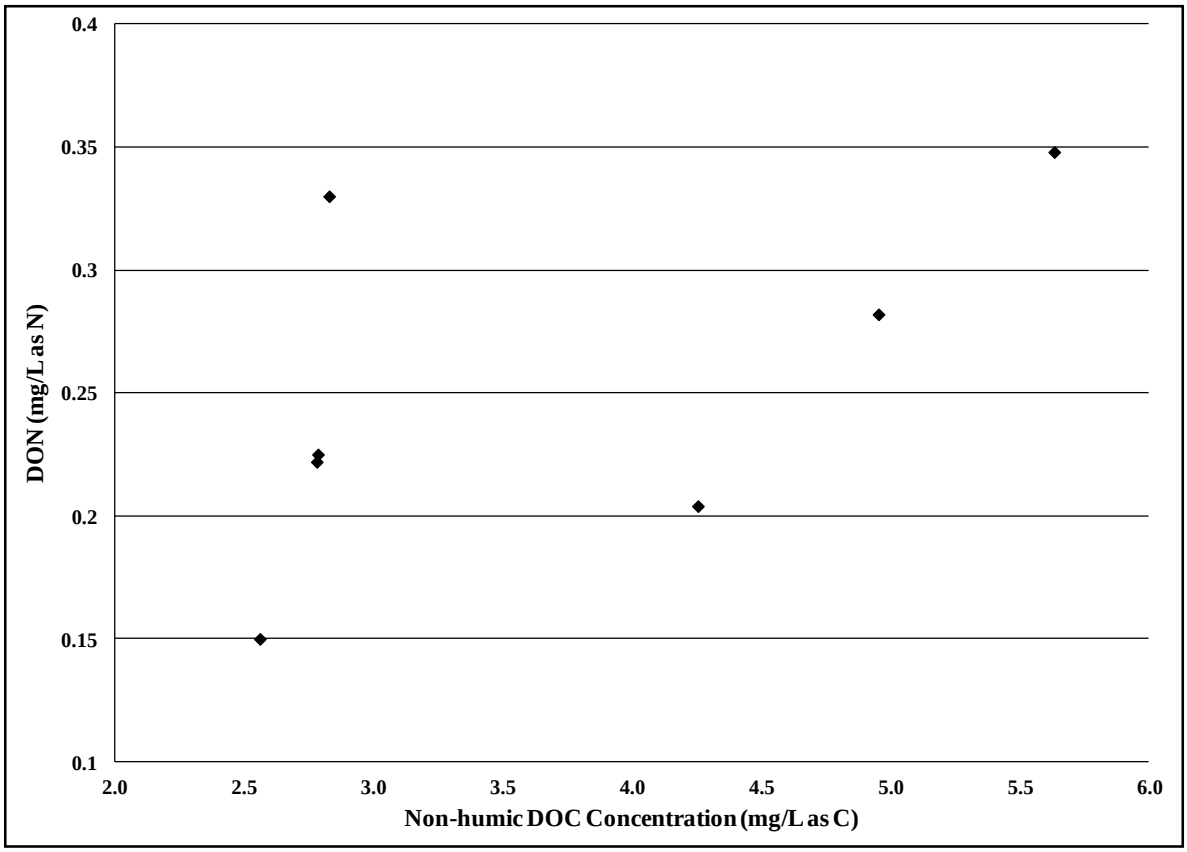


Figure B-1: Nonhumic DOC concentration (XAD8 effluent DOC) relative to dissolved organic nitrogen

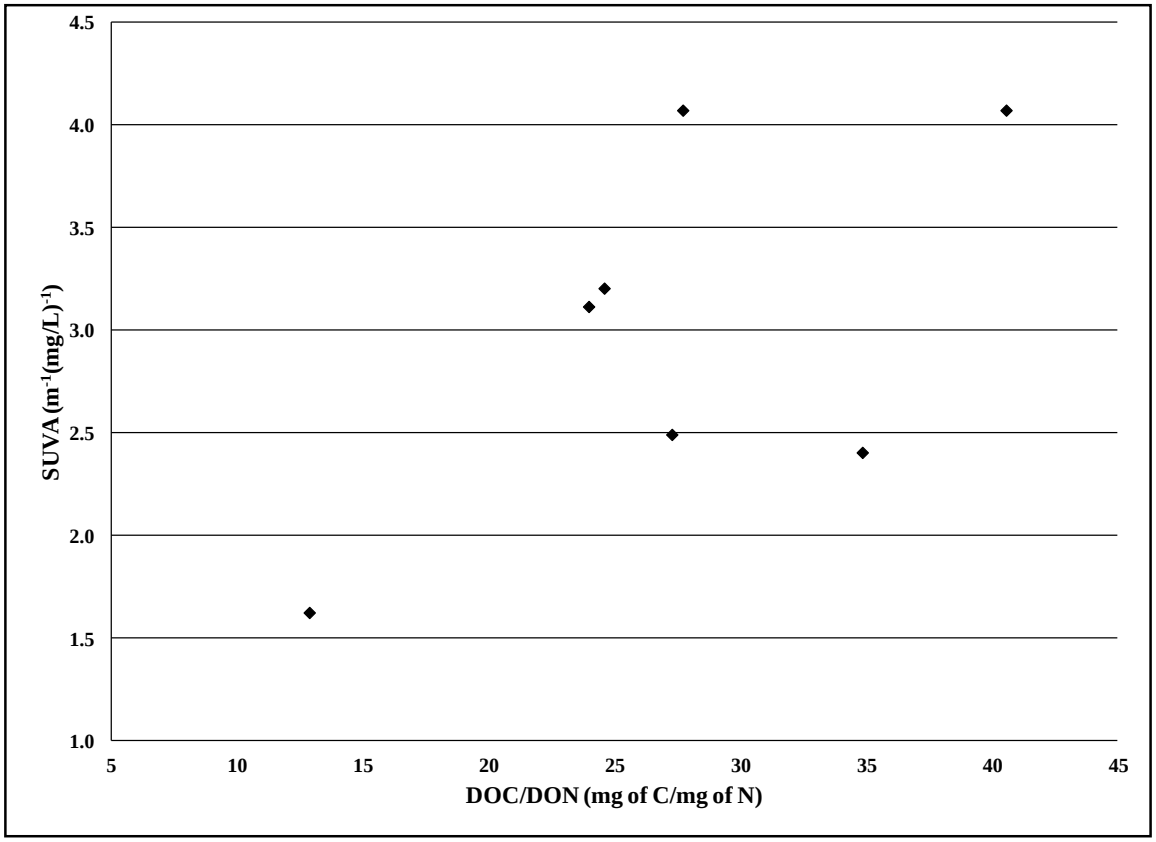


Figure B-2: Ratio of dissolved organic carbon to dissolved organic nitrogen compared to specific UV Absorbance

