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Source Water Quality Characteristics and Implications for Disinfection Byproduct Formation in Colorado Surface Waters

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Source water quality characteristics and implications for disinfection byproduct formation in Colorado surface waters

by

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B.S., Washington State University, 2009

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Source water quality characteristics and implications for disinfection byproduct formation in Colorado surface waters

written by Amanda K. Hohner

has been approved for the

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November 10, 2011

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline

ABSTRACT

Amanda K. Hohner (M.S. Environmental Engineering)

Source water quality characteristics and implications for disinfection byproduct formation in Colorado surface waters

Directed by Professors Fernando L. Rosario-Ortiz and R. Scott Summers

The water quality of lakes and reservoirs can significantly influence the formation of disinfection byproducts (DBPs) upon treatment. Specifically, increased nutrient loads and enhanced algal growth can lead to changed quantity and character of dissolved organic matter (DOM), the primary precursor for DBPs. In this thesis, water quality characteristics, including chlorophyll-a, total organic carbon (TOC), total phosphorus (TP), total nitrogen (TN), and total organic nitrogen (TON), were examined in order to evaluate their effects on the formation of DBPs. Trihalomethane (TTHM), haloacetic acid (HAA5), and haloacetonitrile (HAN) formation were measured. Surface waters located throughout the state of Colorado were studied, and relationships between nutrients, algae, DOM, and carbonaceous and nitrogenous DBPs were explored. Spectrophotometric methods including ultraviolet absorbance and fluorescence were also employed in order to better characterize DOM, and predict DBP formation.

For 10 municipal reservoirs, nutrient and chlorophyll-a relationships were developed, which support the assumption that increased sources of nutrients in surface waters can lead to enhanced algal growth. Chlorophyll-a was further related to TTHM and HAA5 formation; however these relationships are indirect, with an interdependent variable of DOM. A relationship between specific ultraviolet absorbance (SUVA) and C-DBP yield was also developed.

The influences of algal derived organic matter (AOM) and effluent organic matter (EfOM) on DOM character and subsequent DBP formation in 38 Colorado surface waters was assessed. Relationships to haloacetonitrile (HAN) formation were evaluated, and fluorescence analysis was utilized. Sites heavily influenced by wastewater were found to yield the highest levels of HAN and the lowest levels of TTHM and HAA5. The fluorescence index (FI) proved a useful indicator for AOM, organic nitrogen enrichment, and the level of wastewater influence. The FI was also found to indicate DBP reactivity, however DBP species must be taken into consideration as C-DBP and brominated HAN showed opposite trends. Results presented in this thesis suggest that controlling nutrient loadings to drinking water sources could aid in minimization of DOM, and thus presents an approach to DBP control. Results also showed how EfOM and AOM both play an important role in HAN formation.

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CHAPTER 1. Introduction

In order to protect the public from harmful disease-causing pathogens, drinking water is disinfected prior to entering the distribution system. Commonly, a strong oxidant such as chlorine is added during drinking water treatment to inactivate microbial pathogens. Therefore disinfection remains crucial to providing safe drinking water. As an unintended consequence, disinfection byproducts (DBPs) form upon the reaction between dissolved organic matter (DOM) which naturally occurs in water, and a disinfectant. In addition to meeting disinfection requirements to provide safe water, DBPs create another challenge for utilities and a concern for public health, as they have been linked to cancer risks and reproductive developmental effects (Krasner, 1989; Krasner, 2001; Lewis, 2006; Muellner, 2007; Richardson, 2008).

DBPs are ubiquitous in chemically disinfected drinking water, which has been well known since their discovery in 1974 by Rook (Rook, 1974). Since then, over 600 different species have been identified, and even more unknown compounds are likely present (Richardson, 2007). While the exact health risks of DBPs remains somewhat unclear, it is evident that potential adverse health outcomes from DBP exposure exist and efforts towards better understanding DBP formation and control are crucial.

Importance of Disinfection Byproducts

Disinfection byproduct regulation

With the intent of providing safe drinking water, the United States Environmental Protection Agency (USEPA) began regulating DBPs in 1979, shortly after their discovery. The maximum annual average total trihalomethane (TTHM) concentration was set at 100 µg/L, where TTHM is the sum of the four species: chloroform, bromodichloromethane, dibromochloromethane, and bromoform (Table 1.1) (USEPA, 2011). This regulation was then followed by the Stage 1 Disinfectants and Disinfection Byproduct Rule (D/DBPR) in 1998, which decreased the allowable TTHM concentration to 80 µg/L (USEPA, 2001). Five haloacetic acids (HAA5) were also added to the regulation at a maximum contaminant level (MCL) of 60 µg/L. HAA5 represents the sum of monochloroacetic (MCAA) acid, dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA) (Table 1.1). The non-halogenated DBPs, bromate and chlorite, were also added to regulation with MCLs of 10 µg/L and 1000 µg/L, respectively. Under the Stage 1 Rule, the monitoring requirements were changed to running annual averages, where samples from the distribution system over a one year period are averaged. Following this, the Stage 2 D/DBPR was introduced in 2006 and is a modification of the Stage 1 Rule, requiring the same MCLs, but as *locational* running annual averages, with monitoring requirements throughout the entire distribution system (USEPA, 2005). Motivation for this change was due to the concern that some locations in the distribution system were consistently exceeding MCLs. This change has brought about more stringent requirements, and thus significant challenges for utilities.

Table 1.1 Regulated TTHM and HAA5 species and chemical formulas.

DBP Class	Individual Species	Chemical Formula
Trihalomethanes	Chloroform	$CHCl_3$
	Bromodichloromethane	$CHCl_2Br$
	Dibromochloromethane	$CHClBr_2$
	Bromoform	$CHBr_3$
Haloacetic Acids	Monochloroacetic acid	$CH_2ClCOOH$
	Dichloroacetic acid	$CHCl_2COOH$
	Trichloroacetic acid	CCl_3COOH
	Monobromoacetic acid	$CH_2BrCOOH$
	Dibromoacetic acid	$CHBr_2COOH$

DBP regulations are set to protect the health of the public. Thus meeting regulations is vital and represents a challenge for drinking water utilities, which must find a balance between applying sufficient disinfectant to inactivate pathogens, while also minimizing DBP levels.

Emerging disinfection byproducts

To combat stricter TTHM and HAA5 regulations under the Stage 2 D/DBPR, the use of alternative disinfectants to chlorine (i.e. chloramines, ozone, chlorine dioxide) is increasing in order to minimize the formation of regulated DBPs (Seidel, 2005). Subsequently, increased levels of emerging DBPs are occurring as a result (Krasner, 2006). Specifically, the use of chloramines causes concern for elevated levels of nitrogenous DBP (N-DBP) species. Emerging DBPs represent compound classes that are not currently regulated, occur at low to moderate levels, and can be more toxic than THM and HAA. Generally these compounds include haloacetonitriles (HAN), halonitromethanes (HNM), and nitrosamines, among others (Krasner, 2009). The structure of an HAN is shown in Figure 1, where R generally represents Cl^- or Br^-.

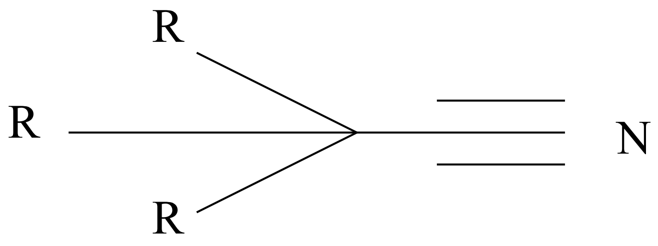

Figure 1.1 Haloacetonitrile (HAN) structure

Traditionally, TTHM and HAA5 were chosen for regulation because they occur at higher concentrations and can be considered proxies for the presence of other DBP species. By regulating these species, it was understood that other known and unknown species would also be reduced (Reckhow and Singer, 1984). However, with the use of alternative disinfectants which preferentially form different species, regulating TTHM and HAA5 may not prove as useful or accurate for ensuring safe DBP levels. Additionally, drinking water sources are becoming increasingly impaired by wastewater discharges and algae, which are both associated with higher organic nitrogen levels. These sources of organic matter can then proceed to form increased nitrogenous DBPs (N-DBPs), thus creating further concern with regards to toxicity. While N-DBPs are not yet regulated by the USEPA, these compounds represent an emerging issue that could affect utilities in the near future.

Toxicology of disinfections byproducts

Disinfection byproducts present a risk to human health as they have been shown to be carcinogenic, and/or mutagenic and genotoxic, and thus are regulated in the U.S., among other countries (Plewa, 2002; Richardson, 2007). Toxicological studies have evaluated the effects of DBPs by exposing bacteria and rodents to DBP doses; however it remains difficult to evaluate actual drinking water DBP levels of human exposure. Additionally, the relationship from rodent carcinogenicity to human health effects also presents another challenge for interpreting toxicological studies. Furthermore, the potential interactions of the vast number of DBP species remain unknown, presenting unclear potential health risks and further challenges for accurately understanding DBP toxicity in a representative way.

From current toxicological studies the most well-known risks of DBP exposure include cancer, particularly bladder cancer (Richardson and Ternes, 2011). The USEPA suggests that between 2-17% of urinary bladder cases can be associated with DBPs (Hrudey, 2009). Liver, kidney, rectal, and colon cancer in rodents exposed to DBPs have also been observed (Boorman, 1999; Villanueva, 2004). Potential reproductive and developmental effects such as spontaneous abortion and fetal anomalies have been associated with long term exposure to chlorinated drinking water (Nieuwenhuijsen, 2000; Richardson and Ternes, 2011). In addition, the emerging role of dermal exposure and inhalation through showering or swimming in pools needs to be studied in more detail, but can represent a significant route of DBP exposure and potentially higher risk than drinking water (Villanueva, 2006).

In a review by Richardson and co-workers evaluating DBP toxicity research, the authors concluded that all regulated DBP species, except for MBAA, have been studied for carcinogenicity in rodents, with results showing all species to be carcinogenic except for MCAA (Richardson, 2007). Together, the USEPA and the International Agency for Research on Cancer

(IARC) have concluded that bromodichloromethane, bromate, bromoform, chloroform, and DCAA are probable human carcinogens (Richardson, 2007).

In addition to THM and HAA, many emerging DBPs have been identified in drinking water and shown to be carcinogenic and even more toxic than the regulated species. In a study by Muellner et al., halonitromethanes (HNM) and haloacetonitriles (HAN) were found to be approximately two orders of magnitude more cytotoxic than HAA, which were concluded to be the least cytotoxic and genotoxic compound class (Muellner, 2007). The study found HAN to cause acute genomic DNA damage in Chinese hamster ovary cells, with the order of declining genotoxicity being: iodoacetonitrile (IAN) > monobromoacetonitrile (MBAN) ~ dibromoacetonitrile (DBAN) > bromochloroacetonitrile (BCAN), monochloroacetonitrile (MCAN) > trichloroacetonitrile (TCAN) > dichloroacetonitrile (DCAN). These findings are consistent with previous work which evaluated the mutagenic toxicity of HAN in *Salmonella typhimurium*, which found brominated di- and tri- HAN to be the most toxic (Bull, 1985; Muller-Pillet, 2000) . In a similar study, Plewa and Wagner also showed that N-DBPs were significantly more toxic than regulated carbonaceous DBPs (C-DBPs) in Chinese hamster ovary cells (Plewa and Wagner, 2009). Other research has shown that in general brominated species are more toxic than their chlorinated analogues (Richardson and Ternes, 2011). Together, these findings support the increasing importance of understanding the formation and role of N-DBP species, in addition to the C-DBP species already regulated.

Chemistry of carbonaceous DBP formation

DBPs are formed from the reaction between a disinfectant, dissolved organic matter (DOM), and an inorganic precursor which is generally a halide ion, either originating from the disinfectant itself (i.e. Cl^-) or from natural sources (i.e. Br^-, I^-). The overall reaction of DBP formation can be represented by the following equation:

$$Disinfectant\ + Precursors\ (DOM, Br^-, I^-) \rightarrow DBPs \quad (1.1)$$

The chemical mechanisms and pathways behind the formation of DBPs relate to the properties of disinfectants, which act as strong oxidants. Oxidation and halogen substitution reactions represent the primary DBP formation pathways (Larson, 1994). The disinfectant oxidizes DOM into simpler, more reactive compounds. These resulting moieties of DOM can then react with the disinfectant in a substitution reaction to form DBPs. In addition to the chemical mechanisms, the rate, speciation, and concentration of DBP formation can all be influenced by pH, dissolved organic carbon (DOC) concentration, organic matter character, reaction time, temperature, disinfectant dose and exposure (Stevens, 1976; Morris, 1978; Reckhow and Singer, 1984; Singer, 1994).

Chlorine as a disinfectant in water generally occurs as $HOCl/OCl^-$, oxidizing organic matter and proceeding to the reduced form as the chloride ion (Cl^-). Chlorine can also initiate substitution reactions and become incorporated into organic molecules to form DBPs. When chlorine reacts with the inorganic halides bromide and iodide, it can undergo an oxidation reduction reaction where hypobromous acid/hypobromite ions ($HOBr/OBr^-$) or hypoiodous acid/hypoiodite ions (HOI/OI^-) are formed. These species then go on to react in similar ways as $HOCl/OCl^-$ to form brominated and iodinated DBPs, however they generally act as weaker oxidants compared to chlorine, but are more effective substitution agents (Amy, 1991).

Chloramines, which are created from the reaction between ammonia and chlorine, can also act as disinfectants and oxidizing agents, thus forming DBPs. Chloramines are much weaker oxidants and substitution agents and therefore form DBPs slower and at lower levels, which is why they are commonly used as an alternative to chlorine (Krasner and Amy, unpublished). However, chloramines can form higher levels of nitrogenous DBPs. Chlorine dioxide, which can also be used as a disinfectant, does not form very high levels of halogenated DBPs, because like chloramines it is a weaker substitution agent (Zhang and Minear, 2000). On the other hand, chlorine dioxide forms chlorite and chlorate as non-halogenated byproducts. Thus, while alternative disinfectants to chlorine can be useful to control regulated species, other byproducts resulting from different chemistry must be considered.

Chemistry of nitrogenous DBP formation

Nitrogenous DBPs (N-DBPs) form through the reaction between oxidants and organic nitrogen moieties that occur as amines, nitriles, and nitro compounds, or heterocyclic and aliphatic structures containing nitrogen (Westerhoff and Mash, 2002). A reaction can occur between chlorine and unprotonated amines, where Cl^+ is rapidly transferred to the amino nitrogen (Mitch, unpublished). For instance, the reaction between a primary amine and hypochlorite would be:

$$HOCl + NH_2R_1 \rightarrow NH_2R_1Cl + H_2O \qquad (1.2)$$

Amines have a higher reactivity with chlorine than amides, which is due to the electron withdrawing nature of the amide carbonyl.

Free amino acids decay into nitriles and aldehydes via the decarboxylation pathway during chlorination (Figure 1.2). The reaction generally proceeds through the substitution of a halogen (Cl^-, I^-, Br^-) for a hydrogen on the nitrogen atom, followed by the formation of a double bond between the nitrogen atom and the adjacent carbon (Larson, 1994). DCAN represents the main product of this pathway, but TCAN also forms if the resulting anion from decarboxylation is chlorinated (Peters, 1990). Additionally, DCAN is an unstable intermediate that forms from the chlorination of amino acids, but can then proceed to form chloroform, DCAA, and TCAA (Trehy, 1981; Ueno, 1996; Glezer, 1999).

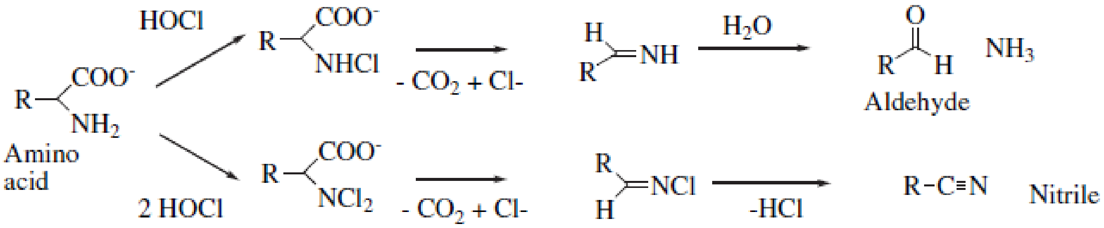

Figure 1.2 Chlorination of an amino acid via the decarboxylation pathway (Deborde and von Gunten, 2008; Bond, et al. 2011)

Nitriles and acetonitriles can also form via the aldehyde pathway from the reaction between monochloramines and aldehydes, as shown in Figure 1.3 (Mitch, unpublished). This pathway differs in that the nitrogen atom is from the monochloramine, representing an inorganic precursor, rather than the organic nitrogen source, which gives rise to the concern of using chloramines as alternative disinfectants.

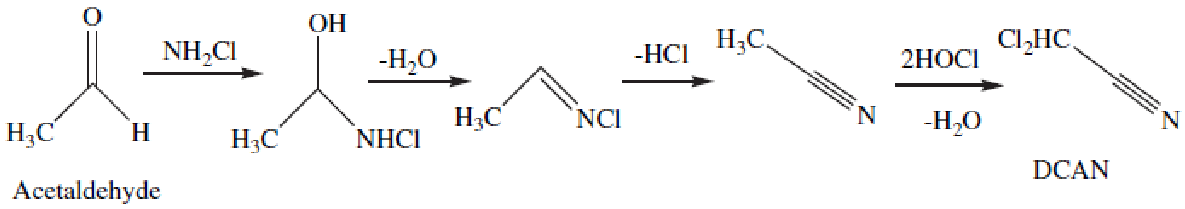

Figure 1.3 The formation of nitriles and acetonitriles via the aldehyde pathway (Mitch, 2008**;** Bond, 2011).

The Role of Dissolved Organic Matter

In an effort to control the formation of DBPs, understanding source water quality interactions with DOM can prove useful for developing approaches to minimize DBP precursor material. To do so, the role of DOM is crucial as it represents the primary precursor for DBPs, and thus insight into its nature, sources, characteristics, and reactivity aids in controlling DBPs in water supplies. This can prove challenging as DOM is a complex, heterogeneous mixture. It consists of both aromatic and aliphatic structures, as well as many functional groups, resulting in a wide range of composition and chemical properties (Leenheer and Croue, 2003).

Sources of DOM

Aquatic DOM can originate from many sources, but two categories, terrestrial and microbial, are traditionally referenced, denoting whether organic matter is produced externally or internally, respectively. Terrestrial sources include plant debris and soil organics that are flushed into surface waters by rainfall; this is commonly referred to as *allochthonous* organic matter and is generally more aromatic with higher humic content (Findlay and Sinsabaugh, 2003). In addition, allochthonous organic matter is generally well removed by conventional treatment processes, whereas microbial organic matter remains more resistant to enhanced coagulation (Archer and Singer, 2006).

Alternatively, internally produced DOM is considered *autochthonous* and derived from algal and microbial productivity within a lake. Autochthonous DOM commonly has lower C:N ratios, a more aliphatic composition, and incorporates more nutrients (Findlay and Sinsabaugh, 2003) (Nyugen, 2005). Nitrogen enrichment is expected for algal produced DOM, as algae contain significant amounts of nitrogen, whereas plant lignin components do not (McKnight, 1994).

DOM characterization

Analytical tools and methods have been developed to better understand characteristics of DOM in water bodies. To quantify DOM a measurement of dissolved organic carbon (DOC) is the common method, as carbon represents approximately 50% of DOM. To further understand DOM properties from a more qualitative perspective, spectrophotometric methods are generally employed, including ultraviolet absorbance (UVA) and fluorescence analysis. The use of UV absorbance can provide insight regarding the aromatic nature of DOM in a water sample, due to the presence of aromatic chromophores which absorb light in the ultraviolet range. In particular, when analyzing aquatic DOM the absorbance at a wavelength of 254 nm (UV_{254}) has been found to correlate well with DOC, and proves a useful surrogate for this parameter, or DOM levels in general (Leenheer and Croue, 2003). DOM contains aromatic structures which consist of carbon double bonds with electron donating and withdrawing groups which tend to absorb light. In addition to providing a useful surrogate measurement for DOC, UV_{254} is known to correlate well with DBP formation (Singer, 1981; Edzwald, 1985; Najm, 1994). Further, the ratio of UV_{254} to

DOC, or the specific ultraviolet absorbance (SUVA) can be a useful indicator of the aromatic content of DOM (Traina, 1990; Weishaar, 2003). Generally, higher SUVA values indicate high absorbance per unit of carbon, and therefore high aromaticity. This index can prove very useful when predicting THM and HAA formation, as terrestrial and aromatic DOM have been shown to yield higher concentrations of these DBP species (White, 1997; Croue, 2000; Archer and Singer, 2006).

