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ORIGINS AND SEASONAL VARIATION OF DISINFECTION BYPRODUCT PRECURSORS

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University of Massachusetts Amherst

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**ORIGINS AND SEASONAL VARIATION OF DISINFECTION BYPRODUCT
PRECURSORS**

A Dissertation Presented

by

RAN ZHAO

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

February 2018

Department of Civil and Environmental Engineering

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**ORIGINS AND SEASONAL VARIATION OF DISINFECTION BYPRODUCT
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RAN ZHAO

Approved as to style and content by:

David A. Reckhow, Chair

John E. Tobiason, Member

Paul K. Barten, Member

Richard N. Palmer, Department Head
Civil and Environmental Engineering Department

DEDICATION

**To my Mom, Li Zhu, and to my Dad, Jian Zhao
and with love, to my husband, Yuefeng Wang**

ACKNOWLEDGMENTS

First, I would like to thank my PhD advisor, Prof. David Reckhow, for his valuable guidance and advice as well as being a great role model for me. His persistent dedication to my educational and professional development has been invaluable. I could not finish my PhD without Dr. Reckhow's help. Second, I would like to thank Prof. John Tobiasson and Prof. Paul Barten for serving on my committee and for their valuable feedback. Third, I would like to extend further gratitude to my friends at UMass Amherst, especially our lab manager, Sherrie Webb-Yagodzinski, with whom I was very happy and fortunate to share the PhD journey. I would also like to thank the entire faculty in the Civil and Environmental Engineering Department for their help.

The PhD study is a long journey and one of a kind experience, and the amount of knowledge and experience I gained is above and beyond what I could have imagined when first joining the program. In these five years, I have learnt that "if it isn't lonely, it isn't research", however, I am really grateful to everyone who helped and supported me during this great journey.

Finally, I would like to thank my parents and my husband for their endless love and encouragement. They always give me great support whenever I face any difficulty or problem. I cannot make it without them.

ABSTRACT

ORIGINS AND SEASONAL VARIATION OF DISINFECTION BYPRODUCT PRECURSORS

FEBRUARY 2018

RAN ZHAO, B.S., SHANDONG UNIVERSITY

M.S., SOUTHERN ILLINOIS UNIVERSITY EDWARDSVILLE

Ph.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor David A. Reckhow

Disinfection byproducts (DBPs) are formed from the disinfectant (e.g., chlorine) reacting with components of natural organic matter (NOM) in water drawn from surface water supplies, and are considered as the cause of potential serious human health problems. DBP precursors originate in large reservoirs from at least three types of sources: (1) watershed or allochthonous, (2) algal or autochthonous, and (3) bottom sediments or benthic. The properties of the NOM and the DBP precursor content of that NOM are unique to each source. Knowledge about the relative importance of these three sources would be valuable for addressing the reasons for the natural variability in DBP precursor occurrence and in managing source waters for the purpose of minimizing DBP precursors.

The first objective of this dissertation was to use temporal and spatial water quality data from a drinking water reservoir to shed light on autochthonous and benthic sources of NOM and DBP precursors. Cannonsville Reservoir (NY) was chosen for this work due to its well documented water quality. To achieve this goal, we developed a series of 2-dimensional contour plots that bring clarity to benthic and near surface (algal)

processes on water quality. Combining conventional water quality parameters with DBP precursor analysis facilitates a more comprehensive understanding of limnological factors that define DBP precursor levels. These data were compared with properties of NOM and related natural biochemical parameters. From this analysis, we conclude that algal-dominated NOM contributes disproportionately to DHAN formation, whereas watershed-dominated NOM is especially rich in THAA and THM precursors as well as UV absorbing substances. The sediment-dominated precursor behaved like a mix of the other two, but generally resembled the watershed NOM most.

The second objective of this dissertation was to identify the seasonal variation and spatial fate of DBP precursors in a drinking water system located in a temperate environment where seasonal variations of surface water quality and water temperature are considerable. The formation potential of trihalomethanes (THM), dihaloacetic acids (DHAA), and trihaloacetic acids (THAA), as well as their hydrophobicity, were examined with water samples collected monthly for a 12-month period in eight reservoirs. The hydrophobic NOM is positively correlated with air temperature of the watershed area whereas the hydrophilic NOM shows a reverse trend. Seasonal climate change (i.e., snowmelt and leaf-off) and microbial decomposition play an important role in variation of NOM fractions, as well as the DBP formation potentials. Generally, the THAA precursors are more hydrophobic and recalcitrant than THM precursors. However, the aged hydrophilic fraction also contributes substantively to the formation of THMs. NOM in spring contains more DHAA precursors, especially the hydrophilic fractions, which is probably linked to the algae growth in the reservoir epilimnion.

Organic matter released from plants is quite likely the most important fraction as potential DBP precursors, especially in heavily forested catchments. However, very few studies have been conducted on plant leachate as DBP precursors. The third objective of this dissertation was to characterize the organic matter that is released by plants, and examine their potentials to form DBPs under light, dark, and dark-with-biocide conditions. Eight-day leaching experiments were conducted for maple and oak leaf litter and pine needle litter. Samples were periodically removed for analysis of DOC, UV absorbance, and DBP precursor content. Significant concentrations of dissolved organic carbon (DOC) were leached from maple, oak, and pine samples. SUVA levels varied considerably among light and dark conditions, suggesting that photolysis has an effect on the breakdown of aromatic content. High levels of specific DBP formation potentials were found in leaf leachate. On average, the biodegraded organic matter formed one to two times higher specific DBP FP levels than the samples with biocide. Maple leaves had the highest yield of DOC and DBP, whereas pine needles had the lowest yield.

The final objective of this dissertation was to determine the comparative significance of DBP (i.e., trihalomethanes, dihaloacetic acids, and trihaloacetic acids) precursors released from profundal sediments of a water supply impoundment under aerobic, hypoxic, and anaerobic conditions. Profundal sediments were collected from Cannonsville Reservoir and incubated under different percentage of dissolved oxygen (DO) saturation (0%, 10%, 20%, and 97%), then chlorinated in the laboratory. The results showed that sediments released increasing DBP precursors in decreasing DO conditions. From the XAD fractionation we concluded that the hydrophobic fraction in anaerobic degradation generally contained more DBP precursors than aerobic degradation. Finally,

the contribution of sediment released NOM to DBP formation was compared with algal cells and leaf leachate. Chloroform and trichloroacetic acid precursors were more prevalent in the plant leachate followed by the sediment and then the algal sources. The sediment-dominated precursor behaved like a mix of the other two.

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CHAPTER 1

INTRODUCTION

Disinfection byproducts (DBPs) are formed from the disinfectant (e.g., chlorine) reacting with components of natural organic matter (NOM) in water drawn from surface water supplies, and are considered as the sources of serious human health problems. The concentration and properties of NOM in reservoirs are affected by both external sources (allochthonous) and internal algae growth (autochthonous). Resolution of the relative contributions of allochthonous and autochthonous DBP precursors in water supply reservoirs is valuable for guiding management decisions to improve or maintain water quality (Stepczuk et al., 1998b; Bukaveckas et al., 2007). Internal production of precursors is the result of autochthonous formation of dissolved and particulate NOM, coupled directly or indirectly with primary production (Stepczuk et al., 1998b; Plummer and Edzwald, 2001; Nguyen et al., 2005; Chen et al., 2008; Hong et al., 2008; Huang et al., 2009; Fang et al., 2010; Lui et al., 2011). As an internal organic matter source in reservoir, algae have long been recognized as DBP precursors (Trehy et al., 1986; Plummer and Edzwald, 1998; Nguyen et al., 2005; Hong, et al., 2008). Allochthonous DBP precursors in reservoirs are derived mostly from terrestrial vegetation from the drainage basin, and are commonly brought to the water supply system through tributaries during runoff events (Stepczuk et al., 1998a; Pomes et al., 1999; Kraus et al., 2010; Beggs and Summers, 2011; Hua et al., 2014; Wang et al., 2015). External organic matter consists of identifiable materials (e.g., polysaccharides and proteins, simple sugars and small acids) and non-identifiable materials, such as humic substances from soil. Humic substances as DBP precursors have been studied for decades (Singer, 1999; Chang et al.,

2001; Liang and Singer, 2003; Nikolaou et al., 2004; Hua and Reckhow, 2007).

However, these naturally-occurring organic substances are a major source of allochthonous natural organic matter (NOM) in surface waters, which are more complex and diverse than autochthonous NOM, and have yet to be fully understood.

NOM is a complex mixture of heterogeneous organic compounds which includes hundreds or thousands of distinct chemical species (Croue, et al., 2000a). It is valuable to isolate NOM into a limited set of categories (fractions) by their homogeneous composition and properties (e.g., hydrophobicity), then characterize the fraction of NOM. Understanding the hydrophobicity of precursors provides knowledge of DBP formation as a function of precursor hydrophobicity, which may help drinking water utilities optimize treatment systems to remove those fractions associated with high DBP yields. The identification, characterization, and quantification of distinct sources of DBP precursors have been documented by several studies (e.g., Stepczuk et al., 1998; Effler et al., 1998; Palmstrom et al., 1988; Martin et al., 1993), however, investigation of origins of DBP precursors and their seasonal behavior has received only limited research attention. It is helpful to identify the seasonal pattern of precursor origins in water supply impoundments and their effect on precursor behavior. Moreover, the seasonal variation of precursor hydrophobicity has rarely been studied, and is informative for the development of predictive models. The goal of this work is to characterize the organic matter that is released by leaf and pine litters as DBP precursors, and also investigate the effect of light exposure and biodegradation on this process.

Substances leached from plants are quite likely the most important fraction as potential DBP precursors, especially in heavily forested catchments, and include a great

diversity of materials (Tukey, 1970). Cellulose and lignin materials from plant structural constituents make up the largest source of allochthonous humic compounds (Wetzel, 2001). The complex compounds undergo a series of decomposition stages. High concentrations of humic substances can be found in upper soil horizons because of the breakdown of surface plant material (Thurman, 1985; Wetzel, 2001). Much has been learned about the sources, transport, and degradation of plant material in the aquatic environment. However, very few studies have been conducted on the fate and transport of DBP precursors originated from these allochthonous sources.

Sediments could also potentially act as a historical sink for humic precursors (Bloesch, 1995; Effler et al., 1998). Dissolved organic carbon released from sediments has been considered as the potential sources of DBP precursors for a long time (Uhler and Means, 1985; Martin et al., 1993). It is possible that release of sediment precursor could be influenced by dissolved oxygen (DO) conditions (Martin, et al., 1993). However, prior research does not provide insight to the characterization of sediment precursors, nor does it compare the properties of sediment precursor (more recalcitrant) with fresh watershed precursors (more labile). It is valuable to quantify and qualify DBP precursors released from sediments under various degradation conditions (e.g., different DO), and to compare the sediment precursors with precursors released from leaf leachate.

CHAPTER 2

SEASONAL VARIATION OF DISINFECTION BYPRODUCTS PRECURSORS IN A LARGE WATER SUPPLY

2.1 Introduction

Disinfection byproducts (DBP) are formed from the reaction of a disinfectant (e.g., chlorine) with components of natural organic matter (NOM) in water. Many of the DBPs are of concern to human health, and as a result, the USEPA has established regulations on two representative groups, the trihalomethanes (THMs) and haloacetic acids (HAAs). Organic matter in reservoirs originates from different aquatic and terrestrial sources. Therefore, NOM in different water bodies has distinct composition and properties, and it produces different concentrations and types of DBPs during chlorination. Identifying the origins of DBP precursors is fundamental to the development of an effective watershed management strategy and reliable mechanistic mathematical models for DBP formation (Effler and Bader, 1995; Chapra, 1997; Hamilton and Schladow, 1997). It is also important for understanding impacts of seasons and climate change on DBPs, since factors such as snow-melt, leaf-off and temperature driven microbial metabolism can be key determinants in NOM export (Thurman, 1985).

Allochthonous DBP precursors are mostly derived from terrestrial vegetation and their microbial degradation products, and their transport to reservoirs primarily occurs during runoff events (Stepczuk et al., 1998a; Wetzel, 2001; Findlay and Sinsabaugh, 2003). Internal production of DBP precursors in reservoirs is the result of autochthonous formation of dissolved and particulate organic matter, coupled directly or indirectly with primary production (Stepczuk et al., 1998b). Previous investigations of organic matter cycling in the water column have highlighted the redistribution of organic matter between

solid and solution phases through sediment resuspension and the organic matter released as a consequence of resuspension-induced desorption (Uhler and Means, 1985; Martin et al., 1993; Bloesch, 1995; Effler et al., 1998; Cantwell et al., 2002; Komada et al., 2002; Eggleton and Thomas, 2004; Yang et al., 2008; Hong et al., 2013). Dissolved organic carbon (DOC) released from sediments can also be considered as an important source of DBP precursors (Uhler and Means, 1985; Martin et al., 1993; Effler et al., 1998; Effler and Matthews, 2004; Hong et al., 2013). The laboratory characterization and quantification of DBP precursors from different origins has been documented by several studies (e.g., Palmstrom et al., 1988; Martin et al., 1993; Hong et al., 2008), however, the field investigation of the origins of DBP precursors and their seasonal behavior have received only limited attention by researchers.

Correlations between the concentration of autochthonous organic matter and indicators of primary productivity (e.g., chlorophyll-*a*) have been widely documented (Walker, 1983; Wetzel 2001). Phosphorus, as the least abundant but most critical nutritional component of most phytoplankton, has been reported to be strongly associated with algal growth in lake photic zones (Vollenweider, 1968; Carlson, 1977; Smith, 1979; Parks and Baker, 1997; Carpenter et al., 1998; Correll, 1998; Wetzel, 2001). Furthermore, the concentration of total organic carbon (TOC) was found to be positively correlated with total phosphorous (TP) in 38 U.S. lakes and reservoirs (Walker, 1983). As the principal internal source of organic matter in surface water, algae have long been recognized as potential DBP precursors. The high content of amino acids and proteins in algal extracellular and intracellular organic matter is likely responsible for high yields of THMs and dichloroacetonitriles (DHANs) in chlorinated eutrophic waters (Trehy et al.,

1986; Plummer and Edzwald 1998; Nguyen et al., 2005). Moreover, algal derived proteins were found to contain more haloacetic acid (HAA) precursors than lipids and carbohydrates. Others have reported that algae cells are richer in dichloroacetic acid (DCAA) precursors on a per-carbon basis compared with humic and fulvic acids (Hong, et al., 2008). However, specific yields of THMs and trihaloacetic acids (TCAA) from humic acids and fulvic acids were higher than those from algal cells (Hong, et al., 2008).

Dissolved organic matter in surface water consists of identifiable materials (i.e., polysaccharides and proteins, simple sugars and small acids) and non-identifiable materials, such as humic substances from soil. The dissolved humic and fulvic acids have clearly recognizable lignin components which are the major constituents in terrestrial vascular plants (Wetzel, 2001). It has been shown that lignin phenols produce more TCAA than chloroform and DCAA as compared to bulk humic substances (Hua et al., 2014).

Another potential reservoir of DBP precursors is particulate organic matter. The partitioning of organic matter between aqueous phase (pore water, overlying water) and solid phase (sediment, suspended particulate matter and biota) is highly affected by hydrodynamics, biogeochemical process, and environmental conditions (redox, pH, salinity, and temperature; Samiullah, 1990; Saulnier and Mucci, 2000; Cantwell et al., 2002). DOC in pore water is released to the water column during sediment resuspension, and additional organic carbon can be released through re-equilibration from the mineral-bound fraction in the resuspended sediment (Komada and Reimers, 2001). Sediment resuspension is a normal process that occurs with dimictic lakes during spring and fall circulation (Wetzel, 2001). Two basic zones of resuspension in lakes have been identified:

a shallow zone that can be directly influenced by wave action, and a deeper area that is associated primarily with internal seiches (Bloesch et al., 1995). Substantial drawdown was another reason for substantial sediment resuspension in reservoirs (Effler et al., 1998). It has been shown that sediments can be the source of significant THM precursors, and littoral sediments (<1 m depth) produce more THMs than profundal sediments (>10 m, Martin et al., 1993). However, to our knowledge, no studies have been conducted that directly compare the relative flux of precursors originating from watershed sources, sediments, and algal biomass at a single study site. Knowledge about the relative importance of these three sources would be valuable for addressing the reasons for the natural variability in DBP precursor occurrence and in managing source waters for the purpose of minimizing DBP precursors.

The purpose of this study is to use temporal and spatial water quality data from a drinking water reservoir to shed light on autochthonous and benthic sources of NOM and DBP precursors. Cannonsville Reservoir was chosen for this work due to its well documented water quality. To achieve this goal, we developed a series of 2-dimensional contour plots that bring clarity to benthic and near surface (algal) processes on water quality. Combining conventional water quality parameters with DBP precursor analysis facilitates a more comprehensive understanding of limnological factors that define DBP precursor levels.

2.2 Materials and Methods

2.2.1 Site Description

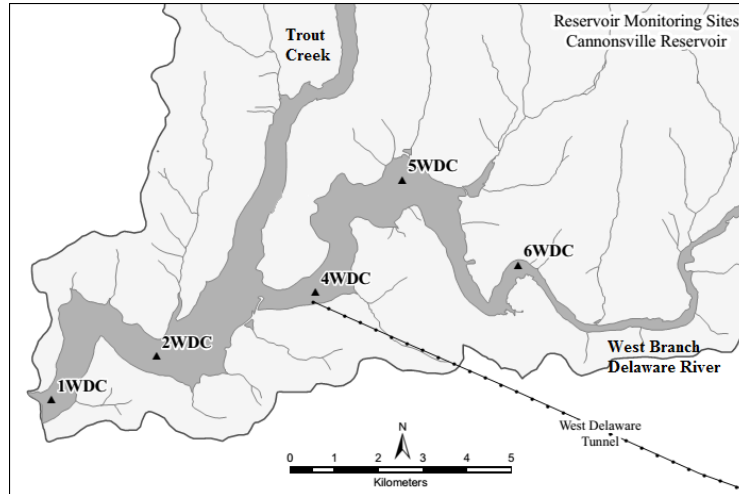


Figure 2.1: Reservoir Monitoring Sites of Cannonsville Reservoir, showing six sampling locations (from NYCDEP, 2009 Watershed Water Quality Monitoring Plan).

Cannonsville Reservoir is a Y-shaped reservoir located in Delaware County, New York. The dam of Cannonsville Reservoir (Latitude 42 02' 46'', Longitude 75 22' 24'') is 5 km downstream from the confluence of the West Branch Delaware River (WBDR) and Trout Creek (Figure 2.1), and the beds of these two streams form the two arms of the reservoir. The reservoir is the third largest in the New York City water supply system. The crest capacity is $373 \times 10^6 \text{ m}^3$, and the surface area is $19.3 \times 10^6 \text{ m}^2$. The maximum depth is about 49 m near the dam (Wood, 1979). Water leaves the reservoir by the following pathways: 1) over the dam spillway when the water level exceeds the crest elevation; 2) through drinking water withdraws (at depth of 10, 20 and 37 m below the spillway elevation); 3) into the downstream portion of the WBDR. The reservoir's watershed, located in the northwestern Catskill section of the Appalachian plateau, drains a 1178 km^2 area. It spans surface elevations from 350 m above sea level at the dam to a

maximum of 1010 m above sea level, with an average slope of 20% (Stepczuk et al., 1998a). The underlying bedrock is made up of consolidated sandstone, siltstone and shales, covered by gravel, sand, unconsolidated fill and clay (Effler and Bader, 1998). WBDR is the principal tributary of Cannonsville Reservoir that contributes about 79% of the inflow to the reservoir and drains a 928 km² watershed. Trout Creek contributes 5% of the inflow and drains a 58 km² watershed, and the remainder consists of smaller tributaries and direct inflow (Owens et al., 1998b). There are seven wastewater treatment plants sited in the Cannonsville watershed region, discharging 1.2×10⁶ m³ per day (Lloyd and Principle, 2006). Vegetative cover is approximately 93.9% of the watershed area (85.2% forestland, 5.5% brush land, and 3.2% grass land; Lloyd and Principle, 2006). Wetlands comprise 1.6% of the watershed. Agriculture use is most prevalent along the watershed's tributaries. Nutrient loading from agricultural runoff and WWTPs was identified as the main source of nutrients feeding algal blooms in the early 1990s, and Cannonsville Reservoir was in relatively poor condition compared with other reservoirs in the NYC water supply system. The NY Department of Environmental Protection (DEP) then initiated several management actions to reduce the amount of nutrient-rich runoff, including WWTP upgrades, septic system remediation and replacement, and watershed agricultural programs (Strickland and Rush, 2011).

2.2.2 Limnological Monitoring Program

NYCDEP conducts a monthly limnology monitoring program from mid-April to December on its Catskill-Delaware system reservoirs including field measurements (dissolved oxygen, pH and temperature) and chemical/biological laboratory analyses (dissolved organic carbon, phosphorous, and nitrogen). Six monitoring sites on the main

arm of the Cannonsville Reservoir are monitored (Figure 2.1) among which Site 4 (4WDC) is at mid-channel across from the intake chamber. Limnology samples are collected at three or four depths, extending from 3m under the surface to 2m above the sediments. WBDR daily inflow data are collected by United States Geologic Survey (USGS, 15km upstream of Walton, NY).

2.2.3 Laboratory Analyses for DBP precursors

Water samples were collected monthly from Site 4 in 2007 and 2013, and were kept in cold room (4 °C) until needed. All samples were treated at bench-scale in the UMass EWRE laboratory. Total and dissolved organic carbon were measured by the high-temperature combustion method based on Standard Methods 5310 (APHA, AWWA and WEF, 1998) using a Shimadzu TOC-VCPH Total Organic Carbon Analyzer (Shimadzu Scientific Instruments, Columbia, Md.). Samples for DOC analysis were filtered through 0.45 micron Whatman GF/F glass fiber filters. UV-visible absorbance spectra were measured on all filtered samples using an Agilent 8453 spectrophotometer. Specific UV absorbance (SUVA) is calculated as the UV absorbance at 254 nm per meter normalized to 1 mg/L DOC.

All water samples were chlorinated in 300mL chlorine demand-free, glass-stoppered bottles and buffered at pH 7 with 0.5mM sodium phosphate. The chlorine doses were determined based on a target chlorine residual of 4 ± 1 mg Cl₂/L after 7 days. A stock solution of sodium hypochlorite (Fisher Scientific, Fairlawn, NJ) was standardized daily by the DPD ferrous titrimetric method according to Standard Methods 4500-Cl F (APHA, AWWA, and WEF, 1998). Samples were stored headspace-free at 20 °C in the dark for 168 h (7days). Then, all samples were quenched with ammonium chloride or

sodium sulfite and partitioned for subsequent analysis of DBPs. Four THMs (CHCl_3 , CHBrCl_2 , CHBr_2Cl , and CHBr_3), three dihaloacetonitriles (dichloro-, bromochloro-, and dibromoacetonitriles), two haloketones (dichloro- and trichloropropanone), and chloropicrin were quantified by liquid-liquid extraction followed by gas chromatography with electron capture detection (GC/ECD). This method was closely aligned with USEPA method 551.1. THM standards were prepared from a halogenated volatiles mix stock solution (Supelco Inc., Bellefonte, PA.). Pentane was used as the extracting solvent, and 1,2-dibromopropane was used as an internal standard. Nine HAAs (monochloro-, nonobromo-, dichloro-, bromochloro-, dibromo-, bromodichloro-, dibromochloro-, trichloro-, and tribromoacetic acid) were analyzed by liquid-liquid extraction in accordance with USEPA Method 552.2. HAA standards were prepared in methyl-tert-butyl-ether (MTBE) from a halogenated acetic acids mix (Supelco Inc., Bellefonte, PA.). MTBE was used as the extracting solvent, and 1,2-dibromopropane was the internal standard. Extracted samples were measured using an Agilent 6890 gas chromatograph equipped with a linearized ^{63}Ni electron capture detector and a J&W DB-5 column for THMs (J&W DB-1 column for HAAs). The carrier gas was ultra-high purity nitrogen.