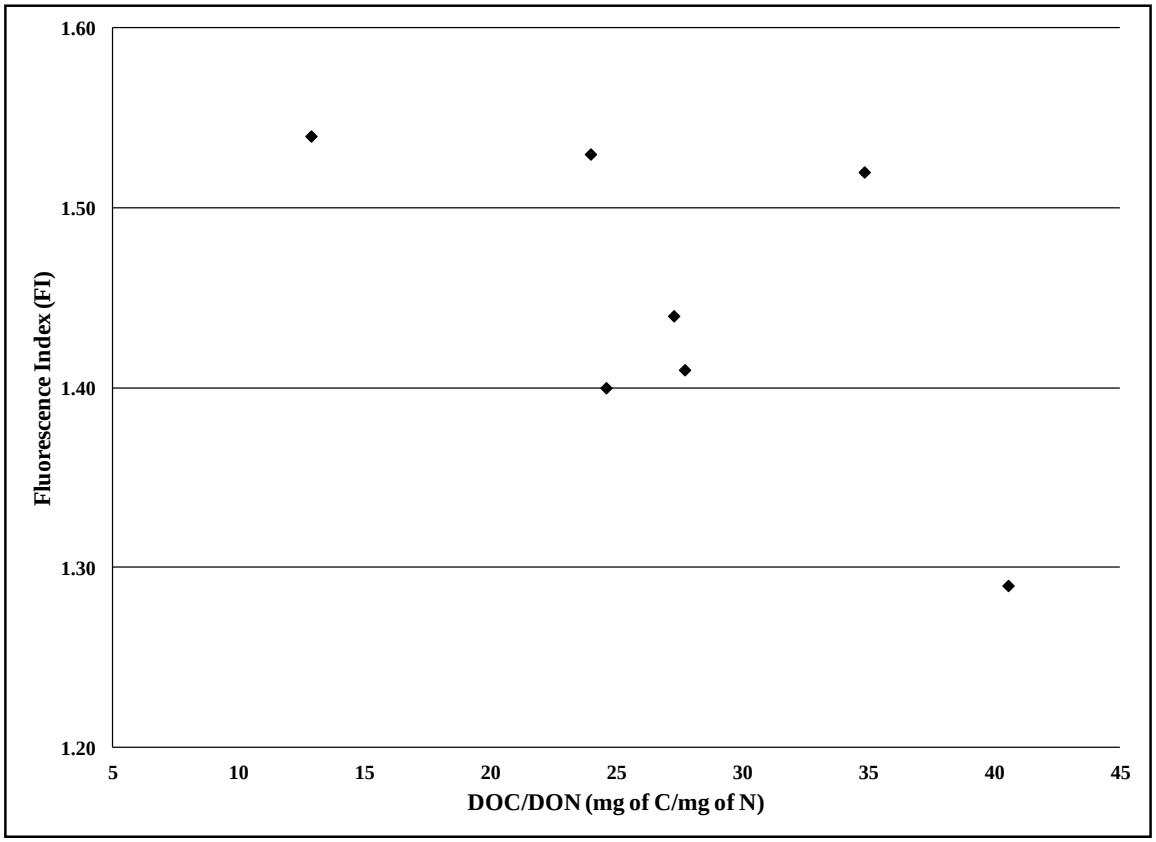


Figure B-3: Ratio of dissolved organic carbon to dissolved organic nitrogen compared to fluorescence index

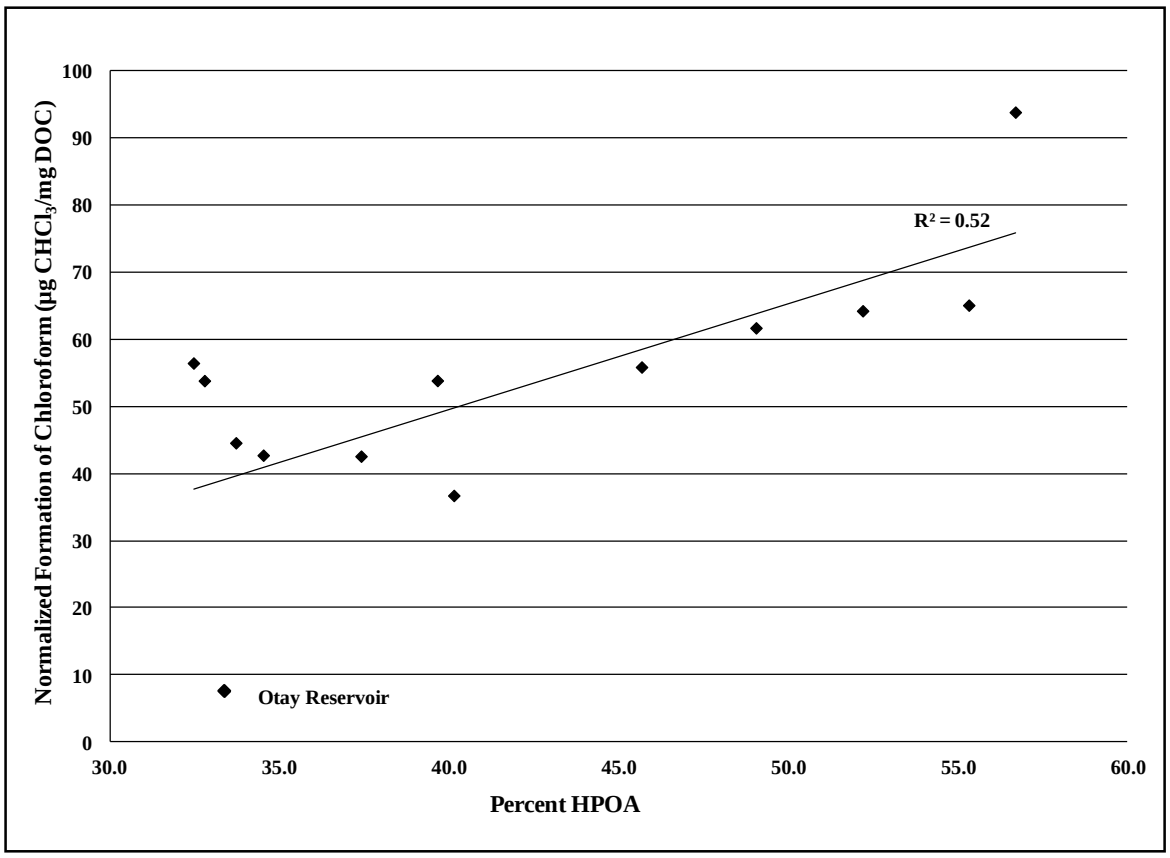


Figure B-4: Normalized formation of chloroform compared to raw water humic content