Fluorescence analysis represents another, more sensitive, spectroscopic method, which can be used to detect fluorophores associated with DOM. The analytical method involves excitation and emission scans at a range of wavelengths, and the fluorescent intensity from each pair of wavelengths as the output (3-D scan). Alternatively, 2-D scans can be applied for a single excitation/emission pair. Two categories of fluorophores are commonly associated with aquatic DOM, including humic-like and protein-like peaks occurring in specific regions of excitation and emission. The protein-like materials that fluoresce include tryptophan and tyrosine, and occur at lower emission wavelengths (Coble, 1995; Leenheer and Croue, 2003). Humic-like fluorophores occur in two “peak” regions, which generally occur at higher emission wavelengths. Furthermore, in a study which analyzed fulvic acids and fluorescent properties of a wide range of water samples, a fluorescence index (FI) was developed (McKnight, 2001). The study found that a ratio of the emission intensity at a wavelength of 450 nm to that at 500 nm and an excitation of 370 nm could serve as a useful index for understanding the character of DOM sources. From this, insight into whether the source of DOM is autochthonous or allochthonous can be obtained. Generally higher FI values, (~1.9) are associated with a more microbial or algal DOM signature, whereas lower FI values (~1.4) indicate a more terrestrial source. This tool can then prove useful to better understand sources of DOM and the associated chemical properties, and therefore potentially provide insight into DBP formation potential.

Contribution of organic nitrogen

Organic nitrogen (ON) represents a component of DOM and can occur in drinking water sources at considerable levels, generating significant interest recently, as it can proceed to react with disinfectants to form N-DBPs. Higher ON concentrations have been shown to produce higher levels of nitromethanes, HAN, and N-Nitrosdimethylamine (NDMA) when chlorinated (Westerhoff and Mash, 2002). Potential sources of ON can include algae, agricultural fertilizers, and wastewater discharges (Westerhoff and Mash, 2002). Soluble microbial products (SMPs) from both natural and engineered systems contribute to the organic nitrogen pool, and consist of proteins, amino acids, and polysaccharides. Bacteria in lakes and reservoirs and biological wastewater treatment processes both create SMPs, and thus can contribute to the ON pool. Blue-green algae fix nitrogen and can excrete up to 45% as organic nitrogen (Westerhoff and Mash, 2002). Green algae species are also capable of excreting organic nitrogen. In addition, the cell walls of both algae and bacteria consist of cross linked peptide chains, containing amino sugars that represent another source of ON. Therefore, the primary productivity and trophic level of surface waters affects ON concentrations.

Common forms of ON generally include amines, nitriles, and nitro compounds (Westerhoff and Mash, 2002). In a review of organic nitrogen in drinking water, Westerhoff and Mash concluded that amino acids can represent 20-50% of organic nitrogen, amides 20%, and heterocyclic organic nitrogen 25%. However, this composition is not well understood and can be highly dependent on ON source, similar to all DOM characteristics. The level of organic nitrogen enrichment can be represented by the ratio of organic carbon to organic nitrogen (C:N). DOM with high ON enrichment (low C:N) has been shown to yield increased levels of N-DBPs (Reckhow, 1990; Dotson and Westerhoff, 2009; Dotson, 2009). Therefore, understanding the contribution of ON to the DOM pool in water sources can prove useful for predicting N-DBP formation potential.

The role of wastewater and effluent organic matter

The unintentional reuse of wastewater for potable purposes has been occurring for quite some time, whether recognized or not (Bunch, 1961). This occurs as wastewater treatment plants discharge effluent into lakes, rivers, and streams, upstream of drinking water sources. This trend is only growing as urban populations are rising and the demand for water is increasing, resulting in less pristine lakes and reservoirs being used for drinking water. Surface waters are becoming increasingly impacted by wastewater discharges, leading to higher organic matter content and nutrient loads. The nitrogen and phosphorus present in wastewater effluent can lead to increased algal blooms, particularly in the late summer season, increasing the contribution of algal derived organic matter (AOM) to the overall DOM pool.

The organic matter present in wastewater discharges, known as effluent organic matter (EfOM), can have different composition and characteristics than other more typical sources of DOM, leading to the formation of higher concentrations of emerging DBPs as these impaired waters are being used for drinking water. Particularly, waters enriched in these sources of organic matter tend to have higher organic nitrogen content, leading to elevated levels of N-DBPs. EfOM is considered relatively fresh compared to DOM, as it has been biologically processed in a wastewater treatment plant during a short time scale with little time for microbial nitrogen removal, whereas DOM degrades over a longer period of time (Mitch, 2008). Typical wastewater effluents contain ON levels around 3 mg_N/L (Westerhoff and Mash, 2002), thus contributing significant N-DBP precursors to surface waters. Additionally, the level of wastewater treatment can influence the presence of DBP precursors in EfOM. Krasner and co-workers found that wastewater treated with nitrification decreased ON levels and precursors for both HAA and HAN, while THM precursors remained unchanged (Krasner, 2009). Therefore, a rising concern for both utilities and the protection of public health exists, due to the increasing levels of EfOM and resulting N-DBP formation.

Algal derived organic Matter

Algal derived organic matter (AOM) represents a significant contributor to the autochthonous DOM pool, particularly during algal bloom seasons or under eutrophic lake conditions. Algae contain organic matter in their physical structure and also release organic matter through metabolic processes, known as extracellular organic matter (EOM). The main pathways of DOM production include: predatory grazing (sloppy feeding on algae where some of the algae is not completely consumed), cell death and senescence, viral cell lysis, and extracellular release (Findlay and Sinsabaugh, 2003). EOM is of particular importance because this material is dissolved and passes through the filtration process in treatment (Plummer and Edzwald, 2001).

The contribution of AOM to a water body is influenced by many factors including: nutrient availability, temperature, and sunlight (Kalff, 2002). As environmental conditions affect the presence of AOM, the microbial contribution to the organic matter pool will also be impacted. For instance, as nutrient loadings increase due to more wastewater discharges and agricultural runoff, algal populations may become more dominant and the role of AOM more significant. Climatic changes such as increases in natural water temperatures will also influence the presence of algae or shift the dominant species. Therefore, although algae have already been recognized as a problem of environmental concern, understanding AOM may become increasingly important for ecosystems that are experiencing significant environmental changes.

Algal derived organic matter has been recognized as a precursor for DBP formation for quite some time, with early studies by Hoehn focusing on the formation of chloroform from AOM (Hoehn, 1980). More recent research has focused on a further evaluation of the reactivity, or DBP yields of certain algal species (Plummer and Edzwald, 2001; Nyugen, 2005; Huang, 2009). Additionally, algal activity has been linked to elevated N-DBP formation, presenting another concern for utilities, which can again be related to wastewater discharges which spawn algal growth (Krasner, 2009; Dotson, 2009). Consequently, the contribution and characteristics of AOM must be taken into consideration when addressing the contemporary challenge of emerging DBPs.

Therefore, understanding the roles of DOM, EfOM, and AOM aids in predicting and controlling DBP formation. Figure 1.4 attempts to further illustrate the contributors to the formation of both regulated and emerging DBPs, in a holistic sense (Krasner, 2009).

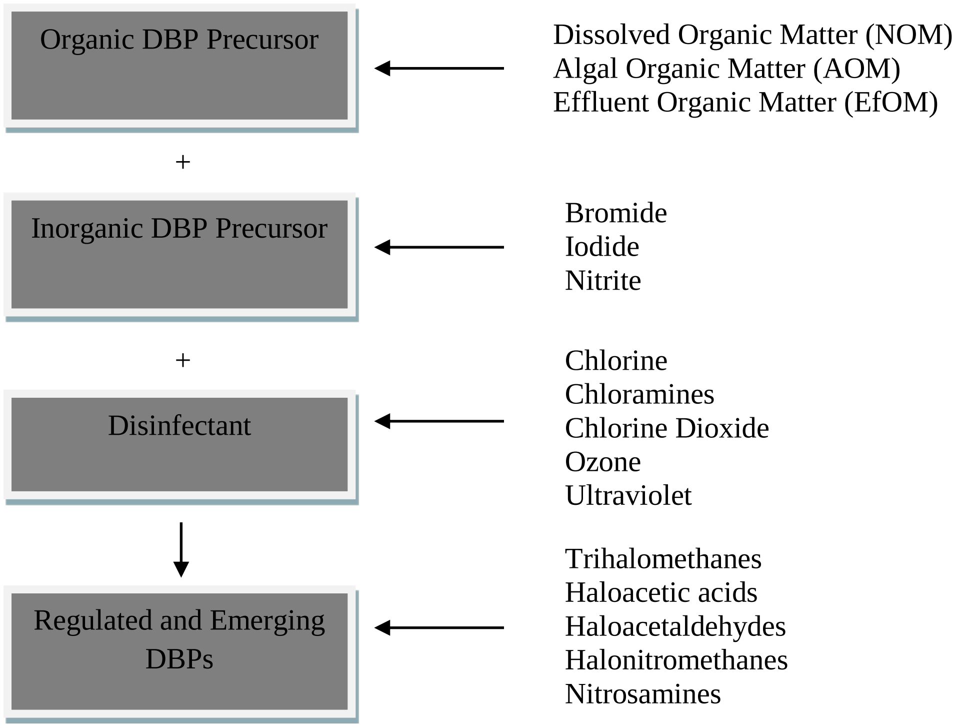

Figure 1.4 Schematic of contributors to the formation of regulated and emerging DBPs.

CHAPTER 2. Thesis Hypotheses and Organization

As has been noted, DBPs represent an important health concern and a significant challenge to utilities providing safe drinking water. The Stage 2 D/DBPR is creating increased pressure for utilities to meet DBP maximum contaminant levels (MCLs), while at the same time surface waters are becoming increasingly impaired by wastewater and algae. Together, the switch to alternative disinfectants coupled with increased levels of effluent organic matter (EfOM) and algal organic matter (AOM) is causing a rising concern for N-DBPs. Though efforts can be made to improve treatment processes for organic matter removal in order to minimize DBP formation, much room for DBP control strategies lies in understanding DBP precursor material. Applying this approach, DBP formation can potentially be minimized through source water quality management, primarily by controlling EfOM and AOM sources.

While both internal and external sources of organic matter exist in lakes and reservoirs, terrestrial sources remain difficult to identify and control, and primarily are related to natural watershed processes. On the other hand, sources such as EfOM and AOM can be related to more anthropogenic influences. Wastewater discharges contain significant amounts of nitrogen and phosphorus, entering and reaching many surface waters, often potable sources. These nutrients spawn algal growth, particularly in the late summer season. As previously discussed, algae represent a source of organic matter (AOM), which can proceed to react with chlorine to form C- and N-DBPs. Additionally, EfOM can react and influence DBP speciation. The combined influences of wastewater and algae on the impairment of drinking water sources are hypothesized to lead to elevated N-DBP levels.

Minimizing nutrient enrichment and algal blooms in surface waters provides an approach for DBP control. If sound relationships can be developed between source water nutrients and algal levels with DBPs, then the potential exists for implementing control strategies for phosphorus and nitrogen loadings, or algal productivity. The main objective of this work was to better understand the interactions between nutrients, algae, and organic matter and how they relate to DBP formation. This would then provide insight into source water control strategies for minimizing DBPs. Additionally, the roles of AOM and EfOM were to be evaluated in order to better understand their influence on C- and N-DBP formation.

Thesis organization

This thesis consists of four chapters which address the hypotheses and objectives previously discussed. In Chapter 3 the role of source water interactions between nutrients, algae, and DOM are explored in ten Colorado drinking water reservoirs. The data set evaluated in this chapter includes average values for each site from May-October, 2010. Subsequently, DBP formation is evaluated and related to source water characteristics, and further implications for the minimization of DBPs from a source water control approach are considered. In Chapter 4, the role of algal and wastewater influences on carbonaceous and nitrogenous DBP formation are considered for 38 lakes and reservoirs that were sampled one time in late July or early August 2010. The use of fluorescence is further used to understand source water characteristics and implications for DBPs. The purpose of Chapter 5 is to draw together and compare the two sets of results, summarizing key findings. Lastly, Chapter 6 introduces approaches to future research and suggestions for more comprehensive analysis in additional studies.

CHAPTER 3. The Contribution of Nutrients and Algae to DBP Formation in Colorado Water Supply Reservoirs: Implications for Source Water Quality Management

Abstract

Drinking water utilities face the challenge of meeting advancing disinfection byproduct (DBP) regulations, in order to provide safe drinking water to the public. Additionally, emerging DBPs, particularly nitrogenous species, are becoming an increasing concern. Meanwhile, changes in source water quality are occurring due to wastewater and algal surface water impairment, resulting in implications for treatment and DBP formation. Rising nutrient concentrations lead to an increase in primary production of algal populations, and more intense bloom periods which can affect the pool of dissolved organic matter (DOM). For drinking water utilities that must meet stringent DBP regulations, understanding source water quality relationships to DBP precursor material is important as it can aid in meeting DBP maximum contaminant levels (MCLs). Also, the potential for revisions of nutrient loading regulations and the development of a chlorophyll-a standard based on drinking water DBP MCLs exists if sound relationships are developed. This study sampled 10 municipal lakes throughout the state of Colorado from May-October 2010. Increased nutrient levels were observed to result in elevated algal activity, and chlorophyll-a was shown to account for at least 81% of the variation in total organic carbon (TOC). DOM contained similar ratios of C:N for the ten sites. Trihalomethane (TTHM) and haloacetic acid (HAA5) concentrations were found to increase with chlorophyll-a and nutrients, however this relationship is not direct, with an interdependent variable of DOM. For a subset of samples analyzed for the fluorescence index (FI) and haloacetonitriles (HAN), total nitrogen (TN) and HAN were strongly correlated ($R^2 = 0.97$). The FI was found to inversely correlate with TTHM and HAA5, and positively correlate with brominated HAN formation. Results from this study suggest that minimizing nutrient levels and algal activity in reservoirs can aid in minimizing carbonaceous and nitrogenous DBP formation.

Introduction

Disinfection byproducts (DBPs) are a series of compounds formed from the reaction between disinfectants and dissolved organic matter (DOM). Due to their toxicity they represent an important health concern and a significant challenge to utilities providing safe drinking water (Krasner, 1989; Krasner, 2001; Krasner, 2006; Lewis, 2006; Muellner, 2007; Richardson, 2008). Currently, the United States Environmental Protection Agency (USEPA) regulates two groups of organic DBPs: total trihalomethanes (TTHM) and haloacetic acids (HAA5) (USEPA, 2001). Although TTHM and HAA5 have been regulated for some time, the Stage 2 Disinfection and Disinfection Byproduct Rule (D/DBPR) now in place will make meeting regulations more complex due to increased monitoring requirements throughout the distribution system (USEPA, 2005). In addition, nitrogenous DBP (N-DBP) species are becoming increasingly important and present further challenges for drinking water treatment in part due to their higher toxicity (Muellner, 2007). Although not yet regulated by the USEPA, this class of compounds represents an emerging issue and could affect utilities in the near future.

Efforts can be made to improve treatment processes for DOM removal in order to minimize DBP formation, but a better understanding of source water DBP precursor material provides additional insight for utilities. Following this approach, DBP formation can potentially be minimized through source water quality control strategies. Both internal (autochthonous) and external (allochthonous) sources contribute to the pool of DOM in lakes and reservoirs, while the exact balance and impact to DBP formation remains difficult to identify in watersheds (Findlay and Sinsabaugh, 2003). External DOM from terrestrial sources is primarily related to natural processes when organic matter is flushed into surface waters by stormwater and snow-melt runoff (Findlay and Sinsabaugh, 2003). In addition, allochthonous organic matter is generally well removed by conventional treatment processes, whereas autochthonous organic matter remains more resistant to enhanced coagulation (Archer and Singer, 2006).

On the other hand, autochthonous organic matter can be associated with more anthropogenic influences, such as nutrient discharges and the subsequent affects on microbial lake dynamics (Westerhoff and Anning, 2000). This commonly is related to nutrient loads in drinking waters which represent an important consideration, including both point and non-point sources entering surface waters. Wastewater effluent contains significant amounts of nitrogen and phosphorus, often discharged into watersheds of drinking water sources. Agricultural runoff can also greatly contribute to nutrient levels in water bodies. These nutrients spawn algal growth, particularly in the mid-summer season. Algae can represent a significant source of autochthonous organic matter, which may then proceed to react with chlorine during treatment and form DBPs (Hoehn, 1980; Plummer, 2001; Nyugen, 2005; Huang, 2009). Additionally, wastewater influence and algal production have both been linked to elevated N-DBP formation, such as haloacetonitriles (HAN), presenting another concern for utilities (Krasner, 2009; Dotson, 2009).

Minimizing nutrient enrichment and algal blooms in surface waters provides an approach for DBP control, and also attempts to address the issue of N-DBPs. If sound relationships can be developed between source water nutrients and algal levels with DBPs, then the potential exists for implementing control strategies for phosphorus and nitrogen loadings, or algal productivity. For instance, if threshold levels for chlorophyll-a are determined to be related to DBP maximum contaminant levels (MCLs), standards for municipal lakes could be incorporated into local regulation. Measures to meet a chlorophyll-a standard would then need to be taken. This could potentially include lowering wastewater effluent nutrient concentrations and/or agricultural runoff nutrients from fertilizer, although this approach would be challenging to implement.

The main objective of this work was to better understand the interactions between nutrients, algae, and organic matter and how they relate to DBP formation in order to gain insight into source water control strategies for minimizing DBPs. Additionally, due to the association of wastewater and algae with nitrogenous DBPs, relationships with haloacetonitriles (HAN) were also evaluated, as well as the use of fluorescence as an indicator of DOM character and precursor material.

Methods

Site description

The study sampling sites included 10 municipal reservoirs located in Colorado. The majority of the sites are primarily located in the Front Range of the Rocky Mountains, including urban areas such as Boulder, Fort Collins, Evergreen, and Greeley, among others. Two sites are located outside the Front Range; including Grand Junction (Juniata Reservoir) is located west of the Continental Divide and Pueblo Reservoir which is much further south than the remaining sites. A detail of the site locations and specific characteristics (elevation, latitude, longitude, area, capacity, and mean depth) are presented in Table 3.1.

Table 3.1 Geographical characteristics of reservoirs sampled

Reservoir	Code	Elevation (ft)	Latitude °N	Longitude °W	Area (acre)	Capacity (acre-ft)	Mean Depth (ft)
Arvada	AV	5759	39.82	-105.21	208	5800	27.9
Boulder	BD	5173	40.08	-105.22	530	13300	25.1
Evergreen	EG	7076	39.63	-105.33	55	669	12.2
Fort Collins	FC	5430	40.55	-105.16	1900	143500	75.5
Grand Junction	GJ	5704	38.97	-108.28	100	2700	27.0
Greeley-Loveland	GL	5006	40.41	-105.09	450	10300	22.9
Greeley-Seaman	GS	5481	40.71	-105.24	140	5008	35.8
Lafayette	LF	5314	40.00	-105.21	240	5300	22.1
Pueblo	PB	4826	38.27	-104.74	5664	357678	63.1
Westminster	WM	5509	39.86	-105.12	1230	42380	34.5

Sampling methods and handling

Grab surface samples were collected approximately bi-weekly May through October of 2010, from 10 drinking water reservoirs in Colorado. For quality assurance and control (QA/QC), 10% of samples were collected in duplicate, including one sample set from each reservoir. Additionally, 10% of samples were analyzed in duplicate to assure analytical QA/QC. Samples for organic analysis and chlorination were collected in pre-cleaned glass amber bottles, while those for nutrient analyses were collected in pre-cleaned polypropylene bottles (VWR, USA). Collected samples were kept on ice until delivery to the analysis lab where they were refrigerated at 4°C. Chlorophyll-a samples were filtered on site through GF/F or GF/C glass fiber filters and were frozen upon receipt until analysis. Samples collected for DBP formation were filtered within 48 hours of receipt through furnaced, 0.7 µm glass fiber filters (GF/F). The volumes required for dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UV_{254}) analysis were further filtered through 0.45 µm pore size polyethersulfone (PES) filters (GE Osmonics, USA). Each PES filter was rinsed with 800 mL of Milli-Q water immediately before use to prevent carbon leaching ($<2.0\ mg_C/L$).

Analytical methods

Total organic carbon (TOC) was measured on raw water samples and DOC was measured on 0.45 µm filtered samples using the Persulfate-Ultraviolet Oxidation method following the standard metthod, with a Sievers 800 TOC analyzer and auto-sampler (APHA; AWWA; WEF, 1998). UV_{254} was measured using a UV-Vis spectrophotometer (Cary 100, Agilent Technologies) with a 1-cm path length quartz cuvette. Total phosphorous (TP) measurements were performed with a Lachat QuikChem 8500 spectrophotometric flow injection. Nitrate and nitrite were measured with an analytical flow solution IV spectrophotometric analyzer (OI Analytical, USA). Total nitrogen (TN) measurements were performed with a Shimadzu TOC-V analyzer. Ammonia was measured using a BioTek Synergy 2 Microplate Reader. Total organic nitrogen (TON) was calculated as the difference between TN and the sum of inorganic nitrogen species. For samples with non-detects for inorganic species, the value was set at the detection limit. This calculation was validated by ensuring that the organic fraction was always greater than 60% (Lee and Westerhoff, 2005). Chlorophyll-a samples were measured following a spectrofluorometric analysis (EPA method 445.0) using a Fluoromax 2 (Horiba Scientific).