2.3 Results and Discussion

2.3.1 Temporal and Spatial Patterns of Limnological Features, 2007

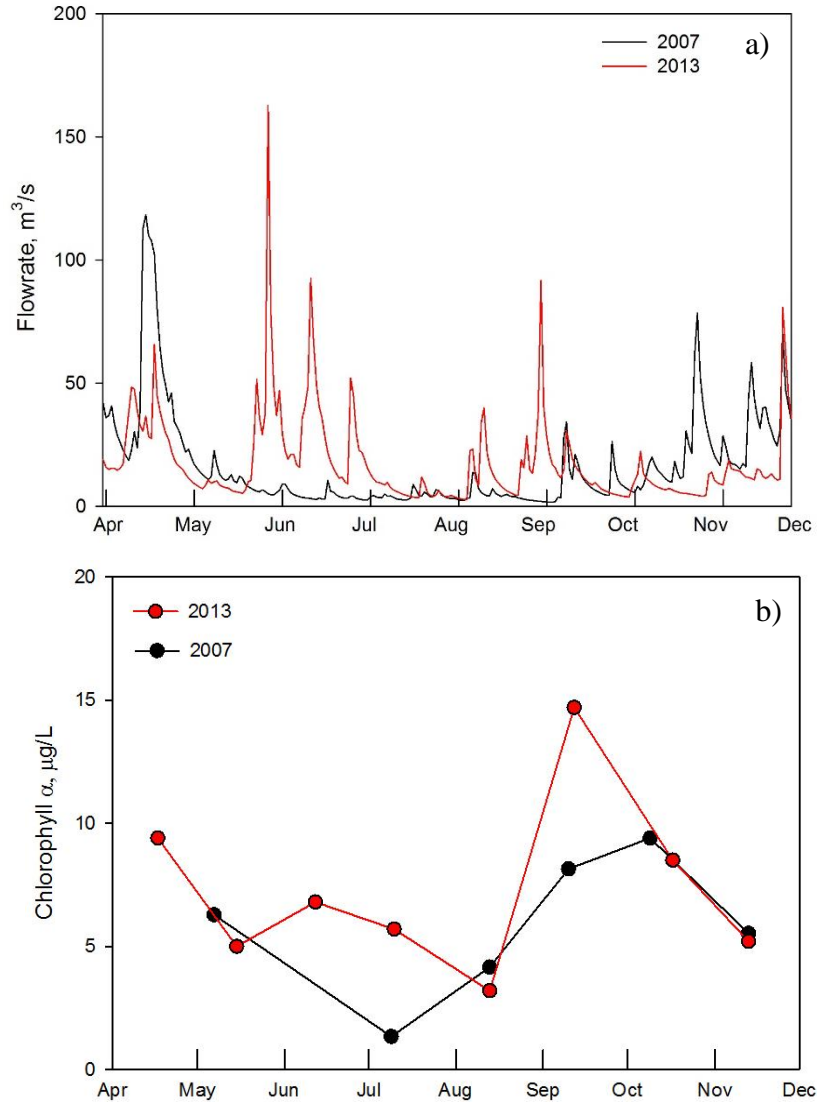
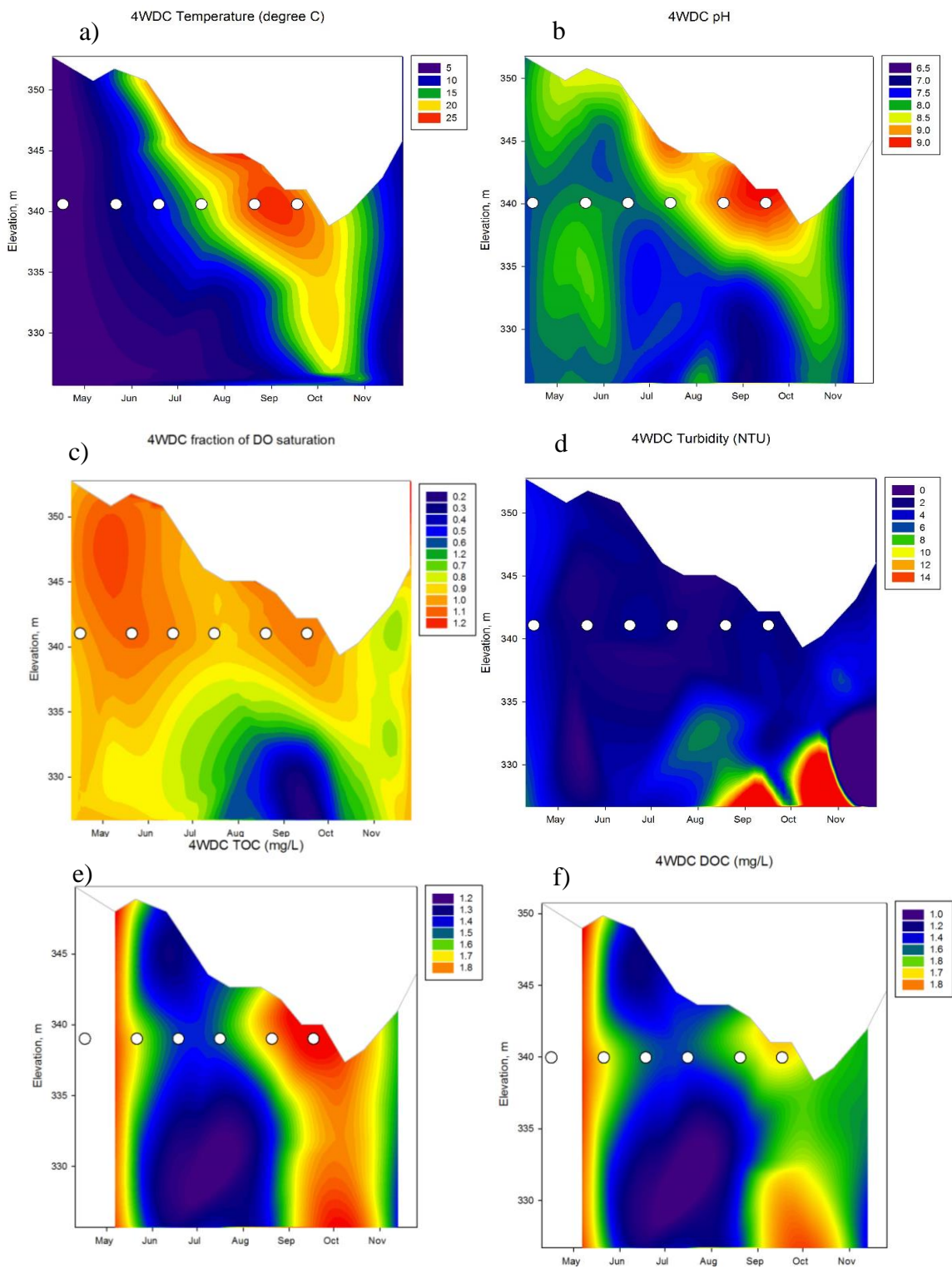


Figure 2.2: Time Series for Cannonsville Reservoir for 2007 and 2013: a) flowrate (measured 15 km upstream of WBDR at Walton, NY); b) Chlorophyll α , measured at site 4, at a depth of 3 m



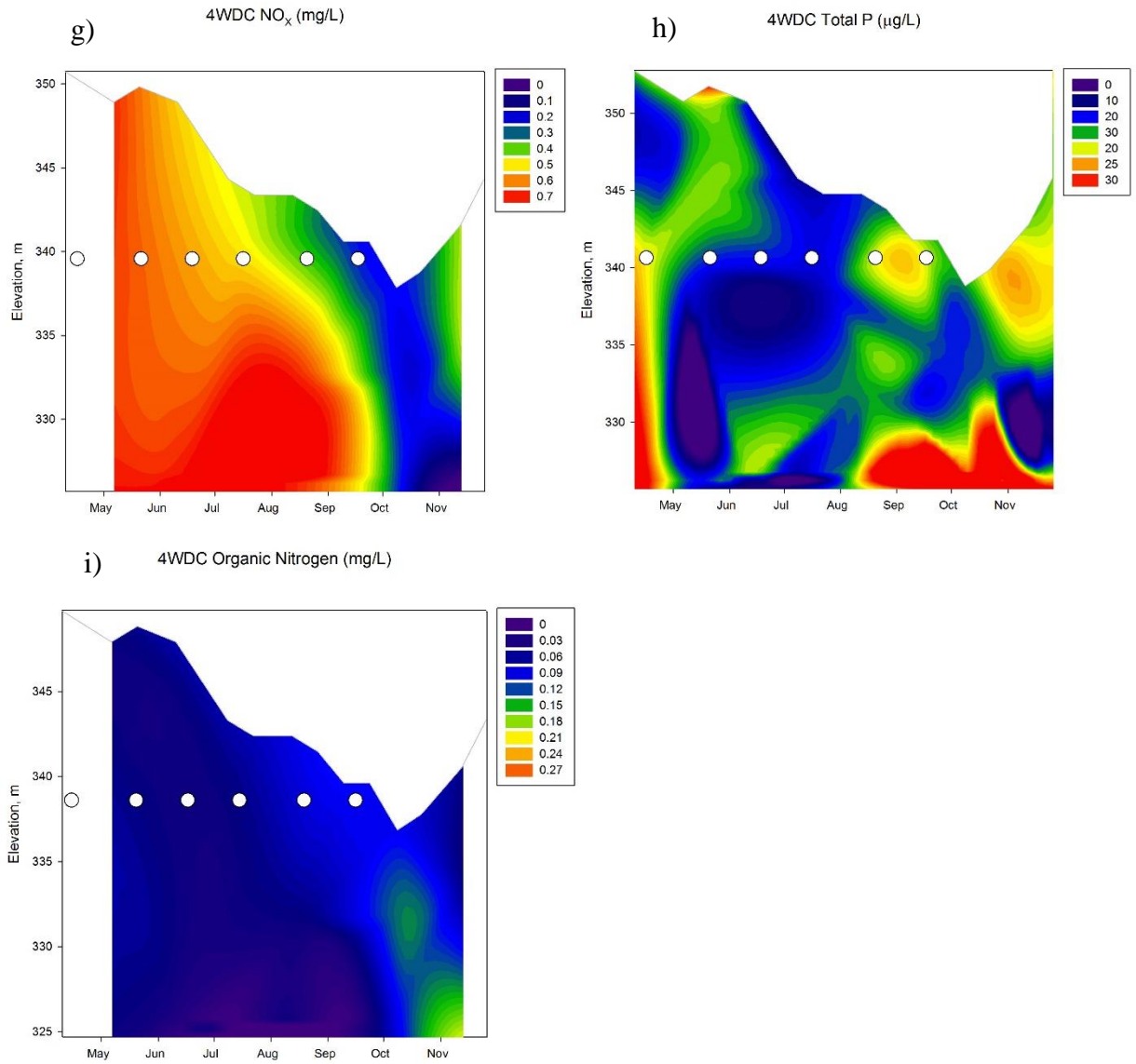


Figure 2.3: Depth and time distribution of limnological data in Cannonsville Reservoir Site 4, 2007 (white dots indicate the sampling sites of DBP analysis): a) Temperature; b) pH; c) % saturation of DO; d) Turbidity; e) TOC; f) DOC; g) NO_x; h) TP; i) Organic nitrogen.

The period from May to September in 2007 is characterized by a lack of substantial runoff events (Figure 2.2a). Significant reservoir drawdown occurred in 2007 as a result of the low inflow. Site 4 of Cannonsville Reservoir, approximately 1km upstream from the confluence of the WBDR and Trout Creek, is adjacent to the intake chamber, where water is transferred into Rondout Reservoir through the West Delaware Tunnel. The water surface elevation (WSE) of Site 4 decreased 14m from nearly full (361m above the sea level) in mid-April to its lowest point in mid-October during the major drawdown. Thermal stratification (Figure 2.3a) lasted from June to October. Surface water warmed rapidly through mid-June with a maximum vertical gradient (15 °C) in early September. The epilimnion was generally 7m in depth during the summer of 2007, with the highest temperature (24 °C) in mid-August. The hypolimnion, which lies below the thermocline, warmed at a lower rate reaching a maximum temperature of 17.6 °C in early October. Warming of the hypolimnion was enhanced in 2007 due to reservoir drawdown. Inflow of WBDR from Site 6 was even warmer during summer stratification, introducing allochthonous NOM into the epilimnion of Site 4. In spring and fall, temperature gradients were lost as the reservoir was completely mixed.

The 2007 data show evidence of primary productivity and autochthonous generation of precursors in the epilimnion. First, near-surface supersaturation of dissolved oxygen (DO) was observed in warm weather (spring, summer, and early fall), a common observation attributable to autotrophic photosynthesis (i.e., algae growth; Figure 2.3c). Several high TP concentrations (Figure 2.3h) were also observed in the epilimnion which reflect the growth of phytoplankton. These were associated with corresponding high Chlorophyll *a* concentrations (Figure 2.2b) in September and November. In contrast

the relatively low concentration of TP in July probably indicated phosphorus limitation of primary production, and this is supported by low chlorophyll α (Chl α) concentrations measured at that same site (July, Figure 2.2b). Note that the relative concentrations of phosphorus to inorganic nitrogen (NO_x) are well below the Redfield Ratio (Wetzel, 2001) for all seasons and depths (Figure 2.3g), supporting the notion that this reservoir is phosphorus limited. Another indicator of primary productivity is the summer-fall increase in epilimnetic pH (Figure 2.3b). This is also a well-known phenomenon resulting from photosynthetic consumption of carbon dioxide (Wetzel, 2001). The key outcome is a modest increase in epilimnetic TOC for the August to October period (Figure 2.3f). It's interesting that no increase in DOC or turbidity are evident for the same space and location. We interpret this as an indication of low levels of algal growth that are a bit too subtle for the rather non-specific and insensitive organic carbon and turbidity parameters, but still could be significant regarding DBP precursor production. The 2007 data also show signs of benthic processes that can inform DBP precursor studies. Turbidity profiles (Figure 2.3d) showed a clear increase near the bottom in late summer and during fall turnover when the WSE was lowest. The measurement of turbidity has been used as a surrogate for re-suspension of bottom sediment in many studies (Gippel, 1989; Bloesch, 1995; Suk et al., 1998; Effler and Matthews, 2004; Cozar et al., 2005; Chung et al., 2009). Hypoxia ($\text{DO} < 30\%$ of saturation) was noted and it lasted for nearly two months in the hypolimnion during summer stratification when the WSE was lowest in 2007. Along with the increase in turbidity are an apparent release of phosphorus (Figure 2.3h), a drop in oxygen concentration (Figure 2.3c) and subtle increases in both TOC (Figure 2.3e) and DOC (Figure 2.3f). This all suggests release of reduced substance from the pore water

and suspended sediments (Hupfer and Lewandowski, 2008; Wetzel, 2001) along with some solubilization of organic matter.

In summary, without allochthonous input of organic carbon (i.e., essentially no runoff events), seasonal increases in epilimnetic organic carbon could be attributed to primary productivity. Similarly, seasonal increases in hypolimnetic organic carbon seem associated with release from sediments.

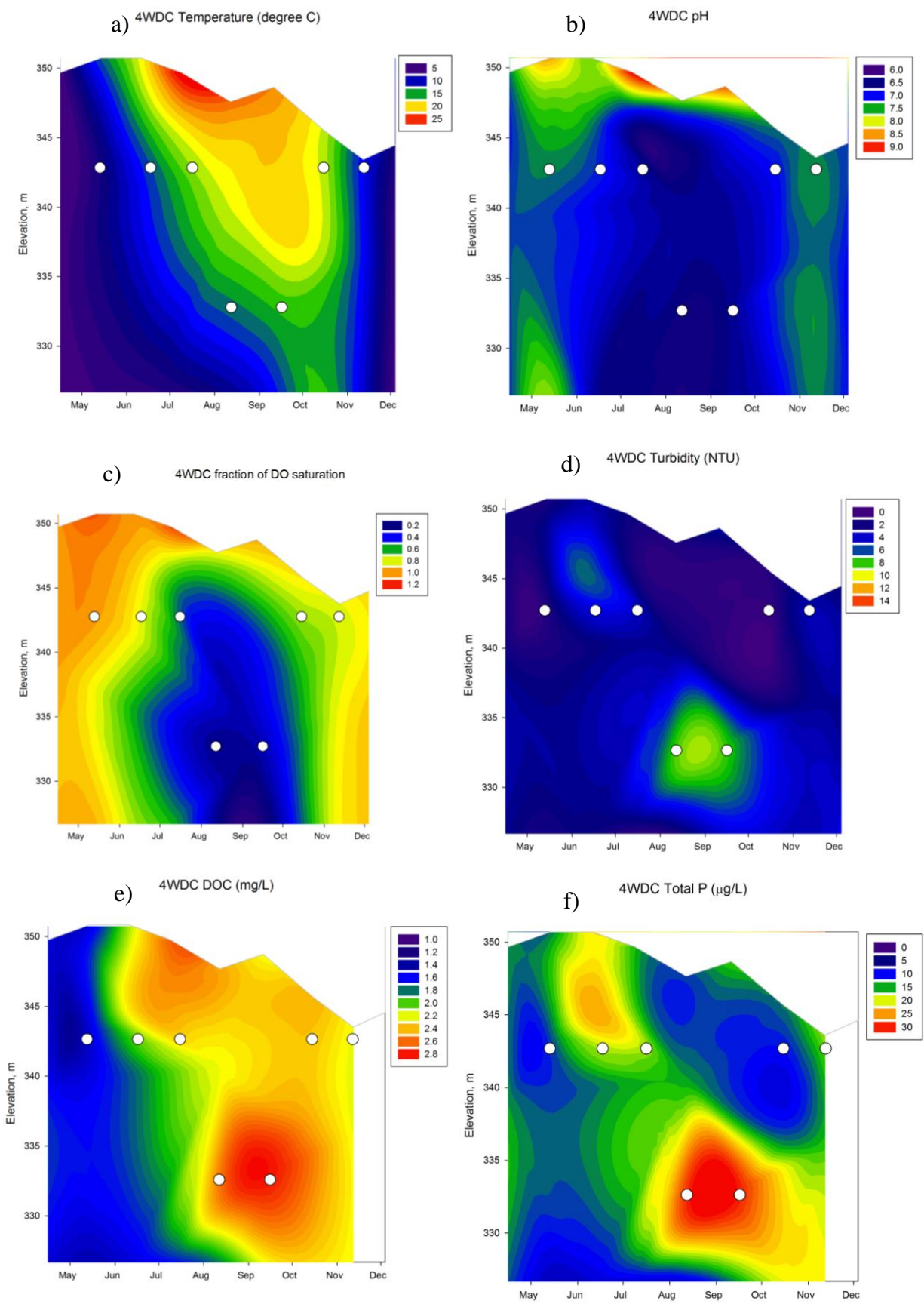
2.3.2 Temporal and Spatial Patterns of Limnological Features, 2013

The year 2013 was substantially different from 2007, as there were six major rain events (Figure 2.2a) between April and November (i.e., in April, June, mid-August to early September, and late November) and far less drawdown. The largest runoff event in 2013 was in early June ($150 \text{ m}^3/\text{s}$). The average water level of site 4 in 2013 was approximately 4 meters higher than in 2007. The WSE at Site 4 was nearly its maximum (359m) in spring and decreased progressively to 352m in early November.

Despite the substantial difference in runoff and storage, some of the same points noted for 2007 are observable again in 2013. First, the evidence for algal activity and autochthonous organic carbon production is clear. Increases in pH, and DO are noted at the surface (Figures 2.4b and 2.4c), especially shortly after major increases in flow (compare with Figure 2.2a). A similar increase in organic nitrogen (Figure 2.4h) is seen which probably occurs at the expense of inorganic nitrogen. Chlorophyll α levels reach a maximum in September (Figure 2.2b). Accompanying these changes are large increases in epilimnetic DOC (Figure 2.4e). However, considering the higher runoff in 2013, it's quite likely that most of the increase in DOC is due to allochthonous organic matter. It

also appears that some of that additional DOC may have contributed to loss of DO in the lower regions of the epilimnion.

Release of benthic DOC and reduced substances is also evident in 2013. Not only is there a strong hypolimnetic hypoxia (Figure 2.3c), but there is also substantial release of phosphorus and organic nitrogen (Figures 2.4f and 2.4h). Accordingly, the DOC increases in the hypolimnion, even beyond the level in the epilimnion (Figure 2.4e).



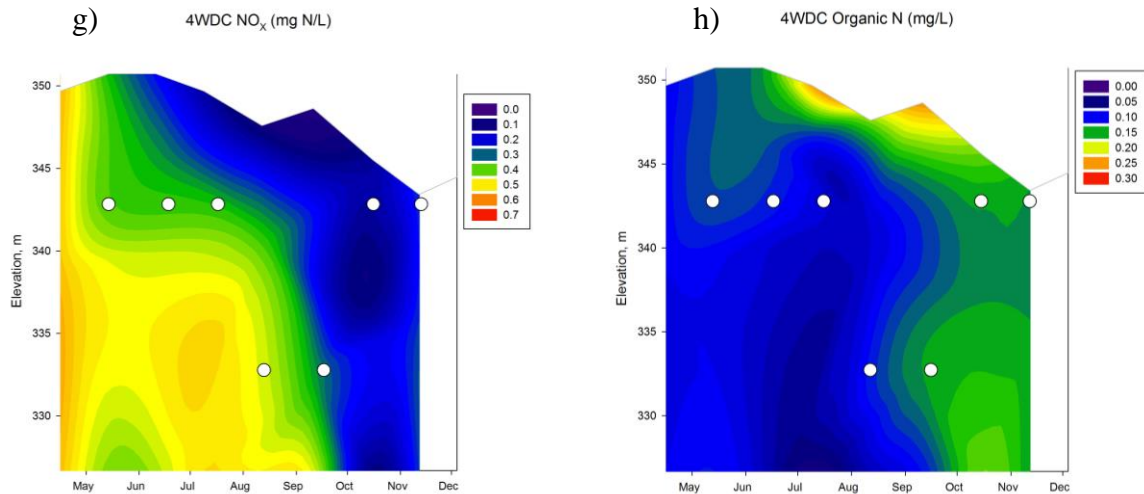


Figure 2.4: Depth-time distribution of limnological indicators in Cannonsville of Site 4, 2013 (white dots indicate the sampling sites of DBP analysis): a) Temperature; b) pH; c) % saturation of DO; d) Turbidity; e) DOC; f) TP; g) NO_x; i) Organic nitrogen.

2.3.3 Spatial Pattern of NOM and Limnology Parameters

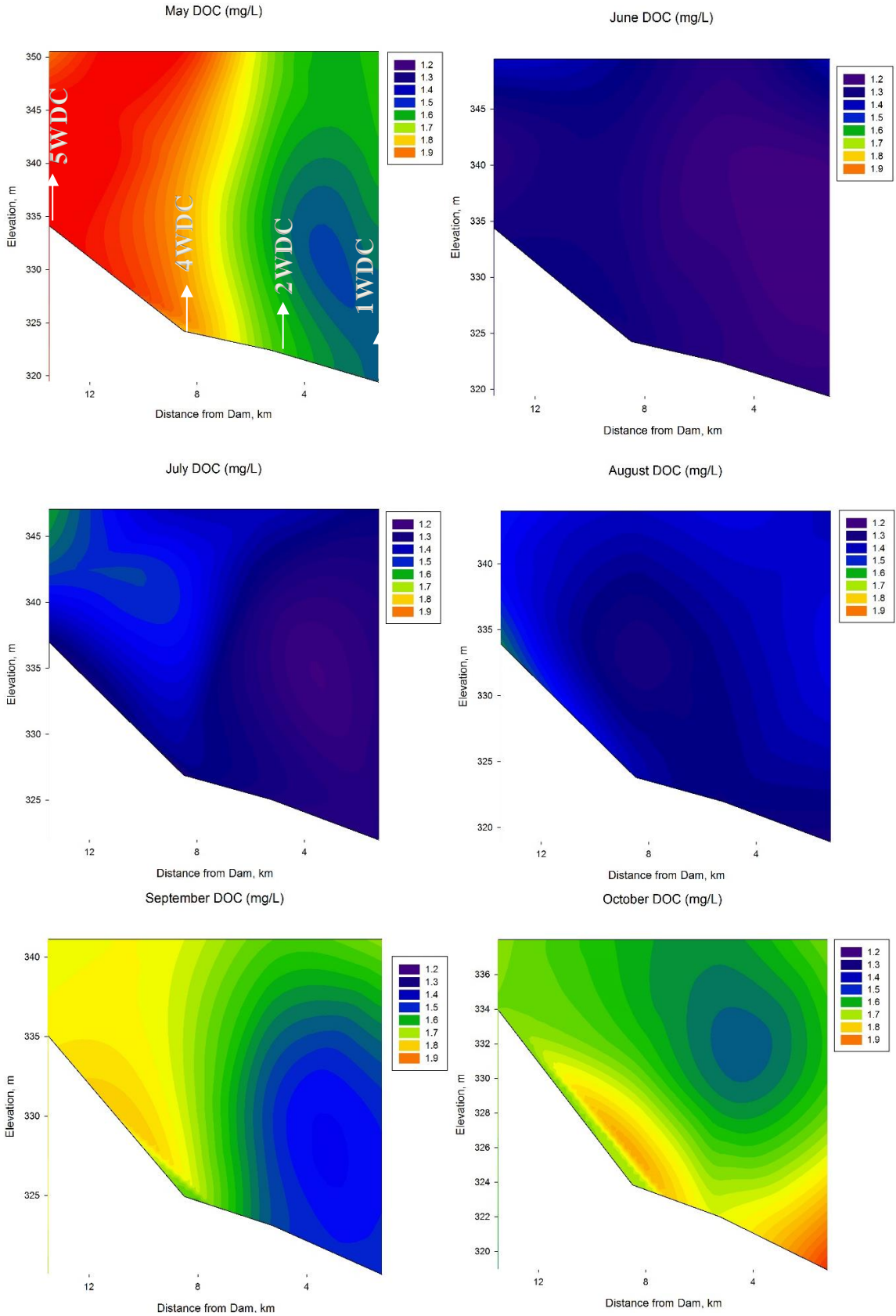
Longitudinal and vertical profiles of monthly DOC and turbidity in 2007 are presented in Figure 2.5 and Figure 2.6, respectively. Runoff in late April resulted in an increase in DOC concentration at all depths in the upstream transition zone. In the lacustrine zone, the longitudinal gradient of DOC along the main axis progressively changed into vertical gradients during the period of summer stratification. Signs of stratification became evident near the dam as early as May, and in the region of 4WDC during the September period. DOC was too low and poorly resolved in June-August to see obvious differences across the vertical temperature gradients. As previously noted this was an exceptionally dry period. Thus, the longitudinal turbidity profiles show very low levels, and only start to increase in the transition zone in August. This hypolimnetic increase in turbidity is quit pronounced in September and diminishes again in October. This may be due to some advective transport of suspended matter in the riverine zone

(e.g., Thornton et al., 1990), perhaps supplemented by some sediment release, both of which could be exacerbated by the extreme drawdown.