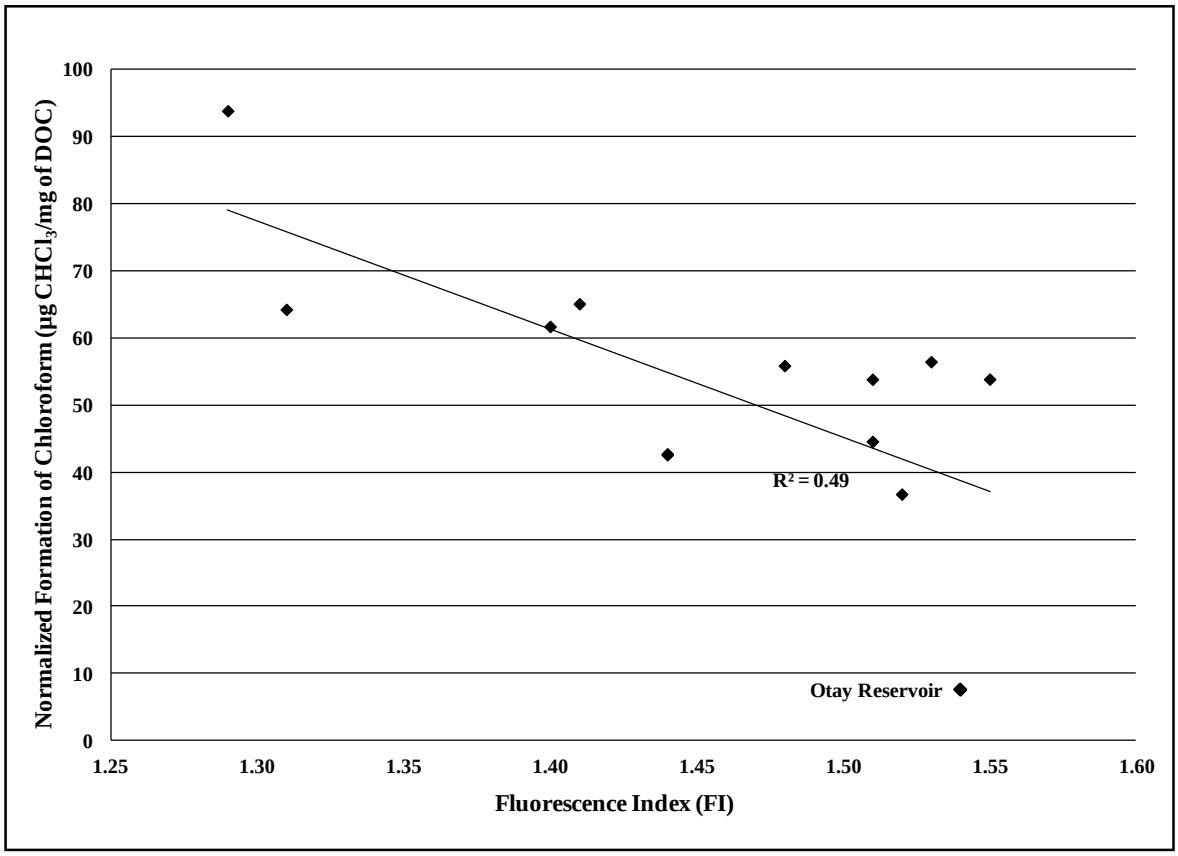


Figure B-5: Normalized formation of chloroform compared to raw water fluorescence index

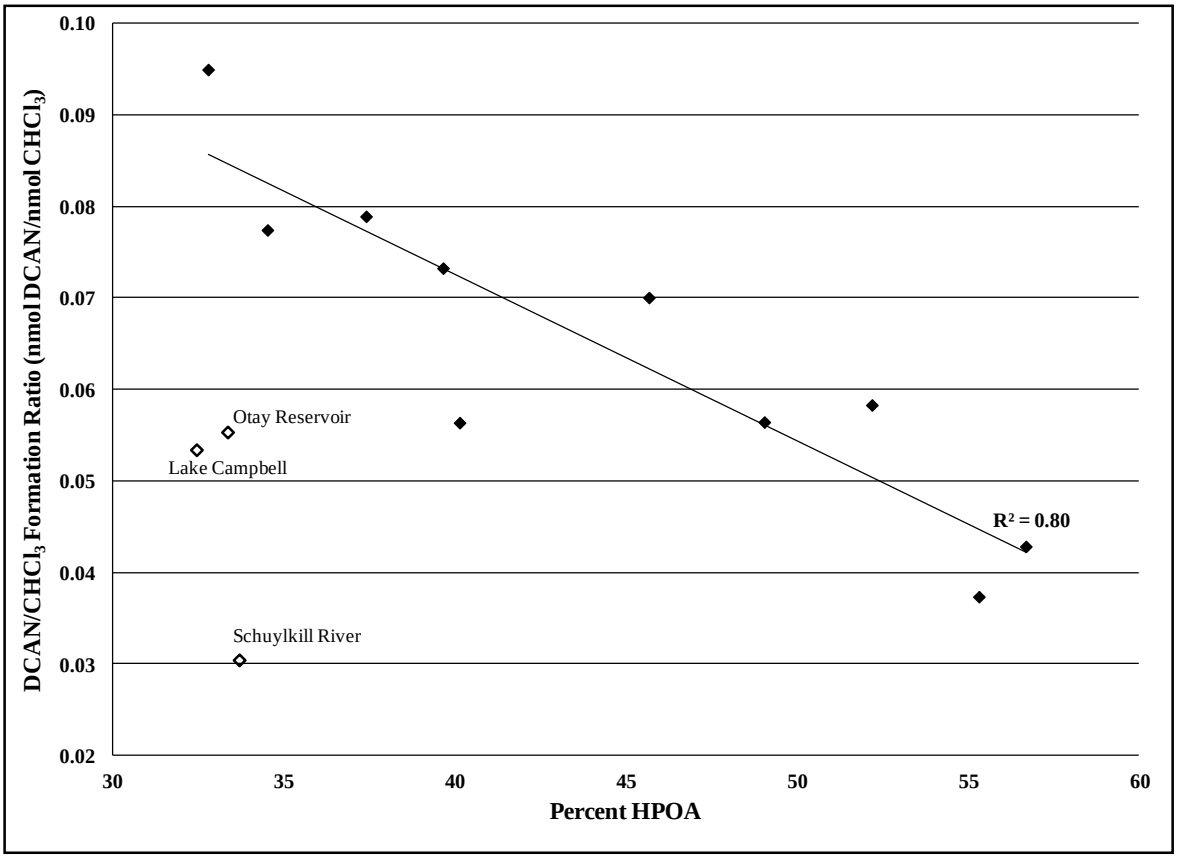


Figure B-6: Impact of humic content upon dichloroacetonitrile-to-chloroform formation ratio