Fluorescence analysis was completed with a Horiba Fluoromax 4. Routine lamp, Raman, and cuvette checks were completed daily. Excitation was from 240-450 nm at 10 nm increments. Emission scans were from 350-550 nm at 2 nm increments. Slit widths were set at 5 nm. The fluorescence index (FI) was calculated as the ratio of the emission intensity at 470 and 520 nm at an excitation of 370 nm (Cory, 2010).

The formation of DBPs followed the chlorination method of uniform formation conditions (UFC) (Summers, 1996). Samples were chlorinated at room temperature with a pH 8, buffered hypochlorite solution. Water samples were buffered with a pH 8 borate buffer and incubated in the dark for 24 hours (± 1 hour) at room temperature (20± 1.0°C). Doses were determined to obtain a chlorine residual of 1.0 mg/L (± 0.4 mg/L). Chlorine residuals were measured with the DPD (N,N-diethyl-pphenylenediamine) colorimetric method (SM4500-Cl G) and were quenched with ammonium chloride, which did not significantly affect the formation of haloacetonitriles (HAN).

DBP analysis was completed within two weeks of chlorination. EPA Method 551.1 (1995) was used for analysis of trihalomethanes (TTHM) and haloacetonitriles (HAN). Species included in HAN analysis were: di-chloroacetonitrile (DCAN), tri-chloroacetonitrile (TCAN), di-bromoacetonitrile (DBAN), and bromo-chloroacetonitrile (BCAN). EPA method 552.2 was followed for analysis of haloacetic acids and reported as the five regulated HAAs (HAA5). An Agilent 6890 Gas Chromatography System with an electron capture detector was used.

Results

Source water quality characteristics

The following results include samples from the 10 municipal reservoirs, with averages determined for each site from May-October, 2010. This study was designed with the intent of developing relationships between source water parameters of interest including nutrients, algae, and organics, with the idea that understanding these interactions could then further be related to DBP formation. Water quality averages, standard deviations, and ranges are shown for each site in Table 3.2. Standard deviations represent the temporal variation for reservoirs as well as any analytical error. DOC concentrations ranged from 2.3 - 7.9 mg_C/L. This indicates a wide range of DOM, and noting that the source waters on the high end of this range will be difficult to treat in order to meet DBP regulations.

Table 3.2 Water quality parameters for 10 reservoirs sampled. Values represent averages, standard deviations, and ranges for the 10 municipal lakes sampled. Averages are for 7 to 11 samples. Standard deviations represent temporal variation and any analysis error.

Municipal Reservoir	**Chl-a** µg/L	**TP** mg_P/L	**TN** mg_N/L	**TON** mg_N/L	**TOC** mg_C/L	**DOC** mg_C/L	**UV_{254}** cm^{-1}
Evergreen	2.7 ± 0.9 (1.6-4.7)	0.010 ± 0.005 (0.002-0.015)	0.343 ± 0.097 (0.194-0.497)	0.276 ± 0.083 (0.159-0.416)	4.1 ± 1.3 (2.2-6.3)	3.9 ± 1.2 (2.3-6.1)	0.122 ± 0.024 (0.092-0.177)
Boulder	3.1 ± 1.4 (1.0-5.6)	0.012 ± 0.005 (0.005-0.017)	0.244 ± 0.017 (0.224-0.279)	0.214 ± 0.022 (0.186-0.262)	3.9 ± 0.3 (3.7-4.4)	3.6 ± 0.2 (3.2-3.9)	0.065 ± 0.006 (0.059-0.075)
Arvada	1.8 ± 1.0 (0.6-3.4)	0.003 ± 0.003 (0.002-0.012)	0.206 ± 0.034 (0.147-0.264)	0.181 ± 0.026 (0.120-0.214)	3.0 ± 0.2 (2.6-3.4)	2.9 ± 0.2 (2.3-3.1)	0.041 ± 0.008 (0.019-0.049)
Greeley-Seaman	9.6 ± 2.9 (6.3-15.0)	0.022 ± 0.013 (0.008-0.042)	0.418 ± 0.073 (0.329-0.558)	0.356 ± 0.055 (0.300-0.439)	7.9 ± 1.5 (6.0-10.2)	7.3 ± 1.3 (5.8-9.5)	0.204 ± 0.058 (0.130-0.275)
Greeley-Loveland	5.3 ± 3.7 (1.8-12.9)	0.011 ± 0.003 (0.007-0.015)	0.348 ± 0.048 (0.294-0.432)	0.302 ± 0.046 (0.253-0.389)	6.6 ± 0.5 (5.8-7.5)	6.1 ± 0.5 (5.4-6.9)	0.139 ± 0.020 (0.118-0.174)
Pueblo	3.3 ± 1.8 (0.5-5.8)	0.012 ± 0.005 (0.006-0.021)	0.291 ± 0.080 (0.197-0.390)	0.153 ± 0.028 (0.094-0.189)	2.9 ± 0.2 (2.6-3.2)	2.6 ± 0.2 (2.3-2.9)	0.058 ± 0.005 (0.051-0.066)
Westminster	2.5 ± 0.9 (1.6-4.5)	0.007 ± 0.004 (0.002-0.015)	0.162 ± 0.011 (0.143-0.178)	0.122 ± 0.011 (0.104-0.138)	2.3 ± 0.2 (2.1-2.5)	2.1 ± 0.2 (1.8-2.4)	0.034 ± 0.005 (0.022-0.042)
Lafayette	NA NA	0.006 ± 0.003 (0.001-0.010)	0.215 ± 0.016 (0.183-0.229)	0.203 ± 0.013 (0.169-0.210)	3.8 ± 0.2 (3.7-4.1)	3.6 ± 0.2 (3.2-4.0)	0.056 ± 0.008 (0.038-0.064)
Fort Collins	2.8 ± 1.7 (1.0-6.8)	0.007 ± 0.003 (0.003-0.013)	0.224 ± 0.035 (0.180-0.278)	0.171 ± 0.030 (0.135-0.211)	4.5 ± 0.5 (4.0-5.3)	4.2 ± 0.4 (3.8-4.8)	0.105 ± 0.011 (0.086-0.121)
Grand Junction	1.7 ± 0.8 (0.9-3.0)	0.009 ± 0.004 (0.002-0.016)	0.279 ± 0.148 (0.153-0.583)	0.246 ± 0.152 (0.107-0.557)	3.0 ± 0.4 (2.6-3.7)	2.8 ± 0.1 (2.6-2.9)	0.057 ± 0.004 (0.051-0.065)

The average values determined for each lake allowed for analysis of potential correlations between source water variables, and regression for evaluation of any relationships. An increase in chlorophyll-a levels was observed as TP concentrations rose (Figure 3.1), supporting the hypothesis that increased nutrient levels correspond to more algal activity and primary productivity, shown by chlorophyll-a. This relationship has been observed before, primarily in limnology research studies (Dillon, 1974; Jones, 1976). A similar trend was also observed with TN, but was not as strong of a linear relationship ($R^2 = 0.58$).

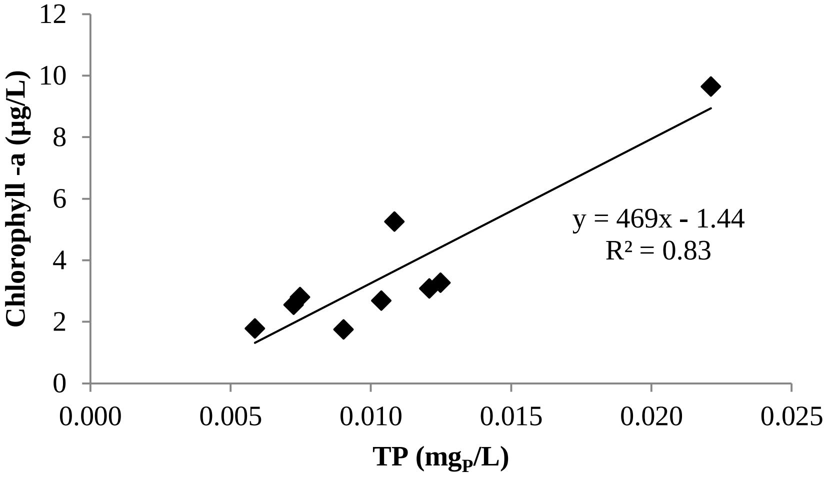

Figure 3.1 Average chlorophyll-a as a function of average total phosphorus levels.

While many sources of organic matter exist, algae can contribute significant amounts through excretion, cell lysis, and predatory grazing (Findlay and Sinsabaugh, 2003). The observed positive correlation between TOC and chlorophyll-a shown in Figure 3.2 suggests chlorophyll-a can account for at least 81% of the variation in TOC, indicating a strong algal influence on organic matter, particularly at higher chlorophyll-a levels. Therefore, the link between nutrients, algae, and organic matter exists, though terrestrial sources of DOM must also be considered.

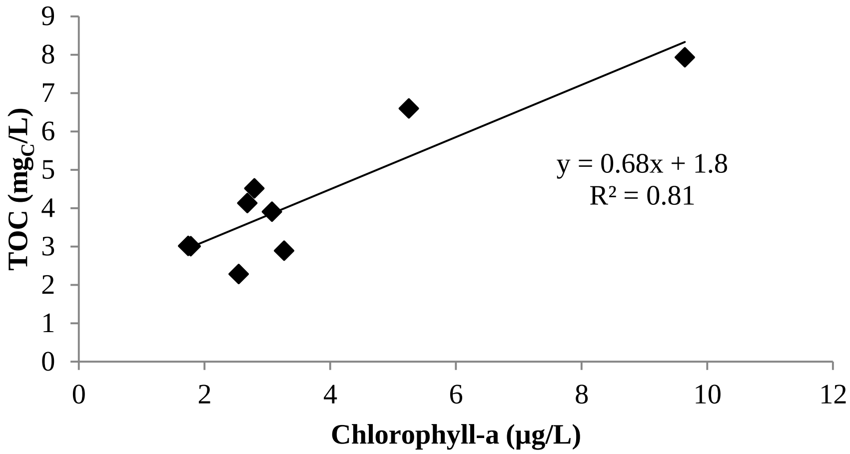

Figure 3.2 Average TOC as a function of average chlorophyll-a concentration.

Additionally, a relationship was observed between TOC and TON concentrations, indicating these two parameters are positively correlated due to overall increases in organic matter containing both carbon and nitrogen at consistently similar ratios for the ten sites (Figure 3.3). Likewise, an increase in chlorophyll-a levels corresponded with TON levels (R^2 = 0.52), suggesting that organic nitrogen can both contribute to algal production and can be produced by algae species, although the direction of this relationship is not well understood. Lastly, a strong relationship was determined between TOC and UV_{254} (R^2 = 0.90) (Najm, 1994; Leenheer, 2003).

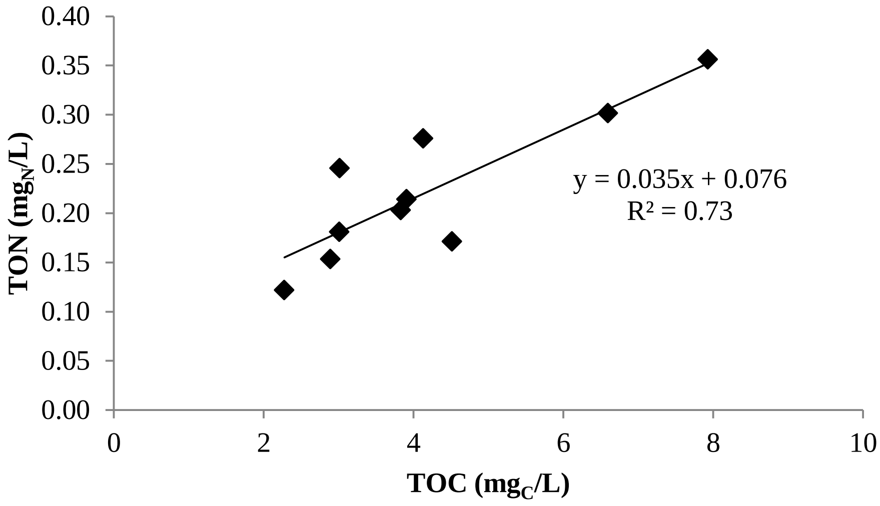

Figure 3.3 Relationship between average TON and TOC concentrations.

These findings all support the lake interactions that were hypothesized between nutrients, algae, and organic matter, and allow insight into the relationships. Although it remains somewhat difficult to draw strong conclusions due to the dependency on DOM, general increasing trends were observed for all parameters of interest, suggesting that nutrients, algae, and organic matter levels are all linked.

Water quality implications for DBP formation

As has been well understood for some time, both DOC and UV_{254} can be useful predictors for DBP formation (Singer, 1981; Reckhow, 1984; Edzwald, 1985; Najm, 1994;). Strong correlations were determined for both TTHM and HAA5 with both parameters (Table 3.3). While these relationships support previous research, this study was designed to further understand other source water parameters and characteristics that could be useful for minimizing DBP formation through source water control measures.

DBP levels were observed to increase with TP and TN concentrations, with correlations shown in Table 3.3; however the TP correlation was strongly dependent on one reservoir with the highest average phosphorous concentration. This could suggest that rising nutrient levels can be related to elevated DBP concentrations, with an interdependent variable of DOC. It must be noted that nutrient levels do not directly relate to increased carbonaceous DBP formation, but rather correspond with organic matter production in turn leading to DBP formation.

Table 3.3 R^2 values for linear correlations with DBPs.

	DOC	**UV_{254}**	**TP**	**TN**	**Chl-a**
TTHM	0.95	0.99	0.60	0.73	0.79
HAA5	0.88	0.99	0.59	0.74	0.76

Similarly, an increase in DBP formation was observed with rising chlorophyll-a concentrations (Figure 3.4), suggesting that algae can be a significant source of organic matter and therefore DBP precursor material.

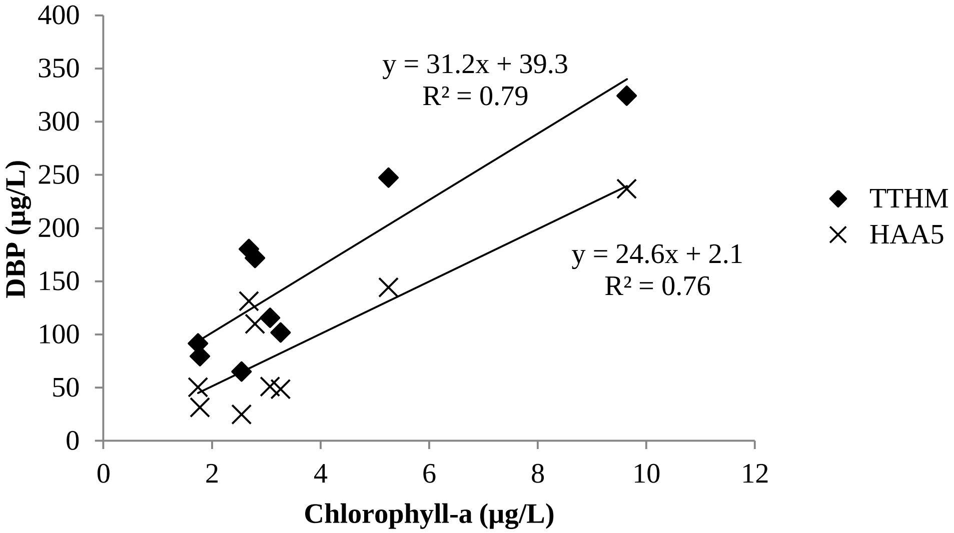

Figure 3.4 Average DBP levels as a function of chlorophyll-a concentration.

In addition, understanding the reactivity of precursor material can be useful when predicting DBP levels from source water quality characteristics. Results showed a very strong relationship between specific ultraviolet absorbance (SUVA) and DBP yields (µg DBP/mg$_C$) for both TTHM and HAA5 (Figure 3.5). This relationship indicates that higher SUVA, generally representative of higher aromatic DOM, yields more DBPs per unit of carbon, shown by previous research (White, 1997; Croue, 2000; Archer, 2006).

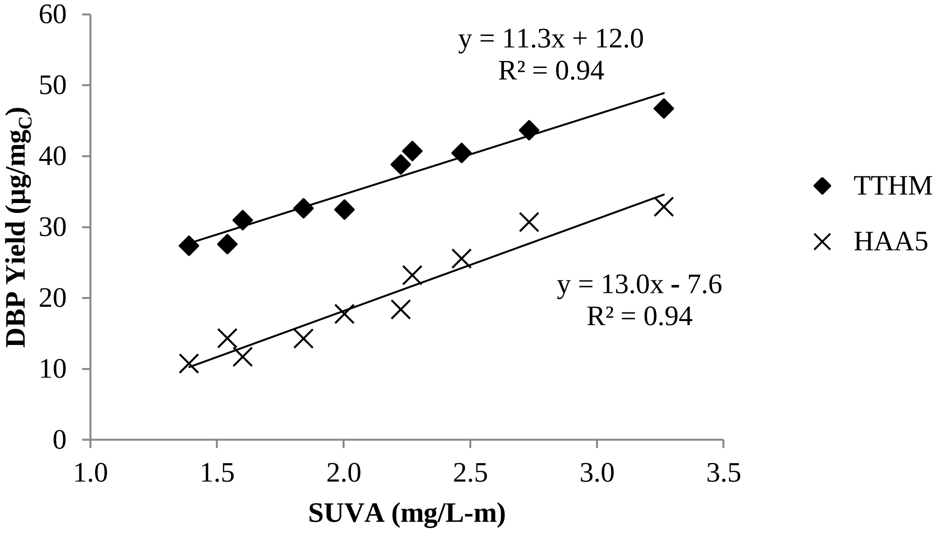

Figure 3.5 Linear correlations between average SUVA and DBP yields.

Together the relationships that exist between lake parameters including nutrients, algae and organic matter can be useful for better understanding source water quality characteristics. Subsequently, these parameters can be further related to DBP formation, noting that all are dependent on DOM as well.

Fluorescence and haloacetonitrile formation

A subset of the samples consisting of one grab sample from each municipal reservoir from mid-summer was further analyzed for fluorescence and HAN concentrations. It must be noted that the following results do not represent averages, as were presented previously for other parameters. The subset is intended to characterize a snapshot of the ten drinking waters during potential algal bloom season when primary productivity is the highest, and the possibility for increased levels of algal derived organic nitrogen exists. A strong relationship was found between TN and HAN concentrations indicating that rising TN levels can lead to increased HAN formation (Figure 3.6). Organic nitrogen can result directly from wastewater discharges and agricultural runoff, but can also be derived from algal sources (Westerhoff and Mash, 2002). TON also correlated with HAN formation to a lesser extent ($R^2 = 0.84$), suggesting that the inorganic nitrogen fraction either directly or indirectly contributed precursor material as well (Table 3.4).

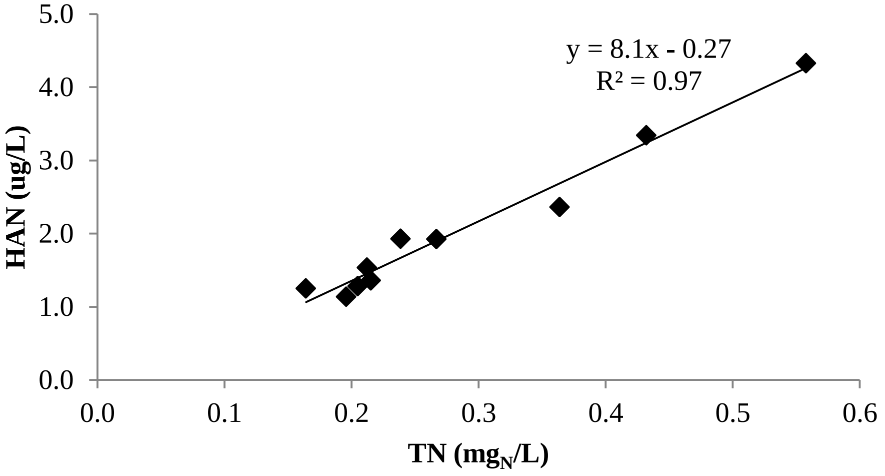

Figure 3.6 TN related to HAN concentrations (single sample set).

DOC and UV_{254} were also found to correlate with HANs, but the relationships were not as strong as for carbonaceous DBPs. Additionally, chlorophyll-a was found to moderately correlate with HAN ($R^2 = 0.52$), whereas no correlation was found between TP and HAN (Table 3.4). This suggests that algal production of organic nitrogen was not a significant contributor to HAN precursor material, but rather TN and chlorophyll-a increase together, explaining the HAN correlation with chlorophyll-a.