In 2013, there was not the large April inflow that had been observed in 2007. Instead, the largest flows came in late May. As a result, heavy allochthonous contributions of DOC were not seen until June and later (Figure 2.7). 2013 year shows similar elevated levels of turbidity and DOC in the hypolimnion in late summer and early fall as in 2007. However, the absolute magnitude of the turbidities is lower than it was during the heavy drawdown in 2007 (i.e., 10 NTU, vs 30 NTU). In contrast, the late summer hypolimnetic DOC in 2013 was higher than in 2007, as it was probably from a combination of allochthonous and benthic organic carbon.

Table 2.1 Dominant source of DBP precursors in Site 4 of Cannonsville Reservoir for each survey in 2007 and 2013

Date	Dominant NOM source
May, 2007	Watershed
June, 2007	Algae
July, 2007	Algae
June, 2013	Watershed
July, 2013	Watershed
August, 2013	Sediment
September, 2013	Sediment
October, 2013	Watershed



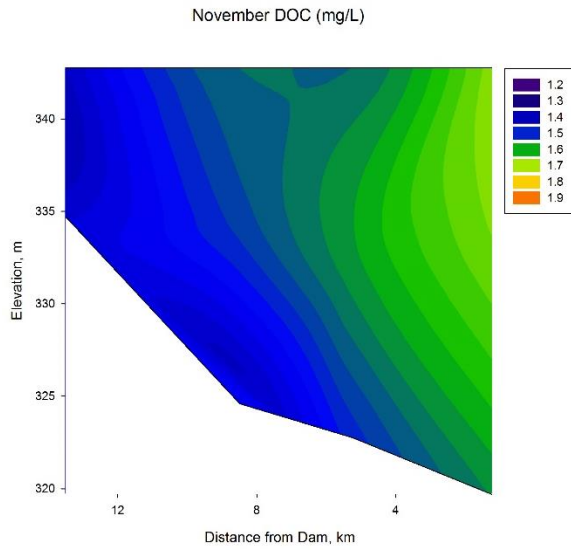
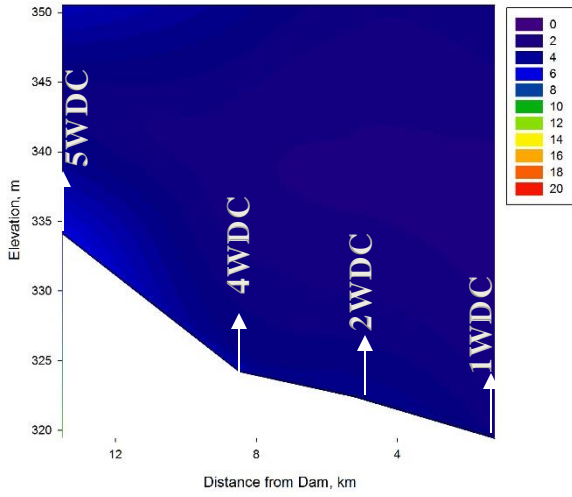
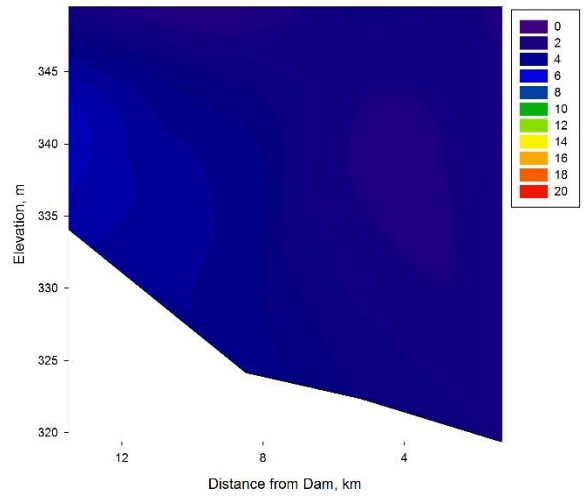


Figure 2.5: Longitudinal and vertical profiles of monthly DOC, 2007

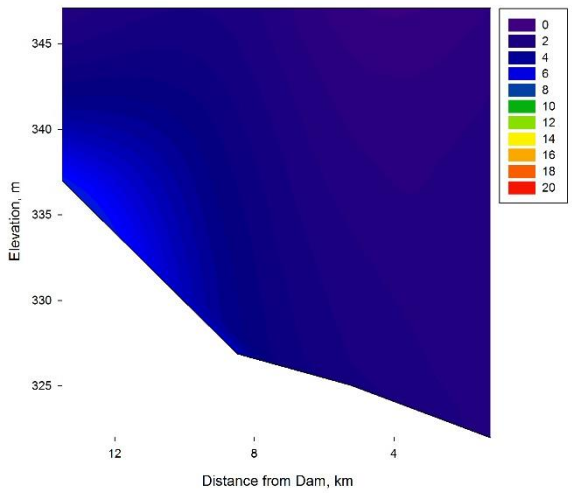
May Turbidity (NTU)



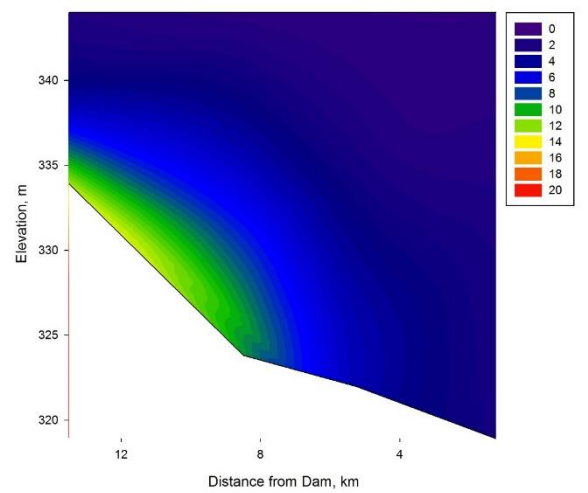
June Turbidity (NTU)



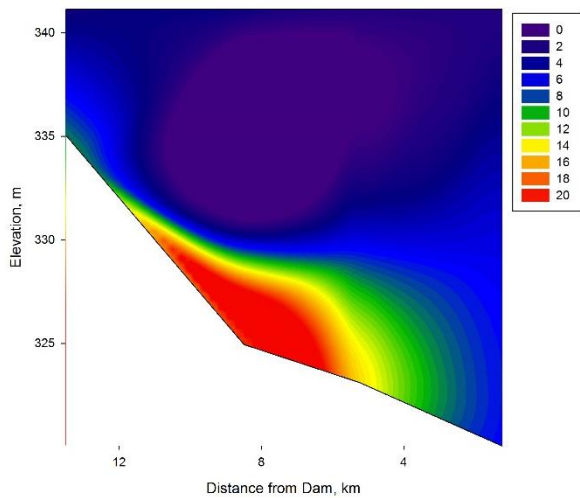
July Turbidity (NTU)



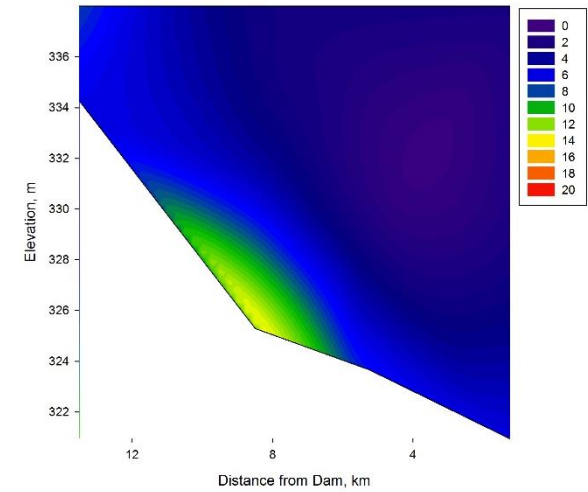
August Turbidity (NTU)



September Turbidity (NTU)



October Turbidity (NTU)



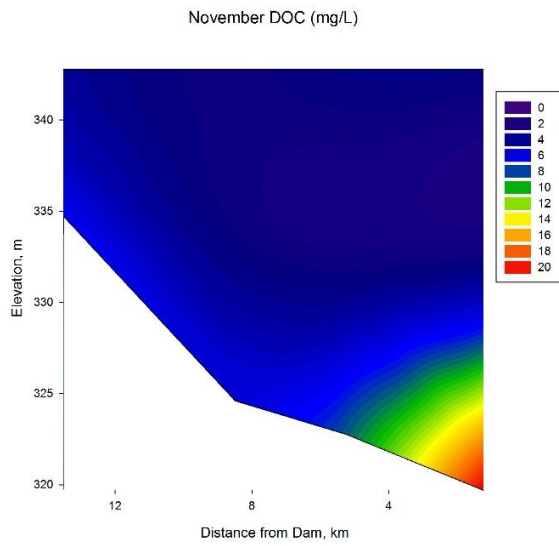
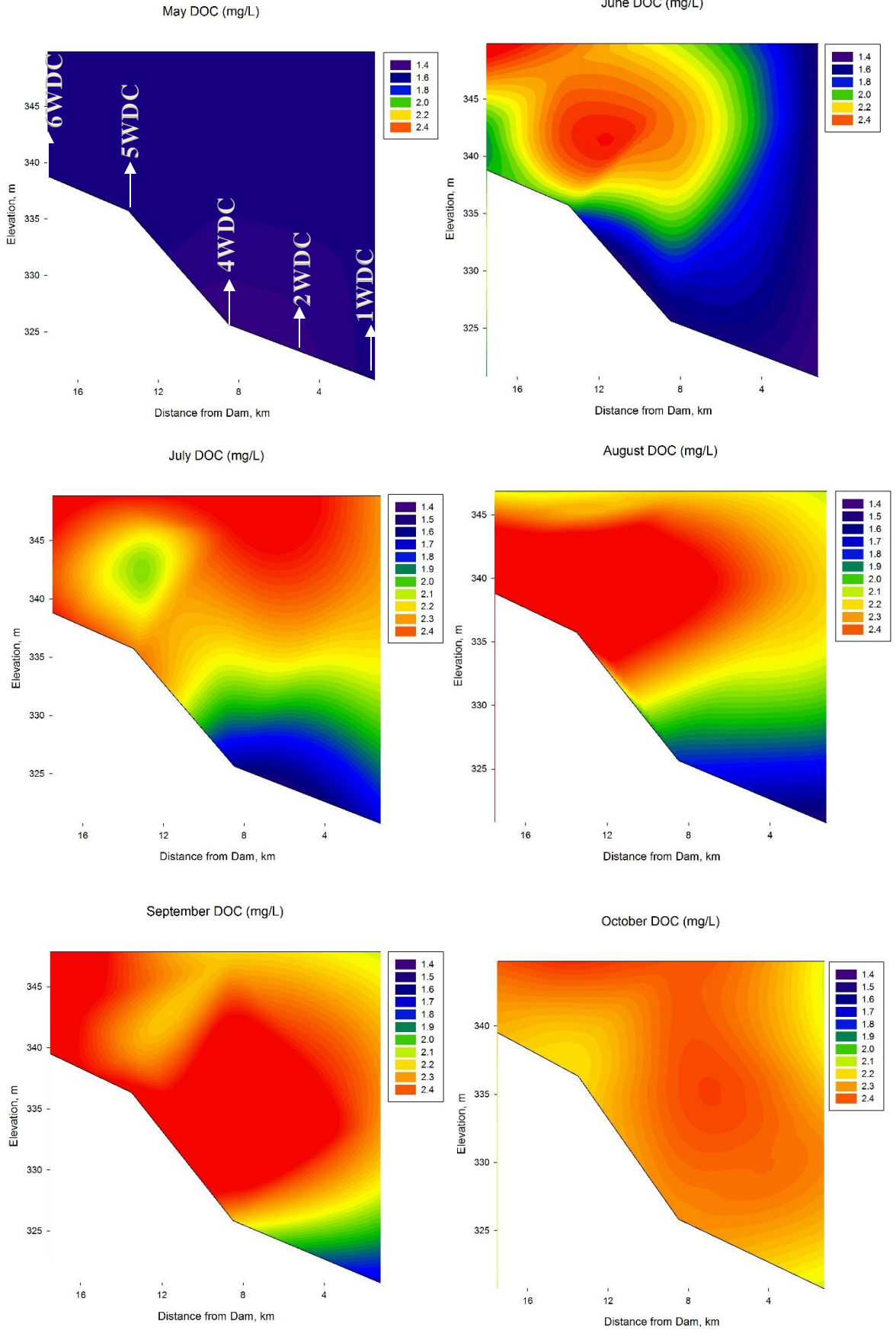


Figure 2.6: Longitudinal and vertical profiles of monthly turbidity, 2007



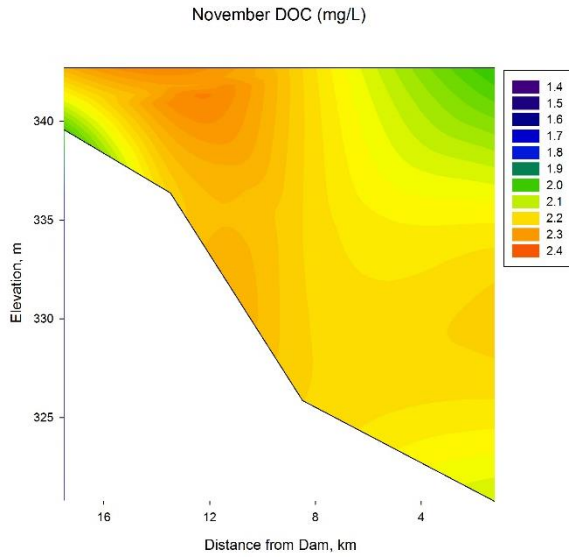
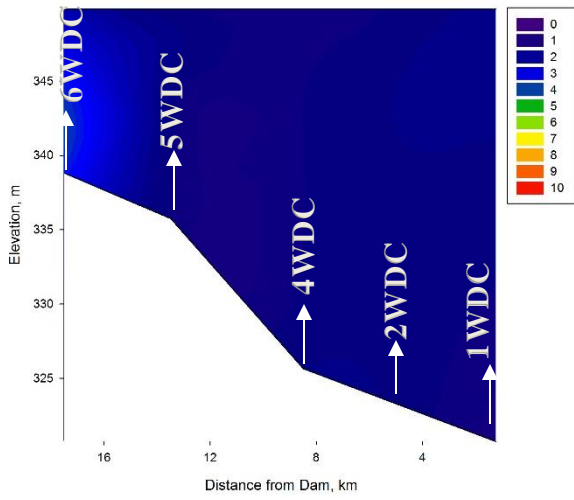
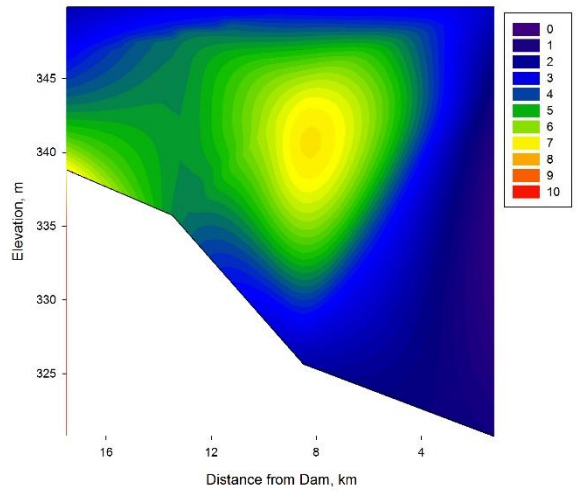


Figure 2.7: Longitudinal and vertical profiles of monthly DOC, 2013

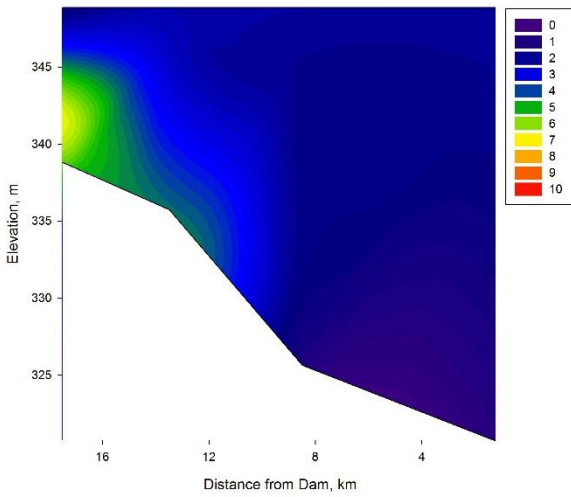
May Turbidity (NTU)



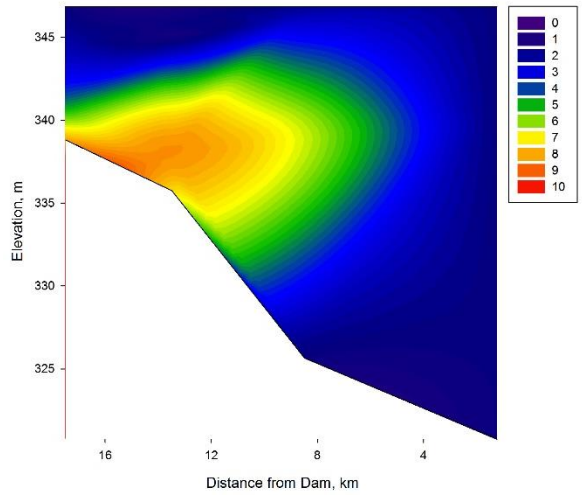
June Turbidity (NTU)



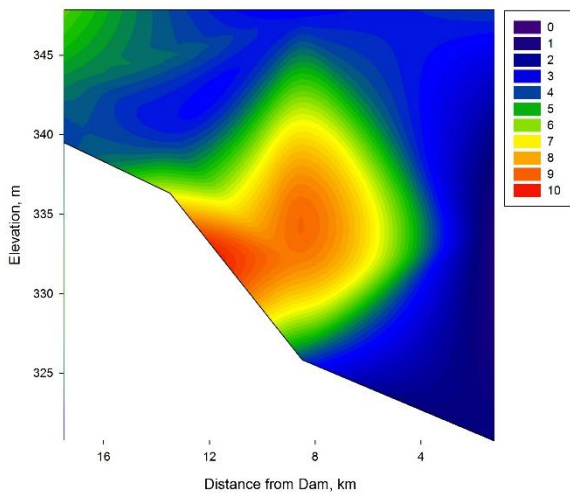
July Turbidity (NTU)



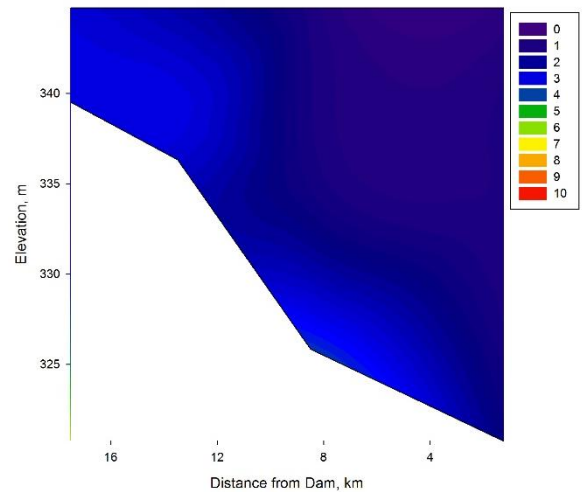
August Turbidity (NTU)



September Turbidity (NTU)



October Turbidity (mg/L)



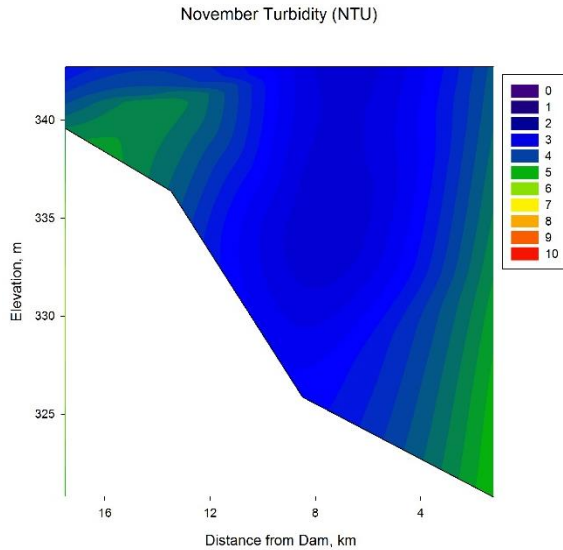


Figure 2.8: Longitudinal and vertical profiles of monthly turbidity, 2013

2.3.4 Analysis of DBP Precursors from Different Origins

Water samples were collected monthly from withdraw locations at two depths (indicated in Figure 2.3 and Figure 2.4 with white dots). Each sample was also analyzed for organic carbon and related NOM parameters. As discussed above, we view NOM in Cannonsville Reservoir as originating from three types of sources: (1) watershed or allochthonous, (2) algal or autochthonous, and (3) lake sediments or benthic. In order to understand the flux and characteristics of NOM from each source, it would be necessary to formulate and validate full system models for NOM in the reservoir, or conduct laboratory studies of all of the relevant environmental processes and compartments. Both are far beyond the scope of this current study, and indeed, to our knowledge, neither has been done to date with any large water system. Instead we aspire to partially deconvolute the separate properties of NOM from these three origins by comparing our most distinct “end members”. These have been listed in Table 2.1, and they include 4 dominated by watershed sources, 2 by algal sources and 2 by sediment sources. The

NOM-based properties for each are grouped by dominant source and presented in Figures 2.9 and 2.10, below.

The concentrations of particulate organic carbon (POC) were relatively constant in 2013 (mean = 0.31 mg/L), with over 80% of the epilimnetic TOC present in the dissolved form (i.e., DOC) in Cannonsville Reservoir. In 2007, the reduced runoff led to lower concentrations of POC (mean = 0.1 mg/L). The median DOC in the sediment-dominated samples (1.69 mg/L) was the greatest (Figure 2.9a) followed by those dominated by watershed sources (1.55 mg/L) and algae sources (1.35 mg/L). Specific UV absorbance (SUVA) showed the same hierarchy (Figure 2.9b). The intensive parameter, SUVA, is considered an indicator of aromatic content in organic matter (e.g., Reckhow et al., 1990). Not surprisingly, watershed and sediment dominated DOC, exhibited higher SUVA values (2.54 and 2.59 L/mg·m, Figure 2.9b), whereas algae dominated NOM exhibited the lowest mean SUVA (1.9 L/mg·m). This supports the contention that algal biomass is rich in hydrophilic materials (Croue et al., 2000), especially proteins and carbohydrates. In contrast, allochthonous NOM contains residues from terrestrial plants that can have substantial lignin and tannin components. This also suggested that NOM in the sediments of Cannonsville Reservoir may be mostly derived from plant detritus rather than algal biomass, and sediments could potentially act as a historical sink for DBP precursors.

The box and whisker plots in Figure 2.10 are all based on DBP analysis of the Cannonsville Reservoir samples. In Figures 2.10a and 2.10c, the values are graphed in absolute concentration units. For the other two (Figure 2.10b and 2.10d), the data have

been normalized to a 1 mg-C/L concentration so that they are intensive parameters, unaffected by the DOC concentrations.

