Disinfection Byproduct (DBP) Precursors In Central MA

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DISINFECTION BYPRODUCT (DBP) PRECURSORS IN A CENTRAL MA WATERSHED AND DBP OCCURRENCE IN MA WATER SUPPLIES

A Master’s Project

Presented by

CYNTHIA M. CASTELLON

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

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In

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September 2008

Department of Civil and Environmental Engineering
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Environmental Engineering
DEDICATION

To Jose Arturo and Janette Castellon, my parents.

To my brothers and sister, Jose, Ivis and Doris.

To Kevin.
ACKNOWLEDGMENTS

Work for this master’s project contributed to two separate studies. The first was a project funded by the Department of Conservation and Recreation (DCR) of the Commonwealth of Massachusetts to monitor the Wachusett Reservoir watershed for sources of disinfection byproduct (DBP) precursors. The second was a project funded by the National Cancer Institute (NCI) of the United States National Institutes of Health to recreate the water exposure history of a gall bladder cancer study group. The University of Massachusetts worked with the National Cancer Institute from 2005 through 2007 to recreate the water exposure history of their gall bladder cancer study group in Massachusetts. This is part of a larger study of the environment and health being conducted in Northern New England by Dartmouth Medical School, the National Institutes of Health, the Departments of Health in New Hampshire, Vermont and Maine and the U.S. Geological Survey. This team of researchers is conducting an epidemiological study to investigate the effect of arsenic, nitrate, and disinfection byproducts on gall bladder cancer incidence.

Thank you to my adviser Dr. David Reckhow for giving me the opportunity to study and work at the University of Massachusetts. Thank you to my co-adviser D. Paula Rees, and to the rest of the Civil and Environmental Engineering faculty for all of their advice, lessons, and support. A million thanks to the following people, who helped me in my laboratory and research work: Gladys Makdissy, Guanghui Hua, Boning Liu, Melissa Brown, Allan Briggs, Russell Adams, Junsung Kim, Safina Singh, Mat Suska, Ken Mercer, Amanda Keyes, and Kirsten Studer. Thank you to Jodi Ozdarski for always patiently answering all my questions. Thank you to the Environmental Engineering graduate students for making ELab II room 312 a fun place to work.
ABSTRACT

DISINFECTION BYPRODUCT (DBP) PRECURSORS IN A CENTRAL MA WATERSHED AND DBP OCCURRENCE IN MA WATER SUPPLIES

September 2008

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Directed by: Professor David A. Reckhow

Controlling disinfection byproduct formation is one of the biggest challenges facing drinking water providers. This report examines two issues regarding disinfection byproducts in public water systems: 1) watershed sources of DBP precursors and watershed characteristics, such as precipitation, season, and land use, which influence DBP formation; and, 2) factors, such as treatment practices, season, and raw water quality, that affect DBP formation at water treatment plants and in distribution systems. In order to analyze these issues, this project utilized two databases, one consisting of DBP precursor data from Wachusett Reservoir located in Central Massachusetts, and the other consisting of historical water treatment data and DBP concentrations from several communities in Massachusetts.

As such, this paper consists of an introductory chapter followed by two main chapters, each dedicated to analyzing one of the databases and each consisting of its own results and conclusions. With respect to watershed influences on DBP precursors, this study shows that: non-aromatic compounds may be significant sources of DBP precursors; DBP precursors and specific DBP-FP are highest during winter months; precipitation tends to favor THM formation rather than HAA formation; rainwater can be a significant source of DBP precursors; specific DBP-FP is significantly correlated with agricultural lands and wetlands (negative) and with urban areas (positive); DOC is significantly correlated with water areas (positive) and urban areas (negative); and, finally, riparian zones probably do not contribute the majority of DBP precursors. With respect to the occurrence of DBPs in public water systems, this study shows that: water sources high in TOC tend to universally filtered while low TOC sources tend to be treated without filtration or by direct filtration; alternative disinfectants are more effective when coupled with multiple precursor removal processes; free chlorine generally results in higher DBP concentrations regardless of precursor removal; ozone is very effective at minimizing DBPs but may result in other unwanted byproducts; high DBP concentrations are observed in systems with low TOC waters if precursor removal is minimal; THM concentrations are highest at water treatment plants during the fall while THM and HAA5 concentrations are highest in distribution systems during the summer; and, finally, DBP formation in distribution systems is considerable and a challenge to water systems.

A fourth chapter of this report examines the usefulness of utilizing results from both databases and the final chapter presents recommendations for future work.
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CHAPTER 1. INTRODUCTION

1.1. Introduction

Disinfection of drinking water is undeniably one of the most important public health advancements of the 20th century (Richardson, 2003). It has greatly helped reduce deaths and illnesses caused by waterborne pathogens in developed countries. Since the late 1970s, however, halogenated organics known as disinfection byproducts (DBPs) have been identified in chlorinated drinking waters (e.g. Rook, 1974). Research has since shown a strong connection between the presence of DBPs in finished drinking water and adverse human health effects such as bladder cancer. The presence of these harmful substances at consumer’s taps is of great concern to watershed managers, environmental officials, drinking water providers, and the general public.

Efforts to control formation of DBPs in municipal water systems have been stimulated by numerous federal regulations (including maximum contaminant levels and monitoring strategies), and many of these have led to the establishment of best treatment practices (such as enhanced coagulation and filtration to remove organic matter prior to disinfection). However, the potential to control watershed sources of compounds that lead to DBP formation (known as DBP precursors) is largely ignored by these measures. In order to develop DBP control strategies at the watershed scale it is necessary to understand how watershed characteristics (such as land use, precipitation, and climate) influence the nature and concentration of DBP precursors. This information can lead to the development of watershed strategies that can be coupled with water treatment practices in order to further reduce the incidence of DBPs. As such, it becomes important to also determine why municipal water
systems are still unable to control DBP formation at water treatment plants and in distribution systems. A critical look into what factors affect DBP formation in public water systems (such as raw water quality or climate) is required, as well as an investigation on the effectiveness (and ineffectiveness) of current treatment practices.

This study attempts to 1) understand the impact of watershed characteristics (such as land use and climate) on disinfection byproduct precursors and raw water quality, and 2) relate the incidence of disinfection byproducts in public water systems to level of treatment, raw water quality, and climate. Wachusett Reservoir, located in Central Massachusetts, and several Massachusetts’ municipal water systems serve as the study sites for this research. Figure 1.1 is a schematic of this project’s approach.

![Figure 1.1: Association between Study Components and Human Health Effects](Image)

Figure 1.1: Association between Study Components and Human Health Effects
1.1.1. **DBP Precursors in a Central MA Reservoir**

Wachusett Reservoir was selected as the target watershed for examining watershed sources of DBP precursors. The University of Massachusetts Amherst has been working with the Department of Conservation and Recreation to monitor Wachusett Reservoir for disinfection byproduct precursors from 2001 through 2007. Wachusett Reservoir, located in Central Massachusetts, is one of the water sources for the Massachusetts Water Resources Authority (MWRA), which supplies drinking water to 48 communities including greater Boston and the MetroWest areas. Since 2005 MWRA has been disinfecting their water sources with ozone, though in the past the primary disinfectant was chlorine (chloramines have been used as a secondary disinfectant since approximately 1932).

This half of the project consisted of sampling the eight main tributaries to Wachusett reservoir for natural organic matter content and disinfection byproduct formation potential. Natural organic matter reacts with disinfectants such as chlorine to produce disinfection byproducts. The focus of this study is to examine how watershed characteristics affect natural organic matter (and, subsequently, raw water quality) and DBP precursors.

1.1.2. **DBP Occurrence in Massachusetts Water Supplies**

Several water systems in Massachusetts were selected in order to examine the effect of treatment practices, raw water quality, and climate on DBP formation at water treatment plants and in distribution systems. In order to compare the effect of several different treatment practices on DBP concentrations, information regarding water sources and water treatment was collected for each system as far back as the 1980s. This time period coincides
with the historical DBP record maintained by the Department of Environmental Protection of Massachusetts for all public water systems.

This half of the project consisted of researching the historical development of 59 public water systems in Massachusetts. For each water system, the project documented what raw water sources were used, the time period during which each water source was used, and the level of treatment each water source received. The historical presence of disinfection byproducts and natural organic matter in each water system was also researched and documented. The focus of this study is to examine how treatment practices and raw water quality affect the occurrence of disinfection byproducts in drinking water systems.

1.2. Research Objectives

The following is a detailed list describing the proposed objectives for this master’s project, making use of the databases from the two previously described studies.

- To relate export of disinfection byproduct precursors to land cover at the watershed and reservoir scale.

- To characterize the impact of environmental and climactic factors on the export and concentrations of disinfection byproduct precursors at the watershed level.

- To understand the relationship between disinfection byproducts and raw water quality (i.e. the effect of natural organic matter characteristics such as concentration and aromaticity on DBP precursor concentrations).
To examine changes in disinfection byproduct levels at water treatment plants and in distribution systems due to different levels of treatment, raw water quality and season.

The overarching goal of this project is to utilize results from both studies in order to develop a meaningful understanding of the incidence of disinfection byproducts and how environmental and climactic factors, drinking water treatment processes, and raw water quality affect disinfection byproduct levels. These results may help drinking water providers in Massachusetts select or develop treatment practices that best comply with federal regulations, even as land uses and climate change.

1.3. Previous Work

Reckhow, Rees, and Bryan (2004) examined characteristics of DBP precursors at Wachusett Reservoir. In this study, they proposed that “freshly leached natural organic matter is relatively poor in DBP precursors due to the abundance of non-reactive carbohydrates” (Reckhow, et al., 2004). They also observed substantial release of DOC and precursors from leaf litter and significant increases in DOC and precursors (sometimes as much as an order of magnitude) as a result of fresh leachate loading from riparian wetlands during rain events.

Bryan (2005) examined changes in water quality parameters (such as total organic carbon, specific ultraviolet absorbance, and disinfection byproduct formation potential) in the different tributaries to Wachusett Reservoir with respect to discharge, temperature, and season: “spatial, temporal, and seasonal variations in precursor and DBP formation potential levels in the Wachusett Reservoir watershed were evaluated in order to better understand critical characteristics of this particular watershed. In addition, laboratory generation of
aquatic precursors using plant material from the Wachusett watershed was performed” (Bryan, 2005).

1.4. Background

The following section contains general information on natural organic matter and disinfection byproducts, including NOM composition, NOM transport and decay processes, DBP formation and classification, DBP control strategies, NOM reactivity with chlorine, and, finally, DBP regulations of interest to municipal water systems.

1.4.1. Natural Organic Matter

Natural organic matter (NOM) is a combination of various dissolved and particulate organic compounds originating from plant, animal, and microbial tissue. Collectively, these organic compounds are referred to as Total Organic Carbon (TOC). The subset of TOC that is dissolved is referred to as Dissolved Organic Carbon (DOC). DOC is the fraction not retained on a 0.45 µm pore-size filter (Wetzel, 2001). DOC accounts for approximately 83 to 98% of TOC in most natural fresh waters (Owen et al., 1995).

The organic compounds that make up total organic carbon include fats, waxes, terpenoids, tannins, lignins, cellulose, hemicelluloses, protein, sugars, and starches (Wetzel, 2001). Each of these compounds can exist at different abundances and with different biodegradation rates. These organic compounds can be classified as humics and non-humics. Non-humic compounds include low molecular weight compounds such as carbohydrates, proteins, amino acids, peptides, fats, waxes, resins, and pigments, which are easily
biodegraded by enzyme-producing microorganisms (Wetzel, 2001). Non-humic compounds fluctuate rapidly, with lifetimes of a few minutes to a few hours, resulting in the accumulation of recalcitrant humic compounds (Wetzel, 2001). Humic compounds include moderate to high molecular weight compounds such as lignins, terpenoids, and cellulose, which are aromatic recalcitrant compounds that account for most of the natural organic matter in surface waters (Wetzel, 2001). They are responsible for most of the color in waters, ranging from yellow to black (Wetzel, 2001).

Natural organic matter transport to water bodies occurs in several different ways with the five main transport mechanisms being direct transport to streams, overland flow, flow from littoral zones, flow from wetlands, and subsurface or groundwater flow. Direct transport may include leaves and plants from overhanging canopies being deposited in the stream and leaching organic material (Wetzel, 2001). Overland flow includes rainfall flushing organic carbon from nearby land surfaces and runoff carrying organic carbon to receiving streams and lakes (Meyer, 1990). Flow from littoral zones includes organic carbon deposited on stream shores and flushed into the stream (Meyer, 1990). Flow from wetlands will contribute DOC from organic soils and woody materials (Hemond, 1990; Meyer, 1990), whereas subsurface or groundwater flow contains organic materials that have leached through the soil (Wetzel, 2001).

Loss of natural organic matter will also occur in natural waters, either from precipitation, microbial degradation, or ultraviolet radiation. Precipitation can lead to absorption of DOC onto soils and sediments suspended in the water, such as clays (Meyer, 1990; Wetzel, 2001). As mentioned previously, certain organic compounds are more susceptible to biodegradation than others. Well-defined biochemicals like sugars, starches,
and proteins are the most biodegradable due, in part, to their ordered and enzymatically mediated synthesis, while woody substances such as cellulose and lignin are the least biodegradable due to their high molecular weight and somewhat disordered structure (Thurman, 1985). Biodegradation rates increase when DOC is exposed to sunlight, thus ultraviolet radiation is likely to facilitate the biodegradation process (Wetzel, 2001).

1.4.2. Disinfection Byproducts

Since 1971 there has been research conducted on the presence of volatile halogenated organics in chlorinated drinking water (Rook, 1974; Symons, 1999). Known as disinfection byproducts (DBPs), they are compounds that form from the reaction of chlorine and bromine with naturally occurring organic matter. Toxicological studies have concluded that some disinfectants and disinfection byproducts have been shown to cause cancer and reproductive effects in lab animals and epidemiological studies have suggested they are associated with bladder cancer and reproductive effects in humans (U.S. EPA, 2001). Given that disinfection is necessary in order to reduce the risk of illnesses caused by waterborne pathogens, DBP control strategies focus on removing DBPs (through adsorption to granular activated carbon or gas stripping, for example) or removing precursors that lead to DBPs prior to disinfection (through coagulation and filtration, for example).

Disinfection byproducts are defined as the group of organic and inorganic compounds that are formed during disinfection (Xie, 2003). Currently, four groups of DBPs are regulated by US EPA include trihalomethanes (THMs), haloacetic acids (HAAs), chlorite, and bromate. However, this is only a subset of the known DBPs. According to Xie, known DBPs are
grouped based on molecular structure, and formation and chemical properties into the following six groups:

Group 1: Trihalomethanes, consisting of a base methane molecule with halogen atoms substituting three of the four hydrogen atoms constitute the first group. Halogen substituents that have been identified are chlorine, bromine and iodine. Common THMs include trichloromethane (CHCl$_3$) (also called chloroform), bromodichloromethane (CHBrCl$_2$), chlorodibromomethane (CHBr$_2$Cl), and tribromomethane (CHBr$_3$) (also called bromoform).

Group 2: Haloacetic acids, consisting of an acetic acid molecule with halogen atoms substituting the hydrogen atoms located next to the COOH group, constitute the next category. Halogen substitutes that have been identified include chlorine and bromine. HAAs are grouped into three categories: monohaloacetic acids (CH$_2$XCOOH) with one halogen atom, dihaloacetic acids (CHX$_2$COOH) with two halogen atoms, and trihaloacetic acids (CX$_3$COOH) with three halogen atoms. These three groups have significantly different chemical and biological properties.

Group 3: Inorganic DBPs make up the third group, including two that are regulated by US EPA (chlorite (ClO$_2^-$) and bromate (BrO$_3^-$)). Chlorite is the product of reactions between chlorine dioxide and NOM while bromate is the product of reactions between bromide and ozone.

Group 4: Other Halogenated DBPs, which include trichloroacetaldehydes and brominated analogues, haloacetonitriles, haloacetones, trihalonitromethane, and cyanogen halides, are the fourth group.
Group 5: Ozonation DBPs, which include products formed from the reaction between ozone and NOM, are the fifth category. Three common types are aldehydes, ketoacids, and carboxylic acids.

Group 6: N-Nitrosodimethylamine (NDMA) is a semi-volatile organic compound that has been found in drinking water and wastewater, though there is little information on the formation of NDMA in drinking waters. It is believed to be a byproduct in chloraminated water.

Xie stresses that the formation of DBPs is not due to a reaction between methane and chlorine in the case of THMs, or between acetic acid and chlorine in the case of HAAs. DBPs are the product of complex reactions between NOM, disinfectants (such as chlorine), and bromine. Formation of disinfection byproducts can be summarized by the following equation (Singer, 1994):

\[ \text{HOCl}^- + \text{Br}^- + \text{NOM} = \text{Trihalomethanes} + \text{Haloacetic Acids} + \text{Other Halogenated DBPs}. \]

There are over 500 known disinfection byproducts (Richardson, 2003). However, 50% of all total organic halides formed during chlorination cannot be accounted for in the known DBPs (Richardson, 2003). Consequently, little is known about the carcinogenic or toxic effects of many DBPs that are present in finished drinking water (Richardson, 2003).

The speciation and concentration of DBPs in drinking water is affected by natural organic matter, chlorine residual, reaction time, inorganic bromide, and pH (Xie, 2003):

- Different fractions of NOM (including humic acids, fulvic acids, hydrophobic acids, hydrophobics neutrals, transphilic acids, transphilic neutrals,
hydrophilic acids, and hydrophilic neutrals) yield different amounts of DBPs under the same chlorine conditions.

- Increasing the chlorine dosage tends to increase the formation of DBPs.

- Formation of THMs and HAAs generally increases with increasing reaction times.

- In general, low pH leads to higher HAAs while high pH leads to higher THMs.

- Bromide itself does not react with NOM, but it reacts with chlorine and ozone to form hypobromous acid and hypobromite. These react with NOM to form brominated DBPs.

Formation of DBPs can be controlled by several means: removal of DBP precursors, reducing reactivity of precursors through the use of alternative disinfectants, and removal of DBPs after formation. Some effective treatment methods for controlling DBP formation include enhanced coagulation, granulated activated carbon (GAC) adsorption, alternative disinfectants (chloramines, ozone, chlorine dioxide, ultraviolet radiation), changing the disinfectant injection point (from prechlorination to postchlorination), biologically active carbon, and membrane filtration (Xie, 2003). Source control can also be a major factor for reducing precursors before they reach treatment plants, provided that the origin and nature of precursors is well understood. Source control is particularly important because precursor removal processes in water treatment plants may be limited in their effectiveness, given a specific water quality.
1.4.3. DBP Formation: Reactivity of NOM with Chlorine

The primary precursor to DBPs is natural organic matter. While the concentration of NOM affects the formation of DBPs (usually higher concentrations of NOM yield higher concentrations of DBPs), the structural characteristics of NOM also impact its reactivity with chlorine. Aromatic and humic NOM compounds are more reactive with chlorine than other NOM fractions and will therefore yield higher DBP concentrations. For this reason, both total organic carbon (an indicator of the amount of NOM) and ultraviolet absorbance at 254 nm (an indicator of the structural features of NOM compounds) are used together as an indicator of DBP formation potential called the specific UV absorbance, or SUVA (Xie, 2003):

\[
\frac{UV_{absorbance} \cdot (m^{-1})}{TOC \cdot (mg / L)} = SUVA \cdot \left(\frac{L}{m \cdot mg}\right)
\]

(1.1).

UV absorbance increases with increasing amount of aromatic and humic organic carbon, the type of organic carbon that yields disinfection byproducts. For a given TOC concentration, as the amount of aromatic NOM increases, the UV absorbance increases and therefore SUVA also increases (from Equation 1.1). Thus higher SUVA values are indicative of aromatic and humic NOM compositions that yield higher DBPs.

The appropriateness of SUVA as a surrogate parameter for DBP formation potential has been debated and questioned (Bryan, 2005). However, it is generally agreed upon that the structural composition and relative concentrations of different NOM fractions affect DBP formation, with certain NOM fractions yielding more DBPs than others. Another intensive property that can reflect the quality of NOM and not just the quantity is the specific disinfection byproduct formation. Similar to SUVA, it is the absolute DBP formation potential normalized to 1 mg/L of TOC. This ratio has also been described as a precursor
yield, representing “the potency of NOM” as a source for DBP precursors (Stepczuk et al., 1998).

1.4.4. DBP Regulations of Interest to Municipal Water Systems

Since the United States Congress passed the Safe Drinking Water Act in 1974, the United States Environmental Protection Agency (US EPA) has established rules and guidelines for drinking water systems in order to protect the public against naturally occurring and man-made contaminants. Table 1.1 contains rules published by EPA since 1989, which address microbial contamination in drinking water systems. The “Surface Water Treatment Rule” of 1989 stated that in order to “assure adequate microbial protection in the distribution system, water systems are required to provide continuous disinfection of the drinking water entering the distribution system and to maintain a detectable disinfectant level within the distribution system” (EPA, 1989). Subsequently, the EPA has also set forth several rules that address the public’s risk of exposure to disinfection byproducts (Table 1.2). Currently, microbial and disinfection byproduct rules go hand in hand and careful balancing is needed in order to comply with both rules.
<table>
<thead>
<tr>
<th>Regulation</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Coliform Rule (1989)</strong></td>
<td>Established maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs) for total coliform levels in drinking water based on the number of samples collected per month, applicable to systems of all sizes.</td>
</tr>
<tr>
<td><strong>Surface Water Treatment Rule (1989)</strong></td>
<td>Requires systems to provide 99.9% (3-log) combined removal and inactivation of <em>Giardia</em> and 99.99% (4-log) of viruses, using combinations of filtration and disinfection. Combined filter water must be less than 0.5 NTU in at least 95% of measurements, never higher than 5 NTU, applicable to systems of all sizes.</td>
</tr>
<tr>
<td><strong>Interim Enhanced Surface Water Treatment Rule (1996)</strong></td>
<td>Requires systems serving 10,000 or more people to provide 99% (2-log) removal of <em>Cryptosporidium</em> through filtration. Strengthens turbidity requirements, where combined filter effluent must be less than 0.3 NTU in at least 95% of measurements, never higher than 1 NTU.</td>
</tr>
<tr>
<td><strong>Filter Backwash Recycling Rule (2001)</strong></td>
<td>Requires that recycled filter backwash be returned to a point in the treatment process such that all processes of the system’s conventional or direct filtration are employed, applicable to system of all sizes.</td>
</tr>
<tr>
<td><strong>Long Term 1 Enhanced Surface Water Treatment Rule (2002)</strong></td>
<td>Requires systems serving less than 10,000 people to provide 99% removal of <em>Cryptosporidium</em>, and a combined filter effluent less than 0.3 NTU in at least 95% of measurements, never higher than 1 NTU.</td>
</tr>
<tr>
<td><strong>Ground Water Rule (2006)</strong></td>
<td>Requires periodic sanitary surveys of groundwater systems, source water monitoring to test for presence of <em>E. coli</em>, enterococci or coliphage, corrective actions for systems with source water fecal contamination, and compliance monitoring to assure treatment technologies meet 99.99% combined inactivation and removal of viruses.</td>
</tr>
<tr>
<td><strong>Long Term 2 Enhanced Surface Water Treatment Rule (2006)</strong></td>
<td>Established monitoring schedule for detection of <em>Cryptosporidium</em> applicable to systems of all sizes, four treatment categories (bins) with varying degrees of treatment requirements, 2 to 3-log inactivation of <em>Cryptosporidium</em> for unfiltered systems, and inactivation requirements of 4-log for viruses, 3-log for <em>Giardia</em>, and 2-log for <em>Cryptosporidium</em> for systems storing water in open reservoirs.</td>
</tr>
</tbody>
</table>
Table 1.2: EPA Regulations Regarding DBPs

<table>
<thead>
<tr>
<th>Regulation Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total Trihalomethane Rule (1979)</strong></td>
<td>Established interim maximum contaminant level (MCL) of 100 µg/L for total trihalomethanes, as a running annual average of the quarterly averages of all samples collected at various points within the distribution system, for community water systems using surface or groundwater and serving at least 10,000 people and using a disinfectant at any point in the treatment process. In 1983, best technologies for removal were promulgated, including chloramination, precursor removal through improved clarification, eliminating prechlorination or using activated carbon.</td>
</tr>
<tr>
<td><strong>Information Collection Rule (1996)</strong></td>
<td>Established in order to collect information on the occurrence and control of pathogens and DBPs in drinking water, applicable to surface water systems or groundwater systems serving more than 100,000 people and to groundwater systems serving 50,000 to 100,000.</td>
</tr>
<tr>
<td><strong>Stage 1 Disinfectants and Disinfection Byproducts Rule (1999)</strong></td>
<td>Applicable to all sizes of community water systems that add a disinfectant, established MCLs of 80 µg/L for total trihalomethanes and 60 µg/L for total haloacetic acids as a running annual average for all monitoring locations in the distribution system. Also contains regulations for DBP monitoring and reporting, best available technologies for DBP control, and enhanced coagulation provisions.</td>
</tr>
<tr>
<td><strong>Stage 2 Disinfectants and Disinfection Byproducts Rule (2006)</strong></td>
<td>Builds upon Stage 1 Rule to reduce exposure to peak DBP levels in distribution systems, changes MCL compliance based on the running annual average measured collectively at all monitoring locations in the distribution system to compliance based on a running annual average for each location in the distribution system. Requires water systems to first identify points in the distribution system with high DBP occurrence.</td>
</tr>
</tbody>
</table>
CHAPTER 2. DBP PRECURSORS IN WACHUSETT RESERVOIR

2.1. Background on NOM and DBPs

As discussed in Chapter 1, disinfectants can react with naturally occurring organic matter to form disinfection byproducts (DBPs), some of which are known human carcinogens. Disinfection byproduct mitigation efforts consist of removing DBPs at the end of the water treatment process (through granular activated carbon or gas stripping), removing precursor material (through filtration and enhanced coagulation) prior to disinfection, or using disinfectants that are less reactive with NOM.