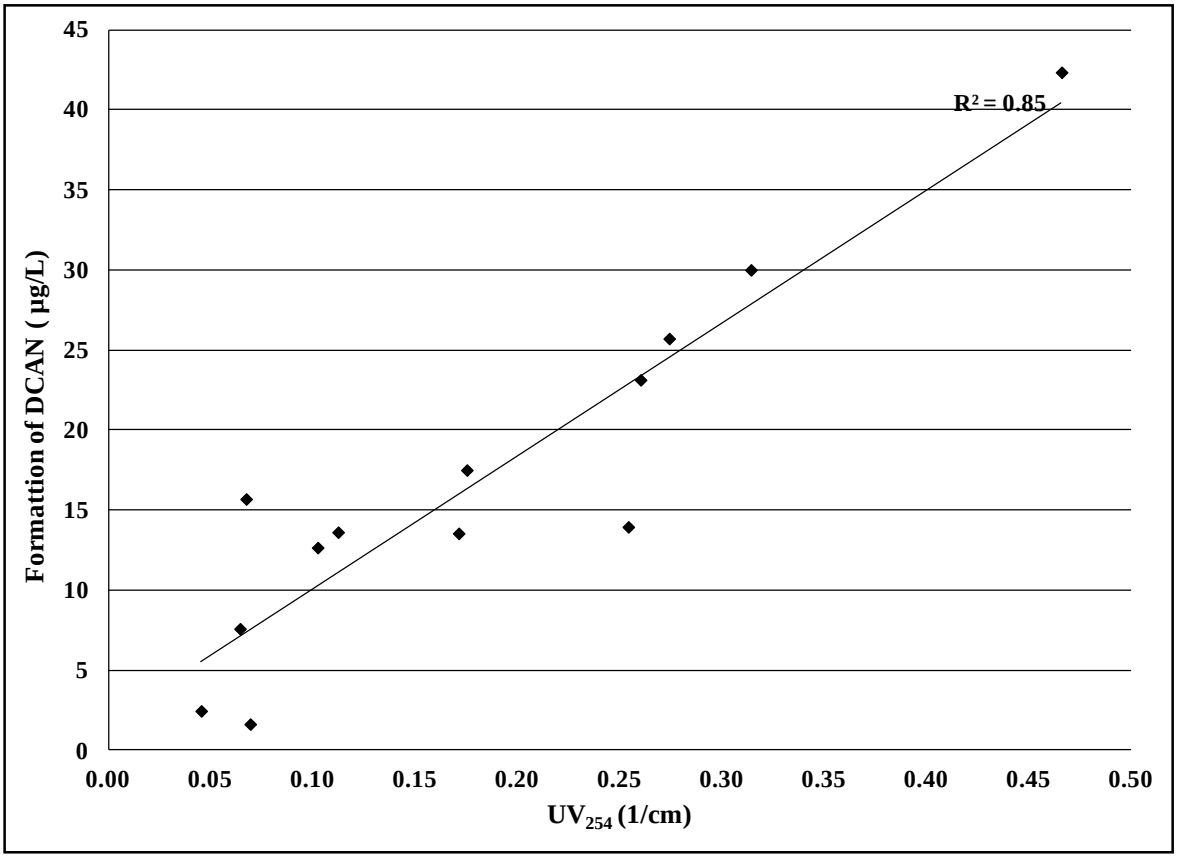


Figure B-7: UV_{254} absorbance compared to formation of dichloroacetonitrile

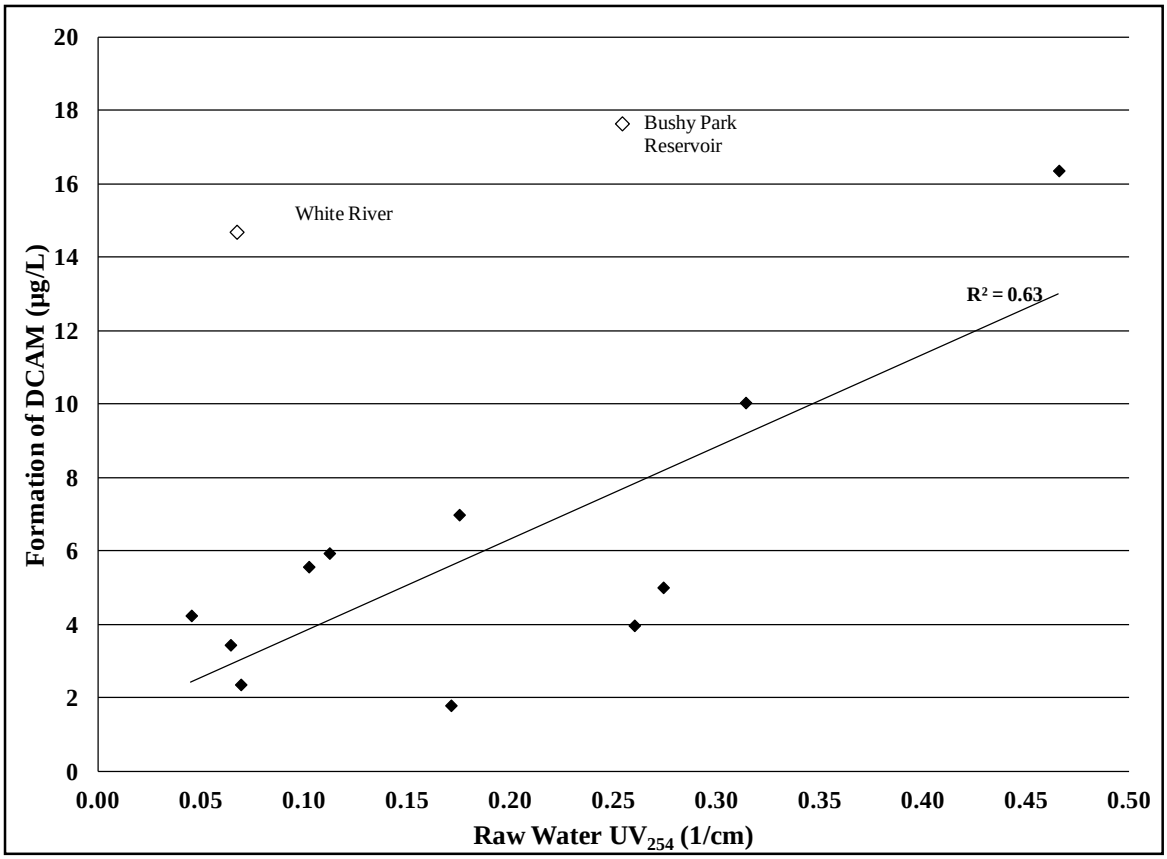


Figure B-8: UV_{254} absorbance compared to formation of dichloroacetamide

APPENDIX C: SUPPLEMENTARY TREATMENT RESULTS