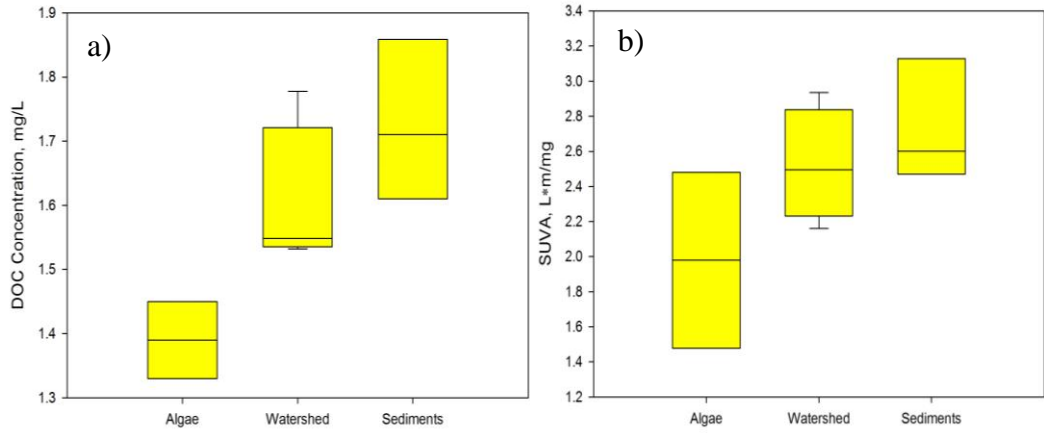


Figure 2.9: Boxplot of DOC and SUVA. a) DOC concentration; b) Specific UV254

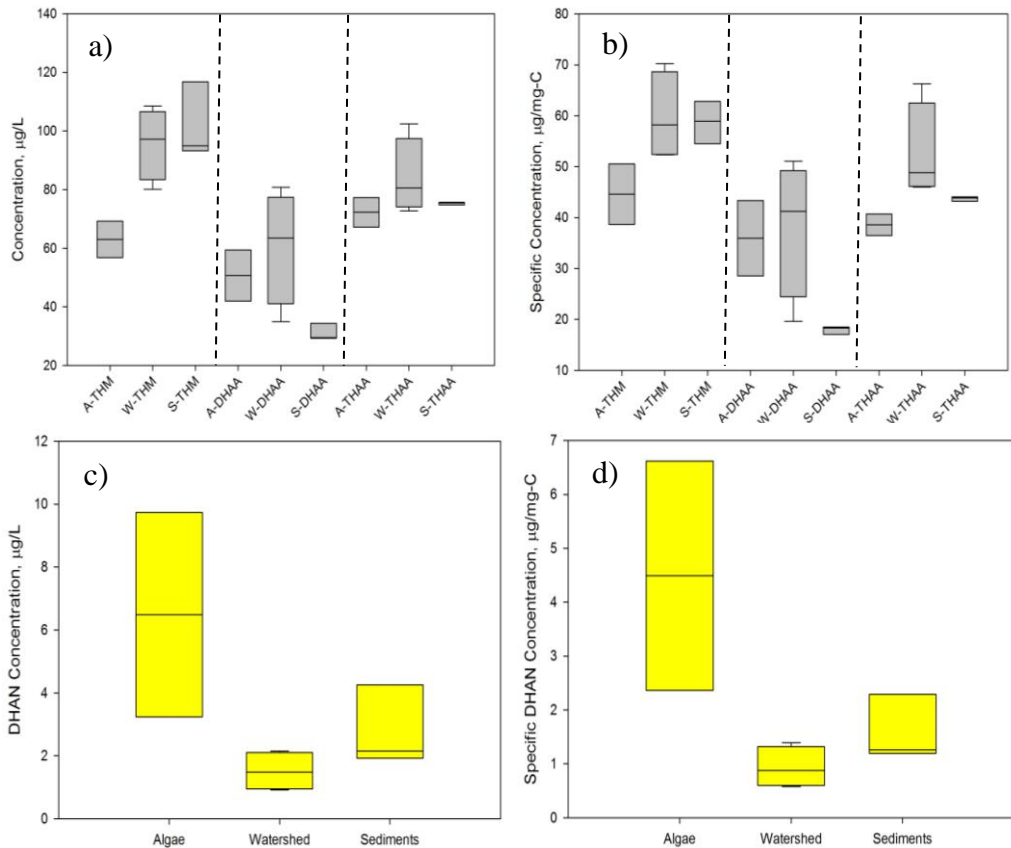


Figure 2.10: Boxplot of DBP and Specific DBP. a) DBP formation potential; b) specific DBP formation potential per carbon; c) DHAN formation potential; d) specific DHAN formation potential per carbon. A: algae; W: watershed; S: sediment

Chloroform (CHCl_3) was by far the most prevalent species of THM, at 92% and 94% of the total THMs in 2007 and 2013, respectively. The other groups are similarly dominated by the fully-chlorinated species. This is because concentrations of bromide are quite low in Cannonsville Reservoir and as a result, little bromine becomes incorporated into the DBPs.

Regardless of whether one considers the extensive or intensive measures, algal dominated waters produce less THM than those dominated by watershed or sediment sources (Figures 2.10a and 2.10b). Dihalooacetic acid (DHAA) precursors seem to be more prevalent in the algal and watershed sources than the sediment sources. Finally, the trihalooacetic acid (THAA) precursor are slightly more prevalent in the watershed sources followed by the sediment and then the algal sources. These relative hierarchies tend to match expectations based on DBP precursor analysis on some laboratory-derived end members. For example, purified lignin and lignin monomers have been shown to be especially rich in THAA precursor, but not in precursors for DCAA and THMs (e.g., Hua et al., 2014). Since lignin is an anticipated component of watershed NOM, but not algal NOM, the THAA results are in agreement with this train of logic. The dihaloacetonitrile (DHAN) data are also supported by model studies. Algal cells are known to have higher abundance of proteins and amino acids than terrestrial plants. In general, nitrogen to carbon ratios from algal cultures are higher than those from terrestrial plant leachate. In particular, aspartic acid residues are well-known DHAN precursor and DHAN formation tests have shown higher formation from algal cells than from aquatic humic substances (e.g., Fang et al., 2010). Thus, the association between algal-dominated NOM and DHAN precursor is easily rationalized on a chemical basis. Unfortunately, we have less

definitive data from the literature concerning other model end members. However, if one accepts that terrestrial or benthic NOM is closer in its characteristics to aquatic humic substances than algal NOM, we can draw from that vast literature. Several researchers have shown that chloroform yields from humic and fulvic acids (42.5 – 56.9 $\mu\text{g}/\text{mg-C}$) are higher than yields from algal-derived organic matter (35.9 $\mu\text{g}/\text{mg-C}$; Reckhow et al., 1990; Hong et al., 2008). When considering DCAA the reverse may be true. Precursor yields from algal cells (29.0 $\mu\text{g}/\text{mg-C}$) have been found to be higher than for fulvic acid (18.6 $\mu\text{g}/\text{mg-C}$; Hong et al., 2008; Reckhow et al., 1990).

2.4 Conclusion

Disinfection byproduct (DBP) precursors originate in large reservoirs from at least three types of types of sources: (1) watershed or allochthonous, (2) algal or autochthonous, and (3) bottom sediments or benthic. The properties of the NOM and the DBP precursor content of that NOM is unique to each source. In this study, we used standard limnological parameters to identify samples from one of the NYC reservoirs that have end-member characteristics. These samples were analyzed in laboratory tests for their DBP precursor content. These data were compared with known properties of NOM and related natural biochemical parameters. From this analysis, we conclude that algal-dominated NOM contributes disproportionately to DHAN formation, whereas watershed-dominated NOM is especially rich in THAA and THM precursors as well as UV absorbing substances. The sediment-dominated precursor behaved like a mix of the other two, but generally resembled the watershed NOM most.

CHAPTER 3

THE SPATIAL AND TEMPORAL DISTRIBUTION OF DBP PRECURSORS CLASSIFIED BY LEVEL OF HYDROPHOBIC BEHAVIOR

3.1 Introduction

Natural organic matter (NOM) reacts quickly with aqueous chlorine to form disinfection byproducts (DBPs), and these compounds have been associated with various human cancers and reproductive problems (Hwang and Jaakkola, 2003). Trihalomethanes (THMs) and haloacetic acids (HAAs) are two regulated groups of DBPs. Chloroform was first considered to be carcinogenic by the U.S. National Cancer Institute in 1976. Other DBP compounds, such as dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), were then found to have carcinogenic properties (NTP, 1985, 1987, 1989; Bull et al., 1990). The US EPA Stage 1 Disinfectants and Disinfection Byproducts Rule (Stage 1 DBPR), established in 1998, included maximum contaminant levels of 80 $\mu\text{g/L}$ for total THMs, and 60 $\mu\text{g/L}$ for five HAAs based on a system water running average. Later, a tightening requirement (the Stage 2 DBPR) for these two groups of DBPs was established in 2006. Stage 2 focuses on locations with high DBP concentrations, resulting in stricter limits for many utilities of all sizes. To optimize management strategy and minimize the concentration of DBPs in water supplies, it is helpful to understand the behavior of DBP precursors (e.g., Palmstrom et al., 1988; Matilainen and Sillanpaa, 2010). It is also important to understand the impacts of seasons and climate change, since factors such as snow-melt, leaf-off and temperature driven microbial metabolism can be key determinants in NOM export.

NOM is a complex mixture of heterogeneous organic compounds that includes hundreds or thousands of distinct chemical species (Croue, et al., 2000a). It is desirable to isolate NOM into a limited set of categories (fractions) by their homogeneous composition and properties and then characterize the different groups of NOM. One common approach is isolating the mixture by differing hydrophobic behavior (e.g., hydrophobic, mesophilic, and hydrophilic) based on adsorption on synthetic resins (e.g., XAD-8 and XAD-4; Aiken et al., 1992; Malcolm and MacCarthy, 1992; Croue et al., 2000a; Hua and Reckhow, 2007). Previous studies suggested that the hydrophilic fraction contain more aliphatic carbon (e.g., carboxylic acids and carbohydrates) and biodegradable nitrogenous compounds (e.g., amino acids, amino sugars, and proteins), and the hydrophobic fraction primarily consists of humic and fulvic acids which are rich in aromatic carbon, phenolic structures, and conjugated double bonds (Aiken et al., 1992; Croue et al., 2000a). It has been documented by several studies that NOM hydrophobicity significantly affects their DBP formation potentials (Croue et al., 2000b; Kitis et al., 2002; Liang and Singer, 2003; Hua and Reckhow, 2007). In general, hydrophobic NOM is found to be a more important source of DBP precursors (Hua and Reckhow, 2007). However, hydrophilic NOM also contributes substantially to the formation of DBPs. These characteristics of DBP precursors are affected remarkably by watershed microbial activities, therefore, it is sensitive to seasonal climate changes, especially temperature and rainfall patterns (Guggenberger and Zech, 1994; Scott et al., 1998; Kalbitz et al., 2000; Aitkenhead-Peterson et al., 2004). It thus becomes important to improve the documentation and understanding of the seasonal variations of DBPs in temperate areas. Not only because they may imply the variations in human exposure to the contaminants

on a seasonal basis, the following development on treatment strategies also worthwhile. However, most of the available data on the topic involves very low sampling frequencies, and the seasonality of hydrophobicity fractions as DBP precursors has not been scrutinized thoroughly. Prior studies do not permit an appropriate analysis of the seasonal changes in these DBP compounds in drinking water supply systems.

The main purpose of this research is to study the occurrence of the two regulated groups of DBPs – THMs and HAAs – in drinking water supplies with an emphasis on their seasonal evolution. Water samples were collected throughout a 12-month period in up-, intermediate, and down-stream reservoirs of the New York City water supply system. The samples were characterized by means of XAD fractionation (Leenheer 1981; Aiken and Leenheer, 1993), and the DBP formation potentials from different NOM fractions were compared.

3.2 Materials and Methods

3.2.1 Site Description

This study includes eight reservoirs (Cannonsville, Pepacton, Neversink, Rondout, Schoharie, Ashokan, Kensico and West Branch) of the New York City supply system that supply drinking water to 9 million people in the NYC area. Schoharie Reservoir is located in the Catskill Mountains of southeastern New York, approximately 190 km from New York City (Gelda and Effler, 2007). The main tributary drains about 314 square miles of watershed (Mehaffey et al., 2005). This is an upstream reservoir in the Catskill system, as water withdrawn travels through Ashokan and Kensico reservoirs before delivery to NYC. Water in Delaware River drains from 1010 square miles of

watershed into three upstream Delaware reservoirs (Cannonsville, Pepacton and Neversink). The upstream Delaware reservoirs supply Rondout reservoir; water then leaves Rondout and travels to West Branch Reservoir. Water from West Branch then flows through the Delaware Aqueduct to the Kensico Reservoir, where it mixes with Catskill Water. As such, West Branch and Kensico are considered as terminal, rather than collecting, reservoirs. Their watershed supplies just 2% or less of the total water volume entering the reservoirs. The Croton Watershed's drainage basin is about 33 square miles, and includes 7% farmland, 66% forestland, and 13% developed lands (more anthropogenically impacted area compared to the Catskill/Delaware watershed). The Catskill/Delaware watersheds consist of 92% forest land, approximately 6% agricultural land, and 1% developed lands (Anandhi et al., 2013). These watersheds are dominated by northern hardwood trees including maple, birch and beech. Other less abundant species present are white/red pine, hemlock, elm, and ash (VanValkenburg, 1996).

3.2.2 Sample Collection

Samples of 2L each were collected on a monthly basis from January 2013 – December 2013 from the intake chamber at each reservoir and shipped overnight to UMass laboratories. All samples were collected in cleaned 2-L borosilicate glass bottles with PTFE-lined septum caps (serum bottles with red caps). The bottles and ice-packs were transported in coolers with foam cushioning. All sampling bottles were acid washed and extensively rinsed with deionized or reverse osmosis water prior to the sampling trip. Once on site, the sampling line was completely flushed prior to collecting the first sample. Bottles were rinsed with the sample at the time of collection. One additional 1L

bottle filled with Milli Q water was transported together with the sampling bottles as the field blank. The samples and blank were kept in a cold room (4 °C) until needed.

3.2.3 XAD-8/4 Resin Extraction

The hydrophobicity of NOM was determined using XAD-8 and XAD-4 resins (Rohm and Haas Company, Philadelphia, PA) based on a method developed by Aiken et al. (1992). The column distribution coefficient (k') of both resins was kept at 50 for all waters. Water samples were acidified to pH 2 using hydrochloric acid and then first passed through XAD-8 resin. The remaining XAD-8 effluent was then passed through XAD-4 resin (Rohm and Haas, Philadelphia, PA). Effluent from the XAD-4 resin was collected, and this was referred to as the hydrophilic fraction. The fractions referred to as hydrophobic and mesophilic organic compounds were retained by XAD-8 and XAD-4 resins, respectively, and sodium hydroxide (NaOH, 0.1N) solution was used to back elute these fractions in reverse direction. The pH of the three fractions was adjusted to 7 using sulfuric acid or sodium hydroxide, and the volume of all fractions was adjusted to the initial sample volume.

3.2.4 Chlorination Procedures

Chlorine doses were determined based on a target chlorine residual of 4 ± 1 mg Cl_2 /L after a 7-day incubation at a temperature of 20 °C. The field blanks used a dose of 4.2mg Cl_2 /L. Samples were buffered at pH 7 with 0.5M phosphate buffer solution. Chlorination was conducted in 300mL glass-stoppered bottles. A stock solution of sodium hypochlorite (Fisher Scientific, Fairlawn, NJ) was standardized by the DPD ferrous titrimetric method according to Standard Methods 4500-Cl F (APHA, AWWA,

and WEF, 1998). After being dosed with chlorine, samples were stored headspace-free at 20 °C in the dark for 168 h (7days). Then, all samples were quenched and partitioned for subsequent analysis of DBPs.

3.2.5 Analytical Methods

Total and dissolved organic carbon (TOC and DOC) were measured by the high-temperature combustion method based on Standard Methods 5310 (APHA, AWWA and WEF, 1998). A Shimadzu TOC-VCPH Total Organic Carbon Analyzer (Shimadzu Scientific Instruments, Columbia, Md.) was used for these measurements at UMass. Samples for DOC analysis were filtered through 0.45 micron Whatman GF/F glass fiber filters. The pH of all samples was adjusted to pH 2 before TOC and DOC measurements. A concentration of 10 mg/L potassium hydrogen phthalate was used as a calibration standard. The UV-visible absorbance spectrum was measured for all waters prior to treatment with disinfectants. Samples were filtered through 0.45 micron Whatman GF/F glass fiber filters. Filtered sample was placed in the 1cm cuvette and measured using an Agilent 8453 spectrophotometer. Specific UV absorbance (SUVA) is calculated as the UV absorbance at 254 nm normalized to 1 mg/L DOC and then multiplied by 100. The liquid-liquid extraction, gas chromatography procedure for the analysis of trihalomethane (THM) in this research is closely aligned with USEPA method 551.1. The THM standard stock solution was prepared from USEPA halogenated volatiles mix stock solution (Supelco Inc., Bellefonte, PA.). Pentane was used as the extracting solvent and 1,2-dibromopropane was used as an internal standard. Stock solutions were stored at -4°C. Extracted samples were measured using an Agilent 6890 gas chromatograph equipped with a linearized 63Ni electron capture detector and Agilent J&W DB-5 column. The

carrier gas was nitrogen of ultra-high purity. Haloacetic acid analysis was performed in accordance with USEPA Method 552.2. The HAA standard stock solution was prepared in methyl-tert-butyl-ether (MTBE) from USEPA Halogenated Acetic Acids Mix (Supelco Inc., Bellefonte, PA.). MTBE was used as the extracting solvent and 1,2-dibromopropane was used as an internal standard. All stock solutions were stored at -4°C. Extracted samples were measured by Agilent 6890 gas chromatograph equipped with a linearized ⁶³Ni electron capture detector and Agilent J&W DB-1 column. The carrier gas was ultra-high purity nitrogen.

3.3 Results and Discussion

3.3.1 Characteristics of Raw Water

The average values of TOC and SUVA₂₅₄ of the hydrophobic, hydrophilic, and mesophilic fractions are summarized in Table 3.1. Relatively high and variable TOC and SUVA₂₅₄ in Schoharie were probably linked to the most part steep, and deep lacustrine clays underlie much of the Schoharie watershed surface that may impact water clarity by minor disturbances (Soil and District, 2013). It is found that, in NYC reservoir system, hydrophobic compounds are the most abundant of the XAD partition-based groups (over 51% in total TOC; Table 3.1), which is in good agreement with the overall median percentage (56%) of hydrophobic acids in dissolved organic matter (DOM) from fresh waters (Perdue and Ritchie, 2003). It is also supported by the previous studies that the sum of the median percentages of humic acids and fulvic acids in fresh waters DOM is 60% (Aiken et al., 1992; Aiken and Leenheer, 1993). Monthly rain events were characterized by USGS in 2013 for NYC reservoirs. The allochthonous organic matter

was probably the primary TOC loading to NYC reservoirs, which are mainly derived from canopy leaching and soil litter decomposition.

The hydrophobic fractions exhibit consistently higher SUVA values than the corresponding hydrophilic and mesophilic (Table 3.1), which is in line with previous forest floor leaching studies. The hydrophilic fractions were found to be largely composed of carbohydrates (e.g., Orem and Hatcher, 1987; Kaiser et al., 2001), whereas the hydrophobic fractions were characterized by large proportions of UV absorbing compounds (e.g., aromatic compounds) and smaller abundances of carbohydrates (Guggenberger et al., 1994; Kaiser et al., 2001).

3.3.2 Seasonal Variation of NOM Hydrophobicity

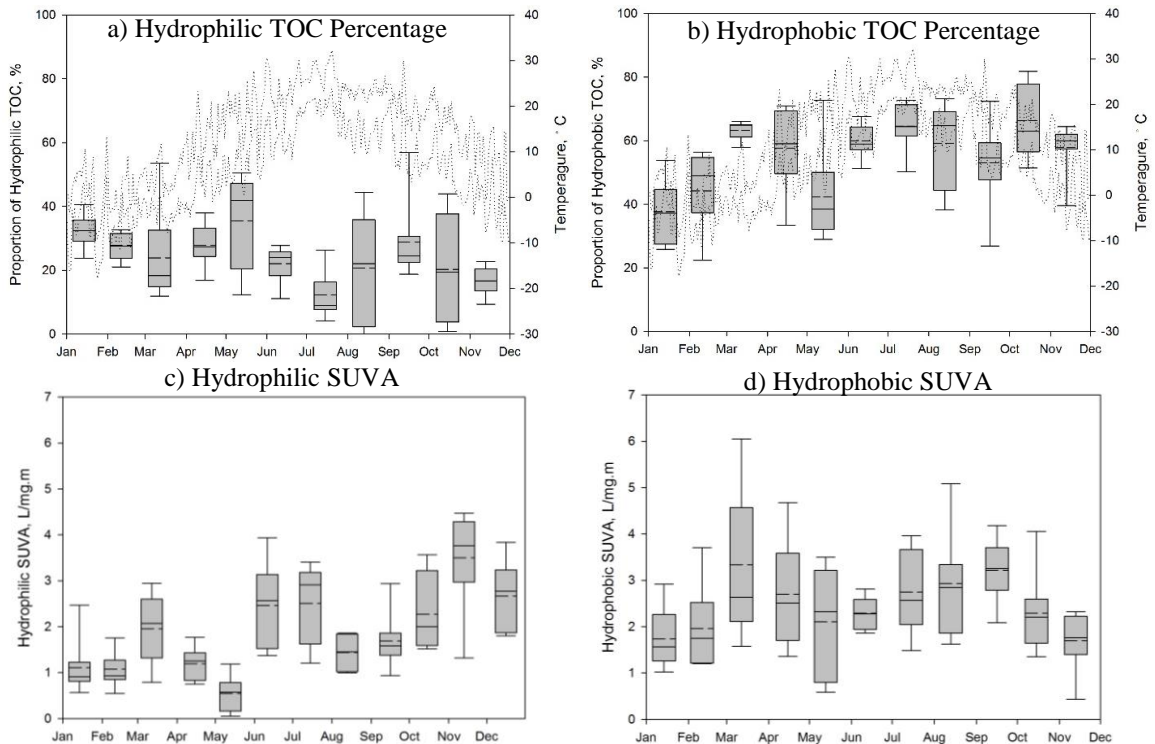


Figure 3.1: Seasonal variation (n=8; solid line: median; dashed line: mean) of hydrophilic TOC percentage (a) and hydrophobic TOC percentage (b) with daily highest and lowest temperatures (°C); seasonal variation (n=8; solid line: median; dashed line: mean) of hydrophilic SUVA (c) and hydrophobic SUVA (d).

Table 3.1 Characteristics of NOM hydrophobicity fractions (average \pm standard deviation) prior to chlorination (n=12months).

Source	Hydrophilic Fraction		Hydrophobic Fraction		Mesophilic Fraction	
	TOC (mg/L)	SUVA ₂₅₄ (L/mg-m)	TOC (mg/L)	SUVA ₂₅₄ (L/mg-m)	TOC (mg/L)	SUVA ₂₅₄ (L/mg-m)
Cannonsville	0.6 \pm 0.4	1.4 \pm 0.5	1.1 \pm 0.7	3.3 \pm 2.3	0.7 \pm 0.6	2.6 \pm 1.1
Neversink	0.8 \pm 0.9	2.6 \pm 1.9	1.5 \pm 1.2	3.5 \pm 2.0	0.4 \pm 0.2	3.1 \pm 1.5
Pepacton	0.4 \pm 0.2	1.7 \pm 1.0	0.9 \pm 0.3	2.6 \pm 1.2	0.5 \pm 0.2	2.4 \pm 1.2
Schoharie	1.1 \pm 2.1	2.0 \pm 1.2	1.3 \pm 0.4	3.8 \pm 2.7	0.7 \pm 0.4	2.3 \pm 1.1
Ashokan	0.8 \pm 1.7	2.2 \pm 2.1	0.9 \pm 0.4	2.8 \pm 1.7	0.4 \pm 0.2	2.2 \pm 1.5
Rondout	0.5 \pm 0.4	2.0 \pm 1.4	1.0 \pm 0.3	2.9 \pm 1.6	0.6 \pm 0.4	2.3 \pm 1.6
Kensico	0.4 \pm 0.2	2.3 \pm 1.4	1.0 \pm 0.4	2.9 \pm 1.6	0.4 \pm 0.2	2.4 \pm 1.9
West Branch	0.5 \pm 0.4	2.2 \pm 0.9	1.3 \pm 0.5	2.7 \pm 1.1	0.6 \pm 0.4	2.5 \pm 1.1

The proportions of hydrophobic and hydrophilic fractions in TOC are presented using the box-and-whisker plots in Figure 3.1a and 3.1b with mean values of daily maximum and minimum air temperatures presented in dashed lines. The air temperatures were monitored by USGS at locations in Catskill, Delaware, and Croton watersheds. The proportions of hydrophobic and hydrophilic fractions in TOC are also presented in the supporting information Figure A.1 and A.2.