Table 3.4 R^2 values for linear HAN correlations

TN	TON	TP	Chl-a	DOC	UV_{254}
0.97	0.84	0.06	0.52	0.53	0.82

Fluorescence analysis was also conducted in order to gain additional water characterization information, particularly on organic matter source (allochthonous vs. autochthonous). The fluorescence index (FI) can be used to indicate whether a water sample is dominated by terrestrial organic matter or microbial/algal derived DOM (McKnight, 2001); high FI values are associated with autochthonous DOM and low FI values are associated with allochthonous DOM. For the 10 municipal lakes sampled, SUVA and FI were inversely related (Figure 3.7). This trend suggests that higher SUVA and higher aromatic content corresponds with lower FI values, supporting previous research that has shown autochthonous DOM is less aromatic (McKnight, 2001).

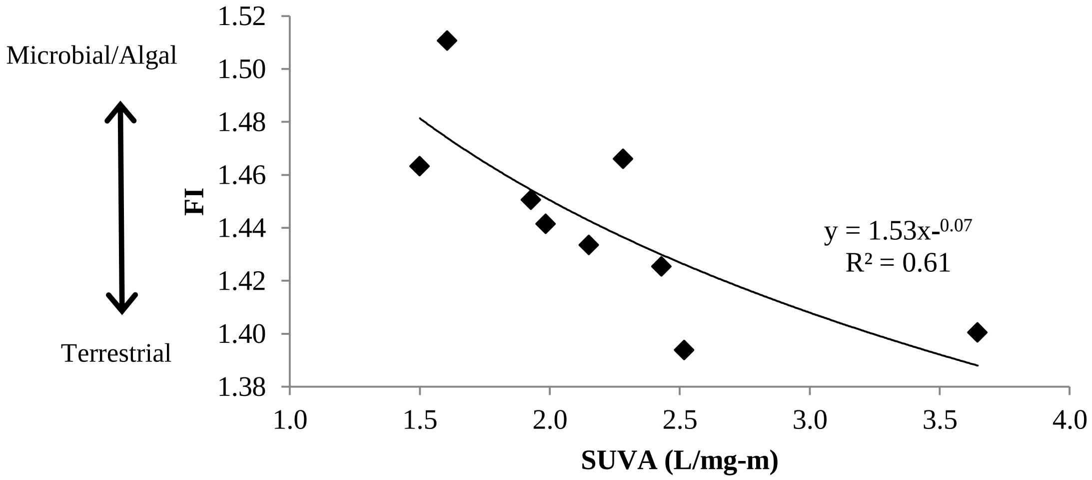

Figure 3.7 FI and SUVA showed an inverse power trend (single sample set).

A decrease in DBP yields for both TTHM and HAA5 was observed with increasing FI, indicating that autochthonous DOM is less reactive for these species than terrestrial allochthonous DOM (Figure 3.8).

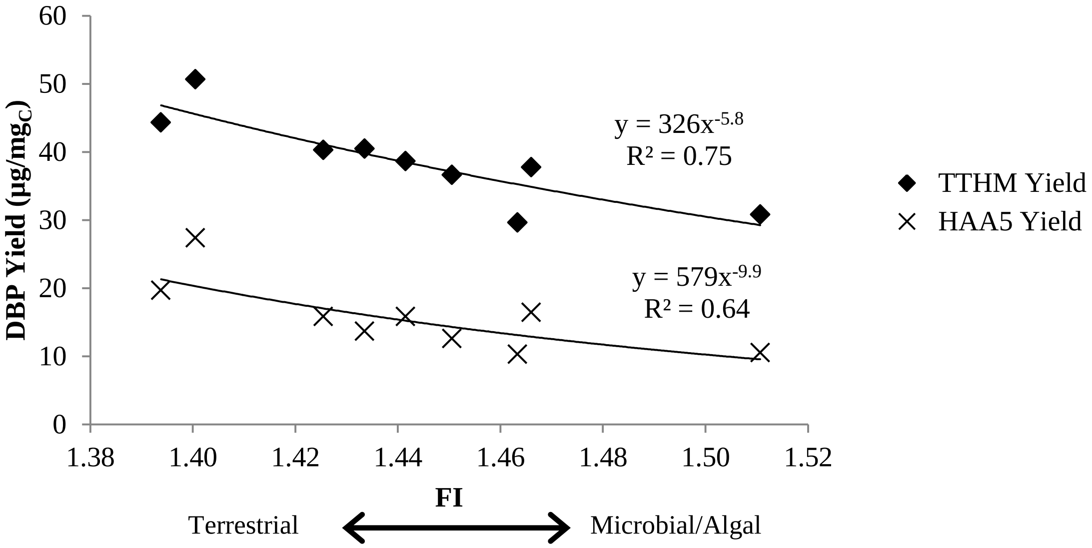

Figure 3.8 Regression of FI and DBP yield correlation (single sample set).

However, for brominated HAN formation (DBAN and BCAN) the opposite trend was observed, with high FI corresponding with high HAN yield (Figure 3.9). This trend suggests that water enriched in algal or microbial DOM can potentially yield higher levels of brominated HANs. Interestingly, a similar trend was not observed between FI and DCAN (TCAN was always <DL). Although the sample sites are minimally influenced by wastewater, many are located in urban areas where wastewater containing nutrient loads and elevated organic nitrogen levels, inevitably reaches surface water sources. Wastewater discharges are also generally sources of bromide, which could possibly explain the association with brominated HANs only.

Another explanation worth considering could be related to brominated HAN species having different precursors than the chlorinated HAN species and that FI is an indicator of these precursors. Regardless, the relationship with FI has significant implications for utilities as N-DBPs are becoming an increasing concern, and in particular, brominated species have been shown to be more carcinogenic than chlorinated species (Plewa, 2002; Komaki, 2009).

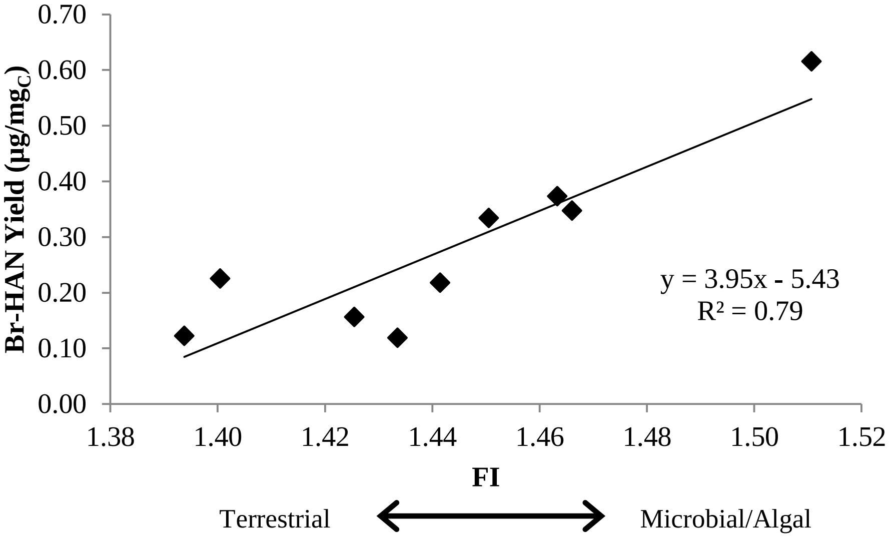

Figure 3.9 Brominated HAN yields related to FI (single sample set).

Discussion

Results from this study suggest that source water characteristics can be useful for understanding and controlling DBP formation. The nutrient and chlorophyll-a relationships support the understanding that wastewater discharges and agricultural sources, which can contribute a significant source of nutrients to surfaces waters, support increased algal blooms (Findlay and Sinsabaugh, 2003). Chlorophyll-a was further related to DBP formation, although it must be understood that this is not a direct relationship, with an interdependent variable of

DOM. The subset of data analyzed for fluorescence and HAN formation showed a strong correlation between TN and HAN ($R^2 = 0.97$). This indicates many HAN precursors exist in TN, and interestingly the correlation with organic nitrogen was not as strong ($R^2 = 0.84$). SUVA and FI were both useful for predicting DBP formation, however relationships are specific. FI was inversely related to both TTHM and HAA5 yields, but positively correlated with brominated HAN yield.

Indices such as SUVA and FI proved useful for understanding source water precursor material. For utilities these tools remain both relatively simple and cheap options. However, if FI is to be used as an indicator of reactivity for DBP formation, speciation must be taken into consideration as different relationships were found for C-DBPs and brominated N-DBPs. Also, a better understanding of the reason behind a relationship with brominated HAN, but not DCAN, needs to be further studied.

Both point and non-point sources of nutrient loadings and subsequent algal production can affect DBP formation indirectly by influencing organic matter production. Results suggest that controlling nutrient loadings to drinking water sources could aid in autochthonous TOC minimization, whereas controlling terrestrial inputs is much less reasonable. Therefore, efforts towards mitigating nutrient levels and resulting algal blooms in drinking waters should be made in order to control DBP formation through source water quality protection measures. Sites more heavily influenced by wastewater, and thus with higher nutrient loadings, should be considered in future work in order to support the results of this study.

These findings further support a *prevention* approach to minimizing DBPs as opposed to a *treatment* approach. While traditionally meeting DBP regulations has been done by improving treatment processes and enhanced removal of DOM, this study proposes an alternative that would aid drinking water utilities in meeting current and future DBP MCLs. Although complex political and logistical issues surround controlling point and non-point nutrient sources, the opportunity exists to protect drinking water sources from these inputs through both nutrient and chlorophyll-a standards. These measures could potentially reduce future treatment costs for municipalities and provide benefits in addition to DBP control, including decreasing influent DOM loadings, possible algal toxins, and taste and odor issues.

As TTHM and HAA5 regulations become more stringent and nitrogenous DBPs potentially move into regulation, pressure on municipalities will increase. Furthermore, due to urban population growth, water demand is rising and surface waters are becoming increasingly impacted by wastewater and nutrients. This will present additional challenges for the water industry. Therefore, source water protection and control measures must become more influential in order to alleviate future pressures on utilities.

Conclusions

From analyzing nutrients, chlorophyll, TOC, UV_{254}, FI, and DBPs in samples from 10 municipal reservoirs in Colorado the following observations were made:

- Increased nutrient levels were observed to lead to an increase in algal activity, and chlorophyll-a was shown to account for at least 81% of the variation in TOC. This supports the link between nutrients, algae, and organic matter.
- TOC and TON concentrations were positively correlated, indicating that DOM contained similar ratios of C:N for the ten sampling sites.

- TTHM and HAA5 levels were observed to increase with TP, TN, and chlorophyll-a. However, these are not direct relationships, due to an interdependency of DOM.
- TN and HAN showed a strong relationship ($R^2 = 0.97$) and TON correlated with HAN to a lesser extent. Additionally, chlorophyll-a was found to moderately correlate with HAN ($R^2 = 0.52$), whereas no correlation was found between TP and HAN.
- TTHM and HAA5 yields were inversely correlated with the FI, whereas brominated HAN yields were positively correlated.

CHAPTER 4. The influence of wastewater and algae on source water quality and implications for C- and N-DBP formation

Abstract

The increasing impairment of drinking water sources by wastewater discharges and enhanced algal blooms presents significant challenges to utilities. Both effluent organic matter (EfOM) and algal organic matter (AOM) can influence the speciation of disinfection byproducts (DBPs), strongly due to enriched levels of organic nitrogen. In particular, nitrogenous DBP species (N-DBPs) are formed from these sources of organic matter, and present an emerging concern for utilities and the protection of public health. This study sampled 38 lakes and reservoirs throughout Colorado with the objective of better understanding the role of wastewater and algal influences on DBP formation. The findings from this study offer insight into nutrient, chlorophyll-a, and organic matter contributions to the formation of total trihalomethanes (TTHM), haloacetic acids (HAA5), and haloacetonitriles (HAN). The fluorescence index (FI) was shown to be an effective indicator of algal activity and organic nitrogen enrichment, and provided insight to the level of wastewater influence. Furthermore, the FI was found to inversely relate to TTHM and HAA5 molar yields, whereas it was positively correlated with brominated HAN yield, further suggesting the importance of algal and wastewater DOM sources, as well as the association of bromide levels with wastewater. The findings of this study provide further insight to how AOM and EfOM can influence carbonaceous (C-DBP) and N-DBP formation, and provide a better understanding of how to apply indicators of these influences.

Introduction

As urban populations are rising and the demand for water is increasing, less pristine lakes and reservoirs are being used for drinking water. Surface waters are becoming increasingly impacted by wastewater discharges, leading to higher organic matter content and nutrient loads. The nitrogen and phosphorus present in wastewater effluent can lead to increased algal blooms, particularly in the late summer season. Both effluent organic matter (EfOM) from wastewater discharges and algal derived organic matter (AOM) can have different composition and characteristics than other more typical sources of dissolved organic matter (DOM), such as from terrestrial runoff. These influences can then affect the speciation of disinfection byproducts (DBPs) that form when disinfectants react with organic matter during treatment. DBPs constitute a significant health concern for drinking water due to their known toxicity (Krasner, 1989; Krasner, 2001; Krasner, 2006; Lewis, 2006; Muellner, 2007; Richardson, 2008). Therefore, increased contributions of EfOM and AOM to the overall DOM pool can significantly influence DBPs, and presents an emerging concern. Particularly, waters enriched in EfOM and AOM tend to have higher organic nitrogen content, which can then lead to increased nitrogenous (N-DBP) formation (Westerhoff and Mash, 2002; Krasner, 2008). These species of DBPs represent an emerging class of compounds which have drawn much attention recently due to their higher toxicity compared to the regulated carbonaceous DBPs (C-DBPs), trihalomethanes (TTHM) and haloacetic acids (HAA5) (Muellner, 2007; Richardson, 2007). Thus, as drinking water sources are becoming increasingly impaired by wastewater discharges and algal activity, a rising concern for DBP formation, specifically N-DBPs, presents new challenges for utilities and the protection of public health.

Organic nitrogen represents a component of DOM, including AOM and EfOM, and can occur in drinking water sources at considerable levels, generating significant interest recently, as it can proceed to react with disinfectants to form N-DBPs. Potential sources of organic nitrogen can include algae, agricultural fertilizers, and wastewater discharges (Westerhoff and Mash, 2002). Soluble microbial products (SMPs) from both natural and engineered systems contribute to the total organic nitrogen (TON) pool, consisting of proteins, amino acids, and polysaccharides. Bacteria in surface waters and in biological wastewater treatment processes create SMPs, resulting in organic nitrogen production. In addition, blue-green algae can fix nitrogen and excrete up to 45% as organic nitrogen; green algae species can also excrete TON (Westerhoff and Mash, 2002). Also, the cell walls of both algae and bacteria consist of cross linked peptide chains, containing amino sugars, representing another source of TON from algae. Therefore, the primary productivity, trophic level, and wastewater impact all affect TON concentrations in surface waters.

Nitrogenous disinfection byproducts (N-DBPs) are currently not regulated by the United States Environmental Protection Agency (USEPA), yet represent an emerging concern for public health and water utilities. This class of compounds includes haloacetonitriles (HANs), nitromethanes, and nitrosamines, among others. While N-DBPs generally occur at much lower levels than the regulated TTHM and HAA5, they have been shown to be more carcinogenic (Richardson, 2007). In a study by Muellner and co-workers., halonitromethanes (HNM) and haloacetonitriles (HAN) were found to be approximately two orders of magnitude more cytotoxic than HAA, which were concluded to be the least cytotoxic and genotoxic compound class (Muellner, 2007). In another study, Plewa and Wagner showed that N-DBPs were more toxic than regulated carbonaceous DBPs (C-DBPs) in Chinese hamster ovary cells (Plewa and

Wagner, 2009). Therefore, a rising need for understanding the factors influencing N-DBP formation exists.

The objective of this study was to better understand the influence of nutrients, algal activity, and organic matter character on the formation of carbonaceous and nitrogenous DBP species. This study sampled and analyzed 38 lakes and reservoirs from throughout the state of Colorado in late July or early August, 2010. All samples were collected at surface locations and analyzed for nutrients, chlorophyll-a, TOC/DOC, UV_{254}, and fluorescence, TTHM, HAA5 and HAN. Findings support the hypothesis that waters impaired by elevated algal activity and wastewater influence will form increased levels of HAN. Furthermore, the fluorescence index (FI) proved useful for better understanding water quality characteristics and DBP precursors. A better understanding of wastewater influence on these parameters was also considered. From this, DBP speciation and precursors were evaluated from a source water quality perspective, in addition to the use of fluorescence analysis for providing an indicator of DBP precursor material.

Materials and Methods

Site description

The 38 lakes and reservoirs sampled in this study were distributed throughout the state of Colorado, encompassing a range of watersheds, geographical locations, and elevations (Figure 4.1). Water bodies sampled varied from high elevation alpine lakes, to sites surrounded by urban areas. A detail of the site locations and specific characteristics (elevation, latitude, longitude, area, capacity, and mean depth) are presented in Table 4.1.

Figure 4.1 Map of Colorado showing site locations.

Table 4.1 Geographical characteristics of lakes and reservoirs sampled.

Lake/Reservoir	Code	Elevation (ft)	Latitude ºN	Longitude ºW	Area (acre)	Capacity (acre-ft)	Mean Depth (ft)
Adobe Creek	AC	4128	38.26	-103.25	5147	62000	12.0
Antero	AN	8940	38.99	-105.91	1930	15880	8.2
Arvada	AV	5759	39.82	-105.21	208	5800	27.9
Boulder	BD	5173	40.08	-105.22	530	13300	25.1
Bear Creek	BE	5553	39.65	-105.14	110	1870	17.0
Blue Mesa	BM	7524	38.47	-107.30	9200	829600	90.2
Barr	BR	5100	39.95	-104.75	1760	32150	18.3
Cherry Creek	CC	5550	39.64	-104.86	845	12805	15.2
Chatfield	CH	5432	39.55	-105.06	1429	27428	19.2
Carter	CR	5763	40.34	-105.22	1100	113500	103.2
Dillon	DL	9022	39.62	-106.06	3258	254036	78.0
Evergreen	EG	7076	39.63	-105.33	55	669	12.2
Eleven Mile	EM	8597	38.93	-105.51	3405	97779	28.7
Fort Collins	FC	5430	40.55	-105.16	1900	143500	75.5
Fruitgrowers	FG	5485	38.83	-107.94	476	4540	9.5
Granby	GB	8285	40.16	-105.87	7300	465600	63.8
Grand Junction	GJ	5704	38.97	-108.28	100	2700	27.0
Greeley-Loveland	GL	5006	40.41	-105.09	450	10300	22.9
Grand	GR	8372	40.24	-105.81	480	60000	125.0
Greeley-Seaman	GS	5481	40.71	-105.24	140	5008	35.8
Henry	HE	4312	38.26	-103.71	1100	8000	7.3
Jumbo	JB	3705	40.92	-102.67	1703	20500	12.0
Jackson	JK	4442	40.39	-104.07	2600	26100	10.0
John Martin	JM	3783	38.08	-103.04	17875	616000	34.5
Lafayette	LF	5314	40.00	-105.21	240	5300	22.1
Lonetree	LT	5131	40.34	-105.13	536	9270	17.3
North Sterling	NS	4065	40.77	-103.29	3080	109000	35.4
Pueblo	PB	4826	38.27	-104.74	5664	357678	63.1
Prewitt	PW	4088	40.42	-103.36	2430	28840	11.9
Road Canyon	RC	9280	37.77	-107.18	140	NA	NA
Ridgway	RW	6851	38.24	-107.76	1000	83000	83.0
Steamboat	SB	8031	40.79	-106.96	1000	23000	23.0
Stagecoach	SC	7210	40.28	-106.84	720	33300	46.3
Skaguay	SK	8915	38.69	-105.05	115	3678	32.0
Sweitzer	SZ	5126	38.71	-108.03	135	1330	9.9
Twin East	TE	9204	39.08	-106.33	2270	54450	24.0
Turquoise	TQ	9875	39.27	-106.39	1800	129400	71.9
Westminster	WM	5509	39.86	-105.12	1230	42380	34.5

While watersheds in Colorado are complex and many, two distinct areas can be separated and were sampled in this study. The South Platte River basin represents a main watershed in Colorado, including Jackson, Prewitt, North Sterling, and Chatfield Lake. The South Platte originates in central Colorado at the Continental Divide and flows 450 miles across the Great Plains (Sprague, 2002). The river is highly influenced by wastewater discharges, agricultural fields, and urban areas. The Arkansas River basin includes Pueblo Reservoir, Turquoise Lake, and Twin Lake East, which are all located east of the Continental Divide. The majority of sites included in the study are located in the eastern slope of the Continental Divide, and primarily central or northern Colorado. Many of the water bodies sampled are located in the Front Range region, including the urban areas of Boulder, Arvada, Fort Collins, and Greeley, among others. However, sampling locations were scattered throughout all regions of the state.