Alternatively, organic matter could be controlled at the source before it reaches water treatment plants. In order for best management practices to be implemented with this goal in mind, a deeper understanding of the nature of DBP precursors (including their origin and composition) is needed. This will involve examining the relationship between DOC (a common NOM surrogate) and subsequent DBP formation.

A first step is to examine the relationship between DOC, DBP-FP precursors and specific DBP-FP (DBP-FP on a per carbon basis). It is usually observed that DOC and DBP concentrations are positively correlated. However, there are indications that DOC quantity alone is not a good indicator of DBP-FP, but that DOC quality (i.e., reactivity) is also important. As discussed in Section 1.4.3, the specific DBP-FP (DBP-FP on a per carbon basis), and the specific UVA (UVA on a per carbon basis, or SUVA) are two parameters that reflect the reactivity of DOC with chlorine. Specific UVA reflects the aromaticity of DOC (higher SUVA values indicate DOC with higher aromatic content and, therefore, higher
propensity to form DBPs) while SpDBP-FP reflects the NOM reactivity (higher SpDBP-FP values indicate NOM with higher reactive carbon content and, therefore, higher propensity to form DBPs). A generally accepted conceptual model for DBP formation is that aromatic carbon is the main source of DBP precursors (Fujii, et al., 1998). For example, a previous study conducted at the University of Massachusetts Amherst for samples collected in the Quabbin Reservoir revealed a weak positive correlation between SpTHM-FP and SUVA (Garvey and Tobiason, 2003).

However, in a study conducted in an agricultural field in the Sacramento-San Joaquin Delta in California, Fujii et al. (1998) reached the conclusion that “dissolved organic carbon aromaticity appears unrelated to trihalomethane formation on a carbon-normalized basis,” even though correlations between DOC, UVA, and THM-FP were positively significant. Their study found no significant correlation between SpTHM-FP (HAA-FP was not measured) and SUVA, indicating that DOC aromaticity was not enough to explain THM precursors. They cite a study by Owen and others (1993) that also observed no correlation between DOC aromaticity and SpTHM-FP, concluding that their results are “somewhat contrary to conventional wisdom… namely that it is the humic fraction that serves as DBP precursor material.”

This is not to say that SUVA is not a good indicator of DOC aromaticity. As Weishaar et al. (2003) report, SUVA “is strongly correlated with percent aromaticity as determined by $^{13}$C NMR spectroscopy for 13 organic matter isolates obtained from a variety of aquatic environments (marine to dark water rivers)...which are representative of aquatic humic substances evolved from a variety of source materials.” However, in their study SUVA did prove to be a weak indicator of DOC reactivity (i.e. it was weakly correlated with THM-FP on
a per carbon basis). Weishaar et al. (2003) observed a wide range of DOC reactivity with chlorine for samples with similar SUVA values and suggest that compositional differences in DOC from different sources are not reflected in the SUVA values, even if aromaticity is. This study did not consider HAA precursors.

Likewise, Stepczuk et al. (1998a) found no correlation between SpTHM-FP and DOC, indicating that DOC concentration was not enough to explain specific THM precursor content. These results seem to suggest that DOC compounds other than aromatics might be significant DBP precursors and, more generally, that variability in DOC quality and composition leads to variability in DBP formation. Therefore, it becomes necessary to examine what factors lead to variability in DOC composition and DBP precursors.

To such end, several studies have examined the impact of land use and land cover on DBP precursors, but “attempts to develop statistically significant land use export coefficient models for precursors have not been successful” (Reckhow et al., 2004). Similarly, season and precipitation can be expected to affect the nature and composition of NOM and DBP precursors. It is these relationships between NOM, DBP precursors, season, precipitation, and land use that are explored in this paper.

In a study examining different DBP predictive models that have been developed over the years, Sadiq and Rodriguez (2004) note that these models have usually included TOC and DOC concentrations, UVA, pH, water temperature, concentration of bromide ion, chlorine dose, and chlorine reaction time as parameters. However, the effects of environmental and climatic factors on DBP levels have also been examined, even if not from a modeling approach.
Stepczuk et al. (1998a) cite studies where seasonal effects on THM precursors were noted, including increased precursor concentrations during fall wet periods and spring snowmelt (Veenstra and Schnoor, 1980), low precursor concentrations in winter and maximum levels in summer (Veenstra and Schnoor, 1980), and precursor peaks during fall and winter wet events (Palmstrom, 1988). Stepczuk and coworkers (1998a) note that in these studies “seasonal changes in TOC concentrations…remained small, suggesting a dependence of precursor production on the nature, rather than simply the quantity, of NOM.” In these studies, wet events (or storm flow periods) contained precursor peaks. In a three-year study conducted at the Chickahominy River Basin in Virginia, Speiran (2000) observed decreases in DOC and DBP precursor concentrations of as much as 50% during base flow events, while peak values of DOC and DBP precursor concentrations were observed during storm flow periods. It is likely that DOC sources are limited to groundwater discharge and riparian litter during base flow periods, but during wet events infiltrating precipitation leaches DOC and DBP precursors from organic litter distributed across the watershed (Speiran, 2000). The UMass Amherst study of Quabbin Reservoir also noted seasonal variations, including increased THM precursors during spring and summer compared to winter (Garvey and Tobiason, 2003).

A recent study by Uyak et al. (2008) commented on the seasonal changes in precursor quality and the effect on formation potential, noting that for three Istanbul surface water reservoirs “the reactivity (specific DBP-FP) of the organic matter changed throughout the year with the lowest reactivity in winter, increasing in spring and reaching a maximum in fall season.” Stepczuk et al. (1998a) also describe seasonal effects on DBPs and DBP precursors observed at their study site at the Cannonsville Reservoir in New York, including: 1) lower
THM-FP concentrations in winter and spring; 2) increases in DOC concentrations during fall events (up to 8 mg/L) accompanied by decreases in specific THM-FP, but an overall lack of correlation between DOC and SpTHM-FP; 3) increases in DOC concentrations during fall events that were not accompanied by similar increases in THM-FP, “indicating a reduced potency of the NOM as a source for precursors;” 4) and, in general, fall wet events with higher concentrations of NOM and THM precursors than spring events, likely influenced by the supply of NOM (fallen leaves in autumn) and microbial metabolic activity driven by temperature. In a Water Resources Investigation Report prepared for the city of Cambridge, Massachusetts, Waldron and Bent (2001) of the US Geological Society studied the water quality of three surface water reservoirs over the course of one year. Their study did not examine seasonal effects to great length, but they did note that dissolved organic carbon concentrations “increased somewhat during the summer months and decreased in the autumn and winter” (Waldron and Bent, 2001).

While some studies allude to variations in NOM, DBP precursors, and DBP reactivity as a result of precipitation and related processes (such as runoff and organic matter leaching during storms), few examine rainwater itself as a source for these compounds. Most studies that examine the incidence of dissolved organic carbon in rainwater stem from disciplines related to atmospheric science. Most studies in these fields seek to identify the sources of atmospheric DOC (anthropogenic vs. natural or terrestrial vs. marine, for example). To such end, several studies have measured dissolved organic carbon concentrations in rainwater samples, uninterrupted by forested canopies. Results from some of these studies include: 1) DOC concentrations ranging from 0.06 to 2.86 mg/L (with DOC concentrations increasing towards the end of the storm) during tropical storm Ernesto when it made landfall over North
Carolina in 2006 (Miller et al., 2008); 2) DOC concentrations averaging 7.14 ± 0.31 mg/L in a mangrove forest in Belize (rainfall samples captured in an open field) (Wanek, et al., 2007); 3) DOC concentrations ranging from 1.58 to 6.48 mg/L at the campus of the University of North Carolina in Wilmington during five different storm events (Avery, et al., 2006); 4) DOC concentrations ranging from 0.12 to 4.81 mg/L during storms over the course of one year at Dunedin, New Zealand (Kieber, et al., 2002); and, 5) DOC concentrations ranging from 1.14 to 2.38 mg/L (TOC concentrations ranging from 1.2 to 2.5 mg/L) in rainwater samples collected during the western Pacific Ocean cruise of R/V Hakuho-Maru (Sempere and Kawamura, 1996). No studies were found where rainwater samples were measured for DBP precursors or DBP yields.

Some studies have also examined environmental factors that may affect DBP formation, namely land use and soil characteristics. In a study conducted at the Sacramento and San Joaquin Rivers in California, Chow et al. (2007) evaluated the quantity and quality (reactivity in forming DBPs) of DBP precursors in the two watersheds. They determined that DOC concentrations correlated significantly and positively with agricultural land, wetland, and grassland ($r^2 = 0.30, 0.27, \text{ and } 0.63$, respectively), and DOC concentrations were strongly negatively correlated with forest cover ($r^2 = 0.67$). There was no significant relationship between DOC concentration and urban area, chaparral, or other categories. “These results suggest that lowland land-cover types (agricultural land and wetlands) contribute more DOC on a per-area basis than upland land-cover types (forests)” (Chow et al., 2007). They also found strongly positive correlations between DOC and THM-FP for both watersheds, but significantly different slopes between the two linear regressions, which suggest that the water sources impacted THM formation. However, Chow et al. (2007) concluded that SUVA, and
therefore DOC quality, were similar for both rivers and attribute the significantly different
THM-FP reactivity to higher concentrations of bromide ion in one river versus the other.

A study by Kaplan et al. (2006) also examined the effect of land use on organic matter
quality in 60 streams supplying New York City drinking water watersheds. The study
revealed distinct regional differences that were related to differences in land use: “percent
agriculture land use in streams west of the Hudson River, and point source discharge and
percent wetland land use in streams east of the Hudson River were the primary land use
characteristics that influences concentrations of OM in the study streams.” Kaplan et al.
(2006) conclude that OM concentrations were related to human activities, which validates
addressing human impacts at the watershed scale in order to improve water quality. However,
this study did not examine DBPs or DBP precursors.

A recent study by Fleck et al. (2007) examines the effect of peat soils under different
management conditions on DOC and THM-FP in California’s Sacramento-San Joaquin Delta.
DOC measurements extracted from peat soils at a constructed wetland and at two agricultural
fields indicated that “the prior history of the soil (length of time since first agricultural use,
abundance of new organic carbon inputs, and oxidation state) all affected the DOC
concentration, aromaticity, and propensity to form THMs.” They found that DOC from the
constructed wetland had a higher propensity to form THMs than DOC from the agricultural
fields. A previous study by Krasner et al. (1994) conducted at the same Delta also observed
wetlands and agricultural peat soils to be significant sources of THM precursors, as well as
HAA precursors. Similarly, Stepczuk et al. (1998a) cite a survey study conducted by Randkte
et al. (1987) that observed higher THM precursor concentrations in agricultural runoff than
urban runoff, as well as other studies that also point to agricultural activity as a source of THM precursors (such as Amy et al. 1990 and Morris and Johnson, 1976).

In the USGS report prepared for Cambridge, Massachusetts, Waldron and Bent (2001) preformed a correlation analysis between water quality parameters (including DOC and THMs, among others) and sub-basin characteristics (including percent area coverage of 28 land-use, land cover, topographic, and geologic features). Their analysis did not find any significant correlation between THM-FP concentrations and any of the sub-basin characteristics (Waldron and Bent, 2001). However, their study did find a significant positive correlation between DOC concentration and percent coverage of forested wetlands. They also identified a significant positive correlation between DOC concentration and percent coverage of fine-grained deposits, but they attribute this relationship to a disproportionately large yield of DOC (“two to three times greater” than any other sampling location) measured at an outlet to a mostly forested wetland watershed with fine-grained deposits (Waldron and Bent, 2001). The largest median concentrations of DOC occurred at an outlet that “drains a large red maple swamp” while the smallest median concentrations occurred at an outlet that “drains a sub-basin with large amounts of paved area and almost no wetland” (Waldron and Bent, 2001). The sub-basin identified as containing large amounts of paved area had the highest concentrations of THM-FP measured, but the sub-basin with the large percent wetland cover had the highest yields of THM-FP (yield being the mean daily load normalized to the sub-basin area) (Waldron and Bent, 2001).

To summarize, studies have identified land use categories that are likely to produce high DBP concentrations (agriculture was identified by Chow et al., 2007 and Randkte et al., 1987), high DOC concentrations (agriculture, wetlands, and forested wetlands were identified
by Chow et al., 2007, Kaplan et al., 2006, and Waldron and Bent, 2001), and increased DBP reactivity (wetlands were identified by Fleck et al., 2007). This study can further explore, and contribute to, these observations. However, those studies considered the full watershed area that drained into their sampling locations. Arguably, rivers and streams are likely to receive most of their DBP precursor and DOC loads from riparian zones. As discussed in Section 1.4.1 (and in greater detail in Bryan, 2005), riparian zones can be significant sources of natural organic matter. Therefore, it is worth examining how land use in the riparian zone contributes to DBP precursors compared to land use in the full watershed.

Also, studies examining the impact of season on DBP precursors and DOC have produced contradictory results (for example, some report increased activity during the fall and others report the least activity in fall). Location likely contributes to opposing results. Therefore, it is important to understand seasonal impacts when characterizing watershed sources of DBP precursors for the particular watershed, as this information may be unique to the watershed but applicable to other watersheds with identical or similar seasonal patterns. Furthermore, seasonal effects on HAA precursors at the watershed scale have not been directly studied. Regarding the effect of precipitation, several studies have observed increased DOC and DBP precursor concentrations during wet events. However, no study has considered the role of rain water as a potential source of DBP precursors.

It is also important to note that some studies (Fujii et al., 1998, Owen et al., 1995, and Stepzcuk et al., 1998a) have raised the question of whether DOC concentration and aromaticity impact DBP formation on a per carbon basis. It is an issue that calls for further analysis. Finally, while some researchers have examined these issues with respect to HAA
precursors, in general there is little work available examining HAA precursors and specific HAA formation.

2.2. Objectives for Wachusett Reservoir Study

The objective of this study is to contribute more data to the Wachusett Reservoir database and to utilize it to better understand the effects of organic carbon and watershed characteristics on DBPs (the database consists of dissolved organic carbon and disinfection byproduct formation potential measurements from water samples taken at 19 locations throughout the Wachusett Reservoir from 2001 through 2007). Specifically, this chapter will examine whether riparian zone land use percentages are better indicators of different NOM compositions and DBP precursors than the full watershed’s land use percentages, while also examining how season and precipitation affect precursor content. With respect to precipitation effects, this study will examine the role of rainwater itself as a source of DBP precursors. Unlike previous studies that have focused mainly on THM-FP, this study will also examine HAA precursors. The extent to which DOC quantity and quality affect DBP formation is also considered.

This Chapter is arranged into two parts. The first part is an analysis of disinfection byproduct precursors and their effect on DBP levels, regardless of watershed characteristics. In order to better analyze the effect of precursor material (namely dissolved organic carbon (DOC)) on DBP levels, a DOC variability experiment was devised in which the composition of the DOC was constant but the DOC concentration was variable. Subsequently, DBP formation was tested as a function of chlorine dose and DOC concentration. This experiment coupled with the Wachusett data is examined in order to understand DBP precursor
characteristics. The second part focuses on how environmental and climatic factors (including season, precipitation, and land use) affect DOC and DBP formation in the Wachusett Reservoir.

Another component of the field study consisted of sampling soil water via lysimeters at different locations throughout the watershed over the course of two years. While this information was outside the scope of the research objectives described above, it is included for documentation purposes as Appendix A. Appendix A describes the soil water sampling methods, presents the results, and discusses problems encountered during sampling.

2.3. Materials and Methods

The following is a description of: 1) the sampling campaign undertaken at Wachusett Reservoir for the period of study (2001-2007); 2) the DOC variability test designed to study the effect of DOC concentration on DBP levels; 3) the laboratory methods for the analysis of dissolved organic carbon, total organic carbon, ultraviolet absorbance, sample chlorination, chlorine residual measurements, and extraction of trihalomethanes and haloacetic acids; 4) data analysis calculations such as SUVA and specific DBP-FP; and 5) the spatial analysis of land use in Wachusett watersheds using ArcGIS.

2.3.1. Wachusett Sampling Campaign

Wachusett Reservoir is one of two drinking water sources for the Massachusetts Water Resources Authority (MWRA), the other being the Quabbin Reservoir. Wachusett is located approximately 35 miles west of Boston (Fig. 2.1). First filled in 1908, it receives water from
the Quabbin Reservoir aqueduct and has a 65 billion gallon capacity (Fig. 2.2). It has 8 main tributaries, most originating “from forested areas which include swamps and bogs, some formed from natural beaver dams; some tributaries flow from urbanized and industrialized areas as well” (Bryan, 2005). Figure 2.2 also shows the amount of land in the watershed that is owned and protected by the State’s Department of Conservation and Recreation (a combined total of 75%) (MWRA, 2008).

Figure 2.1: Location of Wachusett Reservoir and Watershed
All eight main tributaries of Wachusett were sampled, as well as 7 sub-tributaries of the second largest tributary, Stillwater River. Stillwater River was itself sampled at four locations along its stem, for a total of 19 sampling locations (Figure 2.3). Sampling sites were selected by Bryan (2005) and, in general, were chosen based on their accessibility, with most of the sites located near roads and close to the stream outlet. The sites were named according to the tributary or the nearest crossroad. Spatially extensive sampling events were carried out during wet and dry weather events from 2001 through 2007 (Table 2.1).

Stream samples were collected in pre-acid washed amber bottles. Samples were kept in ice-packed coolers during sampling runs and returned to the UMass cold temperature room (4 degrees Celsius) within 5 hours of collection. All samples were tested for UVA, DOC, TOC, THM-FP, and HAA-FP.
Figure 2.3: Sampling Locations at Wachusett Watershed
### Table 2.1: Sampling Events and Types of Sampling

<table>
<thead>
<tr>
<th>Date</th>
<th>Sample Type</th>
<th>Event Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>October 18, 2001</td>
<td>Stream</td>
<td></td>
</tr>
<tr>
<td>December 1, 2001</td>
<td>Stream</td>
<td></td>
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<tr>
<td>January 29, 2002</td>
<td>Stream</td>
<td></td>
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<tr>
<td>April 11, 2002</td>
<td>Stream</td>
<td></td>
</tr>
<tr>
<td>June 7, 2002</td>
<td>Stream</td>
<td></td>
</tr>
<tr>
<td>November 6, 2002</td>
<td>Stream, Leaves</td>
<td>Spatially Based Sampling</td>
</tr>
<tr>
<td>January 21, 2003</td>
<td>Stream</td>
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<tr>
<td>August 18, 2005</td>
<td>Stream</td>
<td></td>
</tr>
<tr>
<td>October 9, 2005</td>
<td>Stream, Soil water</td>
<td></td>
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<tr>
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</tr>
<tr>
<td>November 22, 2005</td>
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</tr>
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<td>April 10, 2006</td>
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<td>May 17, 2006</td>
<td>Stream, Soil water, Rain</td>
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<tr>
<td>July 6, 2006</td>
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<td>February 27, 2007</td>
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<td>April 12-19, 2004</td>
<td>Stream</td>
<td></td>
</tr>
<tr>
<td>April 27-29, 2007</td>
<td>Stream, Soil water, Rain</td>
<td></td>
</tr>
</tbody>
</table>

Stream samples: \(n = 160\)

Leaves, soil, rainwater, groundwater, snow: \(n = 55\)

In addition to stream samples, rainwater samples were collected during a two-day storm event in April 2007. An Intex® Metal Frame 10’ x 30” (Model #56998/E) above ground pool with a plastic cover was installed at the Muddy Pond site to receive and collect rainwater. The pool was equipped with a Teledyne ISCO sampler that collected rainwater hourly. All samples were tested for UVA, DOC, TOC, THM-FP and HAA-FP. On August 4\textsuperscript{th} 2007, the rainwater collector was set up at the University of Massachusetts Amherst. An organic-free glass container was also set up next to the rainwater collector, in order to determine whether the collector itself introduced any organic contamination. Rainwater was collected periodically over the course of the morning. Figure 2.4 contains DOC concentrations.
observed during this test, and indicates that the rainwater collector does not introduce organic contamination.

![Figure 2.4: Rainwater Collector Control Experiment](image)

**Figure 2.4: Rainwater Collector Control Experiment**

### 2.3.2. DOC Impact Test

The purpose of this experiment is to test the DBP formation of water samples with identical DOC composition but variable DOC concentration. In order to accomplish this, a large amount of raw surface water was collected, condensed to 10% the original volume, and diluted to 5 different concentrations. Figure 2.5 is a schematic of this process. Twenty liters of water were collected from the Mountain Street Reservoir, which supplies the neighboring town of Northampton. The water was condensed to 2 liters using a Büchi Rotavapor R-220
evaporator. The instrument was set to a bath temperature of 55 degrees Celsius and a rotational speed of 60 revolutions per minute. The 2 liters were then filtered using a pre-rinsed 0.45 micron glass fiber filter.

The concentrated raw water sample was then diluted into triplicates of 50%, 30%, 20%, 10%, and 5% compositions. All samples were buffered to a pH of 7 using a phosphate buffer. All of the dilutions were chlorinated using a dose of 5, 10, or 20 mg/L of chlorine. For example, three 50% dilutions were prepared and chlorinated with 5, 10, and 20 mg/L, respectively.

Figure 2.5: Schematic of Variable DOC Experiment
Following chlorination and an incubation period of 72 hours, all samples were tested for chlorine residual, pH, trihalomethanes, and haloacetic acids. These procedures are explained below. In addition, the uncondensed raw water sample and the concentrated raw water sample were measured for TOC, DOC, and UVA.

2.3.3. Laboratory Analysis

The following section describes all laboratory procedures as detailed by the Standard Operating Procedures of the Civil and Environmental Engineering Department of the University of Massachusetts Amherst. The complete SOPs can be found at the following website: http://www.ecs.umass.edu/eve/research/sop/index.html.