The results show that the hydrophobic fraction in reservoirs is positively correlated with the air temperature in watershed area (Figure 3.1b) while the hydrophilic TOC shows a reverse trend (Figure 3.1a). Temperature is an indicator of seasonal climate change (snowmelt and leaf-off) in the watershed area, as well as a factor regulating the microbial production of NOM (e.g., Bourbonniere, 1989; Kalbitz et al., 2000; Wetzel, 2001). The increases of the hydrophilic fractions in winter and early spring (Figure 3.1a) are probably caused by the disruption and subsequent leaching of fresh microbial and plant debris upon contact with water from precipitation or snow-melt. Similar increases of hydrophilic compounds during the cold season have been observed for percolation water of forest soils (Dai et al., 1996; Hongve 1999; Kaiser et al., 2001), especially after drastic changes of environmental conditions such as drying or freezing (Christ and David 1994; Guggenberger et al., 1998).

On the other hand, decomposition rates, which remove NOM from soils or waters, decrease in cold seasons but increase in warm seasons. Thus the labile hydrophilic fractions, preferentially used by microbes (Orem and Hatcher, 1987; Dai et al., 1996; Kaiser and Zech, 1997; Kaiser et al., 2001; Massaccesi et al., 2013), decreased rapidly in warm seasons (Figure 3.1a). The hydrophobic fractions consist of recalcitrant compounds

(e.g., Kalbitz et al., 2003; Marschner et al., 2008), and are consequently stable in warm seasons (Figure 3.1b). Another increase of the hydrophobic fraction occurred in the fall (Figure 3.1b). This may probably result from the leaf-off in October and November and subsequent leaching of fresh leaf litter in the NYC watershed.

The hydrophobic fractions contained more UV absorbing content than the hydrophilic fractions in winter and spring, however, their characteristics were relatively similar in summer and fall (Figure 3.1c and 3.1d; Figure A.3 and A.4). This may be mainly regulated by the decomposition rates of UV absorbing content. The decomposition of aromatic components is significantly inhibited by low temperature (Evans, 1963). For example, lignin accumulation was observed by Li et al. (2016) during the snow cover period for litter soil layer. Then lignin and phenolic structures in hydrophobic fractions were degraded and converted into hydrophilic fraction when temperature increased (e.g., Sørensen, 1962; Rutigliano et al., 1996; Austin and Ballaré, 2010).

3.3.3 Seasonal Patterns of Precursor Hydrophobicity

Table 3.2 Characteristics of seasonal water quality parameters (average \pm standard deviation) during the period under study (Spring: March-May; Summer: June-August; Fall: September-November; Winter: December-February; n=24)

	Spring	Summer	Fall	Winter
TOC (mg/L)	2.2 \pm 0.6	1.9 \pm 0.4	1.7 \pm 0.3	1.7 \pm 0.3
DOC (mg/L)	1.7 \pm 0.6	1.5 \pm 0.3	1.4 \pm 0.2	1.3 \pm 0.3
SUVA ₂₅₄ (L/mg·m)	2.0 \pm 0.5	2.6 \pm 0.6	2.5 \pm 0.3	2.7 \pm 0.8
THM FP (μ g/mg-C)	42.3 \pm 12.4	53.2 \pm 9.0	50.7 \pm 5.9	59.1 \pm 8.3
DHAA FP (μ g/mg-C)	31.9 \pm 7.5	27.0 \pm 10.0	14.9 \pm 1.6	17.3 \pm 12.6
THAA FP (μ g/mg-C)	44.2 \pm 17.6	48.1 \pm 15.6	35.4 \pm 6.6	39.7 \pm 17.1

The seasonal characteristics of raw water during the period under investigation are presented in Table 3.2. Among the four THMs (CHCl_3 , CHBrCl_2 , CHBr_2Cl , and CHBr_3), bromoform was the only product not detectable (values lower than the detection limit) in the measured samples whereas chloroform was identified as the predominant compound (over 95% of THM). Among HAAs, dichloroacetic acids (DCAA) and trichloroacetic acids (TCAA) represent 98% and 97% of DHAA (i.e., dichloro-, bromochloro-, and dibromoacetic acid) and THAA (i.e., bromodichloro-, dibromochloro-, trichloro-, and tribromoacetic acid) respectively. All DBP concentrations ($\mu\text{g/L}$) have been normalized to a 1 mg-C/L concentration so that they are intensive parameters, unaffected by actual TOC concentrations.

Monthly measured DBP precursors are plotted for four seasons in Figure 3.2; spring (March-May), summer (June-August); fall (September-November), and winter (December-February). Figure 3.2 presents the seasonal patterns of intensive THM, DHAA, and THAA formation potentials in three partition-based groups using bar plots. The hydrophobic NOM was the predominant fraction in bulk water (Table 3.1), and its characteristics considerably affect the raw water properties. For example, the higher THM yields from hydrophobic fractions in winter (Figure 3.2a; Figure A.6) result in higher THM yields from bulk water in winter (Table 3.2). Similar seasonal differences in THM yields were found in other temperate environments (i.e., Europe and Japan) documented in raw surface water studies (Goslan et al., 2002; Imai, et al., 2003). However, reverse results were observed in treated waters in a distribution system where THM levels in summer and fall were two to five times higher than average concentrations measured in winter (Garcia-Villanova et al., 1997; Chen and Weisel, 1998; Rodriguez et

al., 2004). The possible explanation may be that the hydrophilic fractions in raw water have greater influence on the quality of treated waters as they are less amenable to be removed through conventional coagulation process (Matilainen et al., 2010; Ghernaout, 2014). And they were found to yield more THMs in summer (Figure 3.2a; Figure A.5).

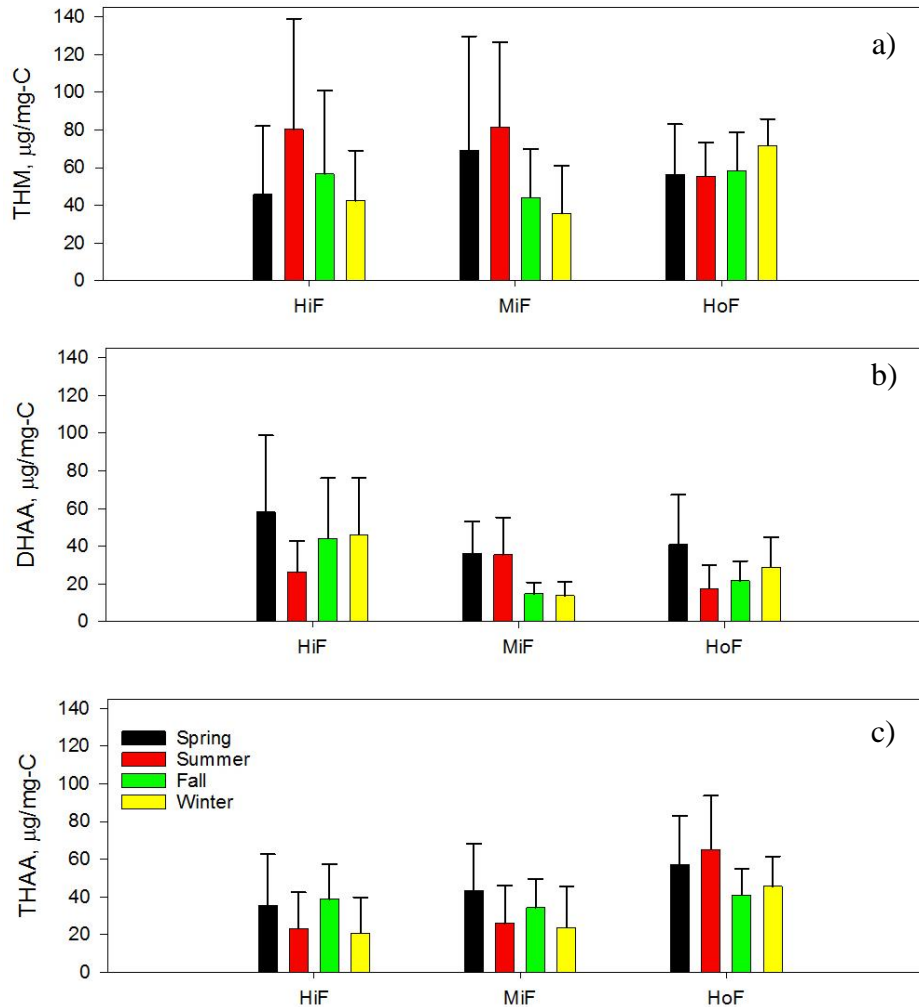


Figure 3.2: Seasonal patterns of DBP yields in three hydrophobicity fractions (HiF: hydrophilic fraction, n=24; MiF: mesophilic fraction, n=24; HoF: hydrophobic fraction, n=24). The error bars represent the standard deviation of all reservoirs in three month period.

Evidence shows that hydrophobic NOM was rich in THAA precursors while hydrophilic NOM was rich in DHAA precursors (Figure 3.2b and 3.2c). This observation has been discussed in previous studies. Hua and Reckhow (2007) found that hydrophilic

and low molecular weight (MW) components tend to be more significant DHAA precursors, and hydrophobic and high MW components are significant THAA precursors. Recently, lignin phenols are reported to be more important as TCAA precursors than as chloroform and DCAA precursors (Hua et al., 2014). Instead, watershed sources derived from terrestrial plants were not considered to be the predominant NOM sources for DHAA precursors. Other researchers found that the algae derived organic matter produces greater amount of DHAA during chlorination than humic or fulvic acids (e.g., Hong et al., 2008).

Figure 3.2 presents seasonal variations of the DBP precursors derived from different hydrophobicity groups. We suggest that the NOM in cold season (fall and winter) is mostly composed of freshly-flushed organic matter, in another word, more labile components, primarily attributed to leaf-off and slow biodegradation rate under low temperature. NOM in warm season (spring and summer) was more decomposed and more recalcitrant. These recalcitrant components are suggested to be quite reactive with chlorine and produce large amounts of DBPs (especially THAA; Table 3.2) during chlorination due to high electron density in the aromatic rings (Larson and Rockwell, 1979; Boyce and Hornig, 1983). The seasonal increases of THAA and THM in summer and winter, respectively, characterize the more recalcitrant property of hydrophobic THAA precursors (Figure 3.2a and 3.2c). A similar hierarchy was characterized for the bulk water (Table 3.2). Furthermore, the hydrophilic fractions yield more THM and THAA in summer and fall. It seems that the hydrophilic THAA precursors were more labile than hydrophilic THM precursors. Moreover, as discussed above, the hydrophobic fractions may be converted into hydrophilic fractions in summer, and some active

reacting structures that form more THMs may have been transferred into the hydrophilic fractions. All three fractions contained more DHAA precursors in spring (Figure 3.2b). This may be caused by an algal bloom in the spring in the epilimnion of reservoirs where we collected the water samples, and these hydrophilic fractions tend to form more DHAA during chlorination.

3.3.4 Locational Variations of DBP Precursors

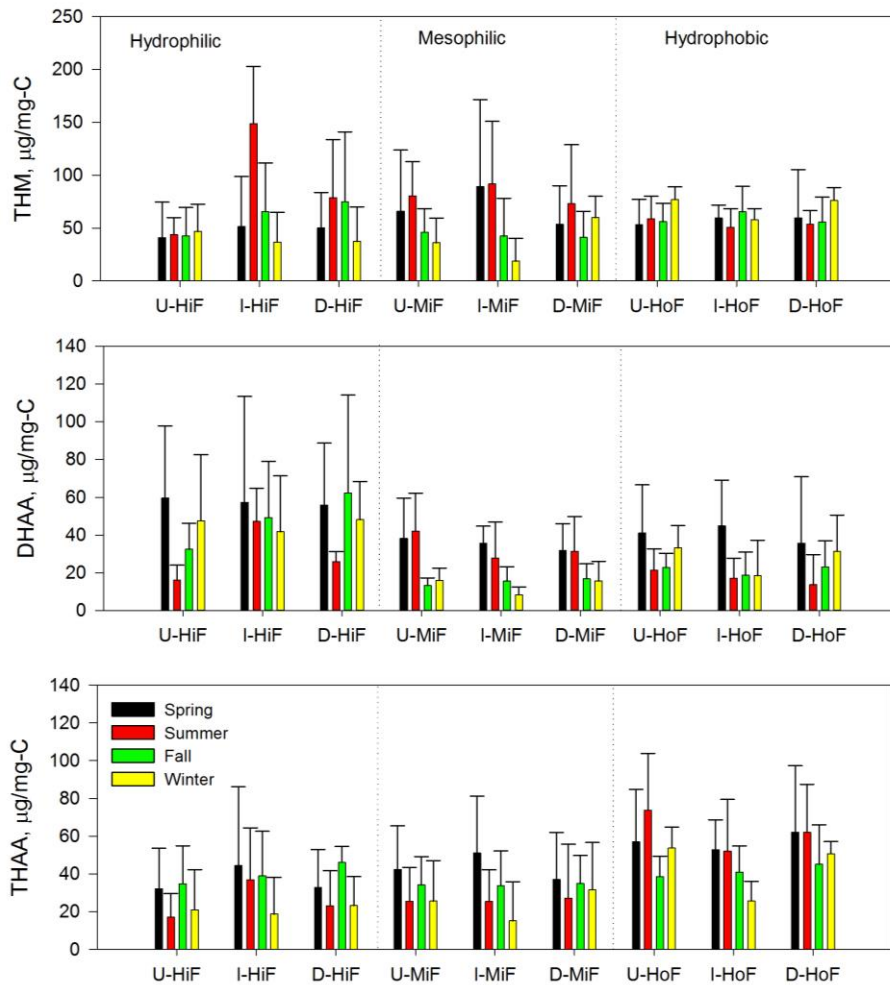


Figure 3.3: Seasonal patterns of intensive DBP concentration in three hydrophobicity fractions (HiF: hydrophilic fraction; MiF: mesophilic fraction; HoF: hydrophobic fraction) from upstream reservoirs (U; n=12): Cannonsville, Neversink, Pepacton, and Schoharie; intermediate reservoirs (I; n=6): Ashokan and Rondout; and downstream reservoirs (D; n=6): Kensico and West Branch. The error bars represent the standard deviation of each reservoir in three month period.

Seasonal patterns of intensive DBP concentrations in up-, intermediate, and down-stream reservoirs are presented in Figure 3.3. Only the hydrophilic fractions show locational variations; the other fractions were relatively stable (Figure 3.3). This result is probably attributed to the most unsteady characteristics of hydrophilic NOM, which may change rapidly during transport from upstream to downstream. The hydrophilic fraction in summer was most recalcitrant and contained considerable amounts of DBP precursors in the intermediate reservoirs compared to others. The labile hydrophilic fractions (i.e., in fall) yielded more DBP precursors in downstream reservoirs, followed by the intermediate, then upstream reservoirs. Thus, to reduce the DBP precursors in water treatment plant, suitable sources could be considered based on the analysis above.

A three-way analysis of variance (ANOVA) test was performed on the DBP formation potential analysis, with season, location, and hydrophobicity as three factors. It is found that season is significantly related to DHAA concentration (P-value: 0.032). The interaction of season and hydrophobicity is significantly related to DHAA and THAA concentrations (P-value: 0.021 and 0.00095). The interaction of location, season, and hydrophobicity is significantly related to THAA concentration (P-value: 0.030).

3.4 Conclusion

This investigation permitted the generation of a portrait of the THM, DHAA, and THAA formation in eight reservoirs located in a temperate environment where seasonal variations of surface water quality and water temperature are considerable. The hydrophobic TOC in reservoir waters were positively correlated with air temperature of the watershed area whereas the hydrophilic TOC shows a reverse trend. The seasonal

climate change (i.e., snowmelt and leaf-off) and microbial decomposition play an important role in the variations of NOM fractions, as well as the yields of DBPs. Generally, the THAA precursors are more hydrophobic than THM precursors, and the DHAA precursors were most hydrophilic. Recalcitrant hydrophobic NOM in summer was very reactive with chlorine and yielded the most amount of THAAs on annual basis. The THM precursors are less recalcitrant. Reservoir waters in spring contained more DHAA precursors than other seasons, which is probably correlated with the algae growth in the epilimnion.

CHAPTER 4

PLANT LEACHATE AS POTENTIAL DBP PRECURSORS

4.1 Introduction

Disinfectants such as chlorine react with organic matter to generate disinfection byproducts (DBPs), which could be potentially hazardous to human health if the water is a public water supply (e.g., Hwang and Jaakkola, 2003). Organic matter released from plants is quite likely the most important fraction as potential DBP precursors, especially in heavily forested catchments. The connection between land cover and NOM generation is at least partly related to leaching of organic material from plant matter. These naturally-occurring organic substances are a major source of allochthonous natural organic matter (NOM) in surface waters, which are more complex and diverse than autochthonous NOM, and have yet to be fully understood.

It has generally been accepted that as a result of immersion in stream water, allochthonous litter displays a pronounced loss of mass of up to 30-50% within the first few days due to leaching of water soluble substances (Petersen and Cummins, 1974; Webster and Benfield, 1986; France et al., 1997). Several investigators have shown a positive correlation between the amount of water-soluble substances in the litter and leaf leachate decomposition during the first months (e.g., Nykvist, 1959; Reckhow et al., 2008). Substances leached from plants include a great diversity of materials (Tukey, 1970). Cellulose and lignin materials from plant structural constituents make up the largest source of allochthonous humic compounds (Wetzel, 2001). The complex compounds undergo a series of decomposition stages. High concentrations of humic can

be found in upper soil horizons as a result of the breakdown of surface plant material (Thurman, 1985; Wetzel, 2001).

Much has been learned about the sources, transport, and degradation of plant material in the aquatic environment. However, very few studies have been conducted on the fate and transport of DBP precursors originated from these allochthonous sources. This research characterizes the organic matter that is released by leaf and needle litters from maple, oak, and pine trees. In order to investigate the effect of light exposure and biodegradation on DBP precursors, we examine the potentials of their leachate to form DBPs under light, dark, and dark-with-biocide conditions.

4.2 Materials and Methods

4.2.1 Leaf Leaching Studies

Oak and maple leaves and pine needles were collected from the top of the leaf pack in Mount Sugarloaf, MA in August, which contained leaves from the previous season's litterfall. The three-species collected were red maple (*A. rubrum*), white oak (*Q. alba*), and white pine (*P. strobus*). All samples were kept in zip lock bags at 4°C before use. Five bottles are prepared for each leaf type (three amber bottles and two clear bottles). Amber bottles were protected from light by surrounding the bottle with aluminum foil. Two replicates were used for light and dark samples. Samples containing biocide were dosed with 1mg/L Sodium Azide. For each bottle, one gram (dry weight) of leaf samples were soaked in 800 mL artificial lake water (0.1587 g NaHCO₃, 0.0992 g MgSO₄, 0.0992 g CaSO₄, 0.0066 g KCl per liter Milli-Q Water). Leaves were dried in an oven at 50°C for 24 hours before being weighed. Moisture contents of the maple and oak

leaves and pine needles were 34.2, 17.9, and 23.1% respectively. During leaching, samples were kept at $20\pm 2^{\circ}\text{C}$ in a constant temperature incubator which is lighted with four 30 watt fluorescent lamps (GRO-LUX). Samples were aerated with zero-grade air (21% oxygen, 79% nitrogen, Airgas, PA). Samples were leached for 8 days, and UV_{254} and DOC measurements were periodically recorded on days 1, 3, 5, and 8. At the end of the leaching phase, the water from all twelve 1L bottles was decanted from the leaves, filtered through $0.45\mu\text{m}$ glass fiber filters and prepared for bench scale chlorination and DBP formation potential analysis.

4.2.2 Chlorination Procedures

The chlorine doses were determined based on target chlorine residual as $4\pm 1\text{mg Cl}_2/\text{L}$ after 7-day incubation at the temperature of 20°C . The field blanks used a dose of $4.2\text{mg Cl}_2/\text{L}$. Samples were buffered at pH 7 with 0.5M phosphate buffer solution. Chlorination was conducted in 300mL glass-stoppered bottles. A stock solution of sodium hypochlorite (Fisher Scientific, Fairlawn, NJ) was standardized by DPD ferrous titrimetric method according to Standard Methods 4500-Cl F (APHA, AWWA, and WEF, 1998). After being dosed with chlorine, samples were stored headspace-free at 20°C in the dark for 168 h (7days).

4.2.3 Analytical Methods

Dissolved organic carbon (DOC) was measured by the high-temperature combustion method based on Standard Methods 5310 (APHA, AWWA and WEF, 1998). A Shimadzu TOC-VCPH Total Organic Carbon Analyzer (Shimadzu Scientific Instruments, Columbia, Md.) was used for these measurements at UMass. Samples for

DOC analysis were filtered through 0.45 micron Whatman GF/F glass fiber filters. The pH of all samples was adjusted to pH 2 before DOC measurements. The concentration of 10 mg/L potassium hydrogen phthalate was used as calibration standard. The UV-visible absorbance spectrum was measured for all waters prior to treatment with disinfectants. Samples were filtered through 0.45 micron Whatman GF/F glass fiber filters. The filtered sample was placed in the 1cm cuvette and measured by Agilent 8453 spectrophotometer. Specific UV absorbance (SUVA) is defined as the UV absorbance of a sample at a specific wavelength normalized by dissolved organic carbon (DOC) concentration. The liquid-liquid extraction, gas chromatography procedure for the analysis of trihalomethane (THM) in this research is closely aligned with USEPA method 551.1. The THM standard stock solution was prepared from USEPA halogenated volatiles mix stock solution (Supelco Inc., Bellefonte, PA.), which contains eleven species. Pentane was used as the extracting solvent and 1,2-dibromopropane was used as an internal standard. Stock solutions were stored at -4°C. Extracted samples were measured by Agilent 6890 gas chromatograph equipped with a linearized ^{63}Ni electron capture detector and Agilent J&W DB-5 column. The carrier gas is nitrogen with ultra-high purity. Haloacetic acid analysis was performed in accordance with USEPA Method 552.2. The HAA standard stock solution was prepared in methyl-tert-butyl-ether (MTBE) from USEPA Halogenated Acetic Acids Mix (Supelco Inc., Bellefonte, PA.), which consisted of nine species. MTBE was used as the extracting solvent and 1,2-dibromopropane was used as an internal standard. All stock solutions were stored at -4°C. Extracted samples were measured by Agilent 6890 gas chromatograph equipped with a linearized ^{63}Ni electron

capture detector and Agilent J&W DB-1 column. The carrier gas is ultra-high purity nitrogen.

4.3 Results and Discussion

4.3.1 Characteristics of DOC Released from Leaf Litter

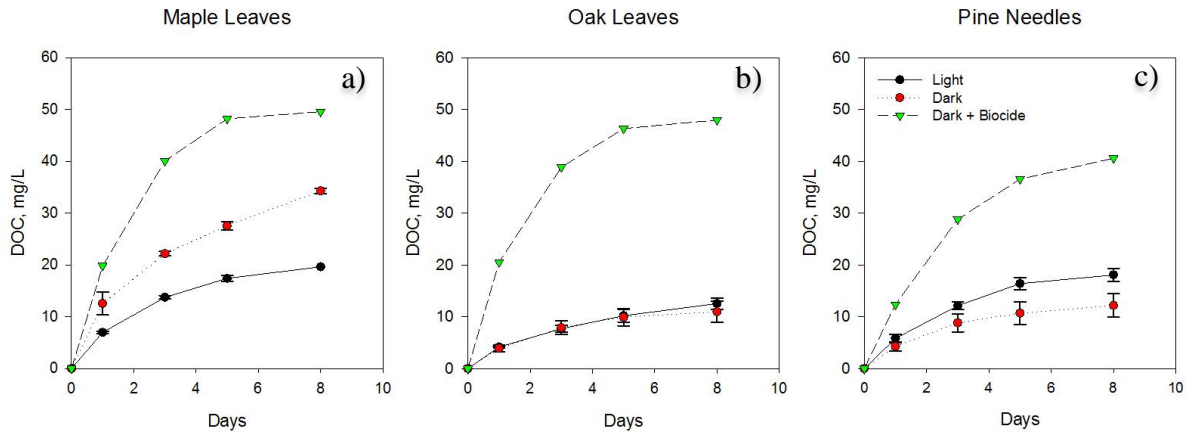


Figure 4.1 Release of DOC. a) Maple leaves; b) Oak leaves; c) Pine needles; vertical bars represent 95% confidence levels.