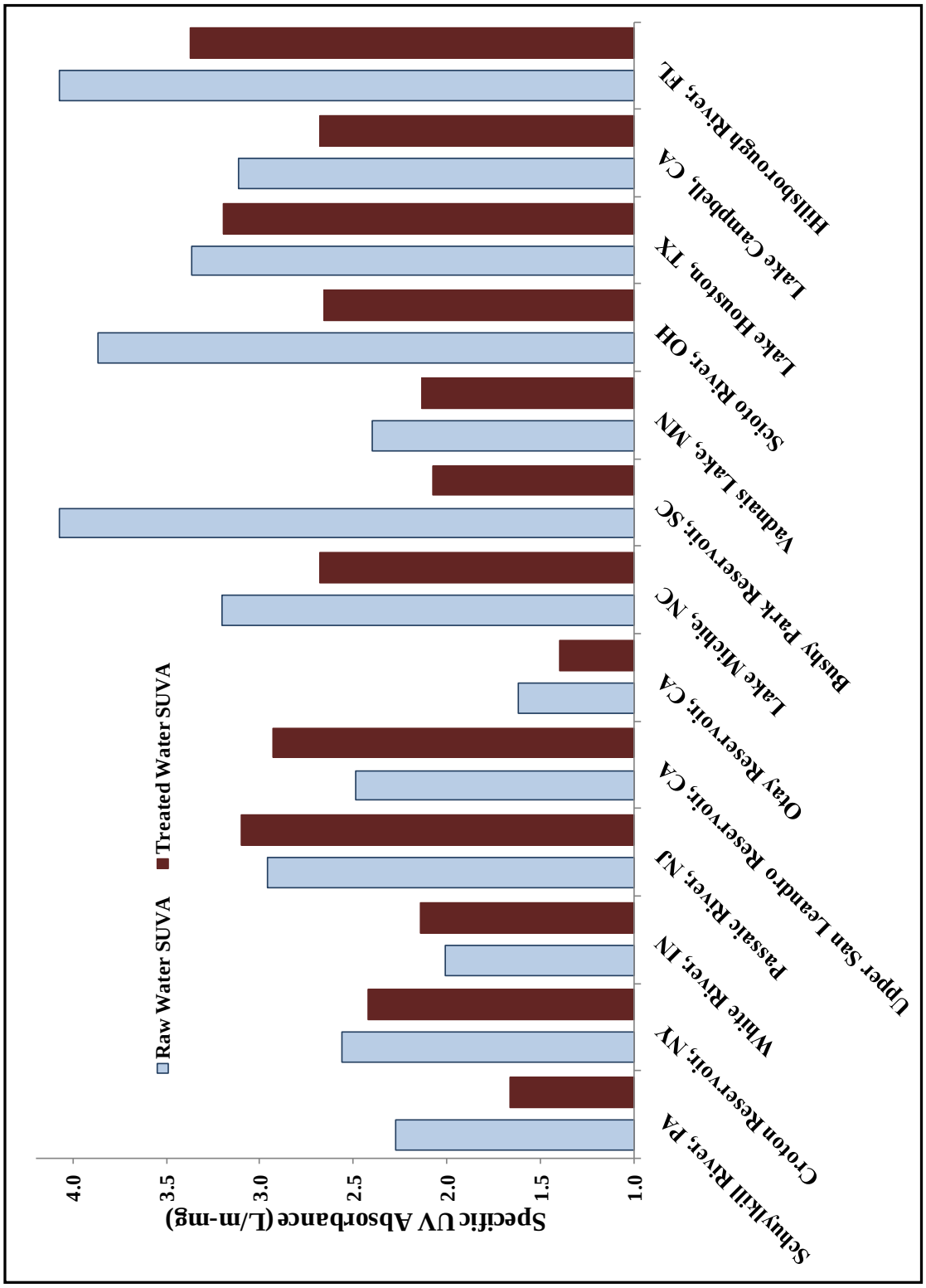


Figure C-1: Specific UV Absorbance before and after treatment by enhanced coagulation

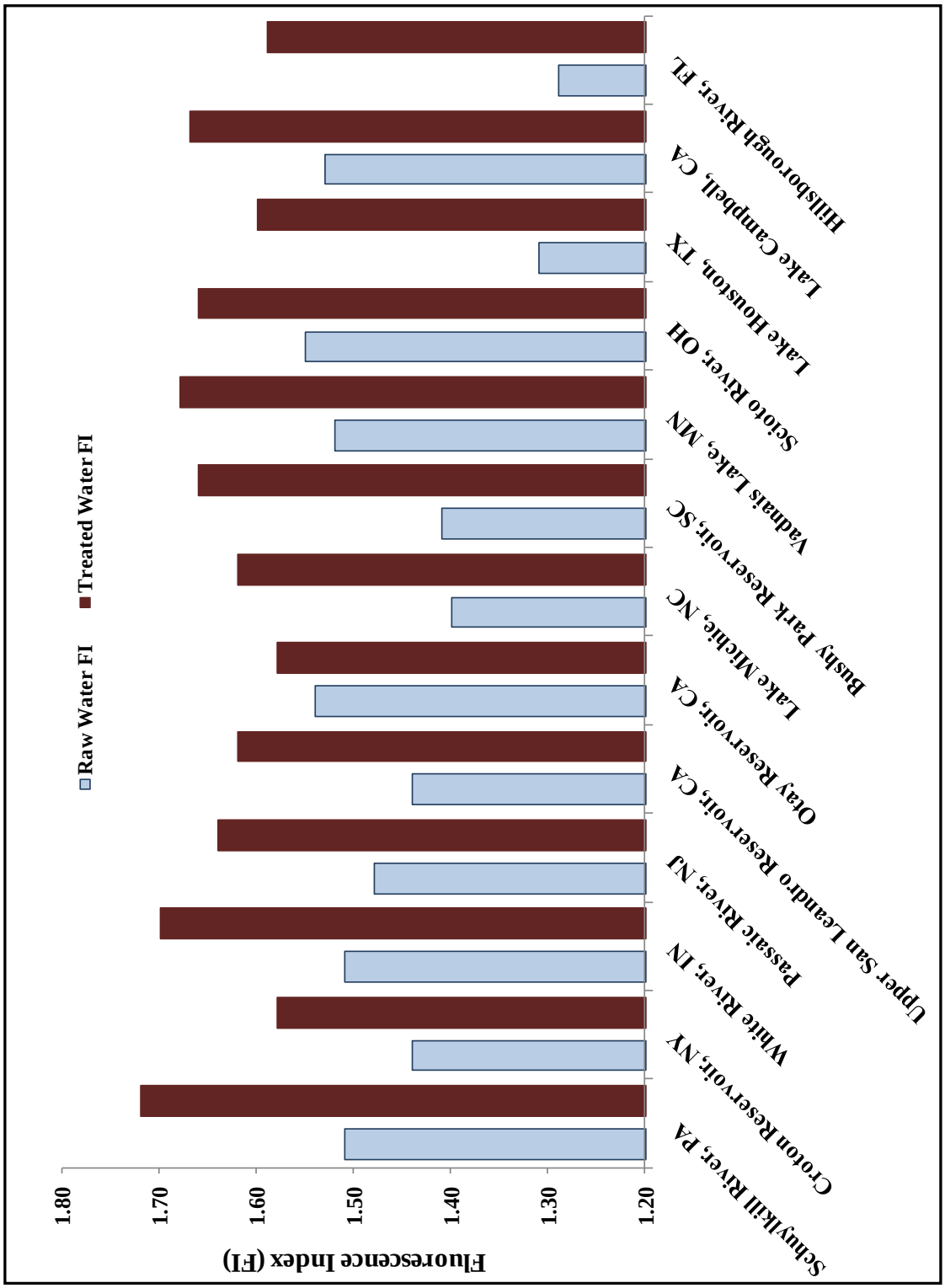


Figure C-2: Fluorescence Index before and after treatment by enhanced coagulation