Total and Dissolved Organic Carbon

The UMass protocol used for analysis of organic carbon is based on Standard Methods’ 5310B, “Total Organic Carbon: High Temperature Combustion Method,” and is described in the Standard Operating Procedure for Organic Carbon (available at the previously listed website). Analysis was conducted within 2 days of sample collection using a Shimadzu TOC-VCPH analyzer. Dissolved organic carbon was measured following filtration with a pre-rinsed 0.45 micron Whatman GF/C glass fiber filter. Calibration standards were prepared in the range 0 to 20 mg/L using a 1000 mg/L stock solution of potassium hydrogen phthalate.
**Ultraviolet Absorbance**

The UMass protocol used for analysis of UV absorbance is based on Standard Method’s 5910B, “Ultraviolet Absorption Method,” and is described in the Standard Operating Procedure for UV Absorbance (available at the previously listed website). Analysis was conducted within 2 days of sample collection using an Agilent 8453 UV Visible System analyzer. Samples were measured following filtration with a pre-cleaned 0.45 \( \mu \)m Whatman GF/C glass fiber filter. Samples with a UV of 4.0 cm\(^{-1}\) were diluted and re-measured.

**DBP Formation Potential Tests**

A standardized method for testing the effect of DBP precursors is the formation potential test (Xie, 2003). The formation potential test consists of adding excess chlorine to ensure maximum DBP levels. The operating procedure for the formation potential test modified by UMass is described in the Standard Operating Procedure for Laboratory Chlorination (available at the previously listed website) and is based on generally accepted methods. The UMass procedure includes an incubation time of 72 hours, a chlorine dose of 20 mg/L, a sample pH of 7 held with a phosphate buffer, and an incubation temperature of 20 degrees Celsius. These parameters have been known to vary between experimenters. The variation of chlorine residuals between samples should not affect DBP formation potential levels because chlorine is added in excess (Xie, 2003). If the chlorine residual is zero or close to zero, however, it cannot be assumed that the reaction was carried out to its full extent.

Samples were chlorinated within 7 days of collection. Prior to chlorination, all samples were brought to room temperature, filtered with a pre-cleaned 0.45 \( \mu \)m Whatman
GF/C glass fiber filter, and diluted to a UVA of approximately 0.15 cm$^{-1}$ if the raw water UVA was above 0.30 cm$^{-1}$. The sample’s pH was adjusted to approximately 7 by first adding 3 mL of 1 M phosphate buffer to 300 mL of sample volume. Final pH adjustments were made by adding either 1 M sulfuric acid or 1 M sodium hydroxide. All pH measurements were made using a calibrated Orion Research Model EA 940 expanded ion analyzer.

For chlorination, a chlorine stock solution was made from sodium hypochlorite. The actual chlorine stock concentration was determined through a colorimetric titration (described below). Samples were chlorinated from the stock solution to a final chlorine concentration of 20 mg/L in 300 mL chlorine-demand-free BOD bottles. Samples were incubated headspace free in the dark for 72 hours at 20 degrees Celsius. A laboratory blank consisting of high-purity chlorinated water was included in every chlorination experiment.

Following the incubation period, samples were preserved for THM and HAA measurements. THM samples were preserved headspace free in 40 mL amber vials containing two quenches, 40 mg of ammonium chloride and approximately 1 mg of phosphate buffer. HAA samples were preserved headspace free in 40 mL clear vials containing one quench, approximately 1 mg of phosphate buffer. Samples were stored in the dark in a refrigerator and analyzed for DBPs within 14 days of quenching.

The remaining sample volume from the BOD bottles was measured for pH and chlorine residual immediately following sample preservation. The UMass protocol used to measure chlorine residual is based on Standard Methods #4500-C1 F, “DPD Ferrous Titrimetric Method,” and is described in the UMass SOP for Chlorine Residual Measurement (available at the previously listed website). A DPD indicator solution and a phosphate buffer are added to 100 mL of sample (in most cases, the sample has to be diluted by a factor of ten).
The sample is titrated with ferrous ammonium sulfate until the pink color of the solution turns clear. The amount of titrant added is directly related to the amount of chlorine available in the sample.

**Trihalomethane Extraction**

The UMass protocol used for extraction of trihalomethanes is based on US EPA Method 551.1, “Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron Capture Detection,” and is described in the Standard Operating Procedure for Trihalomethane Measurement (available at the previously listed website).

THM samples were analyzed within 14 days of chlorine residual measurement and sample preservation. For THM extraction, 20 mL of sample were removed from the 40 mL amber vials prepared during sample preservation and transferred to 40 mL amber vials. The calibration stock solution was prepared using an EPA Method 551 Volatile Organics Mix containing chloroform, bromoform, chlorodibromomethane, and bromodichloromethane. Calibration standards were prepared in the range of 0 to 250 µg/L (per THM compound) using 20 mL of high-purity water in 40 mL amber vials.

Pentane is used as the extraction solvent and 1,2-dibromopropane as the internal standard. After addition of 4 mL of a pre-mixed pentane + internal standard solution and 15 g of sodium sulfate, the samples are shaken vigorously for 15 minutes. The organic layer is extracted using a disposable Pasteur pipette and transferred to 2 mL clear autosampler vials.
The vials are frozen overnight in order to remove any excess water and analyzed the following day using an Agilent 6890 Gas Chromatograph with electron capture detector.

The calibration curve and THM concentrations are determined from the ratio of the compound peak area to the internal standard peak area. Total THM formation potential (TTHM-FP) is the sum of the four THM compounds.

_Haloacetic Acid Extraction_

The UMass protocol used for extraction of haloacetic acids is based on US EPA Method 552.2, “Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatization, and Gas Chromatography with Electron Capture Detection,” and is described in the Standard Operating Procedure for Haloacetic Acid Measurement (available at the previously listed website).

HAA samples were analyzed within 14 days of chlorine residual measurement and sample preservation. For HAA extraction, 30 mL of sample were removed from the 40 mL clear vials prepared during sample preservation and transferred to 40 mL clear vials. Two calibration stock solutions were prepared, one being an EPA Method 552 Haloacetic Acid Mix (containing monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, dibromoacetic acid, trichloroacetic acid, and bromochloroacetic acid) and another being a mixture of three solutions (containing tribromoacetic acid, bromodichloroacetic acid, and chlorodibromoacetic acid). Therefore, one stock solution consists of monohaloacetic acids and dihaloacetic acids, and the other stock solution consists of trihaloacetic acids. Calibration standards were prepared in the range of 0 to 250 µg/L (per mono- and dihaloacetic acid
compound) and 0 to 80 µg/L (per trihaloacetic acid compound) using 30 mL of high-purity water in 40 mL clear vials.

Methyl-tert-butyl-ether (MTBE) is used as the extraction solvent and 1,2,3-trichloropropane as the internal standard. After acidifying the samples with 1.5 mL of concentrated sulfuric acid, the samples are extracted with 3 mL of a pre-mixed MTBE + internal standard solution and 15 g of sodium sulfate. The samples are shaken vigorously for 15 minutes. The organic phase containing the haloacetic acids is extracted, mixed with an acidic methanol solution, and placed in a 50 degrees Celsius water bath in order to convert the HAAs into their methyl esters. The acidic extract is then neutralized with a saturated solution of sodium bicarbonate and shaken vigorously for 2 minutes. The organic layer is extracted a second time using a disposable Pasteur pipette and transferred to 2 mL clear autosampler vials. The vials are frozen overnight in order to remove any excess water and analyzed the following day using an Agilent 6890 Gas Chromatograph with electron capture detector.

The calibration curves and HAA concentrations are determined from the ratio of the compound peak area to the internal standard peak area. HAA9 formation potential (HAA9-FP) is defined as the sum of all HAA compounds listed previously, DiHAA formation potential (DiHAA-FP) is defined as the sum of the dihaloacetic acids, and TriHAA formation potential (TriHAA-FP) is defined as the sum of the trihaloacetic acids.

2.3.4. Data Analysis

In addition to the measurements described above, several other parameters were calculated or obtained from public databases. Precipitation and temperature measurements were obtained from the Worcester Regional Airport Station through the National Climatic
Data Center of the US Department of Commerce. Discharge data for Stillwater River were obtained from a US Geological Survey (USGS) gage located at the intersection of Stillwater River and Muddy Pond Road (site #8 on Figure 2.3). Information related to land use is described below.

SUVA and specific DBP formation potential were calculated for each sample collected. SUVA was calculated by dividing the UV absorbance in m\(^{-1}\) by the respective DOC in mg/L, obtaining SUVA in L/mg-m. Specific DBP formation potential (SpDBP-FP) was calculated by dividing the particular DBP formation potential in µg/L (total THM-FP, TriHAA-FP, or DiHAA-FP) by the respective DOC in mg/L, obtaining SpTHM-FP, SpTriHAA-FP, or SpDiHAA-FP in µg DBP/mg C.

2.3.5. Spatial Analysis with ArcGIS

Watersheds for each sampling point (Fig. 2.3) were manually delineated with ArcGIS by Alison Boutin using 1:100,000 scale hydrology and elevation contour lines as references (Bryan, 2005).

A statewide land use layer from 1999 in ArcGIS format was downloaded from The Official Website of the Office of Geographic and Environmental Information (MassGIS at http://www.mass.gov/mgis/massgis.htm) of the Executvie Office of Energy and Environmental Affairs of the Commonwealth of Massachusetts. This statewide land use shapefile was clipped to the watersheds layer created by Boutin (Bryan, 2005) using ESRI ArcMAP 9.2 in order to isolate the watershed-specific land uses.

Through clipping, land use percentages were determined for each watershed in the watersheds layer. Additionally, the buffer tool was used to create polygons extending 100
meters in either direction of all streams in the watersheds in order to represent the riparian zone of each stream. Land use percentages were determined for these riparian zones in each watershed. Subsequent land use analysis considers the effect of utilizing the full watershed’s land uses versus utilizing the riparian zone’s land uses. Figure 2.6 compares land use percentages for the full watershed with percentages for the riparian zone.

Land use percentages for this project were based on the 21 land use classifications based on 1:25,000 scale aerial photographs from 1999. However, these 21 land use classifications were merged into 6 general categories as given in Table 2.2. Figure 2.7 is a land use map for the full watershed and Figure 2.8 is a land use map for the riparian zones (note only 5 categories are actually mapped, since there were no “Other” areas). Table 2.3 contains the final land use percentages for each sampling location, for both the full watershed and the riparian zone.

Figure 2.6: Full Watershed versus Riparian Zone for Justice Brook
Table 2.2: MassGIS and UMass Land Use Categories

<table>
<thead>
<tr>
<th>21 Classification Codes from MassGIS 1999</th>
<th>Definition</th>
<th>UMass General Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cropland</td>
<td>Agriculture</td>
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<tr>
<td>2</td>
<td>Pasture</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Forest</td>
<td>Forest</td>
</tr>
<tr>
<td>6</td>
<td>Open Land</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Woody Perennial</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Wetland</td>
<td>Wetland</td>
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<td>14</td>
<td>Salt Wetland</td>
<td>Other*</td>
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<td>9</td>
<td>Water Based Recreation</td>
<td>Water</td>
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<td>Water</td>
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</tr>
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<td>5</td>
<td>Mining</td>
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</tr>
<tr>
<td>7</td>
<td>Participation Recreation</td>
<td>Urban</td>
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<td>Spectator Recreation</td>
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<tr>
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<td>Residential Multifamily</td>
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<tr>
<td>11</td>
<td>Residential less than 1/4 acre</td>
<td></td>
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<tr>
<td>12</td>
<td>Residential quarter to half acre</td>
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<td>13</td>
<td>Residential larger than half acre</td>
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<td>Transportation</td>
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<td>19</td>
<td>Waste Disposal</td>
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* This category had 0% land use for all watersheds
Figure 2.7: Land Use Map for Full Watershed
Figure 2.8: Land Use Map for Riparian Zones
Table 2.3: Riparian Zone and Full Watershed Area Percent Land Use Coverage

<table>
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<tr>
<th>Land Use</th>
<th>Agriculture Riparian Area</th>
<th>Agriculture Full Area</th>
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<th>Forest Full Area</th>
<th>Wetland Riparian Area</th>
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<th>Water Riparian Area</th>
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2.4. Results and Discussion

Extensive sampling campaigns at Wachusett Reservoir were undertaken from 2001 through 2007 to measure DOC, THMs, and HAAs to better understand the relationship between DBPs, DBP precursors, environmental factors, and climatic factors. Specifically, since previous studies have shown that DBP formation is linked to DOC composition (and not just concentration), this study seeks to identify the watershed characteristics that most influence DBP precursor quality and subsequent DBP formation.
Prior to examining watershed influences on the Wachusett data, DBP-FP data for all the water samples were grouped together and analyzed with respect to DOC and SUVA. However, preliminary results from this analysis necessitated further analysis through the variable DOC test detailed in Section 2.3.2. The results of this variability test were used to re-examine the Wachusett database, which required re-analyzing DBP-FP data with respect to DOC and SUVA. Therefore, the following sections discuss the analysis of the original Wachusett database, the inclusion of the variable DOC test results, and the re-analysis of a reduced Wachusett database. Finally, this reduced database is used to examine how season, precipitation, and land use affect DBP precursors in the Wachusett watershed.

2.4.1. Original DBP Data for Wachusett Reservoir

The relationship between DBP precursors, DOC, and SUVA were examined for all the stream samples collected. Figure 2.9 illustrates the relationship between DOC and SUVA for all the stream samples collected. Pearson Product Moment and Spearman Rank Order correlation analysis both showed a significant (p < 0.05) negative correlation between DOC and SUVA, indicating that as DOC concentration increases, a smaller fraction of DOC compounds are aromatic. Figure 2.10 illustrates absolute THM-FP, Figure 2.11 illustrates absolute TriHAA-FP, and Figure 2.12 illustrates absolute DiHAA-FP and their relationship with DOC and SUVA (R² values and slopes are included in the figures). Relationships between DBP-FP and DOC are positively correlated but the strength of the relationship is not very high, as indicated by the small R² values. The positive correlation is expected, but the weakness of the correlation is surprising in light of other studies that have reported strong positive correlations. Relationships between DBP-FP and SUVA are very weakly negatively
correlated. A negative correlation between DBP-FP and SUVA is unexpected and inconsistent with other studies, casting doubt on the reliability of the data. Alternatively, there may be other important factors that strongly affect this relationship.

Figure 2.9: Correlation between DOC and SUVA for Original Wachusett Data

Figure 2.10: THM-FP versus DOC and SUVA for Original Wachusett Data
Figure 2.11: TriHAA-FP versus DOC and SUVA for Original Wachusett Data

Figure 2.12: DiHAA-FP versus DOC and SUVA for Original Wachusett Data
The reactivity of all samples was also examined, in particular the propensity of the particular DOC to form DBPs on a per carbon basis, the specific DBP-FP. Figure 2.13 illustrates specific THM-FP, Figure 2.14 illustrates specific TriHAA-FP, and Figure 2.15 illustrates specific DiHAA-FP and their relationship with DOC and SUVA. Relationships between SpDBP-FP and SUVA are weakly correlated (positive), with a wide range of reactivity for similar SUVA values. Relationships between SpDBP-FP and DOC are negatively correlated. These results may indicate both, or either, of two things: 1) samples with higher DOC concentrations tend to be composed of fresh, mostly non-humic material that is less reactive with chlorine than aged NOM (Section 1.4.1); or, 2) samples with high DOC concentrations exhaust the chlorine available in the formation potential test before the reaction is carried out to completion.

Figure 2.13: SpTHM-FP versus DOC and SUVA for Original Wachusett Data
Figure 2.14: SpTriHAA versus DOC and SUVA for Original Wachusett Data

Figure 2.15: SpDiHAA-FP versus DOC and SUVA for Original Wachusett Data
2.4.2. Variable DOC Test and Impact on DBP Levels

The latter possibility was examined through the variable DOC test explained in Section 2.3.2. Untreated surface water was concentrated and re-diluted to five different DOC concentrations. Each DOC concentration was also treated with three different chlorine doses (5, 10, and 20 mg/L) at a pH of 7, incubated for 3 days at 20 degrees Celsius, and measured for THMs and HAAs. Figure 2.16 contains graphs of absolute THM-FP, TriHAA-FP, and DiHAA-FP versus DOC concentration for each chlorine dose. All graphs show a positive correlation. However, as DOC concentration increases, the low and intermediate chlorine dose samples produce lower concentrations of DBPs than the highest chlorine dose samples, indicating that reactions at the low and intermediate dose were not as complete as those of the highest dose. It cannot be assumed with the same certainty that the reaction was carried out to completion for the highest chlorine dose, unless one examines the reactivity of each sample (the DBP formation on a per carbon basis).
Figure 2.16: DBP Precursors in Variable DOC Test
Figure 2.17: Specific DBP in Variable DOC Test
Figure 2.17 contains graphs of the specific THM-FP, TriHAA-FP, and DiHAA-FP formation potential versus DOC concentration. The graphs also include chlorine residual (right axis) measured at the end of the incubation period. Laboratory blanks made during sample chlorination had chlorine residuals of 25.4, 12.5, and 6.5 mg/L. In other words, all samples were chlorinated to a chlorine concentration higher than the intended 5, 10, and 20 mg/L doses, which explains the high chlorine residuals in Figure 2.17. Despite the incorrect chlorine dose, the progression of the actual chlorine doses is similar to that of the intended chlorine doses, such that the experiment is still suitable. The graphs on Figure 2.17 show that samples with the highest chlorine dose always produced more DBPs per mass of carbon, followed by samples with the intermediate dose. The lowest chlorine dose samples always produced the least DBPs per unit carbon. The reactions appear to be second order, with specific DBP formation depending on chlorine concentration. These results emphasize the importance of having excess chlorine in a formation potential test. It is even possible that a 20 mg/L dose is not excessive, but this conclusion is not obvious from this experiment.

Excluding samples with the highest DOC concentration, SpTHM-FP and SpDiHAA-FP levels remained constant with DOC concentration, indicating that the reactivity of the samples was the same regardless of the initial DOC concentration (for all chlorine doses) and dependent only on DOC composition. However, SpTHM-FP and SpDiHAA-FP levels drop for samples with the highest DOC concentration, indicating that for these samples reactivity was diminished (for all chlorine doses). It seems safe to assume that chlorine is not available in excess during the formation potential tests when the DOC concentration is higher than 6 mg/L, thus reactions leading to DBPs are inhibited. For specific TriHAA-FP, reactivity was constant even at high DOC concentrations (with the exception of the high DOC sample with
the lowest chlorine dose), but reactivity was inhibited for samples with low DOC concentrations (particularly for the intermediate and high chlorine doses). The reasons for this observation have not been determined. It may be the result of either laboratory error or DBP formation reactions being impeded by lack of DOC. Low DOC samples should be retested in order to verify whether similar results are observed.

It is not surprising that the lowest chlorine dosed samples had diminished DBP formation at the highest DOC concentration since there was no measurable chlorine available at the end of the incubation period (Fig. 2.17). Nevertheless, it is unclear why DBP formation was also diminished for samples at higher chlorine doses given that there remained considerable chlorine residuals at the end of incubation. Regardless, it can be discerned from the data that above a certain DOC concentration the results of the formation potential test are not reliable (it is possible that below a certain DOC concentration the test is also compromised).

This experiment allows us to define a range of DOC concentrations within which the formation potential test can be expected to produce results that reflect the chemical properties of the NOM and which are not confounded by the concentration of that NOM. Samples with DOC concentrations above that range should then be diluted while samples with DOC concentrations below that range should be concentrated. As a preliminary estimate, this experiment shows that DOC concentrations for a formation potential test should range between 1 and 6 mg/L (until the SpTriHAA-FP results at the low DOC concentrations can be confirmed, it is preferable to keep a low DOC threshold given that SpTHM-FP and SpDiHAA-FP do not exhibit this anomalous behavior at low DOC concentrations).
Currently, the standard operating procedure at UMass for a formation potential test requires that samples be diluted to a UVA of approximately 0.15 cm\(^{-1}\) if the undiluted UVA is 0.30 cm\(^{-1}\) or greater (Section 2.3.3). The SOP does not provide a DOC range for a formation potential test. Figure 2.18 contains specific THM-FP, specific TriHAA-FP, and specific DiHAA-FP versus UVA. These figures show very similar trends to the previous plots against DOC (including the discrepancy at low DOC concentrations for SpTriHAA-FP). As a preliminary estimate, this experiment shows that UVA for a formation potential test should range between 0.01 and 0.10 cm\(^{-1}\). As such, the current SOP should be adjusted. Still, similar tests should be conducted on samples with UVA measurements between 0.10 and 0.18 cm\(^{-1}\), given that this wide UVA range is not covered in this experiment. Such tests might provide a higher UVA threshold than that suggested here.
Figure 2.18: UVA Criteria from Variable DOC Test
2.4.3. Reduced DBP Data for Wachusett Reservoir

SpDBP-FP and DOC concentrations are negatively correlated for the original Wachusett data (Fig. 2.13, 2.14, and 2.15). However, as the variable DOC test shows, this trend might be the result of unreliable formation potential tests conducted when the DOC concentration was too high. As such, any samples with DOC concentrations outside the range of 1-6 mg/L were removed from the database (samples with high DOC concentrations that were diluted to within this range were kept).

The variable DOC test allows us to re-examine the reduced dataset from Wachusett Reservoir. Figure 2.19 illustrates absolute THM-FP, Figure 2.20 illustrates absolute TriHAA-FP, and Figure 2.21 illustrates absolute DiHAA-FP and their relationship to DOC and SUVA. Table 2.4 presents the slopes, intercepts, and \( R^2 \) values of the linear regressions for the original and reduced dataset of absolute DBPs for relationships with DOC and SUVA. Table 2.4 shows a marked improvement in the strength of the relationship between all DBP-FP groups and DOC. With respect to SUVA values the relationships are now weakly correlated (positively rather than negatively correlated), with a wide range of DBP-FP for similar SUVA values. These results indicate (as other studies have shown) that non-aromatic DOC compounds may also contribute to formation potential.

Pearson correlation analysis was also performed to further test the significance of these relationships, the results of which are in Table 2.5 (including correlation coefficient \( r \), coefficient of determination \( R^2 \), and \( t \) values). T-tests show that all absolute DBP-FP levels are significantly correlated (positive) with DOC concentration at the 95% confidence level, as expected. T-tests also show that THM-FP and DiHAA-FP are significantly correlated
(positive) with SUVA at the 95% confidence level. Even though the correlation is not as strong as with DOC concentration, this indicates that aromaticity does influence formation potential for these two DBP groups. TriHAA-FP, however, does not appear to be significantly correlated with SUVA. This result for TriHAA-FP is discussed in more detail below.

Figure 2.19: THM-FP versus DOC and SUVA for Reduced Wachusett Data

Figure 2.20: TriHAA-FP versus DOC and SUVA for Reduced Wachusett Data
Figure 2.21: DiHAA-FP versus DOC and SUVA for Reduced Wachusett Data

Table 2.4: Linear Regressions for Absolute DBP-FP and DOC

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<th></th>
<th>ALL DATA</th>
<th>REDUCED DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>THM</td>
<td>TriHAA</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.449</td>
<td>0.270</td>
</tr>
<tr>
<td>Intercept</td>
<td>126.7 ± 12.3</td>
<td>244.2 ± 31.4</td>
</tr>
<tr>
<td>Slope</td>
<td>24.4 ± 2.2</td>
<td>42.0 ± 5.5</td>
</tr>
</tbody>
</table>

Table 2.5: Pearson Correlation Analysis for Absolute DBP-FP

<table>
<thead>
<tr>
<th></th>
<th>DOC Correlation</th>
<th>SUVA Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Correlation Coefficient $r$</td>
<td>Coefficient of Determination $r^2$</td>
</tr>
<tr>
<td>THM-FP</td>
<td>0.75</td>
<td>0.57</td>
</tr>
<tr>
<td>TriHAA-FP</td>
<td>0.63</td>
<td>0.40</td>
</tr>
<tr>
<td>DiHAA-FP</td>
<td>0.74</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Reduced Data, Critical $t$-value = 1.975 at $\alpha = 0.05$
The reactivity of the reduced dataset is also re-examined on Figure 2.22 for specific THM-FP, Figure 2.23 for specific TriHAA-FP, and Figure 2.24 for specific DiHAA-FP, with respect to DOC and SUVA. Table 2.6 presents the slopes, intercepts, and $R^2$ values of the linear regressions for the original and reduced dataset for specific DBP-FP related to DOC and SUVA. The strength of the linear regression becomes weaker for all specific DBP-FP groups related to both DOC and SUVA, possibly indicating that DOC and SUVA are not good predictors of reactivity (i.e., DBP formation on a per carbon basis), as explained below.