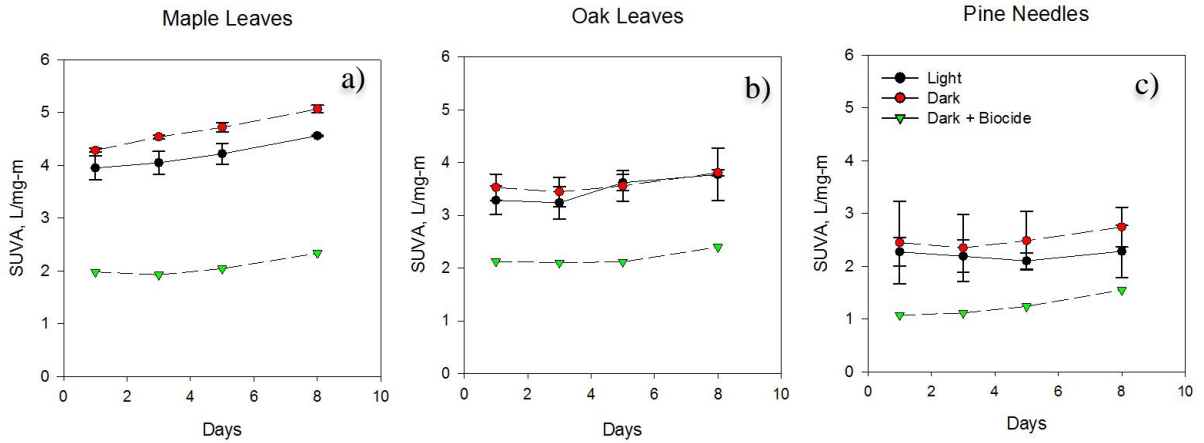


Figure 4.2 Specific UV absorbance. a) Maple leaves; b) Oak leaves; c) Pine needles; vertical bars represent 95% confidence levels.

The results of the leaching of maple and oak leaves, and pine needles are presented in Figure 4.1. All three leaf types were leached under three different

conditions: dark, dark-with-biocide, and light. For all leaf types, the highest DOC was observed in dark-with-biocide condition. Then the maple leaves leached more DOC under dark condition (Figure 4.1a), whereas the pine needles show reverse result (Figure 4.1c). Figure 4.2 shows the slightly increasing trend of SUVA₂₅₄ values with time in all samples. Samples in dark bottles had the highest SUVA₂₅₄ followed by light condition and then the dark-with-biocide condition.

All leaf types exhibited extensive carbon lost due to biodegradation, and 40 to 75% of TOC was lost within eight days (Figure 4.1). The previous literatures show that the organic matter from leaves is rapidly consumed by microorganisms (Wetzel, 2001; Thurman, 2012). Up to 45% of deciduous litter leachate degrades in the first week, and 30% after seven weeks (Hongve, 1999). The low-molecular-weight (MW) compounds initially present in fresh leachate are easily consumed by microbes, utilizing up to 54% of DOC within three days (Meyer, 1990).

The DOC from the maple leaves presents higher SUVA₂₅₄ values than from the oak and pine samples (Figure 4.2). This indicates that the maple leaves released more aromatic humics, whereas oak leaves leached a mixture of hydrophobic and hydrophilic organic matter and pine needles released primarily non-humic materials. McArthur and Richardson (2002) found that among tree species, deciduous species leached more than twice the amount of phenolics than coniferous species. A higher concentration of water-soluble phenolics from deciduous litter than from coniferous species was also observed by Kuiters and Sarink (1986). The decomposition of aromatic humic is much slower, but photolytic processes alter the chemical composition of soluble high molecular weight humics and improve their bioavailability.

Photochemical modification of organic macromolecules can result in major alterations in chemical composition and bioavailability (Wetzel, 2001). Decreases of SUVA₂₅₄ values were observed from the leaf types that were exposed to light (Figure 4.2), which is in agreement with the results of photodegradation of highly conjugated and aromatic compounds (Judd et al., 2007; Helms et al., 2008). Previous research has shown that humic macromolecules with high molecular weight are largely degraded during irradiation (due to bond cleavage and/or disaggregation) resulting in the generation of volatile fatty acids and related simple compounds that serve as excellent substrates for bacterial degradation (Wetzel, 2001; Helms et al., 2008). Similar results have been observed by many laboratory studies of plant matter leaching processes that incorporated light exposure. Fellman et al. (2013) found that the decrease in SUVA₂₅₄ following irradiation was negligible for fresh litter but significant for DOC leachate collected from four-month old litter.

4.3.2 DBP Formation Potentials of Leaf Leachate

The results of DBP formation potentials are presented in Figure 4.3. For all three leaf types, the DBP formation potentials have been normalized by the DOC concentration so that they are intensive yield parameters. The fully-chlorinated species, i.e., chloroform (CHCl₃), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA), were the most abundant species of THM, dihaloacetic acid (DHAA), and trihaloacetic acid (THAA), at 98%, 98%, and 99% of the total concentrations, respectively.

The specific DBP concentrations with biocide were lower than those without biocide (Figure 4.3). This suggests that the NOM responsible for DBP formation from plants may be highly resistant to short-term biodegradation. Reckhow et al. (2008) found

that 81-day biodegradation caused a large increase in SUVA₂₅₄ along with the DBP formation potentials in leaf leachate. Large quantities of low-UV-absorbing material present in the leachate was probably degraded to carbon dioxide or perhaps condensed to form highly recalcitrant humic-like material. This caused considerable increases in specific DBP formation potentials.

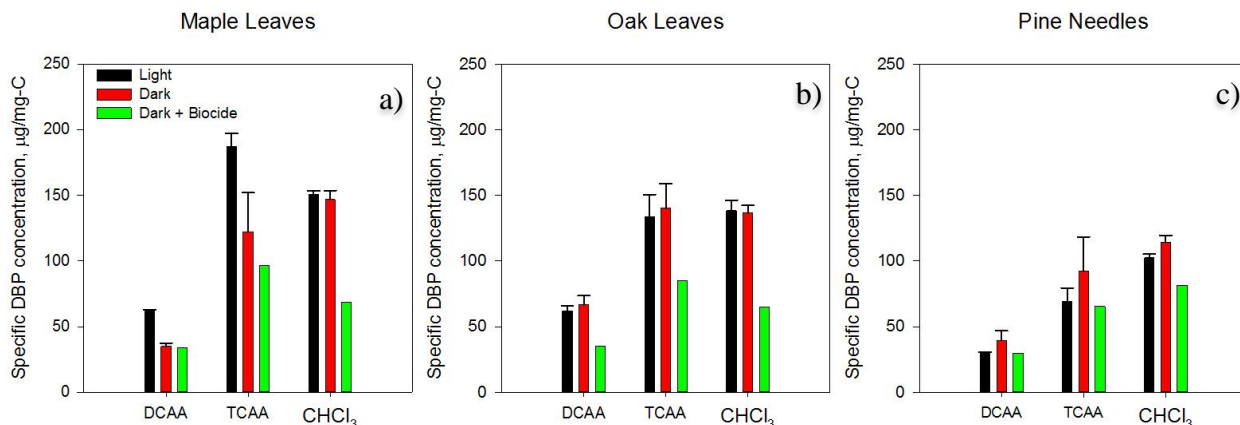


Figure 4.3 Disinfection byproduct formation potential for last day of incubation. a) Maple leaves; b) Oak leaves; c) Pine needles; vertical bars represent 95% confidence levels.

The maple and oak leaf leachates (Figure 4.3a and 4.3b) had higher DBP formation potentials than pine needle leachate (Figure 4.3c). Previous study found maple leaves contained substantial amounts of condensed tannins, phenolic components, and galloyl glucoses, whereas oak leaves contained almost exclusively condensed tannins (Kahkonen et al., 1999). The phenolic components in oak leaves and pine needles were 30% and 45% less than those in maple leaves (Kahkonen et al., 1999; Barbehenn et al., 2006). These phenolic components, especially lignin phenols, are important DBP precursors (Hua et al., 2016). Model lignin phenols generally contained higher TCAA precursors than chloroform and DCAA during chlorination (Hua et al., 2016), which may explain the higher specific concentrations of TCAA and chloroform in the current study.

4.4 Conclusion

During the eight-day maple and oak leaves leaching experiment, and pine needles, significant concentrations of DOC were leached into water under light, dark, and dark-with-biocide conditions. SUVA levels varied considerably between light and dark conditions, suggesting that the photolysis has an effect on the breakdown of aromatic content. High levels of specific DBP formation potentials were formed in leaf leachate. On average, the biodegraded organic matter formed higher specific DBP levels than the samples with biocide. Maple leaves had the highest yield of DOC and DBP precursors, whereas pine needles had the lowest yield.

CHAPTER 5

RESERVOIR SEDIMENTS AS POTENTIAL SOURCES OF TRIHALOMETHANE AND HALOACETIC ACID PRECURSORS

5.1 Introduction

Naturally-occurring organic substances, which constitutes a large fraction of the organic matter in water supplies, was a major source of disinfection byproduct (DBP) precursors. Many of the DBPs are of concern to human health, and as a result, the USEPA has established regulations for two representative groups, the trihalomethanes (THMs) and haloacetic acids (HAAs). In order to control the DBP precursors from sources, it is important to identify and characterize their origins. The allochthonous and autochthonous DBP precursors derived from watershed and algae sources, respectively, have been documented by several studies (e.g., Stepczuk et al., 1998; Hong et al., 2008). Organic matter released from sediments can also be considered as an important source of DBP precursors (Uhler and Means, 1985; Martin et al., 1993; Hong et al., 2013).

Aquatic macrophytes, algae and terrestrial sources are significant sources of organic matter sedimented from water column to sediment (Uhler and Means, 1985; Wetzel, 2001). Sedimentary organic carbon in pore water and soil fraction can be released into the overlying water column under undisturbed and disturbed conditions (e.g., Bloesch 1995; Effler et al., 1998; Komada and Reimers, 2001; Eggleton and Thomas, 2004; Effler and Matthews, 2004). In reservoir sediments, a significant proportion of DOC is disassociated from soil particles and stored in pore water which readily disperses into overlying water column during sediment resuspension (Eggleton and Thomas, 2004). Previous investigations of organic matter cycling in water column have highlighted the redistribution of organic matter between solid and solution phases

through sediment and organic matter release as a consequence of resuspension-induced desorption (Uhler and Means, 1985; Martin et al., 1993; Bloesch, 1995; Eggleton and Thomas, 2004; Yang et al., 2008; Hong et al., 2013). The behavior of organic matter partitioning between aqueous (pore water, overlying water) and solid phase (sediment, suspended particulate matter and biota) is highly affected by hydrodynamics, biogeochemical process, and environmental conditions (redox, pH, salinity, and temperature; Samiullah, 1990; Saulnier and Mucci, 2000; Cantwell et al., 2002). It is found that turbulence on sediments is a major effect that causes rapid DOC release from pore water (Effler et al., 1998; Cantwell et al., 2002; Komada et al., 2002). Sediment resuspension is documented as an annual cycle in dimictic lakes during spring and fall circulation (Wetzel, 2001). The process occurs when bottom shear exceeds a critical shear stress which is sufficient to overcome the cohesion of bottom sediments. Two basic zones of resuspension in lakes have been identified by Bloesch (1995): shallow zones that can be directly influenced by wave action, and turbulence in deeper areas that are associated primarily with internal seiches. Substantial drawdown is another reason that has been documented to cause turbulence on sediments in reservoir (Effler et al., 1998).

When developing the insight and quantitative models, it is important to consider sediments as potential source of DBP precursors. Sediments collected from littoral and profundal zone release different but significant amounts of THM precursors, which are both affected by ambient concentrations of dissolved oxygen (Martin et al., 1993). The components of sediment are very site specific. Sediments from reservoirs in South China were mostly derived from algal biomass due to a considerably high concentration of algae (Hong et al., 2013). This differs from the normal understanding of sediments,

which views them as sinks of humic substances (e.g., Wetzel, 2001). However, to our knowledge, no study has been conducted that directly compares the precursors originating from plant leaching, sediments, and algal cells under similar laboratory conditions. Knowledge about the relative importance of these three sources would be valuable in drinking water management for the purpose of minimizing DBP precursors.

The purpose of this study is to determine the comparative significance of DBP (i.e., trihalomethanes, dihaloacetic acids, and trihaloacetic acids) precursors released from profundal sediments of a water supply impoundment under aerobic, hypoxic, and anaerobic conditions. Finally, the contribution of DOC released from sediment in DBP formation was compared with those from algal cells and leaf leachate.

5.2 Materials and Methods

5.2.1 Sample Collection and Sediment Incubation

Cannonsville Reservoir, a eutrophic water supply reservoir for New York City, was chosen for this work due to its well documented water quality. Sediment samples were collected from a profundal site nearest to the intake chamber (average depth: 20m) with an Eckman dredge, and were mixed to obtain one homogeneous sample. One hundred gram sediment samples were transferred to each of 12 (8 for sediment incubation and 4 for control without sediments) wide-mouth amber 2.5L glass bottles (Thermo Scientific, MA). Two liters of artificial lake water (0.1587g NaHCO₃, 0.0992 g MgSO₄, 0.0992 g CaSO₄, 0.0066 g KCl per liter Milli-Q Water) were added to each bottle. All the chemicals were ACS grade. The sediment organic content in each bottle was 3.9g/L. The bottles were kept in the dark at 20±2°C. Four levels of dissolved oxygen (DO)

concentrations were chosen for this study: 0, 10, 20, and 97% saturation of DO, and two replicates for each DO level. Zero grade compressed air (Airgas, PA) was bubbled into samples at a rate (determined from preliminary experiments) that minimized sediment disturbance yet maintained oxic conditions to maintained DO concentration at 8.6 ± 0.1 mg/L for 97% of DO saturation. Anoxic (DO concentration at 0.1 ± 0.1 mg/L, 0% saturation of DO) were maintained by bubbling nitrogen of ultra-high purity (Airgas, PA) into bottles. The 10 and 20% saturation of DO were maintained by bubbling both DO and nitrogen. Sediments settled for 3 hours before initial TOC samples were taken. Sampling for chlorination occurred every second day and the final samples were collected on Day 26. Samples for XAD fractionation were collected in Day 1, Day 8, and Day 26. All the samples were diluted 4 times with MQ water before future analysis, and the concentrations of each analyte were adjusted to the concentrations in the initial volume to eliminate the impact of volume reduction due to sampling on the accuracy of the results.

After 26 days of incubation, sediments were filtered by GF/F glass fiber filter, then stored in amber bottle under 4°C. The organic content of incubated sediments was tested. Incubated sediments were also chlorinated with particle to Milli-Q water ratio of 400mg/310mL, and their DBP formation potentials were measured. The DBP precursors in sediment particles were calculated based on DBP formation per oven-dry solid weight.

5.2.2 Sediment Characterization

The organic content of homogenous sample was determined by placing 20 g of sediment in pre-weighted and pre-dried aluminum pans, drying at 103°C to constant weight and ashing at 500°C until constant weight was again obtained. Percent organic

matter was calculated from loss of oven-dry weight following combustion. The organic content in sediments from Cannonsville Reservoir is 7.8g per 100g of dry solids.

5.2.3 XAD-8/4 Resin Extraction

The hydrophobicity of the NOM was determined using XAD-8 and XAD-4 resins (Rohm and Haas Company, Philadelphia, PA) based on a method developed by Aiken et al. (1992). The column distribution coefficient (k') of both resins was kept at 50 for all waters. Water samples were acidified to pH 2 using hydrochloric acid and then first passed through XAD-8 resin. The remaining XAD-8 effluent was then passed through XAD-4 resin (Rohm and Haas, Philadelphia, PA). Effluent from XAD-4 resin was collected, and this was referred to as the hydrophilic fraction. The fractions referred to as hydrophobic and mesophilic organic compounds were retained by XAD-8 and XAD-4 resins, respectively, and sodium hydroxide (NaOH, 0.1N) solution was used to back elute these fractions in reverse direction. The pH of the three fractions was adjusted to 7 using sulfuric acid or sodium hydroxide, and the volume of all fractions was adjusted to the initial sample volume.

5.2.4 Chlorination Procedures

Chlorine doses were determined based on target chlorine residual as 4 ± 1 mg Cl_2 /L after 7-day incubation at the temperature of 20 °C. The field blanks used a dose of 4.2mg Cl_2 /L. Samples were buffered at pH 7 with 0.5M phosphate buffer solution. Chlorination was conducted in 300mL glass-stoppered bottles. A stock solution of sodium hypochlorite (Fisher Scientific, Fairlawn, NJ) was standardized by DPD ferrous titrimetric method according to Standard Methods 4500-Cl F (APHA, AWWA, and

WEF, 1998). After being dosed with chlorine, samples were stored headspace-free at 20 °C in the dark for 168 h (7days).

5.2.5 Analytical Methods

Total and dissolved organic carbon was measured by the high-temperature combustion method based on Standard Methods 5310 (APHA, AWWA and WEF, 1998). A Shimadzu TOC-VCPH Total Organic Carbon Analyzer (Shimadzu Scientific Instruments, Columbia, Md.) was used for these measurements at UMass. Samples for DOC analysis were filtered through 0.45 micron Whatman GF/F glass fiber filters. The pH of all samples was adjusted to pH 2 before TOC and DOC measurements. The concentration of 10 mg/L potassium hydrogen phthalate was used as calibration standard. The UV-visible absorbance spectrum was measured for all waters prior to treatment with disinfectants. Samples were filtered through 0.45 micron Whatman GF/F glass fiber filters. Filtered sample was placed in the 1cm cuvette and measured by Agilent 8453 spectrophotometer. Specific UV absorbance (SUVA) is defined as the UV absorbance of a sample at a specific wavelength normalized by dissolved organic carbon (DOC) concentration. The liquid-liquid extraction, gas chromatography procedure for the analysis of trihalomethane (THM) in this research is closely aligned with USEPA method 551.1. The THM standard stock solution was prepared from USEPA halogenated volatiles mix stock solution (Supelco Inc., Bellefonte, PA.), which contains eleven species. Pentane was used as the extracting solvent and 1,2-dibromopropane was used as an internal standard. Stock solutions were stored at -4°C. Extracted samples were measured by Agilent 6890 gas chromatograph equipped with a linearized ⁶³Ni electron capture detector and Agilent J&W DB-5 column. The carrier gas is nitrogen with ultra-

high purity. Haloacetic acid analysis was performed in accordance with USEPA Method 552.2. The HAA standard stock solution was prepared in methyl-tert-butyl-ether (MTBE) from USEPA Halogenated Acetic Acids Mix (Supelco Inc., Bellefonte, PA.), which consisted of nine species. MTBE was used as the extracting solvent and 1,2-dibromopropane was used as an internal standard. All stock solutions were stored at -4°C . Extracted samples were measured by Agilent 6890 gas chromatograph equipped with a linearized ^{63}Ni electron capture detector and Agilent J&W DB-1 column. The carrier gas is ultra-high purity nitrogen.

5.3 Results and Discussion

5.3.1 Characteristics of DOC Released

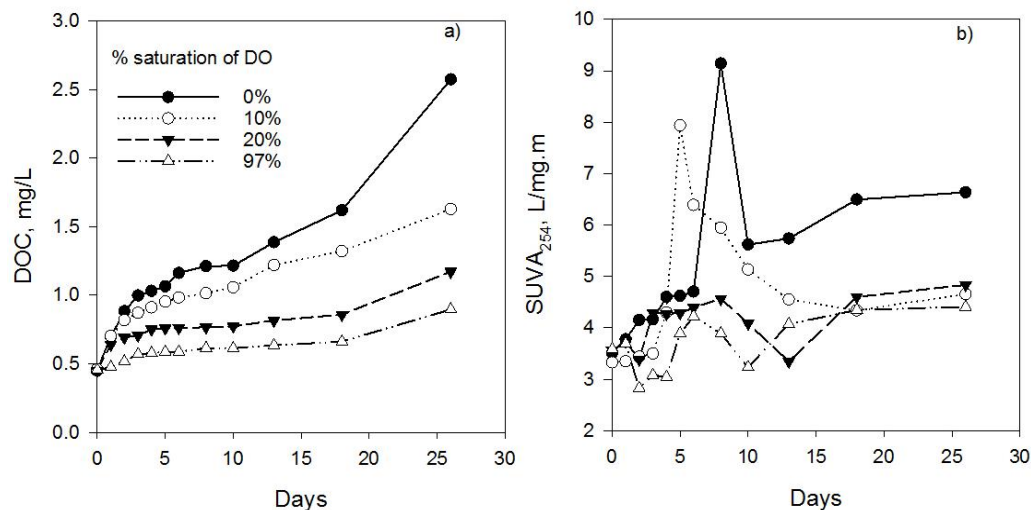


Figure 5.1 Release of DOC from sediments and SUVA₂₅₄ under 0, 10, 20, 97% saturation of DO. a) DOC; b) SUVA₂₅₄

The pilot study of 26-day incubation showed that the sediments released increasing amounts of DOC as the DO content decreased (Figure 5.1a). The proportion of organic content in sediment solids at the end of the experiment were positively correlated

with the DO concentration (Table 5.1). These results show that the absence of DO accelerated the release of organic matter from the sediments. This may be due to rapid DOC desorption from mineral surfaces at low redox potentials in anaerobic condition (0% saturation of DO, Koelmans and Prevo, 2003), and supplemented by a slower anaerobic decomposition rate (Kristensen et al., 1995). Previous evidence showed that iron(III) oxides can be reduced into dissolved form of iron(II) by anaerobic bacteria (Nealson, 1982), and the reduction of Mn(III, IV) to dissolved Mn(II) can also occur in anaerobic conditions (Stumm, 1992). As a result, a release of organic compounds that absorbed onto oxide mineral surfaces occurs in the absence of DO condition. Previous work showed that aerobic decomposition of organic compounds (occurred with 97% saturation of DO) was about 10 times faster than for anaerobic condition, especially when structural components (e.g., lignin and complex lipids) become a dominant fraction of the particulate remains in sediments (Benner et al., 1984; Ding and Sun, 2005). This result supports the finding that UV absorbing substances accumulated in the anaerobic water (Figure 5.1b).

Table 5.1 Characteristics of incubated and raw sediments (after 26 days of incubation)

% saturation of DO	organic content	THM, $\mu\text{g}/\text{mg}\text{-solid}$	DHAA, $\mu\text{g}/\text{mg}\text{-solid}$	THAA, $\mu\text{g}/\text{mg}\text{-solid}$
0%	7.5%	2.05	0.31	0.39
10%	7.6%	2.15	0.66	1.61
20%	7.7%	2.23	0.63	1.81
97%	7.9%	2.25	1.66	1.97
raw*	8.0%	2.74	0.50	1.52

Under anaerobic conditions, the hydrophobic fractions exhibited a slower release rate than hydrophilic fractions, and the proportion of hydrophobic fraction in TOC is in

the range of 28 – 40% (Figure 5.2a). This is similar the hydrophobic proportion under the aerobic condition (30 – 44%; Figure 5.2b). However, these are lower than the sum of the median percentages of hydrophobic fractions in dissolved organic matter from fresh water (63%; Perdue and Ritchie, 2003). Sediments are known to be a historic sink of aquatic macrophytes, algae, and terrestrial sources (Uhler and Means, 1985; Bloesch, 1995; Effler et al., 1998; Wetzel, 2001). The relatively high proportion of hydrophilic components in total TOC (Figure 5.2) may be caused by the substantial algae growth in Cannonsville Reservoir, as its eutrophic status was documented by historic data (Effler et al., 1998; Effler and Matthews, 2004).

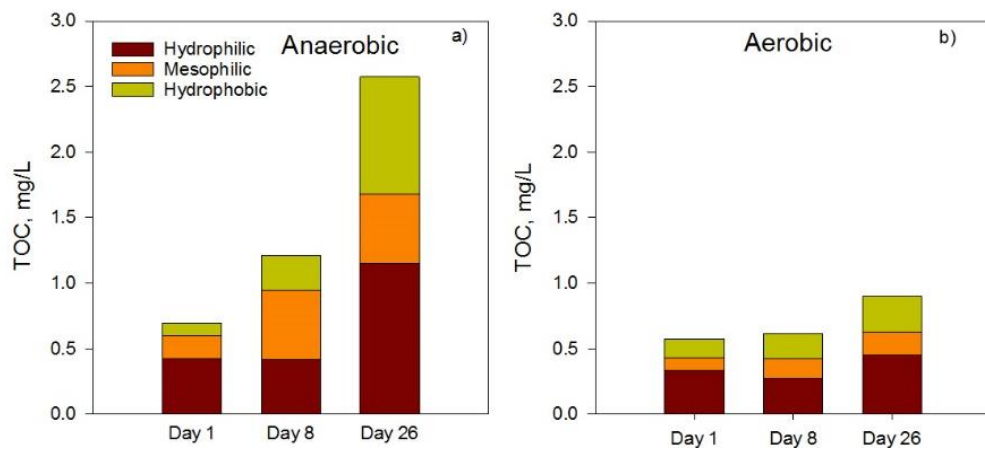


Figure 5.2 Characteristics of hydrophobicity released from sediments. a) anaerobic (0% saturation); b) aerobic (97% saturation).