Sampling methods and handling

Grab surface samples were collected in late July or early August of 2010 from 38 lakes and reservoirs in Colorado. For quality assurance and control (QA/QC), 10% of samples were collected in duplicate. Additionally, 10% of samples were analyzed in duplicate for all parameters to assure analytical QA/QC. Samples for organic analysis and DBP formation were collected in pre-cleaned glass amber bottles, while those for nutrient analyses were collected in pre-cleaned polypropylene bottles (VWR, USA). Collected samples were kept on ice until delivery to the analysis lab where they were refrigerated at 4°C. Chlorophyll-a samples were filtered on site through GF/F or GF/C glass fiber filters and were frozen upon receipt until analysis. Samples collected for DBP formation were filtered within 48 hours of receipt through furnaced, 0.7 µm glass fiber filters (GF/F). The volumes required for dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UV_{254}) analysis were further filtered through 0.45 µm pore size polyethersulfone (PES) filters (GE Osmonics, USA). Each PES filter was rinsed with 800 mL of Milli-Q water immediately before use to prevent carbon leaching (levels < 0.2 mg_C/L).

Analytical methods

Total organic carbon (TOC) was measured on raw water samples and DOC was measured on 0.45 µm filtered samples using the Persulfate-Ultraviolet Oxidation method (Standard methods, 1998) with a Sievers 800 TOC analyzer and auto-sampler (APHA; AWWA; WEF, 1998). UV_{254} was measured using a UV-Vis spectrophotometer (Cary 100, Agilent Technologies) with a 1-cm path length quartz cuvette. Total phosphorous (TP) measurements were performed with a Lachat QuikChem 8500 spectrophotometric flow injection. Nitrate and nitrite were measured with an analytical flow solution IV spectrophotometric analyzer (OI Analytical, USA). Total nitrogen (TN) measurements were performed with a Shimadzu TOC-V analyzer. Ammonia was measured using a BioTek Synergy 2 Microplate Reader. Total organic nitrogen (TON) was calculated as the difference between TN and inorganic nitrogen species. For samples with non-detects for inorganic species, the value was set at the detection limit. This calculation was validated by ensuring that the organic fraction was always greater than 60% (Lee and Westerhoff 2005). Chlorophyll-a samples were measured following a spectrofluorometric analysis (EPA method 445.0) using a Fluoromax 2 (Horiba Scientific).

Fluorescence analysis was completed with a Horiba Fluoromax 4. Routine lamp, Raman, and cuvette checks were completed daily. Excitation was from 240-450 nm at 10 nm increments. Emission scans were from 350-550 nm at 2 nm increments. Slit widths were set at 5 nm. The fluorescence index (FI) was calculated as the ratio of the emission intensity at 470 and 520 nm at an excitation of 370 nm (Cory, 2010).

The formation of DBPs followed the chlorination method of uniform formation conditions (Summers, 1996). Samples were chlorinated at room temperature with a pH 8 buffered, sodium hypochlorite solution. Water samples were buffered with a pH 8 borate buffer and incubated in the dark for 24 hours (± 1 hour) at room temperature (20± 1.0°C). Chlorine doses were determined in order to obtain a chlorine residual of 1.0 mg/L (± 0.4 mg/L) after 24 hours. Chlorine residuals were measured with the DPD (N,N-diethyl-pphenylenediamine) colorimetric method (SM4500-Cl G) and were quenched with ammonium chloride, which did not significantly affect the formation of haloacetonitriles (HAN).

DBP analysis was completed within two weeks of chlorination. EPA Method 551.1 (1995) was used for analysis of trihalomethanes (TTHM) and haloacetonitriles (HAN). The species included in HAN analysis were: dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), dibromoacetonitrile (DBAN), and bromochloroacetonitrile (BCAN). EPA method 552.2 was followed for analysis of haloacetic acids and reported as the five regulated species (HAA5). An Agilent 6890 Gas Chromatography System with an electron capture detector was used.

Results and Discussion

Water quality characteristics and interactions

In order to better understand lake interactions, primary productivity, organic matter character and subsequent DBP formation, nutrients, chlorophyll-a, and organics were analyzed for all samples. The results for each site are shown in Table 4.2, along with UV_{254} and the fluorescence index (FI). These spectrophotometric properties detect humic material, and can be useful for better understanding the character of organic matter, such as source and aromaticity.

Table 4.2 Water quality parameters for the 38 lakes and reservoirs.

Lake/Reservoir	**Chl-a** µg/L	**TP** mg_P/L	**TN** mg_N/L	**TON** mg_N/L	**TOC** mg_C/L	**DOC** mg_C/L	**UV_{254}** cm^{-1}	**FI**
Adobe Creek	21.8	0.039	0.569	0.503	5.8	4.9	0.059	1.62
Antero	2.3	0.020	0.416	0.362	4.7	4.3	0.070	1.54
Arvada	1.6	0.012	0.215	0.184	3.2	3.1	0.042	1.46
Boulder	4.2	0.016	0.267	0.221	4.0	3.2	0.062	1.45
Bear Creek	9.4	0.024	0.536	0.266	5.2	4.6	0.116	1.49
Blue Mesa	0.3	0.004	0.192	0.173	2.8	2.6	0.059	1.48
Barr	31.6	0.415	1.575	1.306	8.3	7.9	0.107	1.64
Cherry Creek	16.8	0.059	0.749	0.709	6.9	5.9	0.093	1.55
Chatfield	2.6	0.007	0.243	0.221	3.8	3.4	0.067	1.47
Carter	3.0	0.008	0.272	0.271	4.0	3.8	0.068	1.43
Dillon	2.3	0.003	0.219	0.102	2.1	2.0	0.045	1.49
Evergreen	2.2	0.002	0.432	0.338	3.6	3.2	0.107	1.40
Eleven Mile	2.8	0.022	0.344	0.296	3.7	3.4	0.051	1.52
Fort Collins	3.7	0.009	0.239	0.206	4.4	4.0	0.101	1.39
Fruitgrowers	25.5	0.038	1.332	1.228	10.1	8.1	0.162	1.54
Granby	1.6	0.009	0.200	0.181	4.7	4.0	0.100	1.41
Grand Junction	1.9	0.002	0.205	0.200	2.8	2.9	0.053	1.44
Greeley-Loveland	1.8	0.013	0.364	0.355	6.7	6.1	0.131	1.43
Grand	3.2	0.005	0.147	0.145	3.7	3.6	0.106	1.35
Greeley-Seaman	15.0	0.014	0.558	0.441	7.8	7.1	0.173	1.43
Henry	31.8	0.081	0.869	0.751	7.4	5.5	0.071	1.62
Jumbo	30.5	0.054	0.997	0.685	7.0	6.6	0.101	1.63
Jackson	48.3	0.126	1.158	1.113	8.2	7.7	0.087	1.69
John Martin	25.2	0.048	0.624	0.467	5.4	4.3	0.083	1.57
Lafayette	NA	0.001	0.196	0.194	4.0	3.6	0.052	NA
Lonetree	0.9	0.005	0.285	0.267	4.2	4.3	0.083	1.46
North Sterling	16.3	0.189	1.387	0.798	6.4	5.6	0.082	1.63
Pueblo	5.7	0.016	0.212	0.140	3.2	2.6	0.060	1.47
Prewitt	9.9	0.093	1.532	1.062	7.7	6.7	0.099	1.63
Road Canyon	16.3	0.272	1.983	1.374	10.1	8.0	0.203	1.49
Ridgway	1.1	0.006	0.133	0.132	2.4	2.1	0.040	1.47
Steamboat	8.6	0.030	0.372	0.331	6.6	5.9	0.173	1.40
Stagecoach	5.1	0.015	0.567	0.460	6.1	6.0	0.160	1.49
Skaguay	NA	0.006	0.197	0.164	2.3	2.2	0.055	1.48
Sweitzer	2.0	0.003	0.787	0.561	6.3	5.7	0.093	1.52
Twin East	0.7	0.002	0.138	0.116	2.0	1.8	0.048	1.44
Turquoise	1.0	0.002	0.187	0.182	3.9	3.3	0.110	1.36
Westminster	1.9	0.006	0.164	0.127	2.5	2.0	0.033	1.51

It was hypothesized that increased nutrient levels would lead to increased organic matter levels, primarily of autochthonous origin (algal derived), and enriched in organic nitrogen. A rise in chlorophyll-a levels was observed as both TN and TP concentrations increased, with R^2 values and corresponding trend equations shown in Table 4.3. Sources of nutrients could potentially be from both wastewater and agricultural sources, in turn influencing the algal activity and primary production. A correlation was also observed between chlorophyll-a and TOC concentrations, suggesting the production of AOM, particularly at higher trophic levels.

Table 4.3 Observed trends (R^2) between nutrients and chlorophyll-a concentrations.

	TN	**TP**	**TOC**
R^2	0.64	0.71	0.59
Equation	$15.2x^{1.3}$	$130x^{0.80}$	$3.17x^{0.25}$

Additionally, an increasing linear trend was observed between chlorophyll-a and TON, shown in Figure 4.2. While there are many sources of organic nitrogen (wastewater, algae, soils, fertilizer), this trend suggests that algal production can account for at least 64% of the variability in organic nitrogen concentrations. However, at higher TON levels the trend shows much more scatter. Several sampling sites are located downstream of urban areas, heavily impacted by wastewater discharges, and do not follow the trend associated with increasing chlorophyll-a concentrations (sites are shown by open symbols), contributing the majority of the scatter to Figure 4.2. This observation suggests these sites are dominated by organic nitrogen from wastewater discharges, rather than algal produced. The direction of the relationship between algae and organic nitrogen can be difficult to understand as algae can use nitrogen as a nutrient for production, but also contain and excrete organic nitrogen.

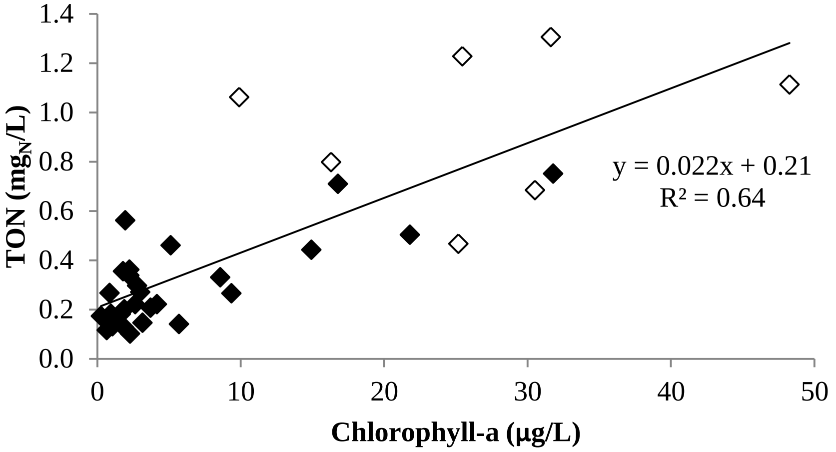

Figure 4.2 Increasing TON concentration with chlorophyll-a levels (regression shown is for all samples). Open symbols indicate sites heavily influenced by wastewater.

TOC and TON were also observed to increase together, with an exponential trend at higher concentrations, as shown in Figure 4.3. This indicates that for elevated levels of carbon and nitrogen, the trend shift to increased nitrogen enrichment and a lower C:N ratio. Also important to note, this observation was significant for sites heavily influenced by wastewater (open symbols), as to be expected from previous work (Mitch, 2008; Dotson and Westerhoff, 2009).

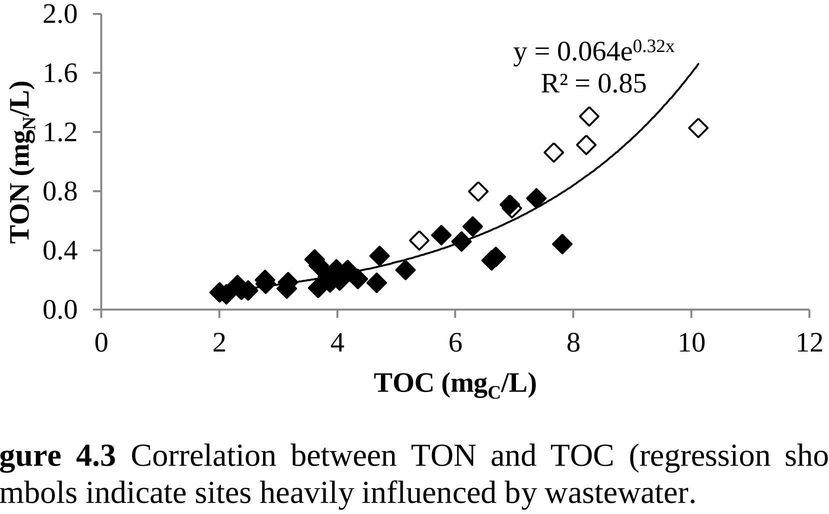

Figure 4.3 Correlation between TON and TOC (regression shown is for all samples). Open symbols indicate sites heavily influenced by wastewater.

Results for this study, showed an average TON concentration of 0.44 mg_N/L and the average C:N ratio was 15.1 mg_N/mg_C. Previous work by Lee et al. found an average dissolved organic nitrogen (DON) concentration of 0.186 mg_N/L and a C:N ratio of 18.0 mg_N/mg_C in municipal waters, whereas Dotson and co-workers conducted a study of wastewater influenced drinking waters and found respective values of 0.290 mg_N/L and 12.6 mg_N/mg_C (Lee, 2006; Dotson and Westerhoff, 2009). When comparing these values, it must be noted that the study presented here sampled both municipal and non-municipal surface waters and also measured TON, rather than DON. Regardless, results showed overall high average organic nitrogen levels and nitrogen enrichment (low C:N). Additionally, this study examined surface waters with a wide range of water qualities and levels of wastewater influence, which must be considered when interpreting averages.

The findings presented above, and notably the distinctions for sites with high wastewater impact, aid in understanding the source water relationships occurring between nutrients, algae, and organics. These relationships remain difficult to understand due to the complex dynamics in water bodies, as well as environmental factors. However, findings presented here provide a better understanding of lake interactions and subsequent AOM and EfOM influences. From this, insight regarding implications for DBP formation related to source water quality can further be evaluated.

Fluorescence and water quality

Fluorescence analysis can prove a useful tool for characterizing source water organic matter. Specifically, the fluorescence index (FI) can be used as an indicator of whether a sample is enriched in DOM from terrestrial sources (lower FI), or DOM derived internally, from microbial and algal sources (higher FI) (McKnight, 2001). An inverse linear relationship between FI and C:N ratios was observed, suggesting that sites enriched in organic nitrogen were associated with higher FI values, and thus a more autochthonous DOM signature (Figure 4.4). Sites heavily influenced by wastewater (open symbols) generally represented the highest FI values and lowest C:N ratios. Previous work has shown higher FI to be associated with wastewater (Nam, 2007). This observation suggests the use of fluorescence for better understanding both nitrogen enrichment and the level of wastewater influence (EfOM), in addition to algal activity (AOM).

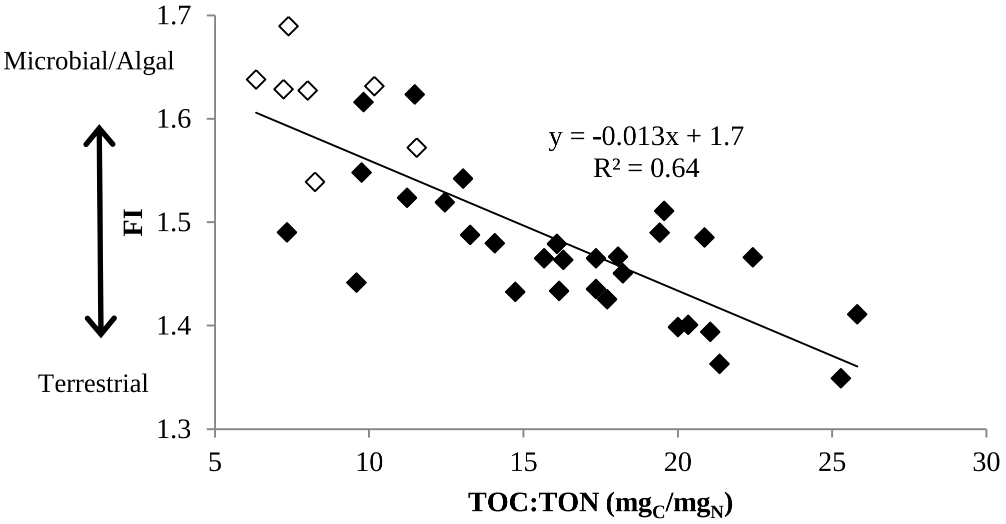

Figure 4.4 Inverse linear relationship between FI and TOC:TON (regression shown is for all samples). Open symbols indicate sites heavily influenced by wastewater.

FI was also found to correlate with both chlorophyll-a and specific ultraviolet absorbance (SUVA) (R^2 values shown in Table 4.4). FI and chlorophyll-a showed a positive relationship, suggesting higher algal levels are associated with a higher FI, and a more autochthonous DOM origin. An inverse linear relationship was observed between FI and SUVA ($R^2 = 0.63$), indicating that samples with greater aromatic content and higher SUVA, were less algal derived and more terrestrial. This is consistent with previous work by McKnight et al. which showed higher aromatic content corresponded with lower FI values (McKnight, 2001). Fluorescence results from this study suggest the use of FI to indicate AOM, organic nitrogen enrichment, aromaticity, and potentially provide insight to the level of wastewater influence and EfOM.

Table 4.4 Linear relationships between water quality parameters and FI.

Linear Trend	**R^2**
FI and Chlorophyll-a	(+) 0.58
FI and SUVA	(-) 0.63
FI and TOC:TON	(-) 0.64

Indicators of carbonaceous DBP formation

Better understanding DBP precursors and the water quality characteristics which lead to increased DBP formation provides insight to utilities which can aid in meeting regulations and protecting public health. As source waters are becoming impaired due to wastewater discharges and enhanced algal activity, research regarding DBP precursor material becomes increasingly important. Previous work has proved UV_{254} a useful surrogate for TTHM and HAA5 formation (Najm, 1994). The results presented here support this finding, however sites heavily influenced by wastewater contributed significant scatter to the trend (open symbols), suggesting the effectiveness of UV_{254} as a surrogate for C-DBP formation will vary depending on the level of wastewater influence (Figure 4.5).

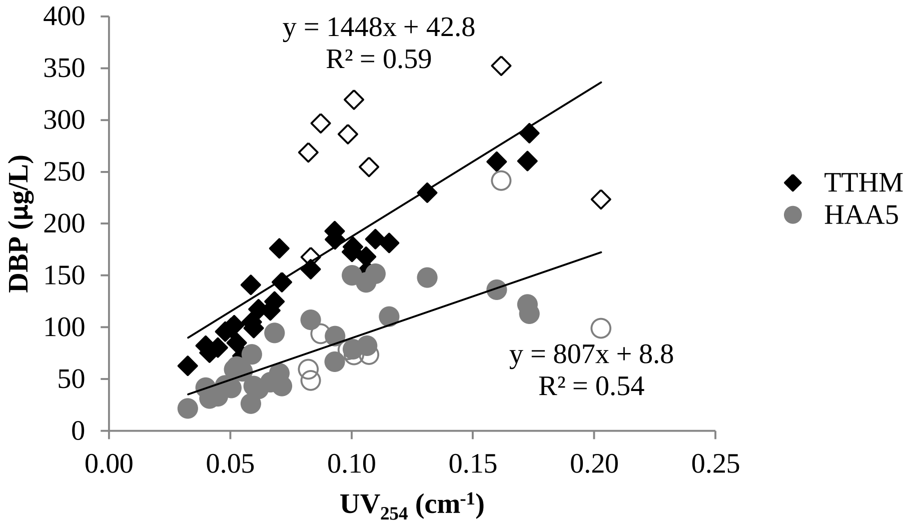

Figure 4.5 Correlation between UV_{254} and DBP concentration for TTHM and HAA5 (regression shown is for all samples). Open symbols indicate sites heavily influenced by wastewater.

However, when SUVA and molar yields of TTHM and HAA5 were considered, the influence of wastewater did not contribute as much scatter, with the exception of one site (Figure 4.6). This trend simply suggests more aromatic content yields more DBPs per unit carbon, supported by previous work (White 1997; Croue, 2000;Archer and Singer, 2006).