To further confirm this conclusion, Pearson correlation analysis was performed between SpDBP-FP (for all three groups of DBPs) and DOC, the results of which are in Table 2.7 (including correlation coefficient $r$, coefficient of determination $r^2$, and $t$ values). T-tests show that the correlation coefficients between any of the specific DBP-FP groups and DOC are not significantly different from zero at the 95% confidence level. In other words, there is no significant correlation between specific DBP-FP and DOC. This result indicates that, as expected, propensity to form DBPs on a per carbon basis (i.e. reactivity of DOC with chlorine) is not determined by DOC concentration alone when the DOC is from different sources.

Similar correlation analysis was performed between SpDBP-FP and SUVA, the results of which are in Table 2.7. T-tests show that SpTHM-FP and SpDiHAA-FP are significantly positively correlated with SUVA at the 95% confidence level, despite the weakness of the linear regressions described previously. These correlation results indicate that propensity to form THM-FP and DiHAA-FP on a per carbon basis is related to the aromaticity as measured by SUVA, albeit weakly. As with absolute TriHAA-FP, the correlation coefficient between specific TriHAA-FP and SUVA is not significantly different from zero at the 95% confidence
level. With respect to TriHAA-FP, the lack of correlation with SUVA (both for absolute and specific formation potential) indicates that non-aromatic compounds may be significant sources of TriHAA precursors.

Figure 2.22: SpTHM-FP versus DOC and SUVA for Reduced Wachusett Data

Figure 2.23: SpTriHAA-FP versus DOC and SUVA for Reduced Wachusett Data
Figure 2.24: SpDiHAA-FP versus DOC and SUVA for Reduced Wachusett Data

Table 2.6: Linear Regressions of Specific DBP-FP

<table>
<thead>
<tr>
<th></th>
<th>ALL DATA</th>
<th>REDUCED DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific DBP vs. DOC</td>
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</tr>
<tr>
<td>SpTHM</td>
<td>0.254</td>
<td>0.010</td>
</tr>
<tr>
<td>SpTriHAA</td>
<td>0.115</td>
<td>0.009</td>
</tr>
<tr>
<td>SpDiHAA</td>
<td>0.307</td>
<td>0.015</td>
</tr>
<tr>
<td>R²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intercept</td>
<td>76.6 ± 2.9</td>
<td>71.2 ± 4.6</td>
</tr>
<tr>
<td>Slope</td>
<td>-3.72 ± 0.5</td>
<td>-1.64 ± 1.3</td>
</tr>
<tr>
<td>Specific DBP vs. SUVA</td>
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<td></td>
</tr>
<tr>
<td>SpTHM</td>
<td>0.123</td>
<td>0.098</td>
</tr>
<tr>
<td>SpTriHAA</td>
<td>0.004</td>
<td>0.002</td>
</tr>
<tr>
<td>SpDiHAA</td>
<td>0.240</td>
<td>0.090</td>
</tr>
<tr>
<td>R²</td>
<td></td>
<td></td>
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<tr>
<td>Intercept</td>
<td>36.2 ± 5.7</td>
<td>48.6 ± 4.9</td>
</tr>
<tr>
<td>Slope</td>
<td>5.15 ± 1.2</td>
<td>3.72 ± 1.0</td>
</tr>
</tbody>
</table>

Table 2.7: Pearson Correlation Analysis for Specific DBP-FP

Critical t-value = 1.975 at α = 0.05

<table>
<thead>
<tr>
<th></th>
<th>DOC Correlation</th>
<th>SUVA Correlation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Correlation Coefficient $r$</td>
<td>Coefficient of Determination $r^2$</td>
</tr>
<tr>
<td>Sp-THMFP</td>
<td>-0.10</td>
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</tr>
<tr>
<td>Sp-TriHAAFP</td>
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<td>0.01</td>
</tr>
<tr>
<td>Sp-DiHAAFP</td>
<td>-0.11</td>
<td>0.01</td>
</tr>
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2.4.4. Watershed Influence on DBP Levels

The following section examines trends in DBP formation due to season, precipitation, and land use. Most analysis is conducted on the reduced Wachusett database, which is summarized in Figure 2.25. Figure 2.25 contains box-whisker plots of all DOC, SUVA, absolute DBP-FP, and specific DBP-FP measurements for the reduced dataset (Figure 2.26 explains the box-whisker plot). Tributaries to Wachusett reservoir tend to be relatively oligotrophic water sources, with DOC values ranging between 2 and 5 mg/L. The NOM composition is fairly aromatic, with SUVA values ranging between 3 and 7 L/mg-m. The highest precursor group on a mass basis tends to be TriHAA-FP, followed by THM-FP and DiHAA-FP. Reactivity also tends to be highest for TriHAA formation, followed by THM and DiHAA formation.
Figure 2.25: Range of Values for Reduced Wachusett Data
Figure 2.26: Box-Whisker Plot Explanation

Seasonal Effects

Figure 2.27 contains seasonal averages of DOC concentrations and SUVA values for all stream samples collected, as well as error bars representing one standard deviation. Figure 2.28 contains absolute and specific DBP-FP levels for the reduced Wachusett dataset, with error bars again representing one standard deviation. Dissolved organic carbon concentrations tend to be higher in summer and lower in winter, while SUVA values tend to be higher in spring and lower in winter. Higher spring SUVA values could be the result of snowmelt leading to flushing of aged plant leachate into receiving waters.

However, despite higher DOC concentrations and SUVA values in the summer, the highest DBP precursor concentrations tend to occur in winter. This may indicate that NOM composition during winter months is abundant in DBP precursors that are not necessarily highly aromatic, thus non-aromatic compounds may be a significant source of DBP precursors as well. Specific DBP-FP values also tend to be higher in winter. Therefore, NOM during
winter months tends to be abundant in highly reactive DBP precursors. SpDBP-FP tends to be lower during the summer when DOC concentrations are highest, signifying that NOM composition is not very reactive.

![Figure 2.27: DOC and SUVA Seasonal Averages (Original Wachusett Data)](image)

![Figure 2.28: DBP-FP and SpDBP-FP Seasonal Averages (Reduced Wachusett Data)](image)
T-tests were performed at the 95% and 90% confidence level to determine if mean seasonal concentrations of specific DBP-FP, DOC, and DOC aromaticity (SUVA) were significantly different over the course of a year. Table 2.8 lists pairs of seasons with significantly different means at the respective confidence level (bold cells represent which of the two means is higher). At the 95% confidence level, only DOC concentrations during the summer were significantly higher as compared to other seasons. Specific UVA values were significantly lower in the winter compared to all other seasons, while spring values were significantly higher than fall and winter (but not significantly different from summer). Again, these results indicate that while summer has high DOC concentrations due to the abundant vegetation, it does not have higher specific aromatic content compared to NOM leached during spring and fall.

With respect to SpDBP-FP, fall and spring were not significantly different from each other for any of the DBP groups at the 95% confidence level, but both fall and spring were significantly higher than summer for all DBP groups at the 90% confidence level. At the 90% confidence level, winter values of SpTHM-FP and SpTriHAA-FP were significantly higher than all other seasons (winter values of SpDiHAA-FP were higher than summer values only). From the regressions calculated in Figures 2.22, 2.23, and 2.24 for SpDBP-FP versus DOC (with slopes not significantly different from zero), the residuals can be calculated and compared by season to distinguish which seasons yield higher or lower DBPs per carbon. These model residuals are plotted in Figure 2.29 as box-whisker plots. This analysis has shown that winter tends to produce the highest DBP yields on a per carbon basis, summer tends to produce the lowest yields, and spring and fall produce comparable yields.
Table 2.8: Comparing Seasonal Averages

For pairs of seasons with significantly different means, the seasons with the highest means are indicated in the following matrices (for DOC, SUVA, and specific DBP-FP at the specified confidence level).

\[ \alpha = 0.1 \]

<table>
<thead>
<tr>
<th>DOC</th>
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<th>Winter</th>
<th>Spring</th>
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<tbody>
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<td>Fall</td>
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<td></td>
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</tr>
<tr>
<td>Winter</td>
<td>*</td>
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<tbody>
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<td>Fall</td>
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<tr>
<td>Winter</td>
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<td>Summer</td>
<td>Fall</td>
<td>Winter</td>
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\[ \alpha = 0.05 \]

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<tr>
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<tr>
<td>Spring</td>
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<td></td>
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<tr>
<td>Summer</td>
<td>Winter</td>
<td>*</td>
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</table>
Figure 2.29: Model Residuals for SpDBP-FP by Season
Precipitation Effects

The Wachusett reduced dataset was analyzed for trends resulting from precipitation effects. Figure 2.30 includes graphs of absolute THM-FP, TriHAA-FP, and DiHAA-FP versus DOC for wet and dry events. Table 2.9 contains $R^2$ values, slopes, and intercepts of these linear regressions separated into wet and dry events.

Figure 2.30 shows a larger range of THM precursors corresponding to similar DOC concentrations under dry conditions than wet conditions. Wet events, on the other hand, tend to consist of similar amounts of THM precursors at the same DOC concentrations. These results correspond to a stronger relationship between THM-FP and DOC for wet events versus dry events. Some of the highest THM precursor values occurred during wet events while some of the lowest values occurred during dry events. Again, these results correspond to a significantly higher slope for wet events versus dry events at the 95% confidence level (a variation of an F-test was performed to determine if regression slopes were significantly different from each other; wherever regression slopes are compared, this F-test variation was used). The amount of THM precursors, therefore, tends to be highly variable and low under dry conditions but relatively homogenous and high during wet conditions.
Figure 2.30: DBP-FP versus DOC for Wet and Dry Events
Table 2.9: Absolute DBP-FP vs. DOC Linear Regressions for Wet and Dry Events

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<tr>
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<th>Dry Events</th>
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<td>TriHAA</td>
<td>DiHAA</td>
<td>THM</td>
<td>TriHAA</td>
<td>DiHAA</td>
</tr>
<tr>
<td>R²</td>
<td>0.645</td>
<td>0.555</td>
<td>0.524</td>
<td>0.496</td>
<td>0.317</td>
<td>0.690</td>
</tr>
<tr>
<td>Intercept</td>
<td>-27.3 ± 28.5</td>
<td>-254.3 ± 72.1</td>
<td>-37.9 ± 20.7</td>
<td>16.5 ± 20.4</td>
<td>-0.584 ± 61.4</td>
<td>23.7 ± 7.6</td>
</tr>
<tr>
<td>Slope</td>
<td>76.81 ± 7.5</td>
<td>168.58 ± 19.2</td>
<td>45.57 ± 5.5</td>
<td>56.99 ± 5.9</td>
<td>118.07 ± 17.8</td>
<td>31.97 ± 2.2</td>
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</tbody>
</table>

Similarly to THM-FP, a larger range of TriHAA precursors is observed for similar DOC concentrations during dry events than wet events. The strength of the TriHAA-FP and DOC relationship is also stronger for wet events than for dry events. However, the slopes between wet and dry events are not significantly different from each other at the 95% confidence level. Like THM precursors, TriHAA precursors tend to be relatively homogenous during wet events but highly variable during dry events. Neither dry nor wet events have significantly higher TriHAA precursors.

DiHAA precursors do not exhibit a similar pattern to THM-FP or TriHAA-FP. The strength of the DiHAA-FP and DOC relationship is stronger under dry conditions, meaning that a wide range of DiHAA-FP values for similar DOC concentrations is not observed during dry events. The slope for wet events, however, is significantly higher than for dry events at the 95% confidence level. These results indicate that DiHAA-FP precursors are relatively homogenous during both wet and dry events, but more abundant during wet events.

While precursors tend to respond to precipitation, DOC concentrations are not significantly different under wet conditions versus dry conditions (Figure 2.31). Figure 2.31 shows averages for DOC concentrations and SUVA values for wet and dry conditions, with error bars representing one standard deviation. SUVA and aromaticity, however, are significantly higher during wet events compared to dry events at the 95% confidence level.
These results signify that wet events bring about more aromatic compounds and more THM and DiHAA precursors than dry events, and that precursors for these two groups include aromatic compounds. However, TriHAA precursors are not significantly higher during wet events despite an increase in aromatic compounds. These results reinforce the notion that non-aromatic compounds may be significant TriHAA precursors.

The reactivity of DOC under wet and dry conditions was also examined. Figure 2.32 contains averages for SpTHM-FP, SpTriHAA-FP, and SpDiHAA-FP for wet and dry events, with error bars representing one standard deviation. SpTHM-FP values were significantly higher during wet events at the 95% confidence level. In contrast, SpTriHAA-FP and SpDiHAA-FP values were significantly higher during dry events at the 95% confidence level.
This shows that NOM flushed into streams during wet events is more reactive in terms of THM formation but less reactive for HAA formation.

Figure 2.33 contains graphs of the three specific DBP groups versus DOC for wet and dry events. Like THM-FP precursors, THM reactivity is highly variable during dry conditions, with a wide range of SpTHM-FP values observed at similar DOC concentrations. During wet events, THM reactivity is fairly constant at all DOC concentrations. TriHAA reactivity also exhibits more variability during dry events than wet events. DiHAA-FP reactivity, on the other hand, is equally variable during wet and dry conditions but higher SpDiHAA-FP values tend to occur during dry events.

![SpDBP-FP Averages for Wet and Dry Events](image_url)
Figure 2.33: SpDBP-FP versus DOC for Wet and Dry Events
To summarize, wet events bring about the following changes: 1) higher THM reactivity and more THM precursors; 2) less DiHAA reactivity but more DiHAA precursors; and, 3) less TriHAA reactivity and no significant increase or decrease in TriHAA precursors. These results signify that NOM flushed from the watershed into streams during storms will most likely favor THM-FP rather than HAA-FP. HAA-FP will most likely be favored by non-aromatic compounds and aged NOM found in the stream itself. Furthermore, dry events represent more diversity in terms of DBP precursors, with a wide range of DBP formation potential observed at the same DOC concentrations. NOM during dry events tends to be highly variable with respect to DBP precursors and DBP reactivity, sometimes favoring formation potential and sometimes not.

As discussed previously, other studies have also investigated the effect of precipitation on DBP precursors. However, none of these studies have considered the contribution of rain water itself to DBP precursors. On April 2007, rain water was collected hourly over a two day storm (excluding a dry 10-hour period, 21 hourly samples were collected). DOC, UVA, THM-FP, and HAA-FP were measured for all rain water samples.

Figure 2.34 contains DOC and SUVA values measured for all rain water samples over the course of the April 2007 storm. The first DOC measurement is high, most likely due to atmospheric deposition on the rain water collector prior to the beginning of the storm. During the first half of the storm DOC values are low. These measurements correspond to a time period when precipitation volumes were the highest, which may have diluted the DOC concentrations of those samples. While the hydrograph on Figure 2.34 shows no precipitation from 6 PM on April 27th through 10 AM on April 28th, there was in fact very light rainfall during that time, enough to allow the ISCO to collect over 150 mL of rainwater per hour.
During the second half of the storm, DOC steadily increases. Given the light rainfall during this period, it is possible that DOC concentrations increased because of accumulation of airborne organic matter on the collector tarp that was not consistently flushed out by the rain. Specific UVA values remained relatively constant throughout the entire storm and are relatively low (averaging 2.2 L/mg-m over the entire event).

Figure 2.35 contains graphs of absolute THM-FP, TriHAA-FP, and DiHAA-FP over the duration of the storm. Patterns for all DBP precursors follow that of DOC concentration, with a spike in formation potential for the very first measurement (again, likely caused by atmospheric deposition), decreasing values during the first half of the storm, and steadily increasing values during the second half of the storm. There is a similar peak in values during the beginning of the second half of the storm. TriHAA precursors are always the highest DBP precursors measured, followed by THM-FP, and DiHAA-FP. DBP values reach considerable levels, greater than 200 ppb of TriHAA-FP, over 300 ppb of total HAA-FP, and approximately 150 ppb of THM-FP. Rain water can be a very significant source of DBP precursors, for all DBP groups. In particular, it seems to be a significant source of TriHAA precursors. It is interesting that for this low SUVA water TriHAA precursors are in fact so abundant. This observation further points to non-aromatic compounds being significant sources of HAA (especially TriHAA) precursors.

The reactivity of rain water was also examined. Figure 2.36 includes graphs of specific THM-FP, TriHAA-FP, and DiHAA-FP over the duration of the storm. Reactivity for all DBP groups was relatively constant throughout the storm (again, there is a peak in values during the beginning of the second half). The pattern closely follows observed SUVA values. NOM reactivity for this low SUVA water was highest for TriHAA formation, followed by
THM formation, and DiHAA formation. Reactivity for all DBP groups was also relatively constant despite increasing DOC concentrations, signifying that the composition of NOM did not change greatly during the event.

Figure 2.34: DOC and SUVA of Rain Water
Figure 2.35: DBP-FP of Rain Water

Figure 2.36: SpDBP-FP of Rain Water
Table 2.10: Comparison between Rainwater and Stream Water

<table>
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Table 2.10 compares the characteristics of rainwater to stream water, including average, median, maximum, and minimum measurements of DOC, SUVA, DBP precursors, and specific DBP formation. It is apparent that rainwater may be a significant source of DOC and DBP precursors, and that it may contain NOM with relatively high specific DBP formation potential. Furthermore, despite the low aromatic content of rainwater, the NOM composition highly favors TriHAA formation over the other DBP groups.

*Land Use Effects*

Figure 2.37 contains DOC and SUVA measurements for all stream samples taken from 2001 through 2007. Locations are arranged along the x-axis according to watershed area (1 being the largest). Note that sites 2, 3, 4, and 5 are different locations along Stillwater River,
with site 2 representing the entire Stillwater watershed. The DOC concentration graph contains lines for the threshold values determined from the DOC variability test. Almost all of the samples outside these thresholds were removed from the database for subsequent analysis. Four samples with DOC concentrations greater than 6 mg/L were retained because they were diluted prior to chlorination; however none of those samples exceeded 8 mg/L prior to dilution.

Larger watersheds have lower DOC concentrations overall and little variability while smaller watersheds exhibit the highest concentrations and high variability (Fig. 2.37). This is expected given dilution effects as water progresses downstream. Similarly, SUVA values are highly variable for the smallest watersheds and fairly constant for the largest watersheds. Both Pearson Product Moment and Spearman Rank Order correlation analysis showed no significant correlation between DOC and watershed area and between SUVA and watershed area. The DOC and SUVA data was not adjusted for seasonal influences in this correlation analysis.

Figure 2.37: DOC and SUVA for Original Wachusett Data, by Location and Year
Figure 2.38: All DBP Precursors for Reduced Wachusett Data, by Location and Year

Figure 2.38 contains absolute THM-FP, TriHAA-FP, and DiHAA-FP levels for stream samples from the reduced Wachusett dataset. The figures also include lines representing the mean values for each location. DBP values exhibit a similar range of values across the watersheds with the exception of Malagasco Brook, which has highly variable DOC concentrations and some of the highest DOC concentrations measured in all the watersheds. TriHAA precursors tend to be higher overall across locations, followed by THM precursors and DiHAA precursors. Both Pearson Product Moment and Spearman Rank Order correlation
analysis showed a very weak positive correlation between all three DBP precursor groups and watershed area, indicating more NOM availability leading to more DBP precursors as watershed size increases.

Figure 2.39 contains specific THM-FP, TriHAA-FP, and DiHAA-FP levels by increasing watershed area. Similarly to DBP precursors, reactivity is highest for SpTriHAA formation, followed by SpTHM and SpDiHAA formation. Again, Malagasco Brook stands out as having the highest specific DBP values. Pearson Product Moment and Spearman Rank Order correlation analysis showed a very weak positive correlation between SpTHM-FP and watershed area and SPTriHAA-FP and watershed area, and a very weak negative correlation between SpDiHAA-FP and watershed area.

Table 2.11 lists averages and one standard deviation for DOC, SUVA, absolute DBP-FP, and specific DBP-FP for each location. These values exclude samples with DOC concentrations outside the range established by the variable DOC test.
Figure 2.39: DBP Reactivity for Reduced Wachusett Data, by Location and Year

Sites ordered by increasing watershed area from left to right (Map ID in parenthesis)
1=Quinapoxet (6), 2=At MPR (8),
3=At Crowley (11), 4=At Rt. 62 (12),
5 = At Stillriver Rd. (15), 6=Wachusett (14),
7=Wauschacum (7), 8=Justice (18),
9=Keyes (19), 10=Gates (4), 11=French (1),
12=Rocky (16), 13=Malden (5), 14=Scalon (10),
15=Houghton (9), 16=Malagasco (2),
17=Ball (13), 18=Muddy (3), 19=Bailey (17)
Table 2.11: Averages and Standard Deviations by Location

Averages and standard deviations exclude high/low DOC samples, locations ordered by increasing watershed area

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Land use percentages were calculated for each of the 19 locations as described in Section 2.3.5, both for the full drainage area corresponding to each sampling point and for a riparian zone area extending 100 meters perpendicular to each stream bank. Land use categories obtained from the Massachusetts Geographic Information Systems website were lumped into 5 general categories including forest, wetland, agriculture, water, and urban (Section 2.3.5, Table 2.2).

In order to remove sample variations caused by seasonal and precipitation effects, Stillwater River at Muddy Pond Road (“At MPR”, location #8 in Figure 2.3) was chosen as a reference index. Specific DBP-FP and DOC values from all other locations were normalized to the MPR site according to calendar date. Several different statistical tests were performed to link specific DBP formation (NOM reactivity) and these five land use categories, including Spearman rank order correlation, Pearson product moment correlation, and stepwise regressions (both forward and backward). The forest category was considered as the background NOM composition and was therefore not included in any statistical test (removing the forest category also has the advantage of avoiding colinearity issues).

Table 2.12 presents results of all statistical tests between specific DBP formation and land use category, for the full watershed area land uses and the riparian zone land uses. For the correlation tests, cells include land use categories for which a significantly positive or negative relationship was observed at the 95% confidence level. For the regression tests, cells include land use categories that could be used to predict SpDBP-FP at the 95% confidence level, with the calculated coefficient in parenthesis.
### Table 2.12: Statistical Analysis between DBP Reactivity and Land Use

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<td></td>
</tr>
<tr>
<td><em>Land Use Category (Coefficient)</em></td>
<td>AG (-0.0176)</td>
<td>AG (-0.0160)</td>
<td>AG (-0.0277)</td>
</tr>
<tr>
<td>R²</td>
<td>0.182</td>
<td>0.183</td>
<td>0.297</td>
</tr>
</tbody>
</table>

AG = agriculture, WL = wetland, WR = water, UR = urban

*For correlations and regression, p < 0.05.*

Except for SpTHM-FP, Pearson product moment correlations gave identical results when using riparian percentages versus full watershed percentages. When using the full watershed percentages no correlation was observed between SpTHM-FP and wetlands. The percentage of wetlands increased for most of the locations when considering the riparian zone since most wetlands are located near streams. Therefore, it might be expected for an analysis considering the full watershed to underestimate the significance of wetlands.