After 26 days of incubation, the TOC of hydrophobic, mesophilic, and hydrophilic fractions under aerobic condition is 63%, 60%, and 58% lower than those in anaerobic environment (Figure 5.2). We interpret this is as caused by the variation of microbial degradation rate for each component. Under anaerobic condition, the hydrophobic compounds were more recalcitrant followed by the mesophilic and then the hydrophilic fractions. This is supported by the previous studies showed that hydrophilic

fractions were most biodegradable under anaerobic condition, and the hydrophobic components (humic substances, lignin residues, and plant-based phenolic compounds) are far less biodegradable (e.g., Benner et al., 1984; Thurman, 1985; Croue et al., 2000; Ding and Sun, 2005).

5.3.2 Release of DBP Precursors

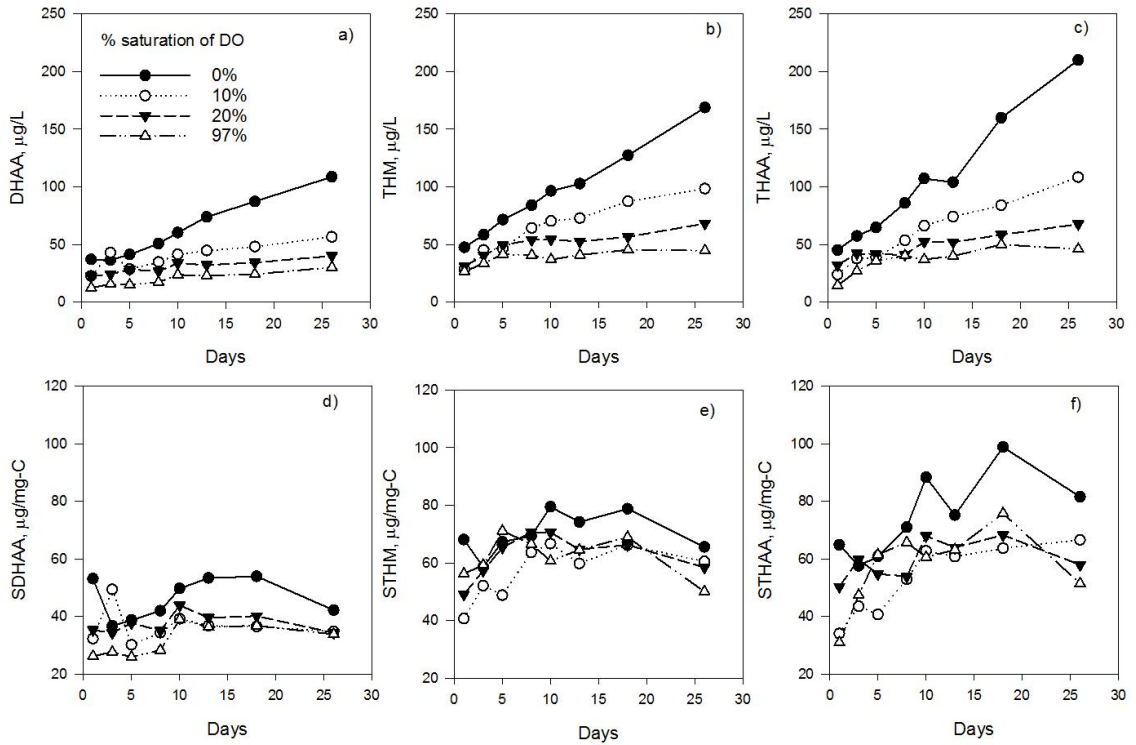


Figure 5.3 Release of DBPs from sediment leachate

Figure 5.3 presents the DBP formation potential results for the organic matter released from sediments under anaerobic (0% DO saturation), hypoxic (10 and 20% DO saturation = 0.9 - 1.8 mg/L DO concentration), and aerobic (97% DO saturation) conditions, where a threshold DO concentration of 2 mg/L has usually been chosen by researchers to define hypoxia because benthic dwelling organisms are strongly affected by oxygen concentrations lower than 2mg/L (Diaz and Rosenberg, 1995; Conley et al.,

2002; Spietz et al., 2015). In Figure 5.3a, 5.3b, and 5.3c, the values are graphed in absolute concentration units. For the other three (Figure 5.3d, 5.3e, and 5.3f), the DBP formation potentials have been normalized to a 1 mg-C/L concentration so that they are intensive parameters which unaffected by actual DOC concentrations. The fully-chlorinated species, i.e., chloroform (CHCl_3), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA), were the most abundant species of THM, DHAA, and THAA, at 97%, 96%, and 99% of the total concentrations, respectively. This is because concentrations of bromide are quite low in Cannonsville Reservoir, and as a result, little bromine becomes incorporated into the DBPs.

Regardless of whether one considers the extensive or intensive measures, sediments produced greater DBP precursors under anaerobic condition than those in presence of free oxygen. This could be attributed to the substantive production of methyl groups during methanogenesis process in anaerobic degradation. Previous study showed that methanogenesis is the predominant step for organic matter dissimilation in profundal sediments of eutrophic lakes during stratification (i.e., DO depletion, Lovley and Klug, 1982). As prevalent intermediate in methanogenesis (e.g., Evans, 1963; Molongoski and Klug, 1980), methyl groups, especially methyl keto and methoxyl, have been found to be important THM, THAA, and DHAA precursors (Morris and Baum, 1978; Hua and Reckhow, 2008; Hua et al., 2014). Hua et al. (2014) found that the methyl keto group produced the highest chloroform, at 2-10 fold more than other phenol structures. The reaction mechanism involves an electrophilic addition of a chlorine atom to the α -carbon of an enolizable carbonyl compound. The subsequent halogenation at the α -carbon and hydrolysis yield chloroform (Morris and Baum, 1978). Furthermore, Table 5.1 shows

lowest DBP production per unit weight of solids under anaerobic condition. This indicates that the release of DBP precursors was enhanced during DO depletion. In addition, the intensive measures for the hypoxic and aerobic conditions were quite similar (Figure 5.3d, 5.3e, and 5.3f). It suggests that the reactivity of NOM released under hypoxic and aerobic conditions were similar. The hydrolysis decomposition is still the dominant degradation pathways in hypoxic settings, although the aerobic respiration is diminished (Middelburg and Levin, 2009).

THAA precursors are more prevalent in sediment leachate followed by the THM and then the DHAA precursors (Figure 5.3). These relative hierarchies tend to match expectations based on DBP precursor analysis on some laboratory-derived end members. For example, terpenoid and lignin are slowly biodegraded in streams and lakes, then are observed to accumulate in sediments (Ishiwatari and Uzaki, 1987; Giri et al., 2015). These aged components have been shown to be especially rich in THAA and THM precursors (e.g., Reckhow et al., 2008; Mitch et al., 2009; Hua et al., 2014).

In summary, it is worthwhile to take into consideration that an anaerobic condition in overlying waters above the profundal sediments was prevalent in the hypolimnion during summer stratification, and this can cause several water quality concerns including phosphorus release (Wetzel, 2001) and the previously noted DBP precursor release.

5.3.3 Characteristics of DBP Precursors

The intensive DBP formation potentials of hydrophobic, mesophilic, and hydrophilic fractions are shown in Figure 5.4. Dashed lines exhibit the maximum and minimum range of DBP yields in the epilimnion water of the Cannonsville Reservoir. Hydrophobic

THAA and THM precursors were more prevalent in sediments than in epilimnion water (Figure 5.4a and 5.4b). This may be due to high THM and THAA formation in the aged hydrophobic fraction.

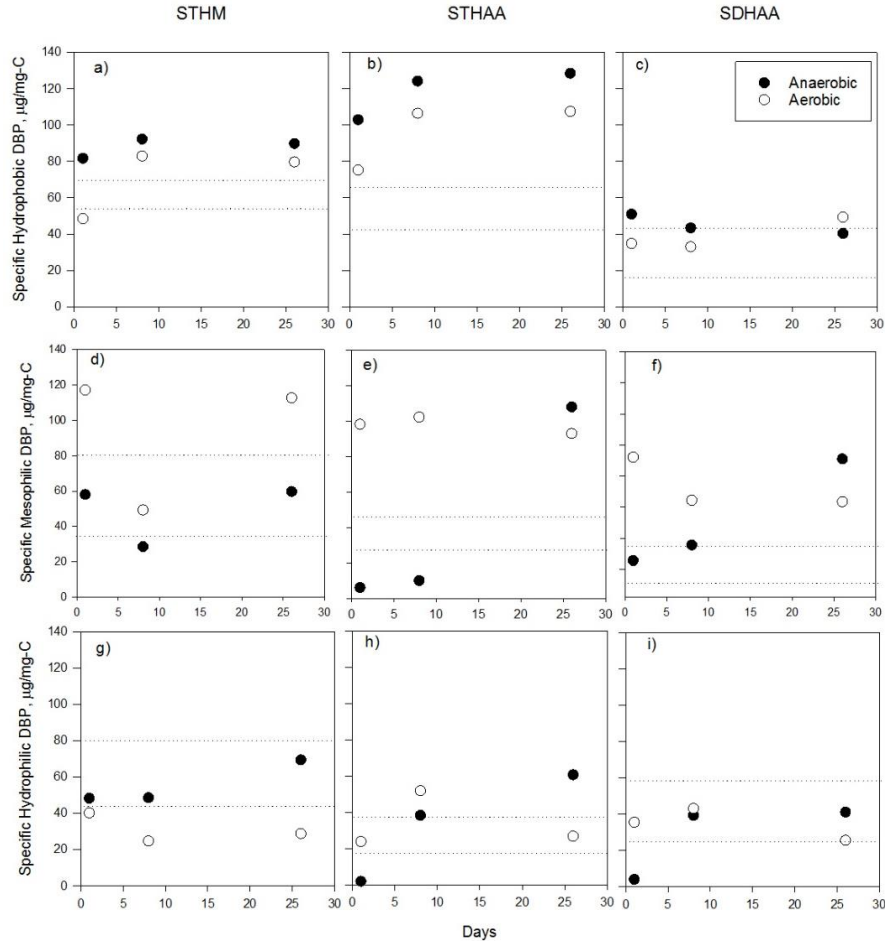


Figure 5.4 Characteristics of hydrophobicity of DBP precursors (dashed line: maximum and minimum range of specific DBP formation of Cannonsville Reservoir).

Hydrophobic fraction in anaerobic condition generally contained more DBP precursors than aerobic degradation (Figure 5.4a, 5.4b, and 5.4c), whereas the DBP yields in mesophilic and hydrophilic fraction were more fluctuating (Figure 5.4d, 5.4e, 5.4f, 5.4g, 5.4h, and 5.4i). The variation is probably caused by the unsteady characteristics of

hydrophilic and mesophilic, especially the latter, which could be in the transition form from hydrophobic to hydrophilic during biodegradation. It is worth noting that the anaerobic hydrophilic fraction contained more THM precursors than the aerobic hydrophilic fraction (Figure 5.4g), whereas their THAA and DHAA specific formation potentials were relatively similar (Figure 5.4h and 5.4i). More attention should be paid to the hydrophilic content of NOM in source waters since this NOM fraction is not amenable to removal by coagulation but can still produce appreciable amounts of DBPs.

5.3.4 Contribution of Sediment Leachate to DBP Precursors

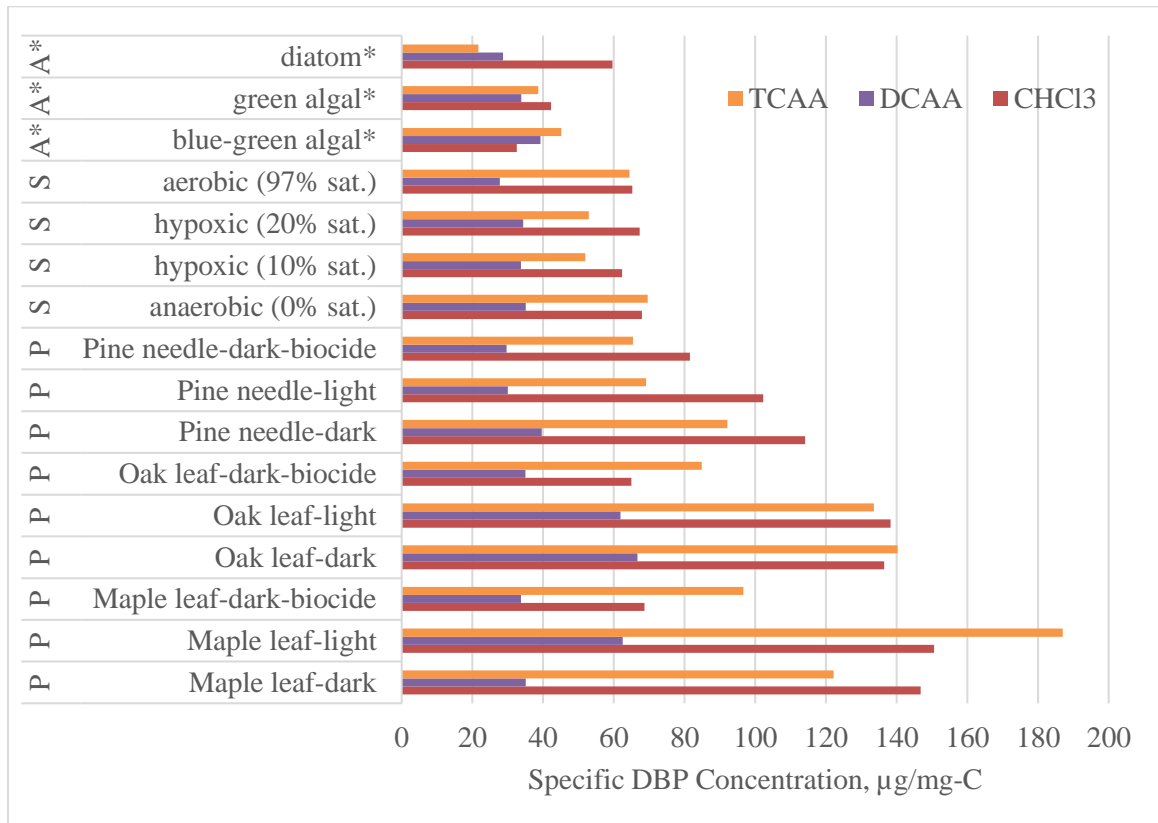


Figure 5.5 DBP formation upon chlorination of organic compounds derived from plant leachate, sediment leachate, and algal cells. A*: Algae (Hong et al., 2008); S: Sediments; P: Plants. (Data from plant and sediment leachate were both collected after 8 days of incubation, chlorination at pH=7, reaction temperature =20°C, Cl₂ contact time = 7days. Algal data were corrected based on data collected by Hong et al., 2008, chlorination at pH =7, reaction temperature =20°C, Cl₂ contact time = 3days.)

We view NOM in a water impoundment as originating from three types of sources: 1) watershed or allochthonous, 2) algal or autochthonous, and 3) lake sediments or benthic. In order to understand the characteristics of NOM from each source, this study compares the DBP formation potentials from these three origins. Data are shown in Figure 5.5 and Table A.1, and include 3 species of leaf leachates representing watershed sources, 4 sediment leachates, and 3 species of algal cells. Data from plant and sediment leachate were both collected after 8 days of incubation, chlorination at pH=7, reaction temperature =20°C, Cl₂ contact time = 7 days. Algal data were corrected based on data collected by Hong et al., 2008, chlorination at pH =7, reaction temperature =20°C, Cl₂ contact time = 3 days. A model¹ was employed to control the difference between chlorination time. All measured DBP levels were adjusted to that which would be expected from a standard chemical environment, where only the organic precursor content (quality or characteristics) affects the specific yields. The values of specific DBP formation potential for leaf leaching were averages of leaf incubation in light and dark conditions after 8 days. Maple, oak, and pine were chosen because they were the major species of the Cannonsville watershed's timberland (over 56% of watershed land cover; Hall et al., 2008). Algal DBP data from Hong et al. (2008) were used for chosen because they were generated under the similar chlorination conditions as the leaching experiments.

The results show that chloroform and TCAA precursors are more prevalent in the plant leachate followed by the sediment and then the algal sources (Figure 5.5). This was

¹ $DBP = a(Br + b)^c(pH + d)^e(temperatur + f)^g(Cl_2dose)^h(time)^i$ (Reckhow et al., 2008 pp.45). The model parameters were shown in Table A.2.

not unexpected as the lignin is an anticipated component of plant tissues, but not algal NOM. Purified lignin and lignin monomers have been shown to be especially rich in TCAA precursors (e.g., Hua et al., 2016). The organic matter released from sediments could be a historic mixed deposit of algae and terrestrial sources, therefore, the formation potentials of DBPs were in the middle of these two sources. Several researchers have shown that TCAA yields from leaf leachate (39-140 $\mu\text{g}/\text{mg-C}$; Reckhow et al., 2008) are higher than yields from algal organic matter (21.5-39.5 $\mu\text{g}/\text{mg-C}$; Plummer and Edzwald, 2001). In contrast, DCAA yields from algal cells were higher than yields from leaf leachate.

5.4 Conclusion

Profundal sediments from Cannonsville Reservoir released increasing levels of DBP precursors as DO levels decreased. Therefore, the hypolimnion DO deficit during summer stratification becomes a more important water quality concern, not only because it results in NOM release, but also a release of obviously higher DBP precursors per unit organic carbon. From the XAD fractionation and chlorination of each fraction, we conclude that hydrophobic fraction in sediment leachate is especially rich in THAA and THM precursors compared with watershed-dominated NOM. The sediment released precursor behaved like a mix of the algal and leaf released precursors.

CHAPTER 6

CONCLUSIONS

It is helpful to identify the seasonal pattern of DBP precursor origins in water supply impoundments and its effects on precursor behavior. The seasonal variation of precursor hydrophobicity has rarely been studied, and is informative for the development of predictive models. Furthermore, the resolution of the relative contributions of the three types of DBP precursor sources (watershed or allochthonous, algal or autochthonous, and bottom sediments or benthic) is valuable for guiding management decisions to improve or maintain water quality.

The summary of the major findings is:

1. Algal-dominated NOM contributes disproportionately to DHAN formation, whereas watershed-dominated NOM is especially rich in THAA and THM precursors as well as UV absorbing substances. The sediment-dominated precursor behaved like a mix of the other two, but generally resembled the watershed NOM most.
2. Hydrophobic TOC in reservoir waters was positively correlated with air temperature of the watershed area whereas the hydrophilic TOC shows a reverse trend. Recalcitrant hydrophobic NOM in summer was very reactive with chlorine and yielded the most amount of THAAs on annual basis. The THM precursors are less recalcitrant. Reservoir waters in spring contained more DHAA precursors than other seasons, which is probably correlated with the algae growth in the epilimnion.

3. Photolysis has an effect on the breakdown of the aromatic content in leaf leachate. Recalcitrant organic matter contained more DBP precursors than labile NOM in maple, oak, and pine leaf leachate. Maple leaves had the highest yield of DOC and DBP precursors, whereas pine needles had the lowest yield.
4. Profundal sediments released increasing DBP precursors as DO levels decreased. Hydrophobic fraction in sediment leachate is especially rich in THAA and THM precursors compared with the watershed-dominated NOM.

Identifying the origins and understanding the behavior of DBP precursors is fundamental to the development of effective management. Therefore, more efforts should be made to build a mechanistic model for DBPs drinking water supply based on the physical and chemical parameters and DBP concentrations. More research needs to be conducted to investigate the speciation distribution of the DBPs in different climatic zones. More detailed research should be conducted to investigate the formation, conversion, and degradation of DBP precursors under different seasonal and spatial conditions.

APPENDIX

SUPPORTING INFORMATION

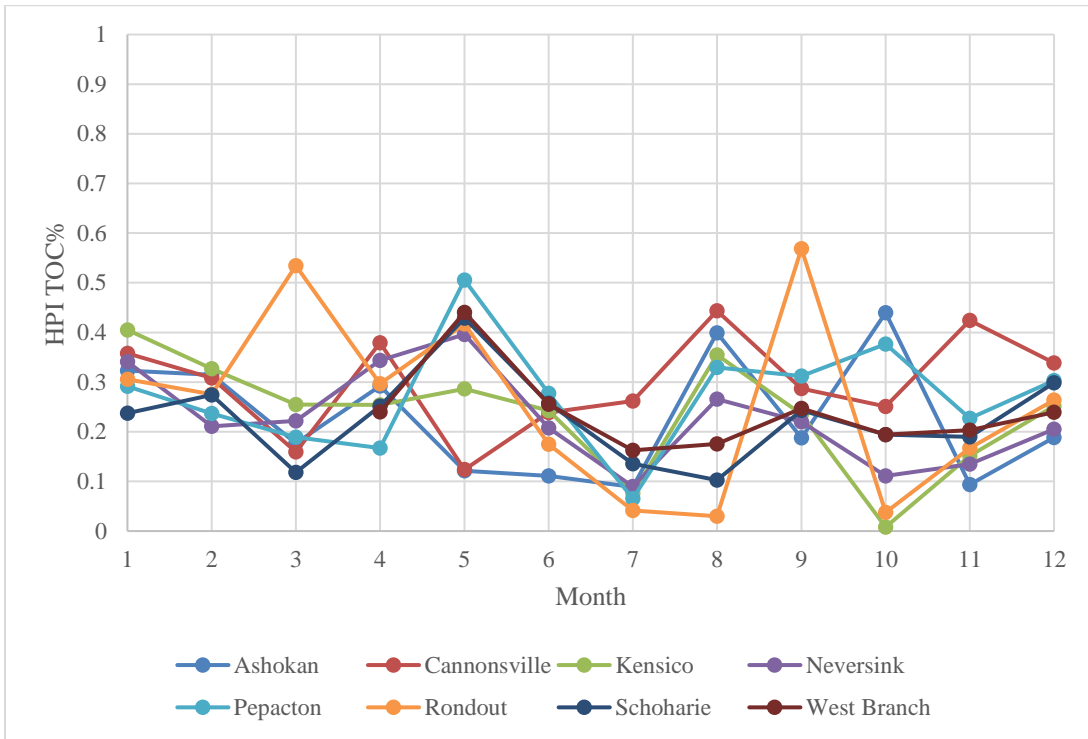


Figure A. 1 Monthly variation of percent of hydrophilic TOC from eight reservoirs

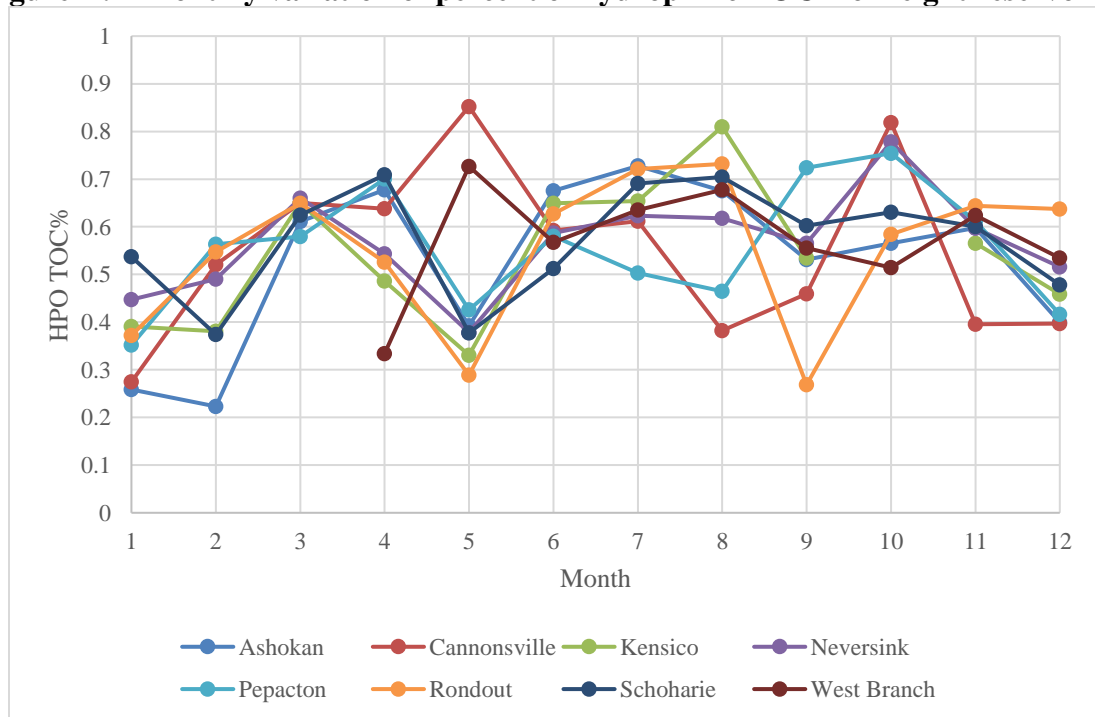


Figure A. 2 Monthly variation of percent of hydrophobic TOC from eight reservoirs