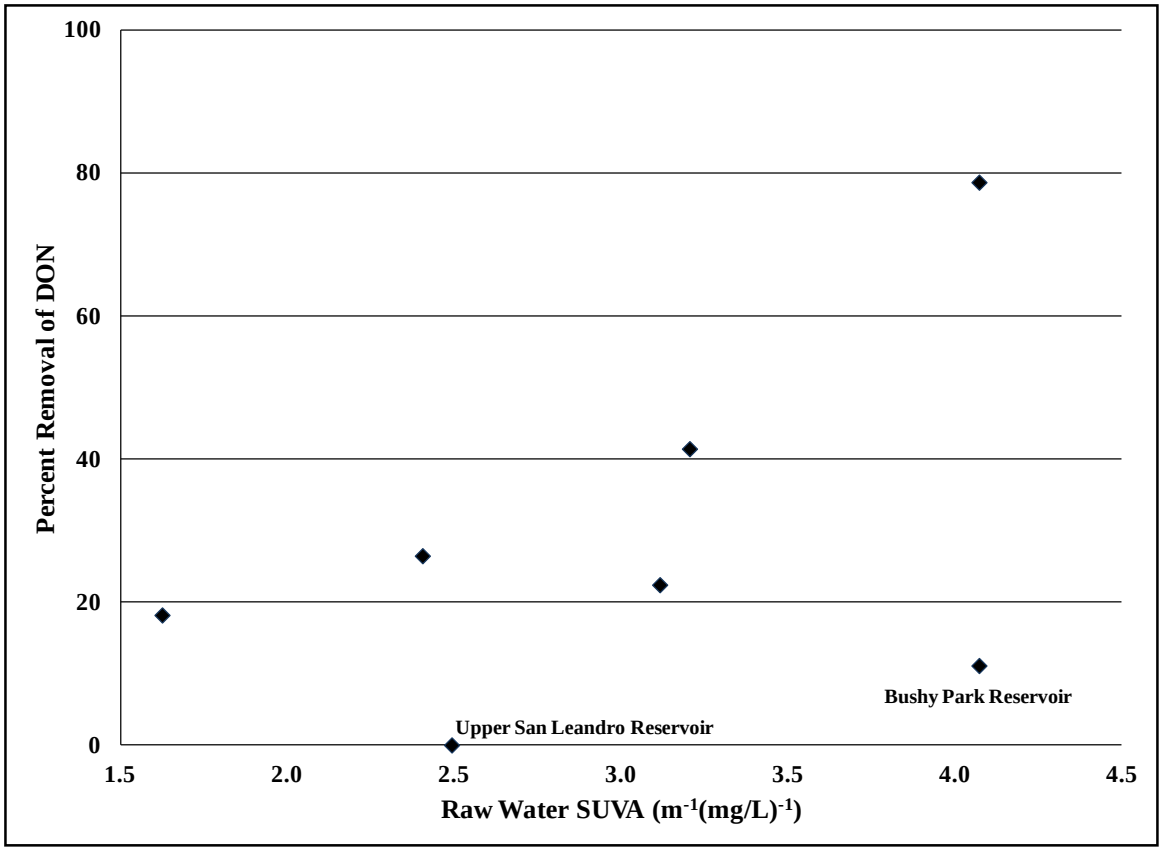


Figure C-3: Raw water specific UV absorbance compared to dissolved organic nitrogen removal by enhanced coagulation

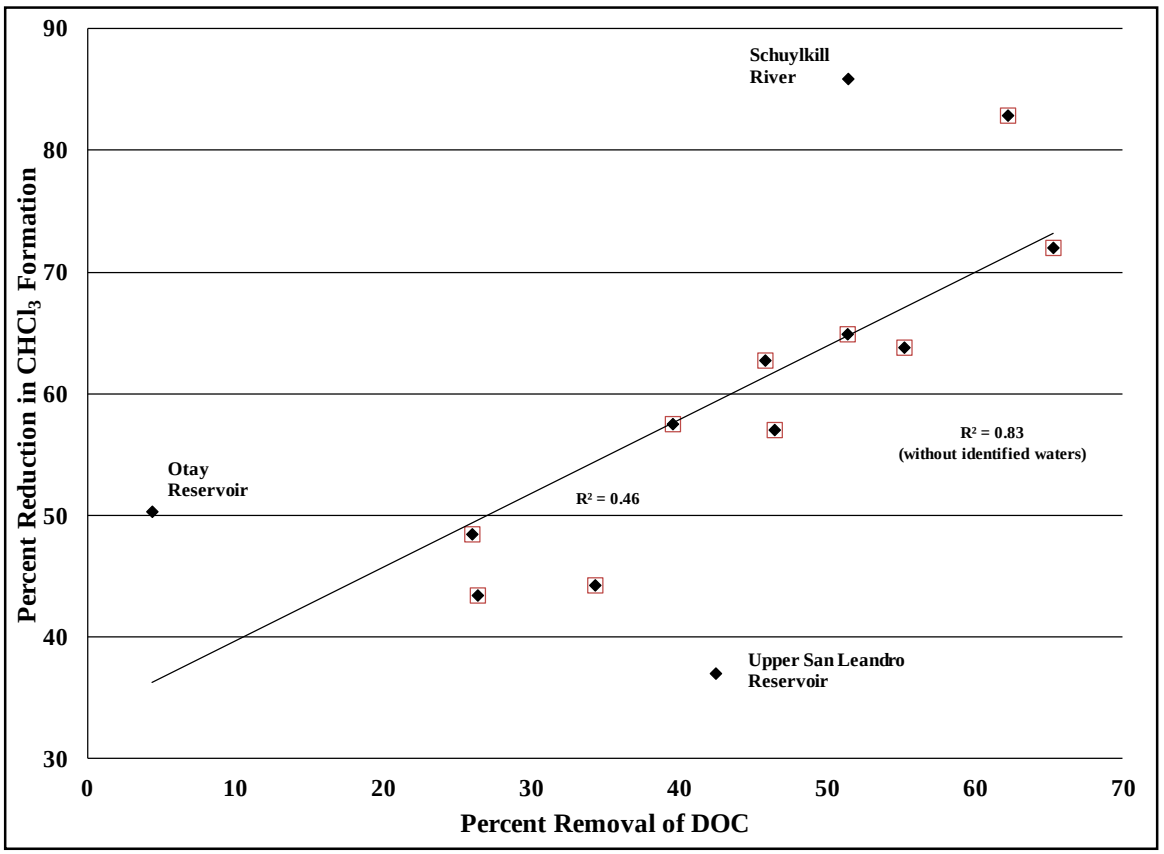


Figure C-4: Removal of dissolved organic carbon relative to reduction in chloroform formation

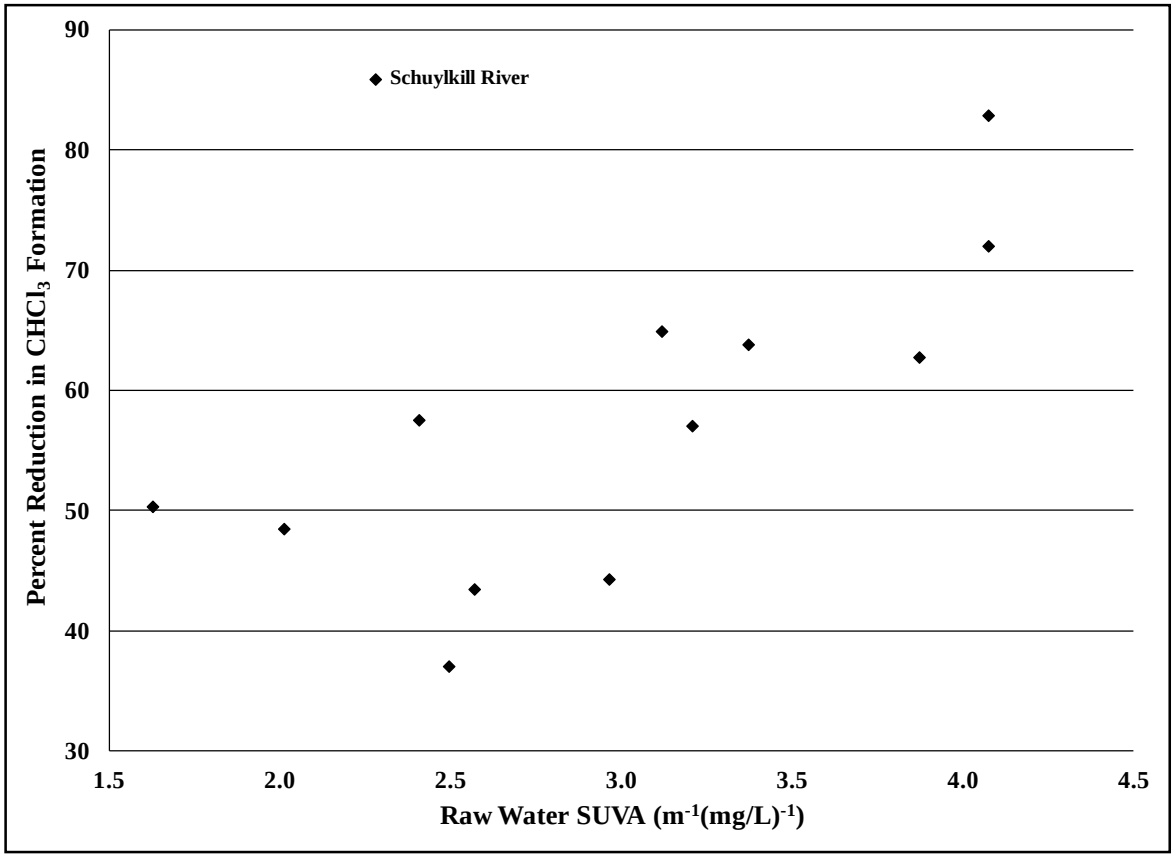


Figure C-5: Impact of raw water specific UV absorbance upon reduction in chloroform formation