For all DBP groups, reactivity was positively correlated with urban zones and negatively correlated with agriculture and wetlands. These results are also observed in the stepwise regression results. These results indicate that NOM from land uses associated with
high DBP precursor content is relatively un-reactive for forming DBPs per carbon. Even though agricultural lands and wetlands are abundant in NOM, it is possible for only a small fraction of those NOM compounds to be reactive with chlorine. The negative correlation between DBP reactivity and these land use categories indicates that the fraction of reactive NOM becomes even smaller as more NOM from these sources is added to streams. These results also show that the most reactive NOM comes from urbanized areas. Urban areas may be contributing DBP-inducing materials such as bromide, or man-made materials that can react with chlorine or enhance DBP formation. However, given that the watershed to Wachusett Reservoir is a highly forested and highly protected area with few urbanized zones, further analysis should be conducted which considers the location of urbanized areas with respect to water bodies. Possibly the few urban areas that do exist are located at such close proximity to receiving streams to affect the strength of the observed correlation with specific DBP formation. Geographic information systems and ArcGIS could be used to conduct a spatial analysis, in order to examine whether trends in specific DBP formation are related to the spatial arrangement of urban areas in the watershed. Unfortunately, this area of analysis lay outside the scope of this particular study, but it should be taken into consideration for any future work related to this project.
<table>
<thead>
<tr>
<th>Riparian Zone %</th>
<th>Full Watershed %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Results of Spearman and Pearson Correlation:</strong></td>
<td><strong>Results of Spearman and Pearson Correlation:</strong></td>
</tr>
<tr>
<td>Significantly correlated with water (positive) and urban (negative)</td>
<td>Significantly correlated with water (positive) and urban (negative)</td>
</tr>
<tr>
<td><strong>Forward and Backward Stepwise Regression:</strong></td>
<td><strong>Forward and Backward Stepwise Regression:</strong></td>
</tr>
<tr>
<td>Predicted from urban (-0.0125)</td>
<td>Predicted from urban (-0.0106)</td>
</tr>
<tr>
<td>$R^2 = 0.111$</td>
<td>$R^2 = 0.102$</td>
</tr>
<tr>
<td><strong>Multiple Linear Regression Model:</strong></td>
<td><strong>Multiple Linear Regression Model:</strong></td>
</tr>
<tr>
<td>$\text{DOC} = 1.132 + (0.00963 \times \text{AG} %) - (0.00429 \times \text{WL} %) + (0.0244 \times \text{WR} %) - (0.00927 \times \text{UR} %)$</td>
<td>$\text{DOC} = 1.190 + (0.00452 \times \text{AG} %) + (0.0283 \times \text{WL} %) + (0.0438 \times \text{WR} %) - (0.00903 \times \text{UR} %)$</td>
</tr>
<tr>
<td>$R^2 = 0.139$</td>
<td>$R^2 = 0.126$</td>
</tr>
</tbody>
</table>

$\text{AG} = \text{agriculture}, \text{WL} = \text{wetland}, \text{WR} = \text{water}, \text{UR} = \text{urban}$

Similar statistical analysis was performed to compare DOC concentrations (Table 2.13). Correlations for both types of land use analysis were significantly positive with the water category and significantly negative with the urban category. All stepwise regression results contained the urban category as the only significant (and negative) predictor of DOC concentration. Multiple linear regressions including agriculture, wetland, urban, and water categories were calculated for both land use groups for DOC concentrations. The strength of the regression is slightly better when using riparian zone percentages. However, the riparian zone regression model calculates a negative contribution to DOC concentration from wetlands, which runs counter to results from other studies showing that wetlands are primary sources of DOC compounds (Wetzel, 2001). On the other hand, the full watershed regression model, though weaker, calculates a high positive contribution from wetlands as expected.

Correlation and stepwise regression results show that DOC concentrations in agricultural lands and wetlands can vary greatly, and that DOC concentrations in these land...
use categories may be dominated by other factors (namely season, as discussed previously). However, water is significantly positively correlated with DOC concentration, indicating that a large source of DOC is the stream itself, and that DOC availability is driven by in-stream biological, chemical, and physical processes. Urbanized areas, on the other hand, are negatively correlated with DOC concentration, which can be expected given that urban areas contain little vegetation that can contribute to organic carbon content. The positive correlation between DBP reactivity and urban areas may indicate that, despite low carbon content, urban areas contribute highly reactive organic matter (possibly synthetic organics). Again, spatial analysis of trends in dissolved organic carbon concentration should be examined to determine how the spatial arrangement of urban areas influences these concentrations.

The most striking observation from this analysis is the lack of a marked improvement in the strength of the relationships when using riparian zone percentages versus the full watershed percentages. In fact, the relationship is stronger for SpTriHAA-FP when considering the full watershed area. Even though a considerable amount of NOM enters streams from littoral zones, it is possible that overland flow during storms carries NOM that is located much farther away than the immediate vicinity of the stream bank.

2.5. Summary

Disinfectants can react with naturally occurring organic matter to form disinfection byproducts (DBPs), which are known human carcinogens. A seldom explored option to control DBP formation in water systems is source control, controlling organic matter at the source before it reaches water treatment plants. In order to implement source control
strategies, it is important to know more about the nature and origin of DBP precursors and how they are influenced by watershed characteristics.

Prior to examining the influence of watershed characteristics on DBP formation, this study examined the effect of DOC concentration and chlorine dose on DBP formation (while maintaining DOC composition constant). It has been shown that as the chlorine dose increases the formation of DBPs on a per carbon basis also increases, such that low chlorine doses always produce less DBPs on a per carbon basis than high chlorine doses. This emphasizes the importance of having excess chlorine in a formation potential test. It was also shown that the reactivity (Specific DBP-FP) of chlorinated waters is the same regardless of DOC concentration and dependent only on DOC composition. This study also showed how the formation potential test produces unreliable results if the DOC concentration is outside the range of 1 – 6 mg/L of carbon. If using ultraviolet absorbance as a surrogate for DOC concentration, results from this experiment suggest sample concentrations should be adjusted to a UVA value between 0.01 and 0.10 cm\(^{-1}\) (as a preliminary estimate), prior to running a formation potential test.

For the reduced Wachusett database, regressions between DBP precursors and DOC concentration were strongly correlated (positive). However, regressions between DBP precursors and SUVA were weakly correlated (positive). This study agrees with other studies (Fujii, et al., 1998, Owen, et al., 1995, Stepaczuk, et al., 1998a), which note that non-aromatic DOC compounds may also contribute to DBP formation potential. In particular, this study has suggested that non-aromatic compounds may be significant sources of TriHAA precursors. This study showed that propensity to form DBPs on a per carbon basis (i.e. reactivity of DOC with chlorine) is not determined by DOC concentration alone when the
DOC is from different sources. Specific UVA was a slightly better predictor of DBP reactivity than DOC concentration, except for TriHAA reactivity, which again indicates the significance of non-aromatic compounds.

Analysis of seasonal effects showed that DOC concentrations were significantly highest during the summer while SUVA values were significantly lower in the winter and higher in spring. This analysis has also shown that winter tends to produce the highest DBP yields on a per carbon basis, summer tends to produce the lowest yields, and spring and fall produce comparable yields. These results indicate that increased DOC loads do not directly translate to increased DBP formation. Rather, DBP formation is favored by aged NOM found during winter months.

Analysis of precipitation effects showed that DOC concentrations are not significantly different under wet conditions versus dry conditions. Aromaticity (i.e. SUVA) is significantly higher during wet events compared to dry events which translated to increased THM reactivity but less DiHAA and TriHAA reactivity. THM and DiHAA precursors tended to increase during wet events, while TriHAA precursors were unrelated to precipitation. Therefore, NOM from runoff will most likely favor THM-FP, while HAA-FP will most likely be favored by non-aromatic compounds and aged NOM found in the stream itself. During dry events, NOM tends to be highly variable with respect to DBP precursors and reactivity, such that it is possible to observe a wide range of DBP formation potential at similar DOC concentrations. This study has also shown that rain water can be a very significant source of DBP precursors, for all DBP groups. In particular, it seems to be a significant source of TriHAA precursors. Dissolved organic carbon concentrations increased during the course of a storm event but
reactivity for all DBP groups remained relatively constant, signifying that the composition of NOM did not change greatly during the event.

Spatial analysis showed that TriHAA precursors tend to be higher overall across all locations, followed by THM precursors and DiHAA precursors. Likewise, reactivity is highest for TriHAA formation, followed by THM and DiHAA formation. This study showed that for all DBP groups, reactivity was positively correlated with urban zones and negatively correlated with agriculture and wetlands. These results indicate that NOM from land uses commonly considered high in DBP precursor content is relatively un-reactive for forming DBPs per carbon. Even though agricultural lands and wetlands are abundant in NOM, it is possible that only a small fraction of those NOM compounds are reactive with chlorine. These results also show that the most reactive NOM comes from urbanized areas. Urban areas may be contributing DBP-inducing materials such as bromide, or man-made materials that can react with chlorine or enhance DBP formation. This study showed DOC concentration to be significantly correlated with water (positive) and urban areas (negative). Therefore, large sources of DOC are the water bodies themselves and DOC availability is driven by in-stream biological, chemical, and physical processes. Urban areas are poor sources of DOC given their lack of vegetation.

Finally, an analysis using land use percentages from riparian zones did not markedly improve the strength of relationships between DBPs and land use, compared to using land use percentages from the full watershed area. Therefore, even though a considerable amount of NOM enters streams from littoral zones, it is possible that overland flow during storms carries NOM that is located much farther away than the immediate vicinity of the stream bank.
CHAPTER 3. DBP OCCURRENCE IN MA DRINKING WATER SYSTEMS

3.1. Background on DBPs in Municipal Water Systems

Disinfection byproducts have been identified in finished drinking water since 1974 (Singer, 1994). Since their discovery, federal regulations under the Safe Drinking Water Act have addressed the need for primary and residual disinfection while also regulating disinfection byproduct formation (Tables 1.1 and 1.2). Drinking water providers must implement disinfection practices in order to protect the public from diseases due to waterborne pathogens while also maintaining DBP concentrations below EPA MCLs to protect the public from illnesses due to carcinogens. Despite some large-scale outbreaks of water-related illnesses in recent years (for example, E. coli related illnesses in Ontario, Canada in 2000 and cryptosporidiosis in Milwaukee, Wisconsin in 1993) the goal of disinfection has been widely accomplished. Deaths and illnesses attributable to waterborne pathogens in finished drinking water are nearly non-existent in developed countries (Richardson, 2003). The latter goal, compliance with DBP regulations, continues to affect most drinking water systems in the United States (Adams et al., 2005; Obolensky et al., 2007). Currently, regulations require monitoring of four trihalomethanes (with an MCL of 80 ppb) and five haloacetic acids (with an MCL of 60 ppb) at points within the distribution system that are known to have high DBP occurrences (Table 1.2). There are also plans for future regulations that might establish lower MCLs.

Meeting disinfection needs while minimizing DBP formation can be particularly challenging if systems are unable to implement DBP control strategies (such as enhanced
coagulation, granular activated carbon or alternative disinfectants) due to increasing costs or lack of resources (Adams et al., 2005). In addition to understanding DBP control strategies, drinking water providers need to be aware of how factors such as raw water quality, season, and typical treatment practices can impact DBP concentrations in distribution systems and DBP formation at water treatment plants. This is necessary to ensure compliance with DBP regulations in the present. Furthermore, understanding the effects of these factors will help water providers plan for future events, such as stricter regulations, changes in climate, or changes in raw water quality as a result of different land uses. To assist water providers, several studies have examined the dynamics of DBP formation in water treatment plants and distribution systems as a function of treatment practices, raw water quality, and season.

In 1981, Singer et al. conducted a two-year survey in which they monitored 13 municipal water systems in North Carolina. The systems were tested for THM formation at several points along the water treatment train. Their study identified “a progressive production of THMs as a result of treatment…the increase in THM concentration during treatment is due to the increase in chlorine contact time as treatment progresses” (Singer et al., 1981). Coagulation and sedimentation were the most effective at removing TOC and THMs while filtration and clear well storage were not as effective (Singer et al., 1981). They also discuss the significant reductions in THMs that can be expected by shifting the point of chlorination to a post-sedimentation or post-filtration location.

Shifting the point of chlorination became one of the main strategies adopted by water providers after the EPA issued the Total Trihalomethane Rule in 1979 (Singer et al., 1994). Other strategies adopted at that time included decreasing the chlorine dose and applying chloramines as an alternative disinfectant, though these modifications often resulted in
violating the Surface Water Treatment Rule and Total Coliform Rule implemented in the late 80s (Singer et al., 1994). More recent strategies include granular activated carbon and enhanced coagulation. These practices, though effective, may be difficult to implement for small utilities due to lack of resources (Adams et al., 2005).

In a study that analyzed the Missouri Department of Natural Resources drinking water database from 1997 to 2001, Adams et al. (2005) compared disinfection practices. Their study found that THM concentrations were significantly lower for plants using chloramines compared to plants using free chlorine (Adams et al., 2005). That study also found that the majority of plants using free chlorine exceeded the 80 ppb regulation for THMs. On the other hand, the majority of plants using chloramines complied with the regulation. Similar results were observed for HAA concentrations when comparing free chlorine and chloramine plants. They also concluded that the majority of THMs were formed at the treatment plant, though a significant contribution had come from the distribution system (Adams et al., 2005). They did not find a statistically significant difference between HAA concentrations at the water treatment plant and in the distribution system. However, it has been shown that HAAs tend to degrade readily within the distribution system while THMs do not, such that HAA control at the water treatment plant is still a concern (Adams, et al., 2005). Adams et al. (2005) reiterate the need to control DBP formation at the water treatment plant, by any of three means: reduction in DBP precursors, use of alternative disinfectants, and removal of DBPs after formation.

With respect to raw water quality, Singer et al. (1981) restate the concept that raw water TOC is a good indicator of THM precursors (THM formation potential). The also note that residual TOC in treated waters is not a good indicator of THM-FP, and surmise that
“coagulation, settling, and filtration remove the constituents comprising the TOC and THM precursors to a different degree and in a non-uniform fashion for different waters” (Singer et al., 1981). In a study by Obolensky, et al. (2000), in which they screened data collected by US EPA as part of the Information Collection Rule of 1996, it was found that influent TOC levels strongly influenced disinfection practices. For example, TOC levels were significantly lower at plants using free chlorine for secondary disinfection than at plants using chloramines for secondary disinfection. They also observed that almost no plants used chloramines if influent TOC was below 2.0 mg/L and almost all plants used chloramines if influent TOC was above 10 mg/L (Obolensky et al., 2000).

As discussed in chapter 2, time of year affects DBP precursors from watershed sources. Similarly, DBP formation within treatment plants and in distribution systems may exhibit seasonal effects. Goslan et al. (2002) examined the formation of THMs through a water facility consisting of coagulation, dissolved air flotation, rapid gravity filtration, chlorination, filtration through a manganese contactor, and residual disinfection. Their study found the lowest reactivity (THM-FP) occurred in January, increased in June, and reached a maximum in November. During November, the water was more difficult to treat because of higher organic loads and increases in humic material (Goslan et al., 2002). Additionally, several other studies have shown THM concentrations in distribution systems tend to increase with increasing temperatures, while HAA concentrations tend to not be correlated with temperature in distribution systems (Adams et al., 2005).

Studies that have examined the effect of treatment practices have focused on generalized categories (such as free chlorine versus chloramines), but rarely on the effect of specific treatment processes or combinations of treatment processes. Studies have also
examined how raw water quality will affect treatment decisions, but have not addressed to a great extent how raw water quality influences DBP formation in distribution systems or in water treatment plants under different treatment practices. Seasonal influences on raw water quality and DBP precursor have been examined in other studies such that climate can be expected to affect DBP formation in water treatment plants and in distribution systems.

3.2. Objectives of Public Water Systems Study

The objective of this study is to utilize a Massachusetts database on public water systems to examine how different treatment practices, different combinations of treatment processes, raw water quality, and season affect DBP formation at the water treatment plant and in the distribution system (the database consists of THM, HAA, and raw water TOC measurements for 59 public water systems from 1988 through 2005). Knowing how these factors influence DBP formation can aid drinking water providers as they face changing climate, changing land uses, and changing regulations. This chapter will examine how DBP levels change at water treatment plants and in distribution systems as a result of treatment practice, raw water quality and season.

An obvious result of this work, which was not one of the main objectives of the study, is the documentation of the historical development of 59 public water systems in Massachusetts from as early as 1920 (though oftentimes as early as the late 1800s) through 2005. These histories are included in Appendix B.
3.3. Materials and Methods

The following is a description of: 1) the Massachusetts towns and public water systems included in the study group; 2) data collection undertaken in 2005 and 2006, including the historical development of public water systems, DBP measurements, and total organic carbon concentrations; and, 3) analysis of DBP measurements according to town, year, raw water quality, treatment practices, and season.

3.3.1. Towns in Study

The historical development of public water systems in Massachusetts was documented from as early as 1920 through 2005. For each water system, this project documented what raw water sources were used, the time period during which each water source was used, and the level of treatment each water source received during its time used. A total of 59 towns were investigated (listed in Table 3.1 in alphabetical order). Of these 59 towns, 35 towns are members of the Massachusetts Water Resources Authority (MWRA). Fourteen of these MWRA towns have been serviced fully by MWRA with finished drinking water since before 1920, nine have been serviced fully by MWRA since after 1920, and twelve have only ever been partially serviced or are serviced only during emergencies (Table 3.1). These 35 member towns share two surface water sources (Quabbin and Wachusset reservoir located in Central Massachusetts) and a water treatment plant (the John J. Carrol Water Treatment Plant). Towns that are only partially serviced by MWRA own and operate separate water sources and treatment plants, while towns that did not become members until after 1920 operated separate water sources and treatment plants prior to joining MWRA. For most of the
subsequent data analysis, MWRA communities are grouped together wherever possible.

Where MWRA members are listed separately, the data refers to non-MWRA water sources and treatment practices.

The historical development of MWRA, including its water sources and water treatment practices, is listed along with the other communities in Appendix B.

<table>
<thead>
<tr>
<th>Table 3.1: List of Communities Included in Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abington-Rockland</td>
</tr>
<tr>
<td>Andover</td>
</tr>
<tr>
<td>Arlington *</td>
</tr>
<tr>
<td>Bedford ***</td>
</tr>
<tr>
<td>Belmont *</td>
</tr>
<tr>
<td>Beverly-Salem</td>
</tr>
<tr>
<td>Billerica</td>
</tr>
<tr>
<td>Boston *</td>
</tr>
<tr>
<td>Braintree ***</td>
</tr>
<tr>
<td>Brockton</td>
</tr>
<tr>
<td>Brookline **</td>
</tr>
<tr>
<td>Burlington</td>
</tr>
</tbody>
</table>

* Members of MWRA before 1920, fully supplied

** Members of MWRA after 1920, fully supplied

*** Only partially supplied by MWRA
### Table 3.2: Data Collection Categories and Questions

<table>
<thead>
<tr>
<th>General Information</th>
<th>Customer Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Utility name and main contact information.</td>
<td>Name of city, town, or village ever served by utility, years of service, source used to provide service.</td>
</tr>
<tr>
<td><strong>Utility Information</strong></td>
<td></td>
</tr>
<tr>
<td>Ownership status, wholesale status, information on who supplies the utility with water and when, information on water treatment plants owned and operated by the utility.</td>
<td></td>
</tr>
<tr>
<td><strong>Source Information</strong></td>
<td></td>
</tr>
<tr>
<td>Years of operation, source name, whether source was treated by utility, type of source, depth of well and aquifer type (if groundwater), source type (if surface water).</td>
<td></td>
</tr>
<tr>
<td><strong>Well Information</strong></td>
<td></td>
</tr>
<tr>
<td>Year of closure (if contaminated), year reopened (if applicable), type of contamination.</td>
<td></td>
</tr>
</tbody>
</table>

### 3.3.2. Data Collection

The following section describes how historical data, DBP measurements, and raw water quality information were collected. Data collection began in the summer of 2005 and was an ongoing process through spring 2007. Table 3.2 lists the different data collection categories and respective questions that served as guidelines for information gathering.

*History of Water Sources and Treatment*

Numerous sources were used to trace the historical development of the municipal water systems. Searches for each town generally began with a search of the literature (primary research literature, grey literature, consulting reports, theses), personal communications (to Dr. Reckhow), consumer confidence reports (annual water quality reports printed by public...
water systems for their consumers), Source Water Assessment and Protection Program (SWAP) Reports, magazine articles, water treatment plant brochures, and questionnaire results from several surveys conducted in the past by UMass directed at water treatment plants. These records exist to varying degree for all communities in Massachusetts.

Other sources included town websites and historical websites. To some extent, historical data was obtained from an Access database provided by the Department of Environmental Protection, though historical data from this source was limited. The bulk of information for most towns was obtained from phone and email communications with water treatment plant operators, heads of Public Works Departments, water department superintendents, and laboratory technicians.

DBPs and Raw Water Quality

Disinfection byproduct data was extracted from an Access database provided by the Department of Environmental Protection. The database contained data from as early as 1988 through 2005. Each sample in the database contained the following information: public water system (PWS) identification number, PWS name, PWS status (active or inactive), address of sampling location, location code, sample characteristics (whether sample was raw or finished water and whether sample was taken at the water treatment plant or the distribution system), sample collection date, laboratory name and state number, analytical method used, chemical name tested for, chemical concentration, concentration units, and date analyzed. Data extracted from the database included total trihalomethanes and haloacetic acid 5 (at the water treatment plant and in the distribution system). Trihalomethane data was available for measurements taken at water treatment plants and in distribution systems, while haloacetic
acid 5 measurements were available for distribution systems only. These reported DBP concentrations represent single samples at a specified location for a given day, not quarterly averages or locational running averages. Such averages were not calculated for this study.

Raw water quality was characterized by total organic carbon content. TOC data was obtained either from the miscellaneous sources noted above or from phone and email interviews with water treatment plant operators. TOC data was available for 24 non-MWRA communities as well as for the MWRA system (data was unavailable for ground water sources supplying nine different communities). Multiple years worth of data were gathered wherever possible in order to calculate monthly averages.

### 3.3.3. Data Analysis

Treatment practices by individual water treatment plants were sorted into any of 16 categories listed in Table 3.3. In general, treatment plants were first sorted into one of four types based on their mechanical treatment: 1) no filtration, 2) direct or inline filtration, 3) conventional filtration consisting of coagulation/flocculation, sedimentation, and sand/anthracite filtration, or 4) conventional filtration including GAC as either a separate step or as part of the main filter. Plants were then sorted into one of eight types based on their disinfection treatment: 1) pre chlorine, where point of free chlorine injection is prior to filtration, 2) post chlorine, where point of free chlorine injection is after filtration, 3) pre chlorine and chloramines, 4) chloramines and ozone, 5) pre and post chlorine, 6) pre and post chlorine and chloramines, 7) post chlorine and ozone, or 8) post chlorine, chloramines, and ozone. Out of all possible combinations, all treatment plants fell into one of 16 categories.
listed in Table 3.3. Table 3.3 also includes the number of plants per category (this number does not reflect how many sources are treated at each plant, which may be several).

Water treatment plants were also sorted by TOC range when describing effects due to water quality, with ranges including less than 2 mg/L, 2 – 4 mg/L, 4 – 6 mg/L, 6 – 8 mg/L, and greater than 8 mg/L.

Samples were distinguished in other ways for different analysis, including by season (with Fall consisting of September, October, and November, Winter consisting of December, January, and February, Spring consisting of March, April, and May, and Summer consisting of June, July and August), by location (at water treatment plant or in distribution system), and by affiliation (MWRA or non-MWRA).

<table>
<thead>
<tr>
<th>Table 3.3: Treatment Categories and Number of Plants per Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional with GAC</td>
</tr>
<tr>
<td>Post Chlorine, Chloramines, Ozone (1)</td>
</tr>
<tr>
<td>Chloramines, Ozone (1)</td>
</tr>
<tr>
<td>Post Chlorine, Ozone (2)</td>
</tr>
<tr>
<td>Pre and Post Chlorine, Chloramines (2)</td>
</tr>
<tr>
<td>Pre and Post Chlorine (5)</td>
</tr>
<tr>
<td>Post Chlorine (5)</td>
</tr>
<tr>
<td>Conventional</td>
</tr>
<tr>
<td>Pre and Post Chlorine, Chloramines (1)</td>
</tr>
<tr>
<td>Pre and Post Chlorine (1)</td>
</tr>
<tr>
<td>Post Chlorine (3)</td>
</tr>
</tbody>
</table>

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3.4. Results and Discussion

The historical development of 59 public water systems in Massachusetts was documented and disinfection byproduct measurements from water treatment plants and distribution systems were collected. The objectives of this study are to examine the effect of treatment practices, raw water quality, and season on DBP formation. Public water system histories are included in Appendix B.