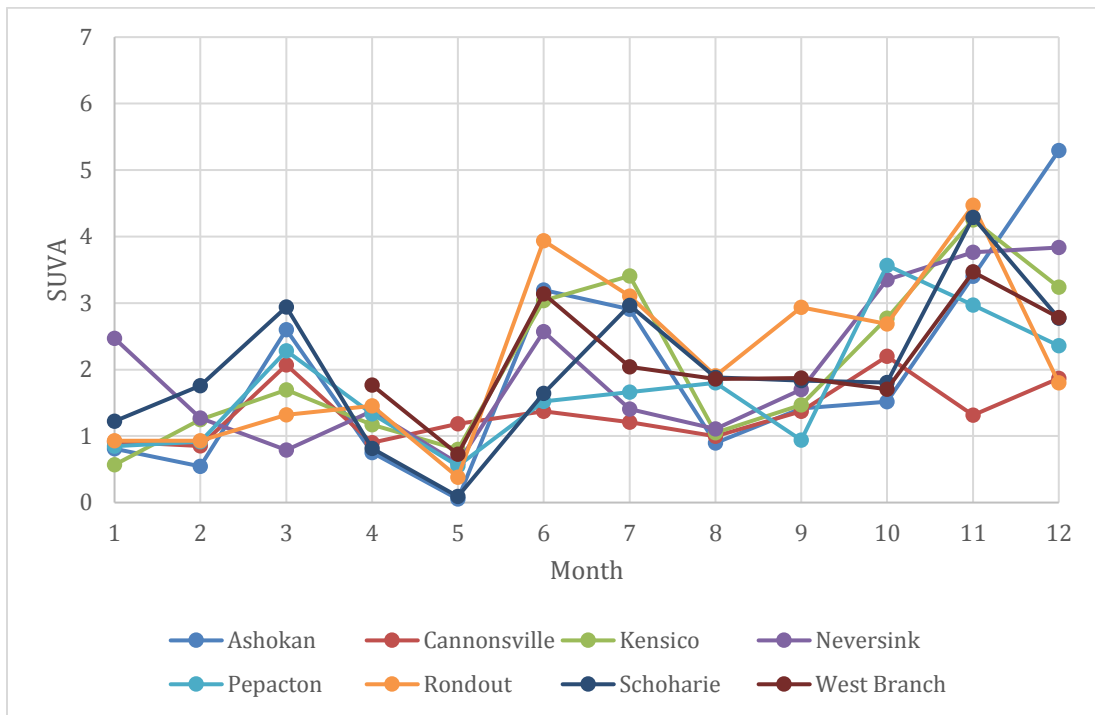


Figure A. 3 Monthly variation of hydrophilic SUVA from eight reservoirs

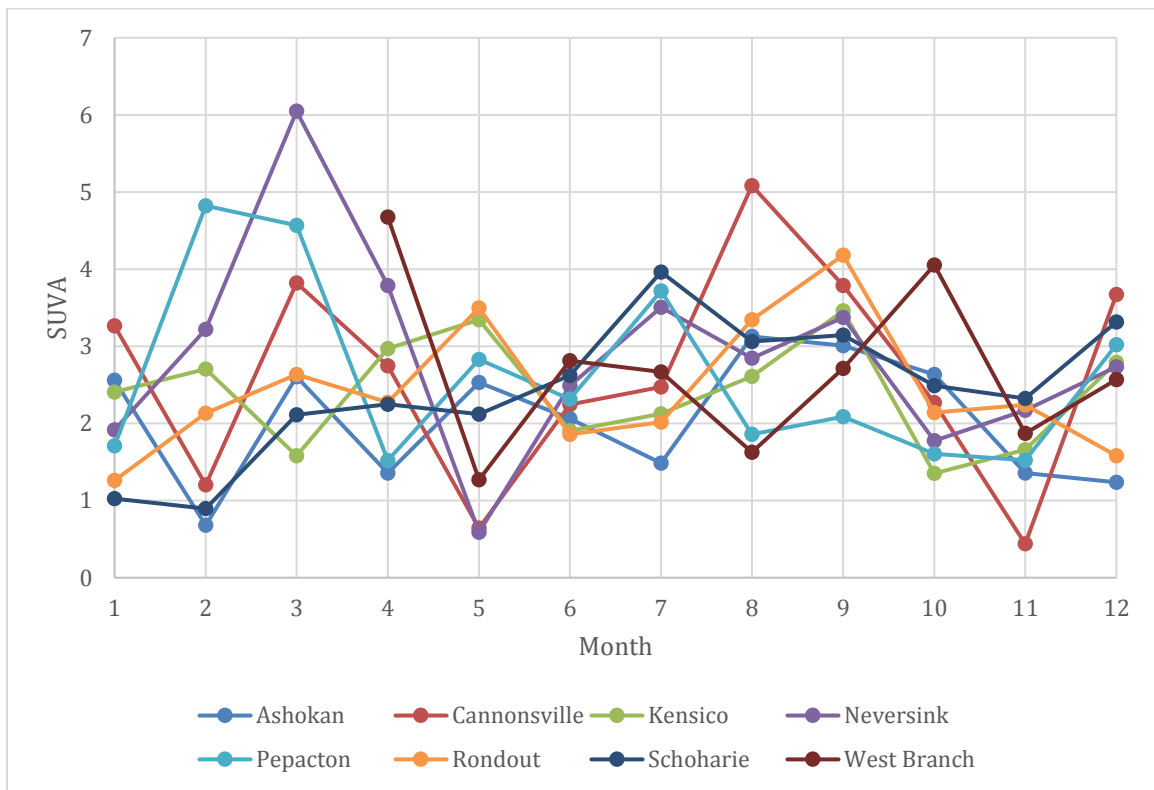


Figure A. 4 Monthly variation of hydrophobic SUVA from eight reservoirs

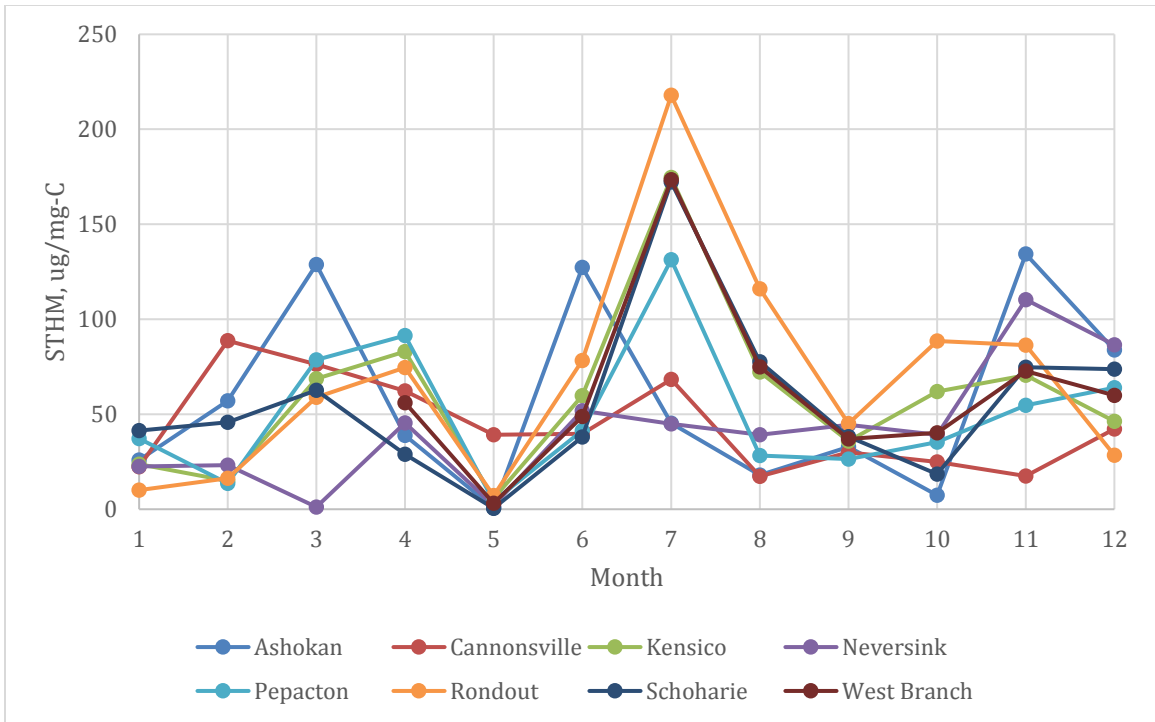


Figure A. 5 Monthly variation of hydrophilic STHM from eight reservoirs

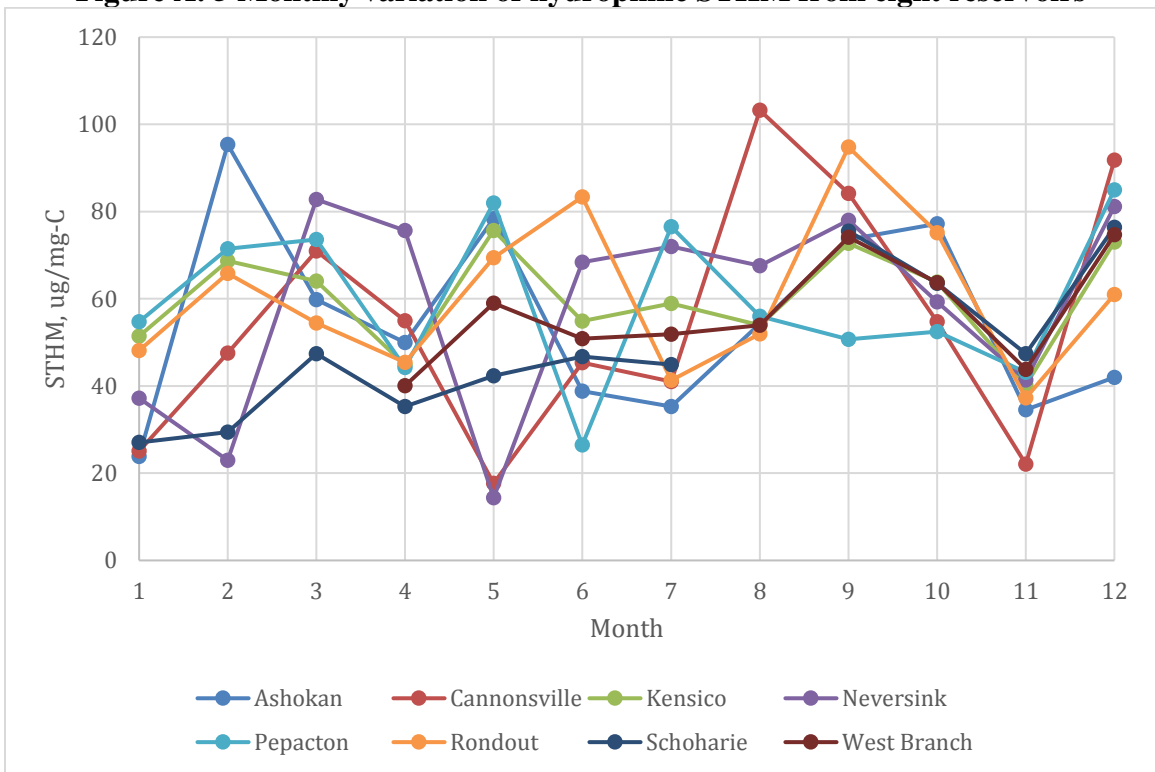


Figure A. 6 Monthly variation of hydrophobic STHM from eight reservoirs

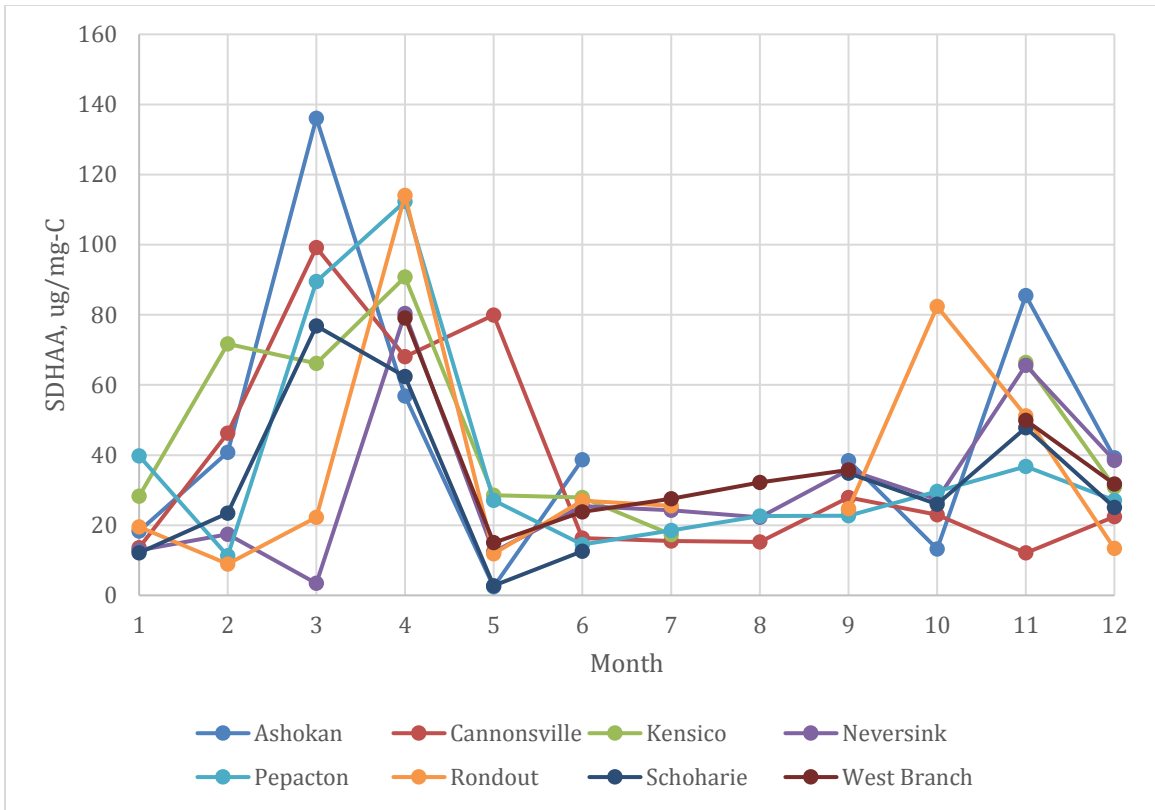


Figure A. 7 Monthly variation of hydrophilic SDHAA from eight reservoirs

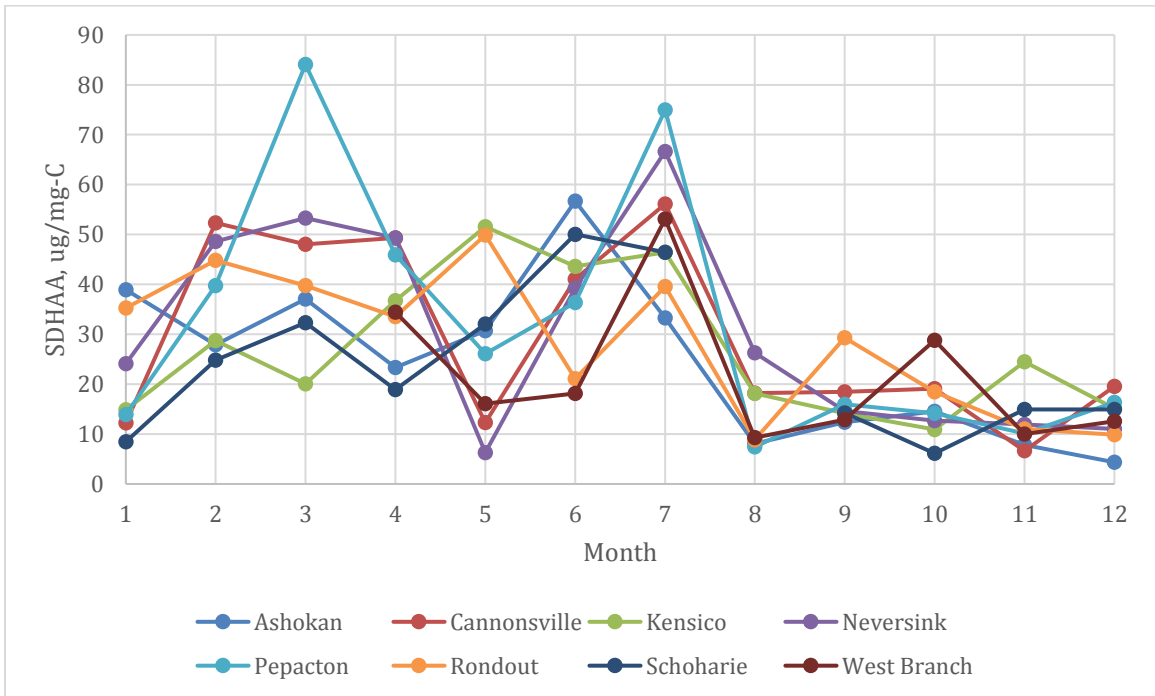


Figure A. 8 Monthly variation of hydrophobic SDHAA from eight reservoirs

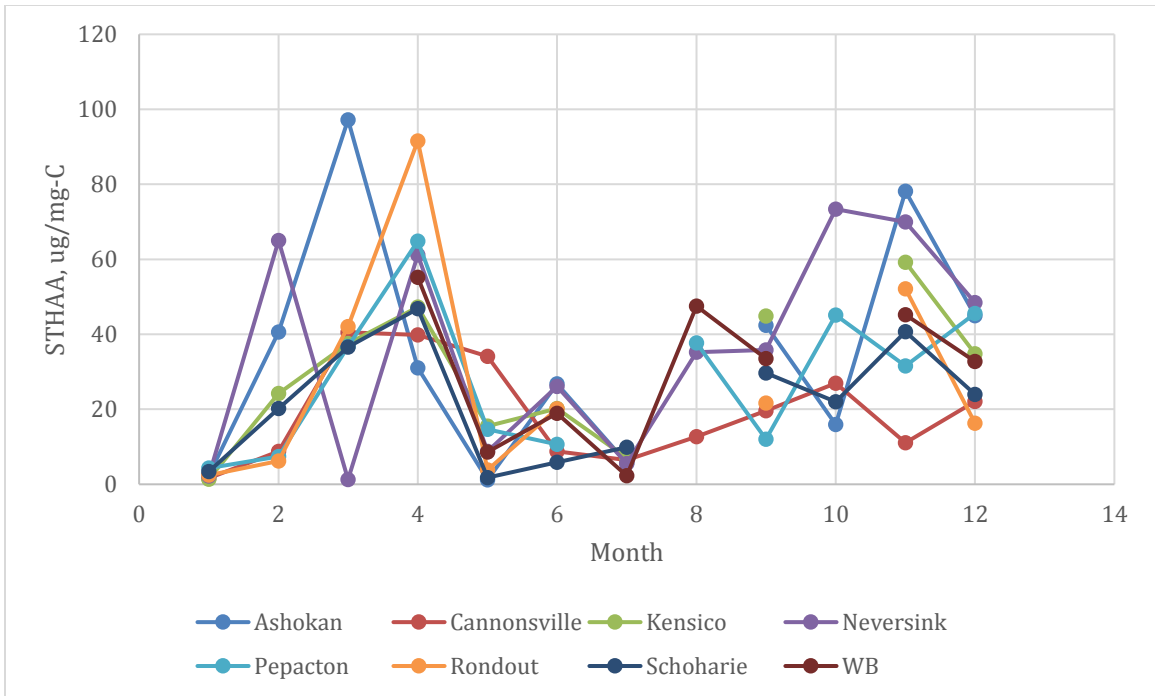


Figure A. 9 Monthly variation of hydrophilic STHAA from eight reservoirs

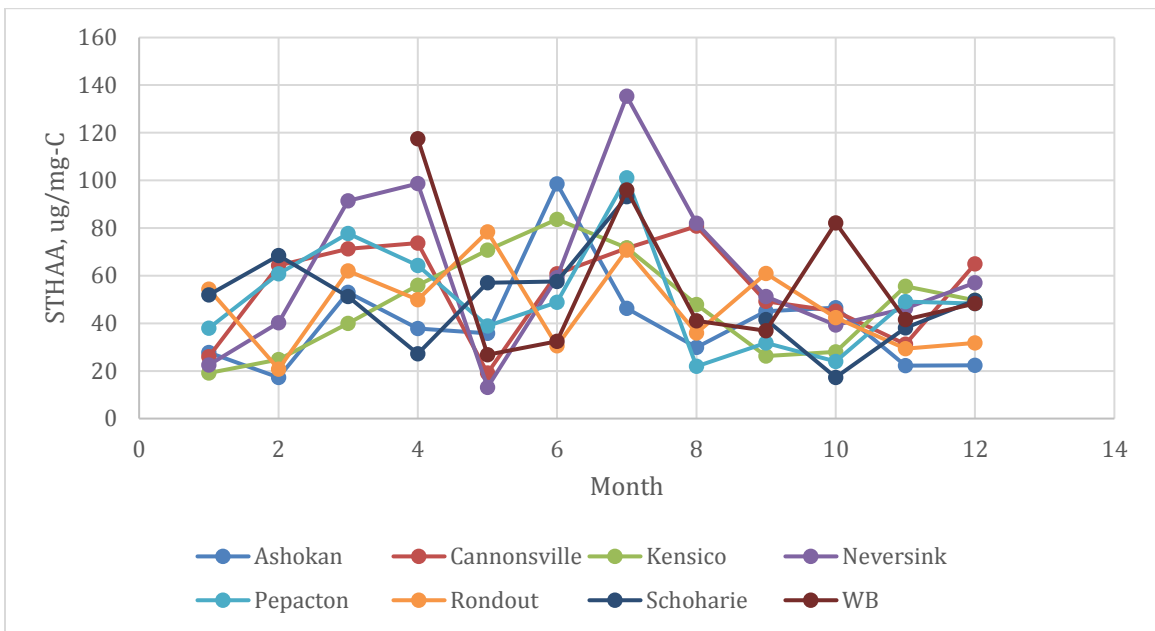


Figure A. 10 Monthly variation of hydrophobic STHAA from eight reservoirs

Table A. 1 DBP formation upon chlorination of organic compounds derived from plant leachate, sediment leachate, and algal cells. (Data from plant and sediment leachate were both collected after 8 days of incubation, chlorination at pH=7, reaction temperature =20°C, Cl₂ contact time = 7days; Algal data were adapted from data collected by Hong et al., 2008, chlorination at pH =7, reaction temperature =20°C, Cl₂ contact time = 3days)

NOM origin	Specific	CHCl ₃	DCAA	TCAA
		μg/mg-C	μg/mg-C	μg/mg-C
plant	Oak leaf-dark	136.5	66.7	140.3
plant	Oak leaf-light	138.3	61.9	133.6
plant	Oak leaf-dark-biocide	65.0	35.0	84.9
plant	Maple leaf-dark	146.8	35.1	122.2
plant	Maple leaf-light	150.6	62.5	187.0
plant	Maple leaf-dark-biocide	68.7	33.7	96.7
plant	Pine needle-dark	114.1	39.6	92.1
plant	Pine needle-light	102.3	30.0	69.1
plant	Pine needle-dark-biocide	81.5	29.7	65.4
sediment	anaerobic (0% sat.)	68.0	35.1	69.6
sediment	hypoxic (10% sat.)	62.3	33.7	51.9
sediment	hypoxic (20% sat.)	67.3	34.4	52.9
sediment	aerobic (97% sat.)	65.2	27.8	64.4
algal cell*	blue-green algal*	32.6	39.2	45.1
algal cell*	green algal*	42.3	33.8	38.6
algal cell*	diatom*	59.6	28.7	21.7

* Hong et al. (2008)

Table A. 2 Model parameters used to adjust DBP yields (Reckhow et al., 2008)

DBP group	Bromide (ug/L)		pH		Temperature (C)		Chlorine dose (mg/L)	Time (hr)
	Offset b	Exponent c	Offset d	Exponent e	Offset f	Exponent g	Exponent h	Exponent i
TTHM	1	0.036	-2.6	0.715	0	0.791	0.272	0.261
THAA	1	0.036	0	-1.495	0	0.307	0.378	0.188
DHAA	1	0.036	0	0.259	0	0.377	0.346	0.186

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