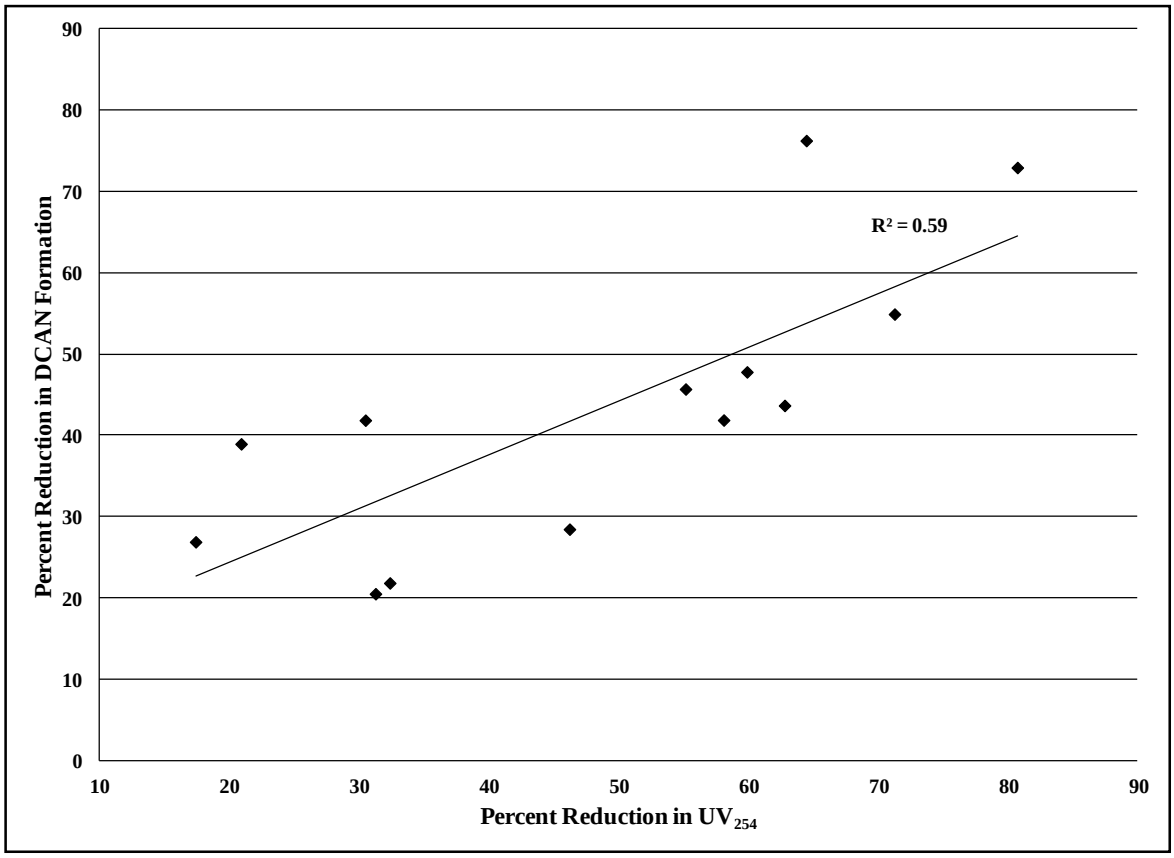


Figure C-6: Correlation of reduction in UV absorbance and reduction in DCAN formation

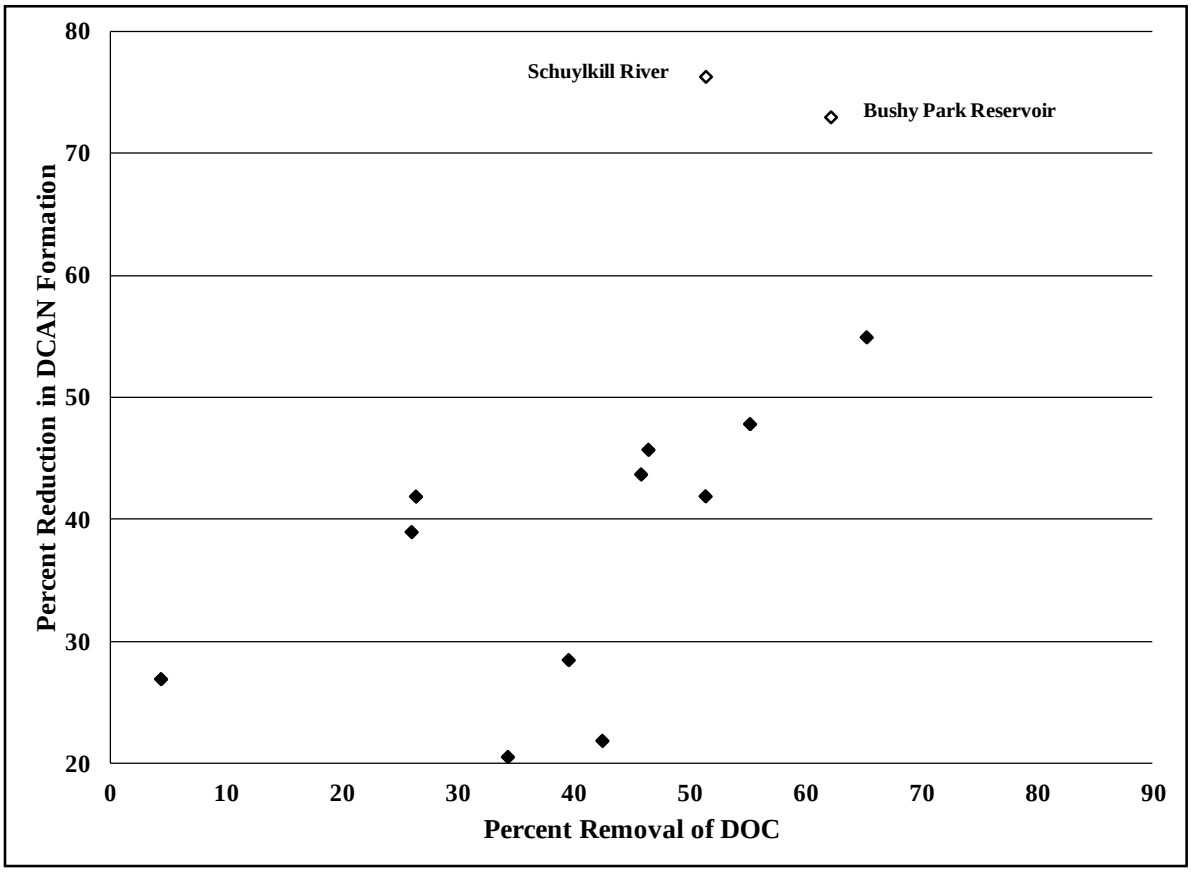


Figure C-7: Removal of dissolved organic carbon relative to reduction in DCAN formation