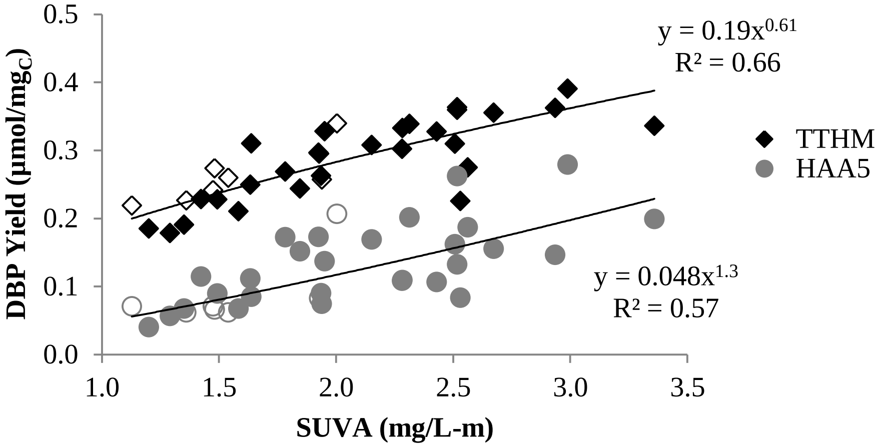

Figure 4.6 Relationship between SUVA and DBP molar yield (TTHM and HAA5) (regression shown is for all samples). Open symbols indicate sites heavily influenced by wastewater.

Also, an inverse relationship was found between FI and C-DBP yields (Figure 4.7), suggesting terrestrially derived organic matter is more reactive for both TTHM and HAA5 formation. This observation remains consistent with the understanding that terrestrial organic matter is generally more aromatic in character, and thus yields higher levels of DBPs, which was also demonstrated by the SUVA relationships shown in Figure 4.6. Additionally, wastewater influenced sites tended to yield lower concentrations of TTHM and HAA5 on a per carbon basis (Sirivedhin and Gray, 2005).

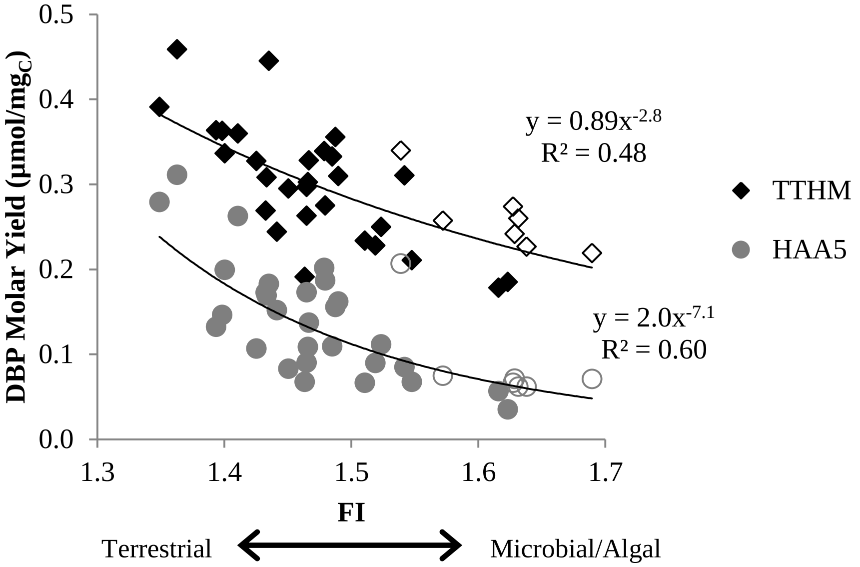

Figure 4.7 Relationship between FI and molar DBP yields (TTHM and HAA5) (regression shown is for all samples). Open symbols indicate sites heavily influenced by wastewater.

Together these findings suggest that spectrophotometric methods can be useful for predicting C-DBP formation and precursor reactivity, however wastewater influence plays a significant role and should be taken into consideration when using UV_{254} as an indicator of DBPs. This will present a growing concern for utility awareness as source waters become increasingly impaired, and utilities should consider alternate surrogates for DBP precursor material.

Haloacetonitrile formation

Previous research has shown that eutrophic lake conditions, algal productivity, and wastewater influence can all be linked to high organic nitrogen content, which can then proceed to form increased levels of N-DBPs (Westerhoff and Mash, 2002; Krasner, 2008; Krasner, 2009). Figure 4.8 shows a correlation between chlorophyll-a and HAN levels, with a generally increasing trend. Interestingly, sites with high wastewater influence (open symbols) did not follow the trend as closely, contributing a significant amount of scatter to Figure 4.8. This suggests when source waters are heavily impacted by wastewater, algae play a much lesser role in HAN formation and chlorophyll-a is not always an effective indicator when the TON source is dominated by wastewater EfOM rather than AOM. This is further supported by the findings previously presented in Figure 4.2.

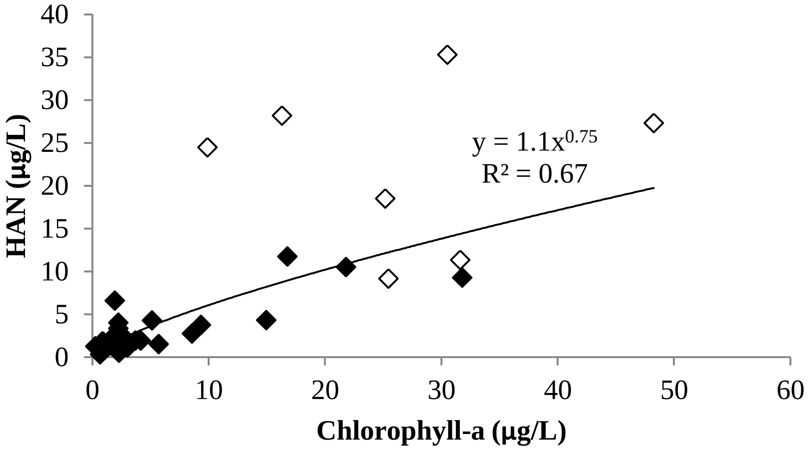

Figure 4.8 HAN concentration as a function of chlorophyll-a levels (regression shown is for all samples). Open symbols indicate sites heavily influenced by wastewater.

HAN concentrations were also observed to increase with TON levels (Figure 4.9), suggesting organic nitrogen moieties as precursors for N-DBPs, which has been shown in previous work (Reckhow, 1990; Lee, 2007; Dotson, 2009). Again, the wastewater influenced sites contribute significant scatter, with no apparent trend for this subset, suggesting TON may not be as useful of a predictor for these sites, whereas for sites with minimal wastewater influence TON proves more useful. This could potentially be attributed to differences between the organic nitrogen character of AOM and EfOM.

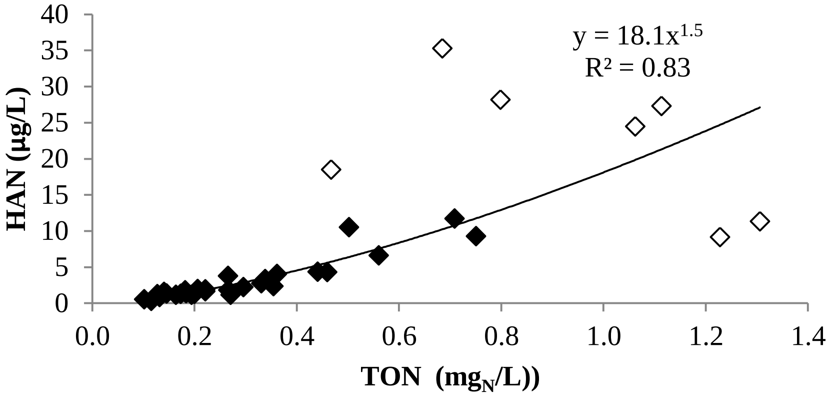

Figure 4.9 HAN concentration as a function of TON (regression shown is for all samples). Open symbols indicate sites heavily influenced by wastewater.

HAN molar yields (μmol/mg_C) were observed to decrease with increasing C:N ratios (Figure 4.10), again indicating that samples enriched in organic nitrogen are more reactive for forming HANs, which has been previously observed by Dotson and co-workers for DCAN (Dotson, 2009). Sites with high wastewater influence generally showed the lowest C:N ratio and highest HAN yields, as expected from previous work (Dotson and Westerhoff, 2009; Dotson, 2009). This observation shows that wastewater influence plays a significant role in the formation of N-DBPs, however the distinction between whether AOM generated from nutrients present in wastewater or EfOM itself contributes to nitrogen enrichment, remains difficult to evaluate.

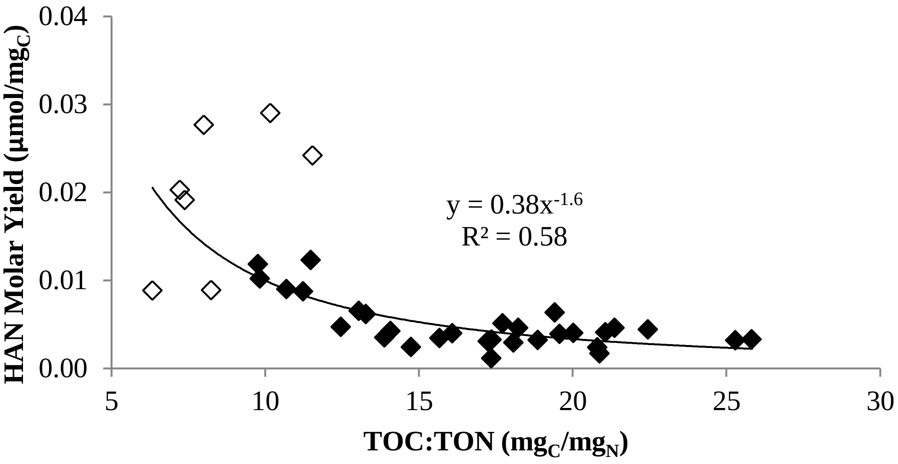

Figure 4.10 HAN molar yield vs. TOC:TON (regression shown is for all samples). Open symbols indicate sites heavily influenced by wastewater.

Furthermore, brominated HAN species, including DBAN and CBAN, showed an increasing relationship with FI (Figure 4.11), opposite to the trend observed for C-DBPs (Figure 4.7). This correlation suggests water enriched in algal or microbial derived organic matter can potentially yield higher levels of Br-HANs. Interestingly, no correlation was observed for FI and DCAN (TCAN was always below detection limit). The trend presented in Figure 4.11 suggests some threshold value of FI, above which Br-HAN yields become significant. A possible explanation for the trend shown in Figure 4.11 can be related to wastewater impacted sources, which tend to be high in both organic nitrogen and bromide. Higher FI values have been linked to wastewater, and therefore could partially explain these results and the lack of a correlation with DCAN (Nam, 2007). Another hypothesis considers different precursors for brominated HAN species rather than the chlorinated HAN species, and that FI is potentially a better indicator for these precursors.

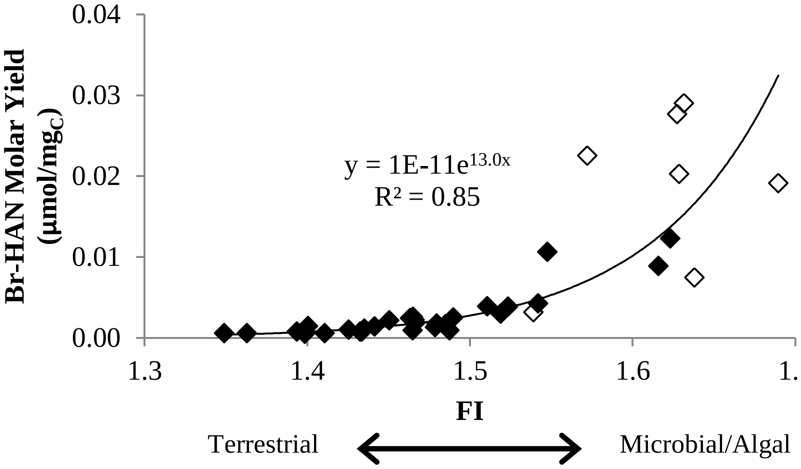

Figure 4.11 Brominated HAN yield as a function of FI (regression shown is for all samples). Open symbols indicate sites heavily influenced by wastewater.

Regardless, the relationship with FI has significant implications for utilities as N-DBPs are becoming an increasing concern, and in particular, brominated species have been shown to be more carcinogenic than chlorinated analogues (Plewa, 2002; Komaki, 2009). Additionally, understanding the role of AOM in HAN formation through measuring chlorophyll-a levels proved useful, but when wastewater influence is significant, the relationship is less clear. The same appeared to be true for TON as an indicator for HAN formation. Therefore, there exists a strong need to better understand the role of EfOM in the formation of C-DBPs and N-DBPs in order to provide utilities with better tools to indicate DBP precursor material.

Conclusions

Wastewater and algal impairment of surface waters and the emerging importance of N-DBP formation is further supported by these findings. While it is well known that both algae and wastewater represent significant sources of TON, further evaluation of their relationship to other lake dynamics and subsequent DBP formation presents challenges. The key implications observed from this study were the following:

- In general, sites heavily influenced by wastewater yielded the highest levels of HAN and the lowest levels of TTHM and HAA5. Therefore, the increasing importance of EfOM and its role in emerging DBP formation must be further considered in the drinking water community. The use of regulated C-DBPs as proxies for all DBPs may no longer be appropriate.
- As drinking water sources are becoming increasingly impacted by wastewater, the use of UV_{254} as a predictor for C-DBP formation should be reconsidered.
- For sites heavily influenced by wastewater, algae played a much lesser role in HAN formation, and therefore the emerging role of EfOM may be more important to consider when dealing with impaired sources.
- The FI can prove a useful indicator for AOM, organic nitrogen enrichment, and the level of wastewater influence. Therefore the FI should be used in the future to better predict emerging DBP precursor material.
- The FI represents a useful tool for DBP reactivity, but DBP species must be taken into consideration as C-DBP and brominated HAN showed opposite trends. Also, the influence of bromide should also be considered.

CHAPTER 5. Summary

The two data sets, which includes averaged values for 10 municipal reservoirs (Chapter 3) and the single sample set for 38 lakes from late July or early August 2010, allowed for comparison between the different relationships which were developed. Table 5.1 shows the correlations between parameters and the corresponding R^2 values and equations for the two data sets. Generally, relationships for the 10 municipal reservoirs showed linear trends, whereas the 38 lakes showed mostly power distributions. This observation can be related to the range of lakes and water qualities for the two different data sets. The municipal reservoirs (Chapter 3) were relatively pristine with generally lower trophic levels, whereas the 38 lakes (Chapter 4) showed a wide range of water qualities and productivity. At lower trophic levels for both of the data sets linear trends were strong, but at higher levels the relationships moved towards more power distributions as well as more scatter from trendlines.

Table 5.1 Summary of relationships between variables of interest for both data sets (Chapters 3 and 4).

Relationship		**10 Municipal Reservoirs**		**38 Lakes**	
x	**y**	**R^2**	**Equation**	**R^2**	**Equation**
TP	Chl-a	0.83	$469x - 1.44$	0.71	$130x^{0.80}$
TN	Chl-a	0.58	$23.5x - 2.93$	0.64	$15.2x^{1.3}$
TOC	TON	0.73	$0.035x + 0.076$	0.85	$0.064e^{0.32x}$
Chl-a	TON	0.52	$0.022x + 0.14$	0.64	$0.022x + 0.21$
Chl-a	TOC	0.81	$0.68x + 1.8$	0.59	$3.17x^{0.25}$
TOC	UV_{254}	0.90	$0.029x - 0.033$	0.60	$0.024x^{0.78}$
DOC	TTHM	0.95	$50.0x -48.0$	0.81	$38.4x^{0.98}$
DOC	HAA5	0.88	$38.8x - 64.0$	0.30	$26.1x^{0.70}$
UV_{254}	TTHM	0.99	$1545x + 11.7$	0.59	$1448x + 42.8$
UV_{254}	HAA5	1.00	$1248x - 21.9$	0.54	$807x + 8.8$
TP	TTHM	0.60	$10871x - 24.8$	0.37	$353x^{0.19}$
TP	HAA5	0.59	$13420x + 8.6$	0.00	$75.7x^{0.01}$
TN	TTHM	0.73	$915x - 102$	0.59	$236x^{0.46}$
TN	HAA5	0.74	$740x - 114$	0.06	$81.9x^{0.16}$
Chl-a	TTHM	0.79	$31.2x + 39.3$	0.39	$116x^{0.22}$
Chl-a	HAA5	0.76	$24.6x + 2.1$	0.00	$70.6x^{0.019}$
SUVA	TTHM Yield	0.94	$11.3x + 12.0$	0.37	$7.9x + 22.1$
SUVA	HAA5 Yield	0.94	$13.0x - 7.6$	0.56	$11.6x - 4.8$
TN	HAN	0.97	$8.1x -0.3$	0.81	$11.4x^{1.4}$
TON	HAN	0.84	$9.3x - 0.2$	0.83	$18.1x^{1.5}$
Chl-a	HAN	0.52	$0.18x + 1.4$	0.67	$1.1x^{0.75}$
TP	HAN	0.06	$42.4x + 1.7$	0.62	$47.4x^{0.63}$
UV_{254}	HAN	0.82	$20.8x + 0.4$	0.22	$75.6x^{1.3}$
DOC	HAN	0.53	$0.47x + 0.3$	0.66	$0.14x^{0.22}$
SUVA	FI	0.61	$1.53x^{-0.07}$	0.63	$-0.11x+1.7$
FI	TTHM Yield	0.75	$326x^{-5.8}$	0.12	$60.8x^{-1.1}$
FI	HAA5 Yield	0.64	$579x^{-9.9}$	0.51	$196x^{-6.1}$
FI	Br-HAN Yield	0.79	$3.95x - 5.4$	0.85	$6E\text{-}10e^{13.6}$

Another finding from the 38 lakes showed when the wastewater influenced sites were not included in the data set the trends tended to be more linear, but when those sites were incorporated into the data set (Chapter 4), the relationships were generally showed power or exponential distributions (Table 5.2). Similarly, this finding can be attributed to the higher trophic levels of the sites heavily influenced by wastewater, and also the higher organic nitrogen concentrations for these sites which tend to not follow the linear trend as tightly and deviate towards a more exponential or power distribution.

Table 5.2. Summary of relationships for 38 lakes, with and without the sites heavily influenced by wastewater.

Relationship		**Wastewater sites not included**		**Wastewater sites included**	
x	**y**	**R^2**	**Equation**	**R^2**	**Equation**
TP	Chl-a	0.82	$365x - 0.13$	0.71	$130x^{0.80}$
TN	Chl-a	0.54	$25.9x - 3.6$	0.64	$15.2x^{1.3}$
TOC	TON	0.71	$0.086x - 0.087$	0.85	$0.064e^{0.32x}$
Chl-a	TON	0.58	$0.018x + 0.20$	0.64	$0.022x + 0.21$
Chl-a	HAN	0.66	$0.33x - 1.3$	0.67	1.1x^0.75
TON	HAN	0.85	$15.8x - 1.6$	0.83	$18.1x^{1.5}$
FI	Br-HAN Yield	0.70	$0.039x - 0.054$	0.85	$6E\text{-}10e^{13.6}$

Together, these two data sets show that depending on the source water quality different correlations were observed, and thus the relationships developed in this thesis should be considered specific for the water bodies studied. Particularly, trophic level and wastewater influence have the potential to significantly influence relationships between parameters.

CHAPTER 6. Future Work and Considerations

In order to better understand source water quality relationships to DBP precursors, advanced DOM characterization and the evaluation of treatment methods is recommended for future work. Additionally, future research on this topic should consider adjustments to the study design which would aid in meeting potential objectives.

Analytical characterization

Further water quality and DOM characterization methods should be employed. Fluorescence can offer a powerful tool in this respect, particularly parallel factor analysis (PARAFAC). This method can identify the respective contributions of different fluorophores to the overall excitation-emission matrix. First, this analysis could potentially provide further insight into source water DOM characteristics, and influence such as wastewater and algae. Furthermore, this tool would aid in understanding DBP precursors, and fluorescent detection of the components relating to these reactive materials. More specifically, certain components could potentially be related to different DBP species. Although not presented in this thesis due to lack of significant conclusions, “peak-picking” approaches to excitation emission matrices (EEMs) could also employed and should at least be considered.

Understanding organic nitrogen composition and precursors for DBPs remains challenging, with current research somewhat inconclusive. However, more information regarding organic nitrogen moieties in drinking water sources would prove useful for further evaluating nitrogenous DBP formation, and relationships to source water quality characteristics.

Specifically, moieties related to wastewater and algal derived organic nitrogen would be of particular relevance. Also, removal of these components during conventional treatment should be considered. Options for characterization could include fractionation of nitrogen enriched isolates, which could then be followed by chlorination and DBP measurements. Additionally, DOM generated in the lab could also be characterized for DBP reactivity. If focusing on algal derived organic nitrogen, algal cultures could be grown in the lab and analyzed. For a similar evaluation, wastewater effluent organic nitrogen composition should be analyzed. There currently exists much room for additional research involving organic nitrogen composition, characterization, and relevance to drinking water and DBPs.