3.4.1. DBPs and TOC by Public Water System

Figures 3.1 and 3.2 contain all available THM and HAA5 data from distribution systems and THM data from water treatment plants, respectively. These figures also distinguish THM samples that exceeded 80 ppb and HAA5 samples that exceeded 60 ppb and contain the percentage of samples that ever exceeded these concentrations (these concentrations mirror EPA MCLs, but the MCLs are based on averages while these samples are single measurements only). Of all THM data available from water treatment plants, 1.9% of measurements exceeded 80 ppb. Of THM data taken at all distribution systems 10.8% of measurements exceeded 80 ppb, while 3.3% of HAA5 data in distribution systems exceeded 60 ppb. THM levels in distribution systems tend to exceed 80 ppb more often than HAA5 levels exceed 60 ppb.

Only a small fraction of public water systems are repeatedly exceeding 80 ppb of THMs at water treatment plants and 60 ppb of HAA5 in distribution systems (Fig. 3.1 and 3.2). However, the majority of systems have exceeded 80 ppb of THMs in distribution systems at some point. Distribution systems tend to have higher THM levels than HAA5
levels. In distribution systems, THM concentrations measured have a maximum of 210 ppb, a median of 38 ppb, and an average of 44 ppb, while HAA5 concentrations measured have a maximum of 120 ppb, a median of 24 ppb, and an average of 25 ppb. A significant portion of THMs are formed at the water treatment plant (THM concentrations measured at water treatment plants have a maximum of 150 ppb, a median of 15 ppb, and an average of 23 ppb). However, THM levels in distribution system tend to be higher than in water treatment plants, indicating that formation within distribution pipes is a concern.
Figure 3.1: THM and HAA5 in Distribution Systems, by Town
Total organic carbon content of raw water sources was obtained for 24 non-MWRA communities as well as for the MWRA system (Fig. 3.3). Raw water sources ranged in TOC from 1 to 11 mg/L, with an average TOC of 4.3 mg/L, a standard deviation of 1.9 mg/L, and a median value of 4 mg/L, for all water sources where TOC data was available (combining surface waters and ground waters). All raw water sources were also arranged according to TOC range (Fig. 3.4). Out of 72 raw water sources for which TOC data was available, the majority of sources (36.1%) are in the 2 – 4 mg/L range, which is a relatively oligotrophic range. However, very few sources (9.7%) are truly oligotrophic with TOC less than 2 mg/L. A quarter of all water sources surveyed have high TOC contents, greater than 6 mg/L.
Figure 3.3: Total Organic Carbon of Raw Water Sources, by Town

Figure 3.4: Percent of Raw Water Sources by TOC Range
3.4.2. DBPs and TOC by Treatment Level

As discussed in Section 3.3.4, all water treatment plants surveyed fell into one of 16 different treatment categories, arranged according to type of filtration and disinfection practices. Raw water quality was found to influence treatment practices (Fig. 3.5), such that low TOC waters (less than 4 mg/L) were generally not filtered or filtered without sedimentation. Higher TOC waters (greater than 4 mg/L) were universally filtered following some type of conventional treatment. The highest TOC waters were not always treated with GAC filters while relatively low TOC waters (less than 4 mg/L) were. It is possible that implementation of GAC filters is driven by cost rather than need.

<table>
<thead>
<tr>
<th>Treatment Level</th>
<th>Raw Water TOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional with GAC</td>
<td>Ozone, Post Chlorine, Chloramine (392)</td>
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<td>Ozone, Post Chlorine (566)</td>
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<td>Pre and Post Chlorine (721)</td>
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<td>Post Chlorine (960)</td>
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<tr>
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<td>Post Chlorine (1073)</td>
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<td>Pre Chlorine (34)</td>
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Figure 3.5: Treatment Level by TOC Range (number of samples in parenthesis)
Figure 3.6 contains observed THM levels at water treatment plants according to level of treatment. With respect to choice of disinfectant, shifting the point of chlorination from pre to post filtration did not decrease THM production in direct filtration plants, but this trend may reflect raw water quality (lower TOC in pre chlorination plants than in post chlorination plants). Use of chloramines usually translated to lower THM levels compared to using chlorine only, except in unfiltered waters. Alternative disinfectants that are less reactive with NOM may not be as effective as possible if THM precursors are not significantly reduced prior to disinfection. Use of ozone almost always resulted in lower THM levels, wherever ozone was used along with any other disinfectant. In conventional plants without GAC, the use of chloramines and of a pre-oxidation step resulted in generally lower THM levels than using post chlorination alone.
With respect to filtration practices, conventional treatment coupled with GAC always resulted in generally lower THM levels (regardless of disinfection practice) compared to conventional treatment without GAC. Unfiltered plants and direct filtration plants had relatively less THM production than conventional plants, but this trend reflects the prevalence of unfiltered plants and direct filtration plants treating low TOC water sources while conventional plants tend to treat high TOC water sources (Fig. 3.5).

Figure 3.7 contains observed THM levels in distribution systems according to level of treatment. THMs in the distribution system can reach much higher levels than THMs at water treatment plants, reinforcing the concept that a significant amount of THMs are formed within the distribution system itself (possibly aided by temperature and microbiological activity within pipes). Treatment practices influenced THM levels in distribution systems to a certain
extent. For example, the use of ozone generally reduced THMs compared to the use of other disinfectants, even for unfiltered waters. These results must be considered carefully, however, because there is a potential for forming potentially dangerous ozonation byproducts.

The use of GAC in conventional plants coupled with chloramines also helped reduce THM levels. However, chloramination plants did not produce lower THM levels compared to free chlorine plants wherever conventional treatment was used without the aid of GAC filtration. Conventional plants with GAC that only used chlorine as a disinfectant produced THM levels comparable to conventional plants without GAC. Overall these results indicate that: 1) alternative disinfectants like chloramines are significantly more effective at curbing THM formation in distribution systems if multiple precursor removal processes (like GAC filtration) are also employed; and, 2) use of free chlorine only is very likely to result in high THM levels regardless of precursor removal practices. Thus, a multiple barrier approach coupled with alternative disinfectants is desirable.

Interestingly, plants with no filtration and with direct filtration produced THM levels comparable to conventional treatment plants despite their lower TOC content. Having high quality water sources, therefore, does not translate to high quality water at the tap if precursor removal is minimal.
Figure 3.8 contains observed HAA5 levels in distribution systems by treatment level.

As mentioned previously, HAA5 concentrations do not reach as high concentrations as THMs in distribution systems, which may reflect the propensity of HAAs to degrade (as noted by Adams et al., 2005). With respect to disinfection, the use of ozone produced low HAA5 levels compared to other disinfectants. Using chloramines did not always result in lower HAA5 levels compared to using free chlorine, particularly for conventional plants without GAC, though this trend may be influenced by raw water quality (higher TOC waters are more likely to be treated with chloramines than with free chlorine only). Unfiltered sources significantly reduced their HAA5 concentrations when they switched from free chlorine and chloramines to ozone and chloramines.

Conventional treatment with GAC (for all disinfection practices) was more likely to produce lower HAA5 levels than conventional treatment without GAC, again signifying the
importance of multiple precursor removal processes. Unfiltered water sources and sources treated with direct filtration produced HAA5 concentrations comparable to filtered water sources, despite low TOC content. This matches the trend observed for THM concentrations discussed previously. Once again, it is important to note the effectiveness of multiple barriers and alternative disinfectants.

Figures 3.9, 3.10, and 3.11 illustrate which type of treatment plants most often exceeded 80 ppb of THMs in water treatment plants, 80 ppb of THMs in distribution systems and 60 ppb of HAA5 in distribution systems, respectively. With respect to THMs at water treatment plants, the following trends are observed (Fig. 3.9): 1) 80 ppb of THMs were most often exceeded by plants using free chlorine only, despite GAC treatment; 2) no ozone plants exceeded 80 ppb of THMs for the period of record; 3) direct filtration and no filtration plants exceeded 80 ppb of THMs the least, though this is likely a result of their low TOC water sources.

Figure 3.9: Samples Exceeding 80 ppb THMs in Water Treatment Plants
In distribution systems, the following trends are observed for THM levels (Fig. 3.10):

1) 80 ppb of THMs were most often exceeded by plants using free chlorine only; 2) plants with a pre chlorination step almost always resulted in more samples above 80 ppb of THMs, despite combinations with other disinfectants; 3) plants utilizing ozone produced the least THMs or none at all; 4) conventional plants with GAC tended to not exceed 80 ppb of THMs in distribution systems.

In distribution systems, the following trends are observed for HAA5 levels (Fig. 3.11):

1) no single disinfection practice consistently produced samples with less than 60 ppb of HAA5; 2) direct filtration and no filtration plants were most often exceeded 60 ppb of HAA5, though conventional chloramine plants (without GAC) had the most samples with HAA5 above 60 ppb; 3) plants are less likely to exceed 60 ppb of HAA5 in distribution systems compared to 80 ppb of THMs.
3.4.3. DBPs by Raw Water Quality

DBPs were sorted by TOC content to examine the effect of raw water quality on DBP formation at water treatment plants and in distribution systems. THM levels at all water treatment plants generally increased with increasing TOC content (Fig. 3.12). However, Figure 3.12 does not include the MWRA system. MWRA data, which falls in the 2 – 4 mg/L TOC range, is included in Figure 3.13. THM levels jump at the 2-4 mg/L range. This jump in THM levels is likely a result of data bias, given that the majority of THM data in that TOC range originates from a “no filtration” plant. Figure 3.12 illustrates the effect of TOC on THM formation, warning drinking water providers that water sources with high TOC contents are more likely to produce THMs, despite treatment level. Figure 3.13, on the other hand, signifies the importance of multiple barrier approaches to water treatment when waters with
low TOC content are capable of producing THM levels comparable to waters with the very highest TOC content.
Figure 3.14 includes THM and HAA5 levels observed in distribution systems by TOC range. THM levels in distribution systems are not as strongly correlated with raw water TOC as THM levels in water treatment plants. However, waters with less than 4 mg/L have lower median THM levels than waters with 6 mg/L or greater. In general, therefore, waters with high TOC content will produce more THMs at water treatment plants, which can translate to higher THM levels in distribution systems. Furthermore, THM levels at water treatment plants tend to be lower than THM levels in the distribution systems, for all TOC ranges. This strengthens the belief that a significant portion of THMs are produced within the distribution system. HAA5 levels in distribution systems are essentially uncorrelated to raw water TOC levels, with most of the TOC ranges producing similar HAA5 levels. While it is not possible to compare HAA5 levels at water treatment plants to levels in distribution systems, Figure 3.14 illustrates that high HAA5 levels can be obtained in distribution systems for all TOC ranges. Thus, control of both THMs and HAA5 in distribution systems is necessary.
Figure 3.14: THM and HAA in Distribution Systems, by TOC Range
3.4.4. DBPs by Season

DBP data was sorted according to season to examine climate effects on DBP formation at water treatment plants and in distribution systems. Figure 3.15 contains THM data from water treatment plants according to season and Figure 3.16 contains THM and HAA5 data from distribution systems according to season. T-tests were performed to determine what seasons had significantly different DBP averages (Table 3.4). Cells with bold words indicate pairs of season with significantly different averages (p < 0.01) (the season indicated in bold had the significantly higher average).

Figure 3.15: THM at Water Treatment Plants, by Season
Figure 3.16: THM and HAA5 in Distribution Systems, by Season
Table 3.4: T-test Results for Seasonal Analysis

For pairs of seasons with significantly different means, the seasons with the highest means are indicated in the following matrices (for DBP precursors at the specified location).

\[ \alpha = 0.01 \]

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<thead>
<tr>
<th>THMs at water treatment plant</th>
<th>THMs in distribution systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fall</td>
<td>Winter</td>
</tr>
<tr>
<td>Fall</td>
<td>*</td>
</tr>
<tr>
<td>Winter</td>
<td>Fall</td>
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<tr>
<td>Spring</td>
<td>Fall</td>
</tr>
<tr>
<td>Summer</td>
<td>Summer</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>HAAs in distribution system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fall</td>
</tr>
<tr>
<td>Fall</td>
</tr>
<tr>
<td>Winter</td>
</tr>
<tr>
<td>Spring</td>
</tr>
<tr>
<td>Summer</td>
</tr>
</tbody>
</table>

THM values at water treatment plants were significantly higher in the fall compared to winter and spring, which agrees with other studies cited here. This trend is most likely due to increased organic matter content and increased humic material from fallen leaves. THM values at water treatment plants were also significantly higher in the summer compared to winter. This trend is likely due to increasing temperatures which foment THM formation as well as increased organic matter content from new vegetation and algal blooms.

In distribution systems, THM levels were significantly higher than summer compared to all other seasons. This indicates the significance of temperature effects on THM formation inside water pipes, particularly due to increased microbiological activity. Fall averages are again significantly higher than spring and winter averages, while spring averages are significantly higher than winter averages. Higher fall and spring averages are likely related to increased organic matter content from fallen leaves and new vegetation.
With respect to HAA5, summer and spring averages in distribution systems were significantly higher than fall and winter. These trends point to the significance of increasing temperatures in HAA5 formation, as observed in other studies. These higher summer and spring averages may also be related to increased vegetation.

3.5. Summary

Public water systems must provide drinking water free of waterborne pathogens while also maintaining DBP concentrations below EPA MCLs. Though there are best treatment practices available (such as GAC filtration, enhanced coagulation, and alternative disinfectants such as chloramines and ozone) drinking water providers need to be aware of how factors such as raw water quality, season, and typical treatment practices can impact DBP concentrations in distribution systems and DBP formation at water treatment plants.

Utilizing Massachusetts water supplies as a source of information, this study has shown that distribution systems tend to have higher THM levels than HAA5 levels. Also, samples exceed 80 ppb of THMs more often than they exceed 60 ppb of HAA5 in distribution systems. Concentrations of HAA5 do not reach as high concentrations as THMs in distribution systems, which may reflect the propensity of HAAs to degrade as compared to THMs (Adams et al., 2005). Furthermore, while a significant portion of THMs are formed at water treatment plants, THM levels tend to be much higher in distribution systems than in water treatment plants, indicating that formation within distribution pipes is a major concern.

This study showed that raw water quality influenced treatment practices, such that low TOC waters (less than 4 mg/L) were generally treated by direct filtration or without the use of granular media filtration (i.e. conventional filtration). Higher TOC waters (greater than 4
mg/L) were universally filtered following some type of conventional treatment. Application of GAC filters was not dictated by need (i.e. the highest TOC waters were not always treated with GAC filters), indicating that cost is the likely driving force.

Analysis of the effect of treatment practices on DBP concentrations showed that alternative disinfectants are significantly more effective at minimizing DBP levels at water treatment plants and in distribution systems if multiple precursor removal processes (like GAC filtration) are also employed prior to disinfection. Use of free chlorine only was shown to result in higher DBP levels regardless of precursor removal practices. Thus, a multiple barrier approach coupled with alternative disinfectants is desirable. While use of ozone almost always resulted in lower DBP levels (wherever it was used along with any other disinfectant), these results must be considered carefully because of the potential to form unwanted ozonation byproducts. Even though plants without a filtration step or with direct filtration had lower TOC water sources, they produced THM levels comparable to conventional treatment plants. Having high quality water sources, therefore, does not translate to high quality water at the tap if precursor removal is minimal.

The effect of raw water quality on DBP formation was also examined. This study showed that THM levels at all water treatment plants generally increased with increasing TOC content, warning drinking water providers that water sources with high TOC concentrations are more likely to produce THMs, despite treatment level. This study also showed how waters with low TOC content are capable of producing THM levels comparable to waters with the very highest TOC content, pointing to the importance of a multiple barrier approach to water treatment. Waters with high TOC content will produce more THMs at water treatment plants,
which can translate to higher THM levels in distribution systems. On the other hand, HAA5 levels in distribution systems are essentially uncorrelated to raw water TOC levels.

Analysis of seasonal effects showed that fall tended to have the highest THM levels at water treatment plants, followed by summer. High THM values during fall are likely the result of increased organic matter content and increased humic material from fallen leaves, while high THM values during summer are likely the result of increasing temperatures and increased organic matter content from new vegetation and algal blooms. In distribution systems, summer tended to have the highest THM and HAA5 levels, possibly as a result of increased organic materials from increased microbiological activity and temperatures.

These results point to the need for multiple treatment barriers coupled with disinfectants that are less reactive with NOM than chlorine, since lower DBP levels at water treatment plants can translate to lower DBP levels in distribution systems. DBP formation in distribution systems should be a major concern for water systems. Even high quality water sources can produce high DBP levels via substantial additional formation in distribution systems.
CHAPTER 4. SYNTHESIS

Controlling disinfection byproduct formation is one of the biggest challenges facing drinking water providers. Past efforts to control DBP levels at consumer taps have consisted of end-of-the-pipe solutions (such as air stripping and granular activated carbon adsorption) and removing precursors to DBP formation prior to disinfection (through enhanced coagulation and filtration). This study has addressed two important issues regarding DBPs in water systems: 1) controlling DBP precursors at the source is another alternative for controlling DBPs, one that has not received as much attention; and, 2) the relationship between treatment practices and DBP concentrations in Massachusetts’ utilities. These issues will be particularly important if water systems are confronted with stricter DBP regulations, changing climate or varying land use.

Source control strategies will necessitate understanding how watershed characteristics can influence DBP precursors and natural organic matter. In general, this study has shown that DBP precursors are strongly correlated with DOC and DBP precursor loadings are driven by the same processes that control DOC loadings. Furthermore, reactivity (specific DBP formation) is affected by the age of natural organic matter, season, precipitation and land use. Specifically, this study has shown that:

- Non-aromatic compounds may be significant sources of DBP precursors (particularly TriHAA precursors).

- DBP reactivity (specific DBP-FP) is highest during winter months due to abundance of aged NOM.

- Precipitation tends to increase NOM aromaticity which favors THM formation but not HAA formation. Dry periods tend to represent a greater
diversity in terms of DBP precursors and reactivity, such that a wide range of DBP formation potential is observed at similar DOC concentrations. Also, rain water itself can be a significant source of DBP precursors.

Specific DBP-FP is positively correlated with urban areas in the watershed and negatively correlated with agricultural land and wetlands. Dissolved organic carbon concentration is positively correlated with water and negatively correlated with urban areas.

Riparian zones probably do not contribute the majority of DBP precursors, such that overland flow during storms carries precursors from throughout the watershed to receiving streams.

Given that many utilities in Massachusetts continue to exceed 80 ppb of THMs and 60 ppb of HAAs in their systems, it is important to take a critical look at what is causing these high concentrations. Factors such as treatment practices, season, and raw water quality will all impact DBP levels observed at water treatment plants and distribution systems. In general, this study has shown that treatment practices are influenced by raw water quality, and in turn DBP formation is affected by treatment practices, raw water quality, and climate. Specifically, this study has shown:

- Low TOC waters in Massachusetts tend to be treated without filtration or by direct filtration, and high TOC waters are universally filtered but the highest TOC waters will not generally be treated with best treatment processes such as GAC.
- Alternative disinfectants are more effective when coupled with multiple precursor removal processes while free chlorine use generally results in higher DBP levels despite precursor removal.

- Ozone is very effective at minimizing regulated DBP levels but may result in other unwanted byproducts.

- Waters with low TOC concentrations are still capable of producing excessive DBP levels if precursor removal is minimal.

- Water treatment plants tend to produce higher THM levels during the fall because of increased organic loading and increased aromaticity while distribution systems tend to produce higher DBP levels during summer because of increased temperatures and increased microbiological activity.

- DBP formation in distribution systems is considerable and may be the most immediate challenge to water systems.

It is outside the scope of this study to recommend precursor control strategies at the watershed level or best management practices for water systems under future political and environmental conditions. However, drinking water providers may benefit from the following considerations:

- Overall, if water systems are faced with stricter DBP regulations, their most effective solution, though certainly not the least expensive, will be to upgrade treatment practices to include multiple precursor removal steps and alternative disinfectants (possibly abandoning free chlorine altogether).
- Water systems will also need to address the distribution system infrastructure where most DBP formation occurs, either through extensive cleaning or replacement.

- Source control will be particularly important during winter when there is an abundance of aged reactive natural organic matter and during droughts when DBP precursors can be highly variable. Hotter temperatures will be particularly problematic as they will lead to increased DBP levels in distribution systems.

- Urban areas were observed to be significant sources of highly reactive DBP precursors, such that watershed management and protection will continue to be important for protecting water supplies.
CHAPTER 5. RECOMMENDATIONS FOR

FUTURE WORK

Both studies presented here will benefit from additional research and input. The following list represents some potential future work studies, though other project ideas may exist.

- Examine correlations between DOC, DBP precursors, specific DBP formation and actual areas of land use categories. The land use percentages calculated for the different sub-watersheds are relatively similar between watersheds. This neglects variations in actual sizes where some watersheds may contain extensive wetlands, for example, while other watersheds contain smaller wetlands. By using the actual land use areas rather than land use percentages it may be possible to obtain stronger correlations or to identify other correlations.

- Land use categories used in this study were obtained in 1999. Therefore, there is a discrepancy between the dates of DBP precursor data and land use categories. Current land use information should be obtained and comparisons made between any new information and that from 1999.

- Perform spatial analysis using geographic information systems (GIS) in order to examine whether specific DBP formation and dissolved organic carbon concentrations are affected by the spatial arrangement of urban areas in the watershed. A strong correlation was observed between specific DBP formation and urban areas (positive relationship) and between DOC and urban areas (negative relationship). It is possible for these correlations to be
affected by the proximity of urban areas to receiving bodies, particularly since Wachusett watershed is heavily forested and highly protected.

- Continue studies to identify and understand the role of different hydrologic compartments, such as rainwater and soil water, as sources of DBP precursors. Methods for extracting soil water via lysimeters will need to be refined in the laboratory and in a controlled outdoor experiment prior to actual field installment.

- Adjust current Standard Operating Procedures of UMass laboratories to require that samples collected for DBP formation potential experiments are diluted to an ultraviolet absorbance range between 0.01 and 0.10 cm$^{-1}$. The DOC variability test could be repeated in order to determine whether a higher UVA threshold is possible.

- Expand the database containing information on municipal water systems, particularly total organic carbon profiles of raw water sources. Total organic carbon data for several communities was limited, particularly for groundwater sources. Obtaining more TOC information will allow for the introduction of more DBP measurements into the results.
APPENDIX A: SOIL WATER DATA

Sampling Methods

Lysimeters were installed at three of the sampling sites in the Wachusett watershed on October 2005. These instruments use suction to collect water as it percolates through soils. Lysimeters were placed at sites #8 (Stillwater River at Muddy Pond Road), #9 (Houghton Brook), and #17 (Bailey Brook) (Fig. 2.3). Two lysimeters were installed at each location, approximately 2 to 5 feet from the stream edge, at depths of 6 and 12 inches (measured from the surface to the bottom of the lysimeter). Portable batteries and vacuum pumps were carted to each location during sampling events. Samples were collected on the same day as scheduled stream sample collection, which may or may not have followed a period of rainfall. During collection, the lysimeter pumps were run for approximately 2 to 6 hours.

On April 27 and 29, 2007, in addition to lysimeter samples, soil water was collected at the three locations by digging a shallow hole (approximately 3 inches deep) near the vicinity of the lysimeters and allowing it to fill with water. This water was collected in order to compare it to the lysimeter samples.

Results

Results are listed in Table A.1, including date of sampling, season, sample location, sample depth, ultraviolet absorbance, dissolved organic carbon, specific UVA, total THM-FP, total HAA-FP, TriHAA-FP, DiHAA-FP, specific THM-FP, specific TriHAA-FP, and specific DiHAA-FP. Specific DBP-FP and DBP precursor data was not available for each sample due
to volume constrains. A future study may utilize these results to consider the contribution of soil water as a source of DBP precursors, and how precursors may vary by depth, season, and land use.