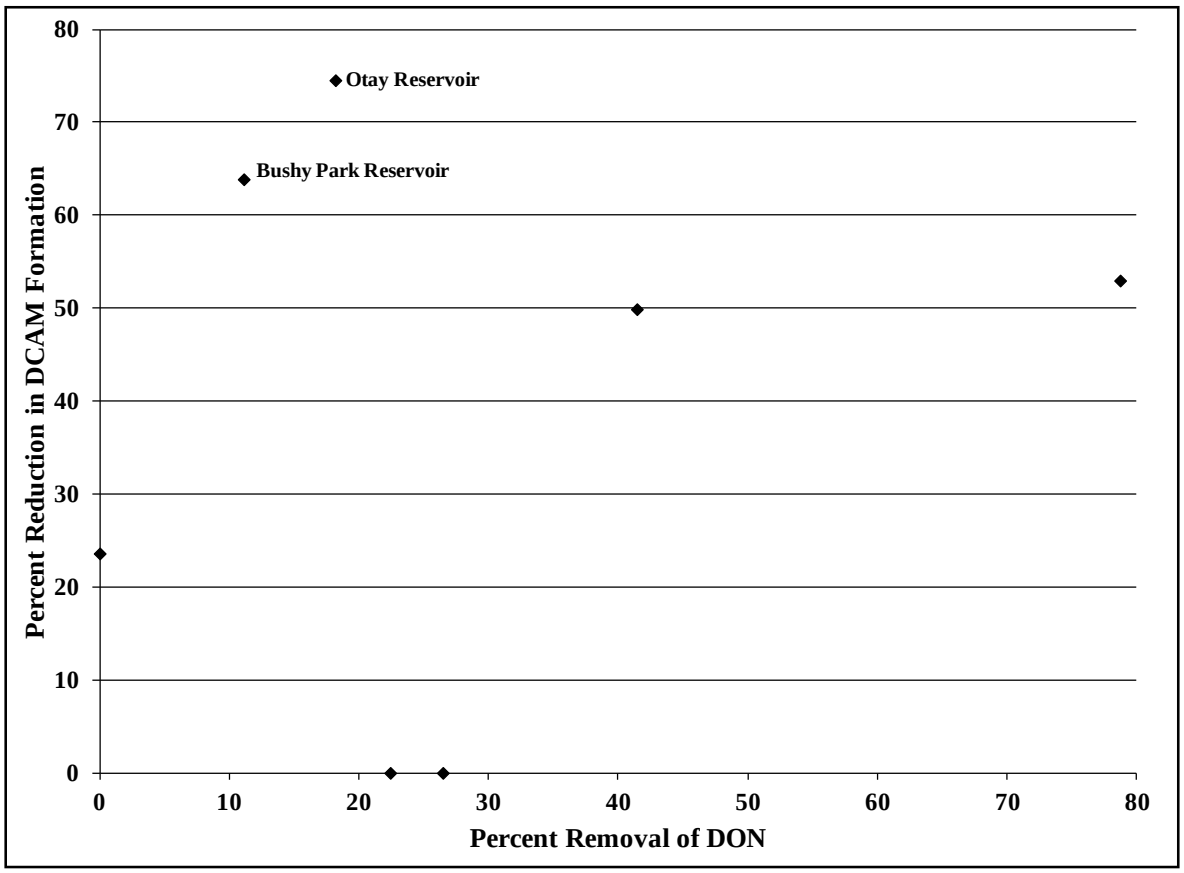


Figure C-8: Reduction of dichloroacetamide relative to removal of dissolved organic nitrogen

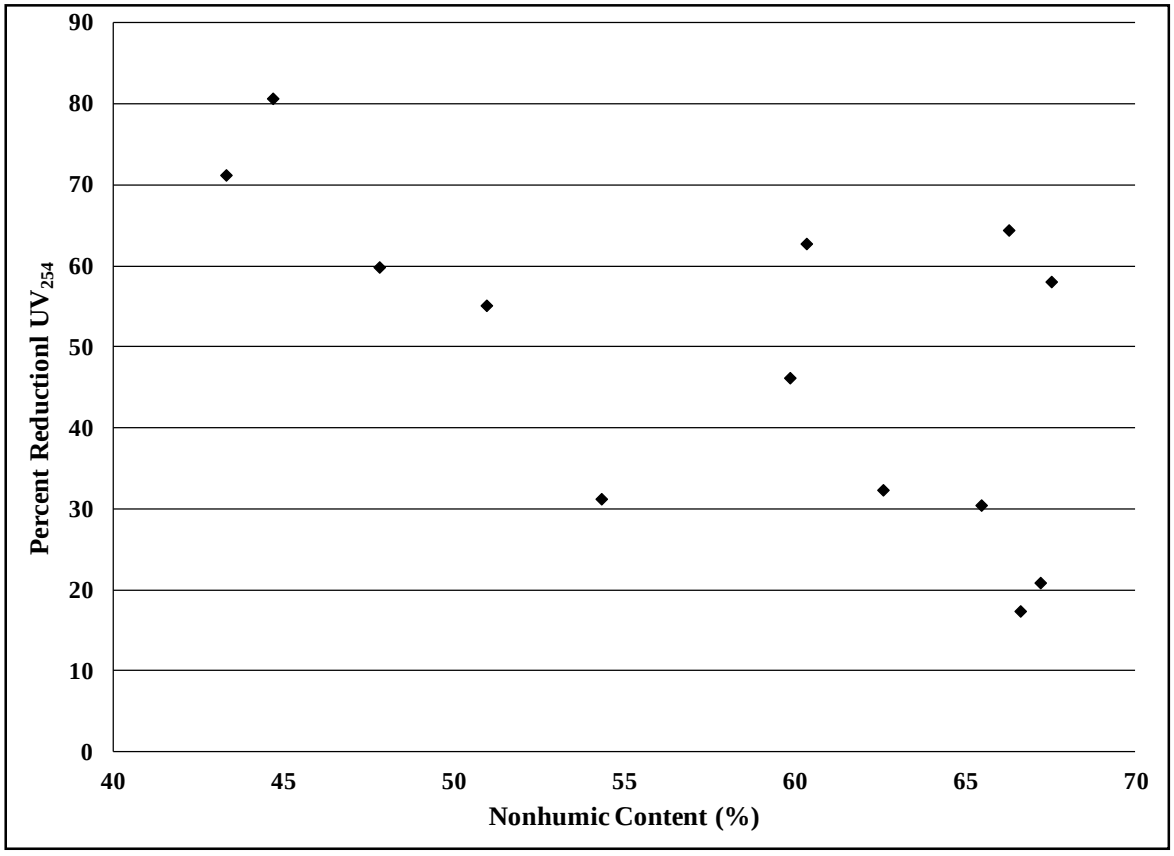


Figure C-9: Reduction of UV_{254} relative to raw water nonhumic content

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