Treatment based analytical approaches

To give a more practical perspective to source water quality implications for DBP formation, the use of a more treatment based approach to analysis would prove useful, particularly if a study is designed to provide insight to utilities and regulatory agencies. Involving coagulation and flocculation at the bench scale would aid in understanding which precursors are well removed by conventional treatment and which are not. Additionally, by measuring DBP formation before and after coagulation/flocculation and analyzing DBP speciation, insights into preferential removal of specific precursors would be gained. Further, DOM characterization should also be conducted before and after treatment in order to better understand source water quality implications to treatment, and further insight into the character of precursors.

As the use of chloramines as an alternative disinfectant to chlorine is rising, a comparison of the DBP formation and speciation of these two oxidants would provide useful and relevant insight. Dosing conditions and parameters would have to be implemented to ensure results are comparable. It may also be worth considering disinfectant kinetics and subsequent DBP formation as well in this analysis. This approach is very appropriate with the onset of the Stage 2 D/DBPR, including monitoring requirements throughout the distribution system, and the switching over of utilities to chloramines.

As the concern of N-DBPs is growing due to current toxicological research, the switch to chloramines, and rising wastewater and algal impairment, a strong need for further research exists. Therefore, analysis of DBP species of emerging importance should be conducted. Future work should analyze for haloacetamides, halonitromethanes, and nitrosamines, among others. Iodinated THM and HAA compounds should also be considered.

Study design considerations

Future work should emphasize a careful original study design in order to meet objectives related to this work, which can be difficult if not well thought out before a sampling campaign begins. Frequency of sampling and season should be considered and directly related to project objectives. An increased sampling frequency should be implemented during algal bloom periods in order to gain more representative data, and provide focused information regarding the role of AOM. Additionally, sites highly impacted by wastewater could be targeted in future studies. From this, an attempt at quantifying the percentage of wastewater influence would prove helpful for drawing conclusions about EfOM. For instance, developing a ranked system of reservoirs based off of quantified wastewater discharges would be recommended. Additionally, when focusing on EfOM the specific wastewater treatment processes (i.e. nitrification and de-nitrification) of respective plants could play an important role in evaluating influences. Lastly, statistical tools should be employed in order to further distinguish source water quality relationships to DBP formation. This would provide a more quantified evaluation of data sets, and strengthen conclusions, which are difficult to draw from dynamic lake interactions.

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APPENDIX A. List of Acronyms

AOM: Algal derived organic matter

BCAN: Bromochloroacetonitrile

Br-HAN: Brominated haloacetonitrile

C-DBP: Carbonaceous disinfection byproduct

DBP: Disinfection byproduct

DBAA: Dibromoacetic acid

DBAN: Dibromoacetonitrile

DCAA: Dichloroacetic acid

DCAN: Dichloroacetonitrile

D/DBPR: Disinfectant and Disinfection Byproducts Rule

DOC: Dissolved organic carbon

DOM: Dissolved organic matter

DON: Dissolved organic nitrgogen

EfOM: Effluent organic matter

EOM: Extracellular organic matter

FI: Fluorescence index

HAA5: Five regulated haloacetic acids

HAN: Haloacetonitriles

HNM: Halonitromethanes

IAN: Iodoacetonitile

IARC: International Agency for Research on Cancer

MBAA: Monobromoacetic acid

MBAN: Monobromoacetonitrile

MCAA: Monochloroacetic acid

MCAN: Monochloroacetonitrile

MCL: Maximum Contaminant Level

N-DBP: Nitrogenous disinfection byproduct

NDMA: N-nitrosdimethylamine

ON: Organic nitrogen

PARAFAC: Parallel factor analysis

PES: Polyethersulfone

QA/QC: Quality assurance and quality control

SUVA: Specific ultraviolet absorbance

SMP: Soluble microbial product

TCAA: Trichloroacetic acid

TCAN: Trichloroacetonitrile

TN: Total nitrogen

TOC: Total organic carbon

TON: Total organic nitrogen

TP: Total phosphorus

TTHM: Total trihalomethanes

UFC: Uniform formation conditions

USEPA: United States Environmental Protection Agency

UV_{254}: Ultraviolet absorbance at 254 nm

APPENDIX B. 10 Municipal Reservoirs Data Set

Table B.1 Arvada data set

Sample ID	Date	Chl-a	TP	TN	NH_4^+	NO_2^-	NO_3^-	TON	TOC	DOC	UV_{254}	SUVA	TTHM	HAA5
		µg/L	mg_P/L	mg_N/L	mg_N/L	mg_N/L	mg_N/L	mg_N/L	mg_C/L	mg_C/L	cm^{-1}	L/mg-m	µg/L	µg/L
AV-01-01-01	5/13/2010	1.5	0.004	0.175	0.009	0.001	0.000	0.164	3.1	2.3	0.019	0.83	57.3	20.8
AV-02-01-01	5/27/2010	0.6	0.004	0.174	0.009	0.001	0.006	0.159	2.8	3.0	0.039	1.28	77.5	46.9
AV-02-01-01d	5/27/2010	NA	0.011	0.147	0.022	0.002	0.004	0.120	2.9	3.1	0.039	1.25	77.7	26.4
AV-03-01-01	6/10/2010	0.7	0.002	0.191	0.023	0.001	0.003	0.163	2.6	2.7	0.039	1.43	80.0	23.6
AV-04-01-01	6/24/2010	0.6	0.003	0.191	0.009	0.001	0.005	0.176	3.2	2.9	0.043	1.46	76.9	30.2
AV-05-01-01	7/8/2010	1.6	0.006	0.231	0.009	0.001	0.014	0.207	2.8	2.9	0.045	1.53	76.6	27.7
AV-06-01-01	7/22/2010	1.6	0.012	0.215	0.023	0.001	0.008	0.184	3.2	3.1	0.042	1.35	75.1	31.2
AV-07-01-01	8/12/2010	3.4	0.008	0.239	0.032	0.001	0.009	0.197	3.2	3.0	0.046	1.50	90.1	31.3
AV-08-01-01	8/26/2010	2.5	0.004	0.264	0.042	0.001	0.007	0.214	3.4	3.0	0.045	1.51	85.0	33.7
AV-09-01-01	9/9/2010	2.8	0.009	0.225	0.025	0.001	0.004	0.194	3.0	3.0	0.045	1.50	87.5	35.9
AV-10-01-01	9/22/2010	2.4	0.003	0.218	0.034	0.001	0.003	0.180	2.8	3.0	0.049	1.67	90.2	36.3
Average		1.8	0.006	0.206	0.021	0.001	0.006	0.178	3.0	2.9	0.041	1.39	79.4	31.3
Stdev		1.0	0.003	0.034	0.011	0.000	0.004	0.026	0.2	0.2	0.008	0.22	9.3	7.1

Table B.2 Boulder data set

Sample ID	**Date**	**Chl-a**	**TP**	**TN**	**NH_4^+**	**NO_2^-**	**NO_3^-**	**TON**	**TOC**	**DOC**	**UV_{254}**	**SUVA**	**TTHM**	**HAA5**
		µg/L	**mg_P/L**	**mg_N/L**	**mg_N/L**	**mg_N/L**	**mg_N/L**	**mg_N/L**	**mg_C/L**	**mg_C/L**	**cm^{-1}**	**L/mg-m**	**µg/L**	**µg/L**
BD-01-01-01	5/11/2010	5.6	0.017	0.245	0.030	0.003	0.001	0.210	4.3	3.8	0.066	1.72	111.5	71.6
BD-02-01-01	6/1/2010	1.3	0.007	0.224	0.028	0.002	0.003	0.191	3.7	3.5	0.061	1.75	116.1	45.6
BD-02-01-01d	6/1/2010	NA	0.005	0.228	0.014	0.002	0.002	0.210	NA	3.6	0.059	1.63	107.3	45.5
BD-03-01-01	6/15/2010	1.0	0.011	0.238	0.035	0.002	0.006	0.194	3.8	3.5	0.060	1.73	106.9	31.5
BD-04-01-01	7/6/2010	2.5	0.017	0.250	0.009	0.001	0.011	0.229	3.7	3.5	0.065	1.88	109.7	58.1
BD-05-01-01	7/19/2010	2.7	0.013	0.279	0.009	0.002	0.006	0.262	4.4	3.9	0.061	1.58	107.7	48.7
BD-06-01-01	8/4/2010	4.2	0.016	0.267	0.041	0.001	0.004	0.220	4.0	3.2	0.062	1.93	117.3	40.4
BD-07-01-01	8/17/2010	3.4	0.007	0.238	0.019	0.002	0.003	0.214	4.0	3.6	0.071	1.98	111.9	57.9
BD-08-01-01	9/13/2010	4.0	0.009	0.231	0.035	0.002	0.008	0.186	3.8	3.5	0.073	2.10	135.9	52.1
BD-09-01-01	9/24/2010	3.1	0.017	0.245	0.025	0.003	0.002	0.215	3.7	3.5	0.075	2.12	131.0	56.4
Average		3.1	0.012	0.244	0.024	0.002	0.005	0.213	3.9	3.6	0.065	1.84	115.5	50.8
Std Dev		1.4	0.005	0.017	0.011	0.001	0.003	0.022	0.3	0.2	0.006	0.19	10.1	11.1

Table B.3 Evergreen data set

Sample ID	**Date**	**Chl-a**	**TP**	**TN**	**NH_4^+**	**NO_2^-**	**NO_3^-**	**TON**	**TOC**	**DOC**	**UV_{254}**	**SUVA**	**TTHM**	**HAA5**
		µg/L	**mg$_P$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_C$/L**	**mg$_C$/L**	**cm^{-1}**	**L/mg-m**	**µg/L**	**µg/L**
EG-01-01-01	5/13/2010	1.8	0.013	0.497	0.062	0.002	0.017	0.416	6.2	5.4	0.114	2.11	212.0	178.5
EG-02-01-01	5/27/2010	1.8	0.015	0.456	0.068	0.003	0.018	0.367	6.3	6.1	0.177	2.90	303.1	225.2
EG-03-01-01	6/10/2010	1.6	0.004	0.433	0.050	0.001	0.018	0.364	4.0	4.0	0.129	3.24	196.9	117.5
EG-04-01-01	6/24/2010	2.6	0.003	0.270	0.015	0.002	0.009	0.244	5.3	4.7	0.136	2.90	210.6	194.9
EG-05-01-01	7/6/2010	2.8	0.008	0.249	0.026	0.001	0.009	0.213	4.4	4.0	0.124	3.07	179.2	117.9
EG-05-01-01d	7/6/2010	NA	0.011	0.308	0.030	0.002	0.010	0.267	4.1	4.1	0.130	3.17	176.5	198.9
EG-06-01-01	7/29/2010	2.2	0.002	0.432	0.079	0.002	0.013	0.338	3.6	3.2	0.107	3.36	154.4	82.0
EG-07-01-01	8/10/2010	3.4	0.015	0.341	0.084	0.007	0.058	0.192	3.9	3.7	0.136	3.65	189.0	102.1
EG-08-01-01	8/24/2010	4.7	0.014	0.283	0.043	0.001	0.010	0.229	3.0	2.7	0.092	3.40	131.0	101.3
EG-09-01-01	9/9/2010	3.1	0.011	0.194	0.024	0.001	0.010	0.159	2.6	2.5	0.097	3.83	126.9	65.4
EG-10-01-01	9/23/2010	2.9	0.008	0.310	0.051	0.002	0.009	0.248	2.2	2.3	0.098	4.29	100.9	58.8
Average		2.7	0.010	0.343	0.048	0.002	0.016	0.276	4.1	3.9	0.122	3.27	180.0	131.1
Std Dev		0.9	0.005	0.097	0.023	0.002	0.014	0.083	1.3	1.2	0.024	0.56	54.4	58.2

Table B.4 Fort Collins data set

Sample ID	Date	Chl-a	TP	TN	NH_4^+	NO_2^-	NO_3^-	TON	TOC	DOC	UV_{254}	SUVA	TTHM	HAA5
		μg/L	mg_P/L	mg_N/L	mg_N/L	mg_N/L	mg_N/L	mg_N/L	mg_C/L	mg_C/L	cm^{-1}	L/mg-m	μg/L	μg/L
FC-01-01-01	5/17/2010	1.0	0.003	0.199	0.009	0.002	0.053	0.135	4.0	3.8	0.086	2.26	124.6	100.5
FC-02-01-01	6/3/2010	1.4	0.004	0.234	0.012	0.002	0.048	0.172	4.5	4.4	0.105	2.36	178.8	111.2
FC-03-01-01	6/14/2010	1.6	0.009	0.259	0.027	0.002	0.054	0.175	5.1	4.7	0.116	2.48	188.8	134.0
FC-03-01-01d	6/14/2010	NA	0.011	0.278	0.084	0.003	0.056	0.135	5.0	4.8	0.121	2.52	192.8	141.0
FC-04-01-01	7/8/2010	3.2	0.010	0.261	0.009	0.003	0.038	0.211	4.9	4.5	0.113	2.50	170.5	143.6
FC-05-01-01	7/20/2010	6.8	0.013	0.216	0.009	0.003	0.004	0.200	5.3	4.6	0.113	2.48	189.3	145.6
FC-06-01-01	8/9/2010	3.7	0.009	0.239	0.026	0.002	0.004	0.206	4.4	4.0	0.101	2.52	177.4	78.8
FC-07-01-01	8/23/2010	2.6	0.005	0.190	0.016	0.001	0.005	0.167	4.1	3.9	0.100	2.58	169.7	83.8
FC-08-01-01	9/13/2010	2.3	0.007	0.180	0.029	0.002	0.006	0.143	4.1	4.0	0.097	2.46	170.2	75.6
FC-09-01-01	9/27/2010	2.6	0.004	0.184	0.041	0.003	0.003	0.137	4.0	3.9	0.097	2.51	155.3	83.1
Average		2.8	0.007	0.224	0.026	0.002	0.027	0.168	4.5	4.2	0.105	2.47	171.7	109.7
Stdev		1.7	0.003	0.035	0.023	0.001	0.024	0.030	0.5	0.4	0.011	0.09	20.1	29.0

Table B.5 Greeley-Loveland data set

Sample ID	**Date**	**Chl-a**	**TP**	**TN**	**NH_4^+**	**NO_2^-**	**NO_3^-**	**TON**	**TOC**	**DOC**	**UV_{254}**	**SUVA**	**TTHM**	**HAA5**
		µg/L	**mg_P/L**	**mg_N/L**	**mg_N/L**	**mg_N/L**	**mg_N/L**	**mg_N/L**	**mg_C/L**	**mg_C/L**	**cm^{-1}**	**L/mg-m**	**µg/L**	**µg/L**
GL-01-01-01	5/13/2010	6.2	0.015	0.397	0.057	0.004	0.065	0.271	7.5	6.9	0.174	2.51	211.8	268.8
GL-02-01-01	6/10/2010	5.6	0.007	0.343	0.023	0.004	0.032	0.284	6.8	6.3	0.153	2.43	167.0	275.5
GL-03-01-01	7/8/2010	2.3	0.011	0.319	0.012	0.004	0.007	0.296	7.1	6.6	0.151	2.30	214.2	281.9
GL-04-01-01	7/8/2010	12.9	0.007	0.331	0.016	0.002	0.008	0.304	6.3	6.0	0.143	2.39	179.0	250.7
GL-05-01-01	7/22/2010	1.8	0.013	0.364	0.009	0.001	0.008	0.346	6.7	6.1	0.131	2.15	147.9	229.5
GL-06-01-01	8/12/2010	3.8	0.013	0.432	0.033	0.001	0.008	0.389	6.3	5.6	0.121	2.15	77.1	227.8
GL-06-01-01d	8/12/2010	NA	0.011	0.294	0.030	0.003	0.008	0.253	NA	5.4	0.118	2.19	76.5	223.2
GL-07-01-01	9/16/2010	4.1	0.010	0.303	0.033	0.001	0.008	0.260	5.8	5.7	0.118	2.07	78.0	220.9
Average		5.3	0.011	0.348	0.027	0.003	0.018	0.300	6.6	6.1	0.139	2.27	143.9	247.3
Stdev		3.7	0.003	0.048	0.015	0.001	0.021	0.046	0.5	0.5	0.020	0.16	59.4	25.2

Table B.6 Greeley-Seaman data set

Sample ID	Date	Chl-a	TP	TN	NH_4^+	NO_2^-	NO_3^-	TON	TOC	DOC	UV_{254}	SUVA	TTHM	HAA5
		µg/L	mg_P/L	mg_N/L	mg_N/L	mg_N/L	mg_N/L	mg_N/L	mg_C/L	mg_C/L	cm^{-1}	L/mg-m	µg/L	µg/L
GS-01-01-01	5/11/2010	6.3	0.012	0.382	0.028	0.003	0.024	0.327	8.6	7.8	0.227	2.90	301.1	266.9
GS-02-01-01	5/25/2010	7.2	0.032	0.409	0.040	0.005	0.005	0.360	8.6	8.0	0.239	2.97	361.6	301.8
GS-03-01-01	6/8/2010	8.0	0.018	0.370	0.055	0.003	0.004	0.307	9.3	8.5	0.272	3.18	427.2	359.5
GS-04-01-01	6/22/2010	8.3	0.032	0.454	0.044	0.003	0.002	0.405	10.2	9.5	0.275	2.89	481.5	460.8
GS-05-01-01	7/5/2010	10.8	0.033	0.487	0.049	0.001	0.008	0.428	8.2	7.5	0.236	3.16	373.3	269.8
GS-06-01-01	8/10/2010	15.0	0.014	0.558	0.115	0.002	0.002	0.439	7.8	7.1	0.173	2.43	287.2	113.0
GS-07-01-01	9/8/2010	12.6	0.042	0.426	0.084	0.006	0.010	0.325	6.5	5.8	0.147	2.54	238.8	161.3
GS-08-01-01	10/5/2010	9.1	0.008	0.346	0.039	0.004	0.002	0.300	6.0	5.8	0.130	2.24	225.6	107.0
GS-08-01-01d	10/5/2010	NA	0.008	0.329	0.012	0.004	0.006	0.307	NA	5.8	0.132	2.28	221.2	91.2
Average		9.6	0.022	0.418	0.052	0.004	0.007	0.356	8.2	7.3	0.204	2.73	324.2	236.8
Stdev		2.9	0.013	0.073	0.031	0.001	0.007	0.055	1.4	1.3	0.058	0.37	92.7	127.7

Table B.7 Grand Junction data set

Sample ID	**Date**	**Chl-a**	**TP**	**TN**	**NH_4^+**	**NO_2^-**	**NO_3^-**	**TON**	**TOC**	**DOC**	**UV_{254}**	**SUVA**	**TTHM**	**HAA5**
		µg/L	**mg$_P$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_C$/L**	**mg$_C$/L**	**cm^{-1}**	**L/mg-m**	**µg/L**	**µg/L**
GJ-01-01-01	6/9/2010	1.2	0.004	0.158	0.026	0.001	0.005	0.126	2.6	2.7	0.051	1.85	79.3	49.2
GJ-02-01-01	6/14/2010	1.2	0.009	0.324	0.032	0.001	0.003	0.288	3.0	2.8	0.056	1.98	103.8	56.6
GJ-03-01-01	6/24/2010	0.9	0.009	0.174	0.053	0.001	0.003	0.117	3.2	2.9	0.061	2.10	105.7	54.8
GJ-04-01-01	6/29/2010	0.9	0.007	0.179	0.009	0.002	0.009	0.160	2.6	2.9	NA	NA	103.3	67.3
GJ-05-01-01	7/15/2010	1.3	0.012	0.241	0.033	0.003	0.007	0.199	2.9	2.8	0.055	1.96	103.7	66.0
GJ-06-01-01	7/26/2010	1.9	0.002	0.205	0.009	0.002	0.003	0.191	2.8	2.9	0.053	1.85	84.9	62.0
GJ-07-01-01	8/12/2010	2.8	0.013	0.369	0.058	0.002	0.003	0.306	2.9	2.6	0.052	1.98	101.7	41.7
GJ-08-01-01	8/24/2010	2.8	0.007	0.583	0.018	0.002	0.005	0.557	3.7	2.8	0.055	1.95	105.8	47.0
GJ-08-01-01d	8/24/2010	NA	0.007	0.541	0.009	0.002	0.008	0.523	3.4	2.9	0.065	2.25	8.0	19.6
GJ-09-01-01	9/7/2010	3.0	0.016	0.243	0.023	0.001	0.004	0.214	3.5	2.9	0.056	1.92	104.2	39.3
GJ-10-01-01	9/21/2010	1.5	0.010	0.172	0.023	0.001	0.006	0.142	2.7	2.9	0.061	2.11	102.2	51.9
GJ-11-01-01	10/13/2010	NA	0.006	0.153	0.041	0.001	0.004	0.107	2.8	2.7	0.058	2.11	93.8	45.7
Average		1.7	0.008	0.279	0.028	0.002	0.005	0.244	3.0	2.8	0.056	2.00	91.4	50.1
Stdev		0.8	0.004	0.148	0.016	0.001	0.002	0.152	0.4	0.1	0.004	0.13	27.6	13.2