**Remarks**

Most of the lysimeter samples had remarkably high dissolved organic carbon concentrations. In order to verify whether these measurements are accurate or the result of contamination and improper lysimeter installation, laboratory experiments and controlled field experiments should be conducted. Controlled experiments can also provide an estimate of the amount of time needed in order to extract a specific volume of water. This will also help determine the best field location for the lysimeter (for example, how far away from the stream it should be located and whether it should be installed on flat or sloped terrain).
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<th>DOC (mg/L)</th>
<th>SUVA (L/mg-m)</th>
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<th>Total HAA-FP</th>
<th>TriHAA-FP</th>
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<td>Abington-Rockland</td>
<td>Great Sandy Bottom Pond</td>
<td>Lake</td>
<td>1887 - present</td>
<td>[1940]: chlorination 1991: coagulation, PAC feed, tube settlers, microfiltration, pH adjustment, pre and post chlorination</td>
<td>PWS operates the John F. Hannigan WTP, the Great Sandy Bottom WTP, and the Myers Ave. WTP</td>
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<td>Hingham St. Reservoir</td>
<td>Reservoir</td>
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<td>1974: filtration, pH adjustment, permanganate addition, pre and post chlorination</td>
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<td>1974: filtration, pH adjustment, permanganate addition, pre and post chlorination</td>
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<td>1974: filtration, pH adjustment, permanganate addition, pre and post chlorination</td>
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<td>1974 - present</td>
<td>1974: filtration, pH adjustment, permanganate addition, pre and post chlorination</td>
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<td>Andover</td>
<td>Ballardvale Well</td>
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<td>[1956] - [1965]</td>
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<td>PWS operates the Robert E. McQuade WTP</td>
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<td>Arlington</td>
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<td>1899 - present</td>
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<td>No additional treatment by PWS</td>
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<td>Bedford</td>
<td>Hartwell Road Well #10</td>
<td>Wells &lt;50 ft</td>
<td>1983 - 1984: closed due to low pH, VOCs and Fe</td>
<td>1983: filtration, pH adjustment, fluoride addition, post chlorination</td>
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<td>Years</td>
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<td>1970: fluoride addition, chlorination</td>
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<tr>
<td>Turnpike Well #7</td>
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<td>[1965] - 1978: closed due to TCE</td>
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<td>1965: fluoride addition, chlorination</td>
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<td>1965: fluoride addition, chlorination</td>
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<td>[1965] - 1978: closed due to TCE</td>
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<td>1965: fluoride addition, chlorination</td>
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<td>[1955] - [1980]: closed due to Fe</td>
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### Belmont

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<td>1895 - present: 100% of current supply purchased year-round</td>
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### Beverly-Salem

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<td>Ipswich River</td>
<td>River</td>
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<td>1913 - present</td>
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<td>1935: aeration, coagulation, sedimentation, PAC feed, filtration, pre and post chlorination, chloramination 1952: pH adjustment, fluoride addition</td>
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<td>Reservoir Type</td>
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<td>1895</td>
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<td>Reservoir</td>
<td>Putnamville</td>
<td>1955 - present</td>
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<td>Wenham</td>
<td>1869 - present</td>
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<td>Farm River</td>
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PWS operates the Billerica Water Works

PWS operates the Great Pond Reservoir WTP
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<td>Upper Great Pond</td>
<td>Reservoir</td>
<td>1922 - present</td>
<td>1926: chlorination 1934: coagulation/flocculation, GAC filtration, pH adjustment, chlorination 1971: sedimentation, permanganate addition, pre and post chlorination 1996: stopped pre chlorinating</td>
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<td>Brockton Avon Reservoir</td>
<td>Reservoir</td>
<td>1880 - 1905, 1994 - present</td>
<td>[1900]: chlorination 1994: coagulation/flocculation, sedimentation, GAC filtration, pH adjustment, permanganate addition, pre and post chlorination</td>
<td>PWS operates the Silver Lake WTP and the Woodland Ave. WTP, also sells water to the Towns of Whitman, Hanson and Halifax since 1905</td>
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<td>Hubbard Ave. Well</td>
<td>Wells 50 - 150 ft</td>
<td>1985 - 1987</td>
<td>1985: permanganate addition</td>
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<td>Silver Lake</td>
<td>Reservoir</td>
<td>1903 - present</td>
<td>1951: chlorination 1969: coagulation/flocculation, sedimentation, filtration, pH adjustment, permanganate addition, post chlorination 1989: GAC filtration</td>
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<td>Brookline Charles River Wellfield</td>
<td>Depth unknown</td>
<td>1895 - 1953</td>
<td>No treatment</td>
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<td>BMWRA System</td>
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<td>1953 - present: 100% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
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<td>Burlington Lexington Well #10</td>
<td>Wells 50 - 150 ft</td>
<td>1998 - present</td>
<td>1999: GAC filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination, chloramination</td>
<td>PWS operates the Mill Pond Reservoir WTP and the Vine Brook WTP</td>
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<td>Lexington Well #11</td>
<td>Wells 50 - 150 ft</td>
<td>1992 - present</td>
<td>1999: GAC filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination, chloramination</td>
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<td>Lexington Well #7</td>
<td>Wells &lt;50 ft</td>
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<td>Main Station Wellfield</td>
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<td>1949 - 1975</td>
<td>1949: chlorination</td>
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<td>Middlesex Pike Well #3</td>
<td>Wells &lt;50 ft</td>
<td>1962 - present: closed between 1981 and 1984 due TCE</td>
<td>1984: air stripping, fluoride adjustment, chlorination 1999: GAC filtration, pH adjustment, permanganate addition, pre and post chlorination, chloramination</td>
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<td>Well</td>
<td>Use</td>
<td>Depth</td>
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<td><strong>Middlesex Pike Well #4</strong></td>
<td>Wells &lt;50 ft</td>
<td>1963 - present: closed between 1981 and 1984 due to TCE</td>
<td>1984: air stripping, fluoride adjustment, chlorination 1999: GAC filtration, pH adjustment, permanganate addition, pre and post chlorination, chloramination</td>
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<td><strong>Middlesex Pike Well #5</strong></td>
<td>Wells &lt;50 ft</td>
<td>1965 - present: closed between 1981 and 1984 due to TCE</td>
<td>1984: air stripping, fluoride adjustment, chlorination 1999: GAC filtration, pH adjustment, permanganate addition, pre and post chlorination, chloramination</td>
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<td><strong>Sandy Brook Well #6</strong></td>
<td>Wells &lt;50 ft</td>
<td>1966 - 1975: closed due to Fe, Mn</td>
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<td><strong>Sandy Brook Well #9</strong></td>
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<td>1970 - 1975: closed due to Fe, Mn</td>
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<td><strong>Terrace Hall Well #1</strong></td>
<td>Wells &lt;50 ft</td>
<td>1958 - present</td>
<td>1999: GAC filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination, chloramination</td>
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<td><strong>Terrace Hall Well #2</strong></td>
<td>Wells &lt;50 ft</td>
<td>1959 - present</td>
<td>1999: GAC filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination, chloramination</td>
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<td><strong>Wyman Well #8</strong></td>
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<td>1968 - 1987: closed due to Fe, Mn, and VOCs</td>
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<td><strong>Cambridge</strong></td>
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<td><strong>Fresh Pond Reservoir</strong></td>
<td>Reservoir</td>
<td>1856 - present</td>
<td>1922: aeration, coagulation, sedimentation, filtration, pH adjustment, post chlorination 1950: flocculation 1974: fluoride addition 2001: new WTP includes aeration, coagulation with dissolved air flotation, GAC filtration, pH adjustment, fluoride addition, post chlorination, chloramination, ozonation</td>
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<tr>
<td><strong>Hobbs Brook Reservoir</strong></td>
<td>Reservoir</td>
<td>1897 - present</td>
<td>1922: aeration, coagulation, sedimentation, filtration, pH adjustment, post chlorination 1950: flocculation 1974: fluoride addition 2001: new WTP includes aeration, coagulation with dissolved air flotation, GAC filtration, pH adjustment, fluoride addition, post chlorination, chloramination, ozonation</td>
<td></td>
</tr>
<tr>
<td><strong>MWRA System</strong></td>
<td>See separate entry</td>
<td>1904 - present: Emergency supply source</td>
<td>No additional treatment by PWS</td>
<td></td>
</tr>
</tbody>
</table>

PWS operates the Walter J. Sullivan WTP (formerly the William H. McGuinness WTP)
<table>
<thead>
<tr>
<th>Reservoir</th>
<th>Well</th>
<th>Depth</th>
<th>Start Date</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stony Brook Reservoir</td>
<td></td>
<td>1887 - present</td>
<td></td>
<td>1922: aeration, coagulation, sedimentation, filtration, pH adjustment, post chlorination 1950: flocculation 1974: fluoride addition 2001: new WTP includes aeration, coagulation with dissolved air flotation, GAC filtration, pH adjustment, fluoride addition, post chlorination, chloramination, ozonation</td>
</tr>
<tr>
<td>Canal Street Well #1</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, closed [1985]</td>
<td>pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Canal Street Well #2</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, closed [1985]</td>
<td>pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Crooked Spring Well #1</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Crooked Spring Well #2</td>
<td>Wells 50 - 150 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Jordan Road Well</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment, chlorination</td>
<td></td>
</tr>
<tr>
<td>Meadowbrook Well #1</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment</td>
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</tr>
<tr>
<td>Meadowbrook Well #2</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Mill Road Well #1</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Mill Road Well #2</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment, chlorination</td>
<td></td>
</tr>
<tr>
<td>Mill Road Well #3</td>
<td>Wells 50 - 150 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment, chlorination</td>
<td></td>
</tr>
<tr>
<td>Riverneck Well #1</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>2004: filtration, air stripping, pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Riverneck Well #2</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>2004: filtration, air stripping, pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Smith Street Well #1</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>1964: filtration, pH adjustment, permanganate addition, post chlorination</td>
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</tr>
<tr>
<td>Smith Street Well #2</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>1964: filtration, pH adjustment, permanganate addition, post chlorination</td>
<td></td>
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<tr>
<td>Turnpike Road Well #1</td>
<td>Wells &lt;50 ft</td>
<td>Dates unknown</td>
<td>pH adjustment</td>
<td></td>
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<tr>
<td>Warren Ave. Tubular Wellfield</td>
<td>Wells &lt;50 ft</td>
<td>Dates unknown</td>
<td>No treatment</td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Source Type</td>
<td>Well Characteristics</td>
<td>Dates</td>
<td>Treatment History</td>
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<tr>
<td>---------------------------</td>
<td>--------------------</td>
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<td>------------------------</td>
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<tr>
<td>Warren Ave. Well #1</td>
<td>Wells &lt;50 ft</td>
<td>Dates unknown</td>
<td>No treatment</td>
<td></td>
</tr>
<tr>
<td>Warren Ave. Well #2</td>
<td>Wells &lt;50 ft</td>
<td>Dates unknown</td>
<td>No treatment</td>
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</tr>
<tr>
<td>Chelsea</td>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1895 - present: 100% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
</tr>
<tr>
<td>Chicopee</td>
<td>Abbe Brook Reservoir</td>
<td>Reservoir</td>
<td>1887 - 1927</td>
<td>No treatment</td>
</tr>
<tr>
<td></td>
<td>Cooley Brook Reservoir</td>
<td>Reservoir</td>
<td>1893 - 1948</td>
<td>1932: filtration</td>
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<tr>
<td></td>
<td>Morton Brook Reservoir</td>
<td>Reservoir</td>
<td>1893 - 1948</td>
<td>1932: filtration</td>
</tr>
<tr>
<td></td>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1948 - present: 100% of current supply purchased year-round</td>
<td>1948: booster chlorination 1993: No additional treatment by PWS</td>
</tr>
<tr>
<td></td>
<td>Sand Bank Pond</td>
<td>Lake</td>
<td>1887 - 1927</td>
<td>No treatment</td>
</tr>
<tr>
<td></td>
<td>Springfield PWS</td>
<td>See separate entry</td>
<td>[1937] - present: Emergency supply source</td>
<td>No additional treatment by PWS</td>
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<tr>
<td>Danvers</td>
<td>Beverly-Salem PWS</td>
<td>See separate entry</td>
<td>Emergency supply source</td>
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<tr>
<td></td>
<td>Emerson Brook</td>
<td>River</td>
<td>1951 - present</td>
<td>1951: fluoride addition, chlorination 1953: pH adjustment 1977: coagulation/flocculation, sedimentation, GAC filtration, permanganate addition, pre and post chlorination</td>
</tr>
<tr>
<td></td>
<td>Middleton Pond</td>
<td>Lake</td>
<td>1876 - present</td>
<td>1934: chlorination 1951: fluoride addition 1953: pH adjustment 1977: coagulation/flocculation, sedimentation, GAC filtration, permanganate addition, pre and post chlorination</td>
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<tr>
<td></td>
<td>South Main St. Well #1</td>
<td>Wells 50 - 150 ft</td>
<td>1960 - present</td>
<td>1960: pH adjustment, fluoride addition, chlorination 2004: air stripping, permanganate addition, post chlorination</td>
</tr>
<tr>
<td></td>
<td>Swan Pond</td>
<td>Lake</td>
<td>1913 - present</td>
<td>1934: chlorination 1951: fluoride addition 1953: pH adjustment 1977: coagulation/flocculation, sedimentation, GAC filtration, permanganate addition, pre and post chlorination</td>
</tr>
<tr>
<td>Dedham-Westwood</td>
<td>Bridge St. A1</td>
<td>Wells 50 - 150 ft</td>
<td>1881 - [1928]</td>
<td>1881: chlorination</td>
</tr>
<tr>
<td>-----------------</td>
<td>---------------</td>
<td>------------------</td>
<td>---------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Bridge St. A2</td>
<td>Wells 50 - 150 ft</td>
<td>1928 - [2000]</td>
<td>1928: chlorination</td>
<td></td>
</tr>
<tr>
<td>Bridge St. B1</td>
<td>Wells 50 - 150 ft</td>
<td>1964 - present</td>
<td>1991: coagulation/flocculation, filtration, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination 2005: slat tray aeration</td>
<td></td>
</tr>
<tr>
<td>Bridge St. D1</td>
<td>Wells 50 - 150 ft</td>
<td>1966 - present</td>
<td>1991: coagulation/flocculation, filtration, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination 2005: slat tray aeration</td>
<td></td>
</tr>
<tr>
<td>Bridge St. E</td>
<td>Wells 50 - 150 ft</td>
<td>1954 - present</td>
<td>1991: coagulation/flocculation, filtration, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination 2005: slat tray aeration</td>
<td></td>
</tr>
<tr>
<td>Bridge St. F</td>
<td>Wells 50 - 150 ft</td>
<td>1954 - present</td>
<td>1991: coagulation/flocculation, filtration, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination 2005: slat tray aeration</td>
<td></td>
</tr>
<tr>
<td>Dover Road Well</td>
<td>Depth unknown</td>
<td>1951 - 1981</td>
<td>1951: chlorination</td>
<td></td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>2005 - present: Emergency supply source</td>
<td>No additional treatment by PWS</td>
<td></td>
</tr>
<tr>
<td>Rock Meadow Well #11</td>
<td>Wells &lt;50 ft</td>
<td>1953 - present</td>
<td>1953: pH adjustment, fluoride addition, chlorination</td>
<td></td>
</tr>
<tr>
<td>White Lodge Well #1</td>
<td>Wells 50 - 150 ft</td>
<td>1954 - present</td>
<td>1987: filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre chlorination</td>
<td></td>
</tr>
<tr>
<td>White Lodge Well #2</td>
<td>Wells 50 - 150 ft</td>
<td>1959 - present</td>
<td>1987: filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre chlorination</td>
<td></td>
</tr>
<tr>
<td>White Lodge Well #3</td>
<td>Wells 50 - 150 ft</td>
<td>1962 - present: closed between 1978 and 1987 due to TCE</td>
<td>1987: filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre chlorination</td>
<td></td>
</tr>
<tr>
<td>White Lodge Well #4</td>
<td>Wells 50 - 150 ft</td>
<td>1966 - present</td>
<td>1987: filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre chlorination</td>
<td></td>
</tr>
<tr>
<td>White Lodge Well #5</td>
<td>Wells 50 - 150 ft</td>
<td>1997 - present</td>
<td>1997: filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre chlorination</td>
<td></td>
</tr>
<tr>
<td>Everett</td>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1895 - present: 100% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
</tr>
</tbody>
</table>

PWS operates the Bridge St. WTP, White Lodge WTP, and Rock Meadow Treatment Facility.
|----------------|----------------|-----------|----------------|----------------------------------------------------------------------------------------------------------------------------------|

PWS operates the Regional Water Filtration Facility and the Falulah Water Filtration Facility, also sells water to Town of Westminster since 1890.
<table>
<thead>
<tr>
<th>Framingham</th>
<th>Birches St. Wells #1-3</th>
<th>Wells 50 - 150 ft</th>
<th>1939 - [1985]</th>
<th>[1939]: pH adjustment, metaphosphate addition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sudbury Aqueduct</td>
<td>Reservoir</td>
<td>1906 - 1946</td>
<td>No treatment</td>
</tr>
<tr>
<td>Haverhill</td>
<td>Chadwick Pond</td>
<td>Lake</td>
<td>1897 - 1976: closed but retained as emergency supply source</td>
<td>[1900]: diatomaceous earth filtration</td>
</tr>
<tr>
<td></td>
<td>Crystal Lake</td>
<td>Lake</td>
<td>1884 - present</td>
<td>1933: chlorination 1971: fluoride addition 1980: coagulation/flocculation, sedimentation, GAC filtration, pH adjustment, chloramination</td>
</tr>
<tr>
<td></td>
<td>Johnson Pond</td>
<td>Lake</td>
<td>1897 - 1976: closed but retained as emergency supply source</td>
<td>[1900]: diatomaceous earth filtration</td>
</tr>
<tr>
<td></td>
<td>Kenoza Lake</td>
<td>Lake</td>
<td>1867 - present</td>
<td>1933: chlorination 1971: fluoride addition 1980: coagulation/flocculation, sedimentation, GAC filtration, pH adjustment, chloramination</td>
</tr>
<tr>
<td></td>
<td>Lake Saltonstall</td>
<td>Lake</td>
<td>1867 - 1932</td>
<td>No treatment</td>
</tr>
<tr>
<td></td>
<td>Millvale Reservoir</td>
<td>Reservoir</td>
<td>1895 - present</td>
<td>1933: chlorination 1971: fluoride addition 1980: coagulation/flocculation, sedimentation, GAC filtration, pH adjustment, chloramination</td>
</tr>
<tr>
<td></td>
<td>Round Pond</td>
<td>Lake</td>
<td>1802 - present</td>
<td>1933: chlorination 1971: fluoride addition 1980: coagulation/flocculation, sedimentation, GAC filtration, pH adjustment, chloramination</td>
</tr>
</tbody>
</table>

PWS operates the Haverhill WTP, sells water to Plaistow, NH since 1960.
<table>
<thead>
<tr>
<th>Lawrence</th>
<th>Merrimac River</th>
<th>River</th>
<th>1873 - present</th>
<th>1893: filtration, chlorination 1938: aeration, coagulation/flocculation, sedimentation, pH adjustment, fluoride addition 1972: GAC filtration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>PWS operates the Lawrence Water Works, sold water to Town of Methuen between 1942 and 1983</td>
</tr>
<tr>
<td>Lexington</td>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1903 - present: 100% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
</tr>
<tr>
<td>Lowell</td>
<td>Black Brook Wells</td>
<td>Depth unknown</td>
<td>[1870] - 1961</td>
<td>No treatment</td>
</tr>
<tr>
<td></td>
<td>Hadley St. Wells</td>
<td>Depth unknown</td>
<td>[1870] - 1961</td>
<td>No treatment</td>
</tr>
<tr>
<td></td>
<td>Lower Black Brook Wells</td>
<td>Depth unknown</td>
<td>[1870] - 1961</td>
<td>No treatment</td>
</tr>
<tr>
<td></td>
<td>Merrimac River</td>
<td>River</td>
<td>1961 - present</td>
<td>1961: coagulation/flocculation, sedimentation, GAC filtration, pH adjustment, fluoride addition, pre and post chlorination</td>
</tr>
<tr>
<td>Lynne</td>
<td>Birch Pond</td>
<td>Reservoir</td>
<td>1873 - present</td>
<td>1983: pH adjustment, fluoride addition, chlorination 1989: coagulation/flocculation, GAC filtration, pre and post chlorination</td>
</tr>
<tr>
<td></td>
<td>Breeds Pond</td>
<td>Lake</td>
<td>1870 - present</td>
<td>1983: pH adjustment, fluoride addition, chlorination 1989: coagulation/flocculation, GAC filtration, pre and post chlorination</td>
</tr>
<tr>
<td></td>
<td>Hawkes Pond</td>
<td>Lake</td>
<td>1895 - present</td>
<td>1983: pH adjustment, fluoride addition, chlorination 1989: coagulation/flocculation, GAC filtration, pre and post chlorination</td>
</tr>
<tr>
<td></td>
<td>Ipswich River</td>
<td>River</td>
<td>1918 - present</td>
<td>1983: pH adjustment, fluoride addition, chlorination 1989: coagulation/flocculation, GAC filtration, pre and post chlorination</td>
</tr>
<tr>
<td></td>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1998 - present: Emergency supply source</td>
<td>PWS operates the Raymond Reardon WTP, sold water to Town of Saugus from 1885 through 1946</td>
</tr>
<tr>
<td></td>
<td>Saugus River</td>
<td>River</td>
<td>1898 - 1938: closed but retained as emergency supply source</td>
<td>1983: pH adjustment, fluoride addition, chlorination 1989: coagulation/flocculation, GAC filtration, pre and post chlorination</td>
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<tr>
<td></td>
<td>Walden Pond</td>
<td>Reservoir</td>
<td>1889 - present</td>
<td>1983: pH adjustment, fluoride addition, chlorination 1989: coagulation/flocculation, GAC filtration, pre and post chlorination</td>
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<tr>
<td>Malden</td>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1895 - present: 100% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
</tr>
<tr>
<td></td>
<td>Dug Wells</td>
<td>Depth unknown</td>
<td>[1885] - 1956: closed due to salt</td>
<td>[1885]: filtration</td>
</tr>
<tr>
<td>------------</td>
<td>-----------</td>
<td>---------------</td>
<td>---------------------------------</td>
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</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1956 - present: 100% of current supply purchased year-round</td>
<td>1994 - 1998: booster chlorination</td>
<td></td>
</tr>
<tr>
<td>Swampscott Road Wells</td>
<td>Depth unknown</td>
<td>[1885] - 1956: closed due to salt</td>
<td>[1885]: filtration</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Wells 50 - 150 ft</th>
<th>Startup date unknown, still used</th>
<th>pH adjustment, post chlorination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Church Street Well</td>
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<td></td>
</tr>
<tr>
<td>Duxbury PWS Municipal System</td>
<td></td>
<td>Emergency supply source, startup date unknown, still used</td>
<td>No additional treatment by PWS</td>
<td></td>
</tr>
<tr>
<td>Ferry St. Well</td>
<td>Wells 50 - 150 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Furnace Brook Well #1</td>
<td>Wells 50 - 150 ft</td>
<td>Startup date unknown, still used</td>
<td>PAC feed, GAC filtration, pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Furnace Brook Well #2</td>
<td>Wells 50 - 150 ft</td>
<td>Startup date unknown, still used</td>
<td>Air stripping, pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Furnace Brook Well #3</td>
<td>Wells 50 - 150 ft</td>
<td>Startup date unknown, still used</td>
<td>GAC filtration, pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Furnace Brook Well #4</td>
<td>Wells 50 - 150 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment, post chlorination</td>
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</tr>
<tr>
<td>Mt. Skirgo Wellfield</td>
<td>Wells &lt;50 ft</td>
<td>Dates unknown, no longer used</td>
<td>PAC feed, pH adjustment, post chlorination</td>
<td></td>
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<tr>
<td>Parsonage St. Well #1</td>
<td>Wells &lt;50 ft</td>
<td>Dates unknown, no longer used</td>
<td>Treatment unknown</td>
<td></td>
</tr>
<tr>
<td>Parsonage St. Well #2</td>
<td>Wells &lt;50 ft</td>
<td>Dates unknown, no longer used</td>
<td>Treatment unknown</td>
<td></td>
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<tr>
<td>School St. Well</td>
<td>Wells 50 - 150 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>South River St. Well</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Spring St. Well</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Union Station #1</td>
<td>Wells 50 - 150 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Union Station #2</td>
<td>Wells 50 - 150 ft</td>
<td>Startup date unknown, still used</td>
<td>pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Depth</td>
<td>Wells</td>
<td>Startup Date</td>
<td>Pre-Treatment Processes</td>
</tr>
<tr>
<td>---------------------</td>
<td>-------</td>
<td>-------</td>
<td>--------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Webster Well #1</td>
<td>50 - 150 ft</td>
<td>Still Used</td>
<td>pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Webster Well #2</td>
<td>&lt;50 ft</td>
<td>Still Used</td>
<td>pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Medfield</td>
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<tr>
<td>Elm St. Well #3</td>
<td>Depth unknown</td>
<td>Still Used</td>
<td>pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Elm St. Well #4</td>
<td>Depth unknown</td>
<td>Still Used</td>
<td>pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Main St. Well #1</td>
<td>Depth unknown</td>
<td>Still Used</td>
<td>1997: air stripping, pH adjustment, pre chlorination</td>
<td></td>
</tr>
<tr>
<td>Main St. Well #2</td>
<td>Depth unknown</td>
<td>Still Used</td>
<td>1997: air stripping, pH adjustment, pre chlorination</td>
<td></td>
</tr>
<tr>
<td>Medfield State Hospital</td>
<td>Private System</td>
<td>1932 - 1956</td>
<td>Treatment unknown</td>
<td></td>
</tr>
<tr>
<td>Route 27 Well #6</td>
<td>Wells 50 - 150 ft</td>
<td>1998 - present</td>
<td>pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Medford</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1895 - present: 100% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
<td></td>
</tr>
<tr>
<td>Melrose</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1895 - present: 100% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
<td></td>
</tr>
<tr>
<td>Methuen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lawrence PWS</td>
<td>See separate entry</td>
<td>1942 - 1983: 100% of supply purchased year-round</td>
<td>1942: pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Merrimac River</td>
<td>River</td>
<td>1983 - present</td>
<td>1983: coagulation/flocculation, sedimentation, PAC feed, GAC filtration, pH adjustment, pre and post chlorination</td>
<td></td>
</tr>
<tr>
<td>Private wells</td>
<td>Depth unknown</td>
<td>1894 - 1942</td>
<td>Treatment unknown</td>
<td></td>
</tr>
<tr>
<td>Milford</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clark Island Wellfield</td>
<td>Wells &lt;50 ft</td>
<td>1949 - present</td>
<td>1949: filtration and post chlorination 1996: coagulation/flocculation, pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Dilla St. Wellfield</td>
<td>Wells &lt;50 ft</td>
<td>1949 - present</td>
<td>1949: filtration and post chlorination 1996: coagulation/flocculation, pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Echo Lake</td>
<td>Lake</td>
<td>Startup date unknown, still used</td>
<td>1996: filtration, coagulation/flocculation, pH adjustment, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Godfrey Brook Well #1</td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>1984: filtration, air stripping, pH adjustment, permanganate addition, post chlorination</td>
<td></td>
</tr>
</tbody>
</table>