Table B.8 Lafayette data set

Sample ID	Date	Chl-a	TP	TN	NH_4^+	NO_2^-	NO_3^-	TON	TOC	DOC	UV_{254}	SUVA	TTHM	HAA5
		µg/L	mg_P/L	mg_N/L	mg_N/L	mg_N/L	mg_N/L	mg_N/L	mg_C/L	mg_C/L	cm^{-1}	L/mg-m	µg/L	µg/L
LF-01-01-01	5/18/2010	NA	0.002	0.183	0.009	0.002	0.003	0.169	4.1	3.2	0.038	1.20	109.5	68.3
LF-02-01-01	6/1/2010	NA	0.003	0.219	0.010	0.001	0.004	0.205	3.8	3.7	0.056	1.51	52.1	40.0
LF-03-01-01	6/29/2010	NA	0.002	0.229	0.009	0.003	0.007	0.210	NA	3.7	0.053	1.46	93.0	45.3
LF-05-01-01	7/27/2010	NA	0.001	0.196	0.009	0.002	0.003	0.182	4.0	3.6	0.052	1.42	101.8	59.2
LF-07-01-01	8/10/2010	NA	0.010	0.227	0.018	0.002	0.005	0.203	3.7	3.5	0.064	1.84	108.5	41.5
LF-07-01-01d	8/10/2010	NA	0.008	0.222	0.009	0.001	0.003	0.208	3.7	3.6	0.062	1.70	106.0	43.3
LF-08-01-01	8/26/2010	NA	0.008	0.213	0.010	0.001	0.006	0.196	3.7	3.5	0.056	1.59	101.4	70.7
LF-09-01-01	9/8/2010	NA	0.009	0.216	0.009	0.001	0.003	0.203	3.9	3.6	0.060	1.65	107.5	43.1
LF-10-01-01	9/28/2010	NA	0.006	0.228	0.019	0.001	0.007	0.201	3.8	4.0	0.061	1.50	109.9	48.2
Average		NA	0.006	0.215	0.011	0.002	0.005	0.198	3.8	3.6	0.056	1.54	98.9	51.1
Stdev		NA	0.003	0.016	0.004	0.001	0.002	0.013	0.2	0.2	0.008	0.18	18.4	11.9

Table B.9 Pueblo data set

Sample ID	Date	Chl-a	TP	TN	NH_4^+	NO_2^-	NO_3^-	TON	TOC	DOC	UV_{254}	SUVA	TTHM	HAA5
		µg/L	mg_P/L	mg_N/L	mg_N/L	mg_N/L	mg_N/L	mg_N/L	mg_C/L	mg_C/L	cm^{-1}	L/mg-m	µg/L	µg/L
PB-01-01-01	5/19/2010	0.5	0.011	0.390	0.024	0.006	0.209	0.150	2.8	2.6	0.051	1.97	94.5	30.3
PB-02-01-01	6/1/2010	1.1	0.010	0.369	0.027	0.005	0.197	0.140	2.9	2.5	0.057	2.24	96.5	48.1
PB-03-01-01	6/16/2010	2.4	0.021	0.379	0.035	0.006	0.160	0.177	3.2	2.9	0.065	2.25	118.3	61.4
PB-03-01-01d	6/16/2010	NA	0.013	0.380	0.049	0.007	0.156	0.169	3.2	2.9	0.066	2.27	115.0	65.2
PB-04-01-01	7/6/2010	3.5	0.006	0.263	0.017	0.006	0.051	0.189	2.8	2.7	0.061	2.25	111.5	78.3
PB-05-01-01	7/20/2010	3.6	0.019	0.197	0.009	0.004	0.010	0.173	3.0	2.8	0.061	2.20	106.7	42.4
PB-06-01-01	8/3/2010	5.7	0.016	0.212	0.058	0.001	0.014	0.139	3.2	2.6	0.060	2.28	98.9	43.1
PB-07-01-01	8/26/2010	3.8	0.015	0.211	0.077	0.001	0.039	0.094	2.6	2.4	0.054	2.23	94.7	42.6
PB-08-01-01	9/9/2010	5.8	0.009	0.228	0.018	0.002	0.044	0.164	2.7	2.4	0.053	2.18	91.5	35.1
PB-09-01-01	9/30/2010	3.1	0.006	0.280	0.013	0.001	0.139	0.127	2.6	2.3	0.056	2.39	89.9	37.8
Average		3.3	0.012	0.291	0.033	0.004	0.102	0.152	2.9	2.6	0.058	2.23	101.8	48.4
Stdev		1.8	0.005	0.080	0.022	0.002	0.078	0.028	0.2	0.2	0.005	0.11	10.3	15.1

Table B.10 Westminster data set

Sample ID	**Date**	**Chl-a**	**TP**	**TN**	**NH$_4^+$**	**NO$_2^-$**	**NO$_3^-$**	**TON**	**TOC**	**DOC**	**UV$_{254}$**	**SUVA**	**TTHM**	**HAA5**
		µg/L	**mg$_P$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_N$/L**	**mg$_C$/L**	**mg$_C$/L**	**cm^{-1}**	**L/mg-m**	**µg/L**	**µg/L**
WM-01-01-01	5/17/2010	1.7	0.012	0.172	0.032	0.002	0.007	0.130	2.4	1.8	0.022	1.22	51.3	21.4
WM-02-01-01	6/8/2010	1.9	0.002	0.172	0.048	0.002	0.014	0.107	NA	2.1	0.042	1.95	77.1	23.2
WM-03-01-01	6/22/2010	1.6	0.006	0.158	0.022	0.002	0.012	0.122	2.5	2.4	0.033	1.40	74.5	27.6
WM-04-01-01	7/16/2010	2.1	0.004	0.178	0.026	0.003	0.020	0.130	2.2	2.2	0.038	1.71	73.4	25.8
WM-05-01-01	7/19/2010	3.4	0.008	0.162	0.009	0.002	0.013	0.138	2.4	2.2	0.036	1.60	66.9	27.5
WM-06-01-01	8/3/2010	1.9	0.006	0.164	0.032	0.002	0.003	0.127	2.5	2.0	0.033	1.61	62.6	21.4
WM-07-01-01	8/17/2010	2.6	0.005	0.147	0.022	0.001	0.004	0.120	2.3	2.3	0.035	1.51	62.0	23.3
WM-08-01-01	9/1/2010	2.4	0.015	0.155	0.026	0.001	0.004	0.124	2.2	2.1	0.033	1.58	59.6	25.3
WM-08-01-01d	9/1/2010	NA	0.007	0.143	0.023	0.001	0.004	0.115	NA	2.0	0.034	1.66	61.8	27.4
WM-09-01-01	9/13/2010	3.4	0.006	0.162	0.043	0.001	0.008	0.110	2.1	1.9	0.034	1.78	62.0	23.0
WM-10-01-01	10/5/2010	4.5	0.010	0.170	0.051	0.009	0.007	0.104	2.2	2.0	0.032	1.61	63.7	23.6
Average		2.5	0.007	0.162	0.030	0.002	0.009	0.121	2.3	2.1	0.034	1.60	65.0	24.5
Stdev		0.9	0.004	0.011	0.013	0.002	0.005	0.011	0.2	0.2	0.005	0.19	7.5	2.3

APPENDIX C. 38 Lakes Data Set

Table C.1 Nutrient levels

Sample ID	**TP**	**TN**	**NO_2^-**	**NO_3^-**	**TON**
	mg_P/L	**mg_N/L**	**mg_N/L**	**mg_N/L**	**mg_N/L**
AC-01-01-01	0.039	0.569	0.003	0.005	0.503
AN-01-01-01	0.020	0.416	0.001	0.005	0.362
AV-06-01-01	0.012	0.215	0.001	0.008	0.184
BD-06-01-01	0.016	0.267	0.000	0.004	0.221
BE-01-01-01	0.024	0.536	0.009	0.200	0.266
BM-01-01-01	0.004	0.192	0.001	0.003	0.173
BR-01-01-01	0.415	1.575	0.004	0.009	1.306
CC-01-01-01	0.059	0.749	0.003	0.008	0.709
CH-01-01-01	0.007	0.243	0.001	0.022	0.221
CR-01-01-01	0.008	0.272	0.002	0.003	0.271
DL-01-01-01	0.003	0.219	0.003	0.114	0.102
EG-06-01-01	0.0020	0.432	0.002	0.013	0.338
EM-01-01-01	0.022	0.344	0.001	0.007	0.296
FC-06-01-01	0.01	0.24	<DL	<DL	0.206
FG-01-01-01	0.038	1.332	0.002	0.003	1.228
GB-01-01-01	0.009	0.200	0.001	0.005	0.181
GJ-06-01-01	0.00	0.20	<DL	<DL	0.200
GL-05-01-01	0.0130	0.364	0.001	0.008	0.355
GR-01-01-01	0.005	0.147	0.002	0.003	0.145
GS-06-01-01	0.0145	0.558	0.002	<DL	0.441
HE-01-01-01	0.081	0.869	0.008	0.005	0.751
JB-01-01-01	0.054	0.997	0.007	0.033	0.685
JK-01-01-01	0.126	1.158	0.003	0.007	1.113
JM-01-01-01	0.048	0.624	0.010	0.020	0.467
LF-05-01-01	0.001	0.196	0.002	<DL	0.194
LT-01-01-01	0.005	0.285	0.002	0.003	0.267
NS-01-01-01	0.189	1.387	0.026	0.098	0.798
PB-06-01-01	0.02	0.21	0.00	0.01	0.140
PW-01-01-01	0.093	1.532	0.016	0.188	1.062
RC-01-01-01	0.272	1.983	0.007	0.010	1.374
RW-01-01-01	0.006	0.133	0.001	0.003	0.132
SB-01-01-01	0.030	0.372	0.002	0.004	0.331
SC-01-01-01	0.015	0.567	0.004	0.019	0.460
SK-01-01-01	0.006	0.197	0.001	0.017	0.164

SZ-01-01-01	0.003	0.787	0.007	0.102	0.561
TE-01-01-01	0.002	0.138	0.001	0.021	0.116
TQ-01-01-01	0.002	0.187	0.001	0.004	0.182
WM-06-01-01	0.006	0.164	0.002	0.003	0.127

Table C.2 Water quality parameters

Sample ID	Chl-a	TOC	DOC	UV_{254}	SUVA	FI
	µg/L	mg_C/L	mg_C/L	cm^{-1}	mg/L-m	--
AC-01-01-01	21.8	5.8	4.9	0.059	1.20	1.62
AN-01-01-01	2.3	4.7	4.3	0.070	1.64	1.54
AV-06-01-01	1.6	3.2	3.1	0.042	1.35	1.46
BD-06-01-01	4.2	4.0	3.2	0.062	1.93	1.45
BE-01-01-01	9.4	5.2	4.6	0.116	2.51	1.49
BM-01-01-01	0.3	2.8	2.6	0.059	2.31	1.48
BR-01-01-01	31.6	8.3	7.9	0.107	1.36	1.64
CC-01-01-01	16.8	6.9	5.9	0.093	1.58	1.55
CH-01-01-01	2.6	3.8	3.4	0.067	1.94	1.47
CR-01-01-01	3.0	4.0	3.8	0.068	1.78	1.43
DL-01-01-01	2.3	2.1	2.0	0.045	2.28	1.49
EG-06-01-01	2.2	3.6	3.2	0.107	3.36	1.40
EM-01-01-01	2.8	3.7	3.4	0.051	1.49	1.52
FC-06-01-01	3.7	4.4	4.0	0.101	2.52	1.39
FG-01-01-01	25.5	10.1	8.1	0.162	2.00	1.54
GB-01-01-01	1.6	4.7	4.0	0.100	2.52	1.41
GJ-06-01-01	1.9	2.8	2.9	0.053	1.85	1.44
GL-05-01-01	1.8	6.7	6.1	0.131	2.15	1.43
GR-01-01-01	3.2	3.7	3.6	0.106	2.99	1.35
GS-06-01-01	15.0	7.8	7.1	0.173	2.43	1.43
HE-01-01-01	31.8	7.4	5.5	0.071	1.29	1.62
JB-01-01-01	30.5	7.0	6.6	0.101	1.54	1.63
JK-01-01-01	48.3	8.2	7.7	0.087	1.13	1.69
JM-01-01-01	25.2	5.4	4.3	0.083	1.94	1.57
LF-05-01-01	NA	4.0	3.6	0.052	1.42	NA
LT-01-01-01	0.9	4.2	4.3	0.083	1.93	1.46
NS-01-01-01	16.3	6.4	5.6	0.082	1.48	1.63
PB-06-01-01	5.7	3.2	2.6	0.060	2.28	1.47
PW-01-01-01	9.9	7.7	6.7	0.099	1.47	1.63
RC-01-01-01	16.3	10.1	8.0	0.203	2.53	1.49
RW-01-01-01	1.1	2.4	2.1	0.040	1.95	1.47
SB-01-01-01	8.6	6.6	5.9	0.173	2.94	1.40
SC-01-01-01	5.1	6.1	6.0	0.160	2.67	1.49
SK-01-01-01	NA	2.3	2.2	0.055	2.56	1.48
SZ-01-01-01	2.0	6.3	5.7	0.093	1.63	1.52
TE-01-01-01	0.7	2.0	1.8	0.048	2.70	1.44
TQ-01-01-01	1.0	3.9	3.3	0.110	3.30	1.36
WM-06-01-01	1.9	2.5	2.0	0.033	1.61	1.51

Table C.3 TTHM and HAA5 Speciation

Sample ID	Chloroform	DCBM	CDBM	Bromoform	MCAA	DCAA	TCAA	MBAA	DBAA	TTHM	HAA5
					µg/L						
AC-01-01-01	49.9	42.5	37.7	10.5	0.8	19.2	6.2	<DL	<DL	140.7	26.3
AN-01-01-01	120.3	43.4	12.2	<DL	2.3	29.6	17.9	1.3	4.3	175.9	55.4
AV-06-01-01	57.5	15.0	2.6	<DL	0.9	19.1	11.3	<DL	<DL	75.1	31.2
BD-06-01-01	100.6	16.3	0.4	<DL	1.2	21.5	14.9	0.4	2.4	117.3	40.4
BE-01-01-01	144.0	33.0	4.1	<DL	4.2	55.8	50.2	<DL	<DL	181.1	110.2
BM-01-01-01	98.3	6.7	<DL	<DL	6.3	34.6	32.8	<DL	<DL	105.0	73.7
BR-01-01-01	130.2	79.3	39.6	5.6	2.6	45.7	25.1	0.2	<DL	254.7	73.6
CC-01-01-01	68.2	59.9	53.7	10.7	1.4	29.1	14.8	<DL	21.2	192.4	66.5
CH-01-01-01	88.5	23.0	4.6	<DL	1.8	29.7	15.2	<DL	<DL	116.1	46.7
CR-01-01-01	118.0	6.7	<DL	<DL	7.9	42.9	43.6	<DL	<DL	124.7	94.5
DL-01-01-01	72.9	7.4	<DL	<DL	<DL	22.5	10.7	<DL	<DL	80.2	33.3
EG-06-01-01	141.3	13.1	<DL	<DL	2.3	38.2	39.0	0.3	2.1	154.4	82.0
EM-01-01-01	74.6	21.2	3.3	<DL	5.0	20.0	12.6	0.7	2.9	99.2	41.2
FC-06-01-01	165.0	9.4	3.0	<DL	2.4	38.1	36.0	0.3	2.1	177.4	78.8
FG-01-01-01	267.8	71.8	12.7	<DL	15.6	109.7	114.7	<DL	1.7	352.3	241.6
GB-01-01-01	166.4	6.1	<DL	<DL	9.6	62.1	78.3	<DL	<DL	172.5	149.9
GJ-06-01-01	78.8	6.1	<DL	<DL	6.4	30.9	24.8	<DL	<DL	84.9	62.0
GL-05-01-01	210.4	19.1	<DL	<DL	12.7	70.8	64.4	<DL	<DL	229.5	147.9
GR-01-01-01	161.0	4.6	2.2	<DL	7.9	61.9	73.5	<DL	<DL	167.8	143.2
GS-06-01-01	255.5	31.7	<DL	<DL	4.0	55.3	50.9	0.5	2.3	287.2	113.0
HE-01-01-01	68.5	42.0	28.1	5.0	8.2	24.4	10.6	<DL	<DL	143.5	43.2
JB-01-01-01	38.7	77.2	123.2	80.4	1.4	20.3	7.2	4.1	40.1	319.6	73.2
JK-01-01-01	58.7	80.9	105.4	51.7	7.2	28.1	9.1	3.2	46.3	296.8	93.8
JM-01-01-01	67.5	50.8	39.5	9.9	0.6	29.2	18.9	<DL	<DL	167.7	48.7

LF-05-01-01	91.2	10.7	<DL	<DL	6.2	29.0	24.0	<DL	<DL	101.8	59.2
LT-01-01-01	145.6	10.2	<DL	<DL	8.2	48.5	50.5	<DL	<DL	155.8	107.1
NS-01-01-01	48.6	73.2	100.5	46.4	1.6	19.4	8.6	4.4	25.4	268.7	59.5
PB-06-01-01	83.1	15.4	0.4	<DL	1.7	23.6	14.9	0.4	2.4	98.9	43.1
PW-01-01-01	51.3	78.0	104.4	52.6	7.0	25.0	8.7	4.5	32.9	286.3	78.1
RC-01-01-01	195.4	28.0	<DL	<DL	3.4	45.6	46.9	0.7	2.4	223.4	99.0
RW-01-01-01	75.5	6.6	<DL	<DL	1.7	23.6	16.4	<DL	<DL	82.1	41.7
SB-01-01-01	241.7	14.0	4.5	<DL	5.9	55.9	57.3	0.6	2.2	260.2	121.8
SC-01-01-01	238.2	21.4	<DL	<DL	10.7	79.9	45.5	<DL	<DL	259.6	136.2
SK-01-01-01	66.0	6.2	<DL	<DL	6.1	28.9	22.3	<DL	<DL	72.2	57.3
SZ-01-01-01	136.4	39.4	8.7	<DL	9.3	47.7	34.2	<DL	<DL	184.5	91.2
TE-01-01-01	92.2	3.0	0.3	<DL	4.7	23.1	14.0	0.1	2.0	95.5	43.9
TQ-01-01-01	177.2	4.7	3.0	<DL	5.3	66.3	79.8	<DL	<DL	184.9	151.4
WM-06-01-01	42.7	15.9	3.9	<DL	<DL	11.1	6.9	0.4	3.0	62.6	21.4

Table C.4 DBP yields

Sample ID	TTHM Yield	HAA5 Yield	TTHM Molar Yield	HAA5 Molar Yield
	µg/mg$_C$	µg/mg$_C$	µmol/mg$_C$	µmol/mg$_C$
AC-01-01-01	28.9	5.4	0.18	0.04
AN-01-01-01	41.0	12.9	0.31	0.08
AV-06-01-01	24.5	10.2	0.19	0.07
BD-06-01-01	36.7	12.6	0.30	0.08
BE-01-01-01	39.3	23.9	0.31	0.16
BM-01-01-01	41.2	28.9	0.34	0.20
BR-01-01-01	32.3	9.3	0.23	0.06
CC-01-01-01	32.7	11.3	0.21	0.07
CH-01-01-01	33.8	13.6	0.26	0.09
CR-01-01-01	32.6	24.7	0.27	0.17
DL-01-01-01	40.7	16.9	0.33	0.11
EG-06-01-01	48.7	25.9	0.34	0.20
EM-01-01-01	29.3	12.2	0.23	0.09
FC-06-01-01	44.4	19.7	0.36	0.13
FG-01-01-01	43.7	29.9	0.34	0.21
GB-01-01-01	43.3	37.7	0.36	0.26
GJ-06-01-01	29.7	21.7	0.24	0.15
GL-05-01-01	37.6	24.2	0.31	0.17
GR-01-01-01	47.3	40.3	0.39	0.28
GS-06-01-01	40.3	15.8	0.33	0.11
HE-01-01-01	26.0	7.8	0.18	0.06
JB-01-01-01	48.7	11.2	0.26	0.06
JK-01-01-01	38.3	12.1	0.22	0.07
JM-01-01-01	39.1	11.4	0.26	0.07
LF-05-01-01	28.0	16.3	0.23	0.11
LT-01-01-01	36.1	24.8	0.30	0.17
NS-01-01-01	48.4	10.7	0.27	0.07
PB-06-01-01	37.7	16.5	0.30	0.11
PW-01-01-01	42.9	11.7	0.24	0.07
RC-01-01-01	27.9	12.4	0.23	0.08
RW-01-01-01	40.0	20.3	0.33	0.14
SB-01-01-01	44.3	20.7	0.36	0.15
SC-01-01-01	43.4	22.8	0.36	0.16
SK-01-01-01	33.6	26.7	0.27	0.19
SZ-01-01-01	32.3	16.0	0.25	0.11
TE-01-01-01	53.7	24.7	0.44	0.18
TQ-01-01-01	55.5	45.5	0.46	0.31
WM-06-01-01	30.8	10.5	0.23	0.07