PWS operates the Methuen WTP and PWS operates the Dilla St. WTP and Godfrey Brook WTP, also sells water to Town of Hopedale since 1881.
<table>
<thead>
<tr>
<th>MWRA System</th>
<th>Reservoir/Lake</th>
<th>Wells</th>
<th>Startup Date</th>
<th>Treatment History</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Godfrey Brook Well #2</strong></td>
<td>Wells 50 - 150 ft</td>
<td>Startup date unknown, still used</td>
<td>1984: filtration, air stripping, pH adjustment, permanganate addition, post chlorination</td>
<td></td>
</tr>
<tr>
<td><strong>Godfrey Brook Well #4</strong></td>
<td>Wells &lt;50 ft</td>
<td>Startup date unknown, still used</td>
<td>1984: filtration, air stripping, pH adjustment, permanganate addition, post chlorination</td>
<td></td>
</tr>
<tr>
<td><strong>Lake Cochituate</strong></td>
<td>Reservoir</td>
<td>1848 - 1951</td>
<td>1928: chlorination</td>
<td></td>
</tr>
<tr>
<td><strong>Mystic Lakes</strong></td>
<td>Lake</td>
<td>1870 - 1908</td>
<td>No treatment</td>
<td></td>
</tr>
<tr>
<td><strong>MWRA System</strong></td>
<td>See separate entry</td>
<td>1954 - present: 15% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
<td></td>
</tr>
<tr>
<td><strong>Needham</strong></td>
<td>Charles River Well #1</td>
<td>Wells 50 - 150 ft</td>
<td>1936: pH adjustment, chlorination 2000: filtration, post chlorination</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Charles River Well #2</td>
<td>Wells 50 - 150 ft</td>
<td>1936: pH adjustment, chlorination 2000: filtration, post chlorination</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Charles River Well #3</td>
<td>Wells 50 - 150 ft</td>
<td>1936: pH adjustment, chlorination 2000: filtration, post chlorination</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dedham Ave. Dug Wells</td>
<td>Wells &lt;50 ft</td>
<td>1900 - 1936</td>
<td>No treatment</td>
</tr>
<tr>
<td><strong>New Bedford</strong></td>
<td>Acushnet Reservoir</td>
<td>Reservoir</td>
<td>1869 - 1899</td>
<td>No treatment</td>
</tr>
<tr>
<td></td>
<td>Assawompsett Pond</td>
<td>Reservoir</td>
<td>1924 - present</td>
<td>[1940]: pH adjustment, fluoride addition, chlorination 1978: coagulation/flocculation, sedimentation, PAC feed, GAC filtration, permanganate addition, post chlorination 1980: stopped fluoride addition</td>
</tr>
<tr>
<td></td>
<td>Great Quitticas Pond</td>
<td>Reservoir</td>
<td>1899 - present</td>
<td>[1940]: pH adjustment, fluoride addition, chlorination 1978: coagulation/flocculation, sedimentation, PAC feed, GAC filtration, permanganate addition, post chlorination 1980: stopped fluoride addition</td>
</tr>
</tbody>
</table>

PWS operates the John J. Carroll WTP, PWS operates the Quitticas WTP, also sells water to Acushnet since 1924, to Dartmouth and to Freetown since 1975.
<table>
<thead>
<tr>
<th>Reservoir Name</th>
<th>Type</th>
<th>Age</th>
<th>History</th>
</tr>
</thead>
<tbody>
<tr>
<td>Little Quitticas Pond</td>
<td>Reservoir</td>
<td>1886 - present</td>
<td>[1940]: pH adjustment, fluoride addition, chlorination 1978: coagulation/flocculation, sedimentation, PAC feed, GAC filtration, permanganate addition, post chlorination 1980: stopped fluoride addition</td>
</tr>
<tr>
<td>Long Pond</td>
<td>Reservoir</td>
<td>1924 - present</td>
<td>[1940]: pH adjustment, fluoride addition, chlorination 1978: coagulation/flocculation, sedimentation, PAC feed, GAC filtration, permanganate addition, post chlorination 1980: stopped fluoride addition</td>
</tr>
<tr>
<td>Pocksha Pond</td>
<td>Reservoir</td>
<td>1924 - present</td>
<td>[1940]: pH adjustment, fluoride addition, chlorination 1978: coagulation/flocculation, sedimentation, PAC feed, GAC filtration, permanganate addition, post chlorination 1980: stopped fluoride addition</td>
</tr>
<tr>
<td>Artichoke Reservoir</td>
<td>Reservoir</td>
<td>1908 - present</td>
<td>1908: filtration 1933: chlorination 1971: GAC filtration, fluoride addition 1985: coagulation/flocculation, sedimentation, pH adjustment, post chlorination</td>
</tr>
<tr>
<td>Ferry Road Well #1</td>
<td>Depth unknown</td>
<td>1956 - present</td>
<td>1956: pH adjustment, fluoride addition, post chlorination</td>
</tr>
<tr>
<td>Ferry Road Well #2</td>
<td>Depth unknown</td>
<td>1956 - present</td>
<td>1956: pH adjustment, fluoride addition, post chlorination</td>
</tr>
<tr>
<td>Indian Hill Reservoir</td>
<td>Reservoir</td>
<td>1979 - present</td>
<td>1979: GAC filtration, fluoride addition, chlorination 1985: coagulation/flocculation, sedimentation, post chlorination</td>
</tr>
<tr>
<td>Jackman Ravine Dug Wells</td>
<td>Wells &lt;50 ft</td>
<td>1893 - [1953]</td>
<td>1893: filtration</td>
</tr>
<tr>
<td>Trout Brook Wellfield</td>
<td>Wells &lt;50 ft</td>
<td>1881 - [1953]</td>
<td>1881: filtration</td>
</tr>
<tr>
<td>Trout Brook Wells</td>
<td>Wells 50 - &gt;150 ft</td>
<td>1903 - [1953]</td>
<td>1903: filtration</td>
</tr>
<tr>
<td>Charles River Dug Wells #1</td>
<td>Wells &lt;50 ft</td>
<td>1911 - 1954</td>
<td>1911: filtration 1935: chlorination</td>
</tr>
<tr>
<td>Charles River Dug Wells #2</td>
<td>Wells &lt;50 ft</td>
<td>1927 - 1954</td>
<td>1927: filtration 1935: chlorination</td>
</tr>
<tr>
<td>Charles River Dug Wells #3</td>
<td>Wells &lt;50 ft</td>
<td>1938 - 1954</td>
<td>1938: filtration, chlorination</td>
</tr>
</tbody>
</table>

**Newburyport**

- PWS operates the Artichoke Reservoir WTP, sells water to Town of West Newbury since 1908.
<table>
<thead>
<tr>
<th>Source</th>
<th>Location</th>
<th>Depth</th>
<th>Years</th>
<th>Treatment History</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charles River Infiltration Gallery</td>
<td>Wells &lt;50 ft</td>
<td>1875 - 1954</td>
<td>1875: filtration 1935: chlorination</td>
<td></td>
</tr>
<tr>
<td>Charles River Wellfield</td>
<td>Wells 50 - 150 ft</td>
<td>1889 - 1954</td>
<td>No treatment</td>
<td></td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1954 - present: 100% of current supply purchased year-round</td>
<td>1963: fluoride addition 1984: stopped fluoride addition</td>
<td></td>
</tr>
<tr>
<td>North Reading</td>
<td>Andover PWS</td>
<td>See separate entry</td>
<td>[1900] - present: 60% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
</tr>
<tr>
<td>Central St. Wellfield</td>
<td>Wells &lt;50 ft</td>
<td>1954 - present</td>
<td>1971: pH adjustment, fluoride addition, permanganate addition, pre chlorination</td>
<td></td>
</tr>
<tr>
<td>Lakeside Boulevard Wellfield</td>
<td>Wells &lt;50 ft</td>
<td>1962 - present</td>
<td>1971: pH adjustment, fluoride addition, permanganate addition, pre chlorination 1981: filtration</td>
<td></td>
</tr>
<tr>
<td>Railroad Bed Wellfield</td>
<td>Wells &lt;50 ft</td>
<td>1980 - present</td>
<td>1971: pH adjustment, fluoride addition, permanganate addition, pre chlorination 1999: filtration, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Route 125 Wellfield</td>
<td>Wells &lt;50 ft</td>
<td>1976 - present</td>
<td>1971: pH adjustment, fluoride addition, permanganate addition, pre chlorination 1981: filtration</td>
<td></td>
</tr>
<tr>
<td>Stickney Well</td>
<td>Wells &lt;50 ft</td>
<td>[1965] - 1978: closed due to TCE</td>
<td>1971: pH adjustment, fluoride addition, permanganate addition, pre chlorination</td>
<td></td>
</tr>
<tr>
<td>Norwood</td>
<td>Buckmaster Pond</td>
<td>Lake</td>
<td>1880 - 1954: kept as emergency supply source till 1979, abandoned in 1979 due to VOCs</td>
<td>1936: aeration, GAC filtration</td>
</tr>
<tr>
<td>Ellis Wellfield</td>
<td>Depth unknown</td>
<td>1904 - 1954: kept as emergency supply source till 1979, abandoned in 1979 due to VOCs</td>
<td>1936: aeration, GAC filtration</td>
<td></td>
</tr>
<tr>
<td>Location</td>
<td>Source Type</td>
<td>Depth</td>
<td>Years in Operation</td>
<td>Treatment History</td>
</tr>
<tr>
<td>-------------------</td>
<td>-------------</td>
<td>-------</td>
<td>--------------------</td>
<td>--------------------------------------------------------</td>
</tr>
<tr>
<td><strong>Peabody</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ipswich River</td>
<td>River</td>
<td></td>
<td>1927 - present</td>
<td>1974: aeration, coagulation/flocculation, sedimentation, filtration, pH adjustment, permanganate addition, pre and post chlorination  1983: fluoride addition</td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1957 - present: 10% of current supply purchased year-round</td>
<td>1974: aeration, coagulation/flocculation, sedimentation, filtration, pH adjustment, permanganate addition, pre and post chlorination  1983: fluoride addition</td>
<td></td>
</tr>
<tr>
<td>Spring Pond Reservoir</td>
<td>Reservoir</td>
<td>1797 - present</td>
<td>[1915]: filtration, permanganate addition, chlorination  1997: aeration, coagulation/flocculation, filtration, pH adjustment, fluoride addition, pre and post chlorination</td>
<td></td>
</tr>
<tr>
<td>Suntaug Lake</td>
<td>Lake</td>
<td>1906 - present</td>
<td>1974: aeration, coagulation/flocculation, sedimentation, filtration, pH adjustment, permanganate addition, pre and post chlorination  1983: fluoride addition</td>
<td></td>
</tr>
<tr>
<td>Winona Pond Reservoir</td>
<td>Reservoir</td>
<td>1974 - present</td>
<td>1974: aeration, coagulation/flocculation, sedimentation, filtration, pH adjustment, permanganate addition, pre and post chlorination  1983: fluoride addition</td>
<td></td>
</tr>
<tr>
<td><strong>Quincy</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1895 - present: 100% of current supply purchased year-round</td>
<td>1974: aeration, coagulation/flocculation, sedimentation, filtration, pH adjustment, permanganate addition, pre and post chlorination  1983: fluoride addition</td>
<td></td>
</tr>
<tr>
<td><strong>Reading</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-Line Well</td>
<td>Wells 50 - 150 ft</td>
<td>1961 - 2006</td>
<td>1961: aeration, coagulation/flocculation, filtration, pre chlorination  1981: sedimentation, pH adjustment, fluoride addition, permanganate addition, post chlorination</td>
<td>PWS used to operate the Louanis Groundwater Facility</td>
</tr>
<tr>
<td>Ipswich River Wellfield</td>
<td>Depth unknown</td>
<td>1891 - 1931</td>
<td>1896: coagulation/flocculation, filtration</td>
<td></td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>2006 - present: 100% of current supply purchased year-round</td>
<td>1974: aeration, coagulation/flocculation, sedimentation, filtration, pH adjustment, permanganate addition, pre and post chlorination  1983: fluoride addition</td>
<td>No additional treatment by PWS</td>
</tr>
<tr>
<td>Well #</td>
<td>Wells</td>
<td>Water Level</td>
<td>Year Range</td>
<td>Treatment History</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>-------------</td>
<td>------------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Revay Well #2</td>
<td>Wells &lt;50 ft</td>
<td>1931 - 1958: VOCs discovered in 2002</td>
<td>1935: aeration, filtration</td>
<td></td>
</tr>
<tr>
<td>Well #15</td>
<td>Wells 50 - 150 ft</td>
<td>1966 - 2006</td>
<td>1966: aeration, coagulation/flocculation, filtration, pre chlorination 1981: sedimentation, pH adjustment, fluoride addition, permanganate addition, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Well #66-8</td>
<td>Wells &lt;50 ft</td>
<td>1966 - 2006</td>
<td>1966: aeration, coagulation/flocculation, filtration, pre chlorination 1981: sedimentation, pH adjustment, fluoride addition, permanganate addition, post chlorination</td>
<td></td>
</tr>
<tr>
<td>Well #82-20</td>
<td>Wells 50 - 150 ft</td>
<td>1985 - 2006</td>
<td>1985: aeration, coagulation/flocculation, sedimentation, filtration, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination</td>
<td></td>
</tr>
</tbody>
</table>

**Revere**

| MWRA System | See separate entry | 1895 - present: 100% of current supply purchased year-round | No additional treatment by PWS |

**Saugus**

| Lynn PWS Municipal System | 1885 - 1946: 100% of supply purchased year-round | No additional treatment by PWS |

<p>| MWRA System | See separate entry | 1946 - present: 100% of current supply purchased year-round | No additional treatment by PWS |</p>
<table>
<thead>
<tr>
<th>Location</th>
<th>MWRA System</th>
<th>See separate entry</th>
<th>Years of Operation</th>
<th>Treatment History</th>
</tr>
</thead>
<tbody>
<tr>
<td>Somerville</td>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1895 - present: 100% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
</tr>
<tr>
<td></td>
<td>Littleville Reservoir</td>
<td>Reservoir</td>
<td>1965 - present: Emergency supply source</td>
<td>1965: aeration, coagulation/flocculation, sedimentation, filtration, chlorination 1974:</td>
</tr>
<tr>
<td>Stoneham</td>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1895 - present: 100% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
</tr>
<tr>
<td>Sudbury</td>
<td>Well #1</td>
<td>Depth unknown</td>
<td>1936 - 2003: closed due to salt</td>
<td>No treatment</td>
</tr>
<tr>
<td></td>
<td>Well #10</td>
<td>Wells 50 - 150 ft</td>
<td>1996 - present</td>
<td>1996: pH adjustment, fluoride addition, chlorination</td>
</tr>
<tr>
<td></td>
<td>Well #2A</td>
<td>Wells 50 - 150 ft</td>
<td>1956 - present</td>
<td>1997: air stripping, pH adjustment, fluoride addition, post chlorination 2003: filtration</td>
</tr>
<tr>
<td></td>
<td>Well #3</td>
<td>Wells 50 - 150 ft</td>
<td>1959 - 2004</td>
<td>1965: pH adjustment, fluoride addition, post chlorination</td>
</tr>
<tr>
<td></td>
<td>Well #4</td>
<td>Wells 50 - 150 ft</td>
<td>1962 - present</td>
<td>1965: pH adjustment, fluoride addition, post chlorination</td>
</tr>
<tr>
<td></td>
<td>Well #5</td>
<td>Wells 50 - 150 ft</td>
<td>1965 - present: closed between 1986 and 1990 due to VOCs</td>
<td>1965: pH adjustment, fluoride addition, post chlorination 1990: air stripping</td>
</tr>
</tbody>
</table>

PWS operates the West Parrish WTP, also supplies Ludlow since 1994, Agawam since 1913, East Longmeadow since 1913, Southwick since 1929, Chicopee since 1913, Westfield since 1954.
<table>
<thead>
<tr>
<th>Well</th>
<th>Wells &amp; Depth</th>
<th>Years</th>
<th>Treatment Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Well #6</td>
<td>Wells 50 - 150 ft</td>
<td>1972 - present</td>
<td>1972: fluoride addition, chlorination</td>
</tr>
<tr>
<td>Well #7</td>
<td>Wells 50 - 150 ft</td>
<td>1980 - present</td>
<td>1980: filtration, pH adjustment, fluoride addition, pre chlorination</td>
</tr>
<tr>
<td>Well #8</td>
<td>Wells 50 - 150 ft</td>
<td>1983 - present</td>
<td>1983: pH adjustment, fluoride addition, pre chlorination 1999: filtration</td>
</tr>
</tbody>
</table>

**Wakefield**

<table>
<thead>
<tr>
<th>Location</th>
<th>Wells &amp; Depth</th>
<th>Years</th>
<th>Treatment Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bay State Rd. Well</td>
<td>Wells &lt;50 ft</td>
<td>1943 - 1976: closed due to Fe and Mn contamination</td>
<td>No treatment</td>
</tr>
<tr>
<td>Crystal Lake</td>
<td>Lake</td>
<td>1883 - present</td>
<td>1930: aeration, filtration, pH adjustment, post chlorination, chloramines 1978: fluoride addition</td>
</tr>
<tr>
<td>Lake Quannapowitt</td>
<td>Lake</td>
<td>1958 - present</td>
<td>Emergency supply source</td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1957 - present</td>
<td>85% of current supply purchased year-round 1998: booster chlorination, stopped in 2005</td>
</tr>
<tr>
<td>Sexton Ave. Wellfield</td>
<td>Wells &lt;50 ft</td>
<td>1930 - 1968: closed due to Fe and Mn</td>
<td>No treatment</td>
</tr>
</tbody>
</table>

**Walpole**

<table>
<thead>
<tr>
<th>Location</th>
<th>Wells &amp; Depth</th>
<th>Years</th>
<th>Treatment Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mine Brook #1</td>
<td>Wells &lt;50 ft</td>
<td>1954 - present</td>
<td>1976: filtration, pH adjustment, fluoride addition, permanganate addition, pre chlorination</td>
</tr>
<tr>
<td>Mine Brook #3</td>
<td>Wells 50 - 150 ft</td>
<td>1977 - present</td>
<td>1977: filtration, pH adjustment, fluoride addition, permanganate addition, pre chlorination</td>
</tr>
<tr>
<td>Mine Brook #5</td>
<td>Wells 50 - 150 ft</td>
<td>1987 - present</td>
<td>1987: filtration, pH adjustment, fluoride addition, permanganate addition, pre chlorination</td>
</tr>
<tr>
<td>Neponset #1</td>
<td>Wells &lt;50 ft</td>
<td>1992 - present</td>
<td>1998: filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination</td>
</tr>
<tr>
<td>Neponset #2</td>
<td>Wells &lt;50 ft</td>
<td>1992 - present</td>
<td>1998: filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination</td>
</tr>
<tr>
<td>South St. Well</td>
<td>Wells &lt;50 ft</td>
<td>1958 - 1965</td>
<td>No treatment</td>
</tr>
<tr>
<td>Washington Well #1</td>
<td>Wells &lt;50 ft</td>
<td>1895 - 1980</td>
<td>No treatment</td>
</tr>
<tr>
<td>Washington Well #10</td>
<td>Wells &lt;50 ft</td>
<td>1988 - present</td>
<td>1998: filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination</td>
</tr>
</tbody>
</table>

PWS operates the Wakefield WTP

PWS operates the H.E. Willis WTP and the Edward F. Delaney WTP
| Washington Well #2 | Wells <50 ft | 1918 - 1980 | No treatment |
| Washington Well #3 | Wells <50 ft | 1930 - 1980 | No treatment |
| Washington Well #4 | Wells <50 ft | 1944 - 1980 | No treatment |
| Washington Well #5 | Wells 50 - 150 ft | 1953 - 1967 | No treatment |
| Washington Well #6 | Wells 50 - 150 ft | 1969 - present | 1998: filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination |
| Washington Well #7 | Wells <50 ft | 1973 - present | 1998: filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination |
| Washington Well #8 | Wells <50 ft | 1976 - present | 1998: filtration, air stripping, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination |
| Washington Well #9 | Wells 50 - 150 ft | 1982 - present | 1990: GAC filtration, post chlorination, ozone 1998: air stripping, pH adjustment, fluoride addition, permanganate addition, pre and post chlorination, stopped ozone |

**Waltham**

| Charles River | River | 1873 - 1949 | 1880: filtration |
| MWRA System | See separate entry | 1949 - present: 100% of current supply purchased year-round | No additional treatment by PWS |

**Weymouth**

<p>| Great Pond | Lake | 1883 - present | 1936: coagulation/flocculation, sedimentation, filtration, pH adjustment, permanganate addition, post chlorination 1972: fluoride addition |
| Libbey park Well | Wells &lt;50 ft | 1959 - present: Emergency supply source | 1959: pH adjustment, chlorination 2001: aeration, coagulation/flocculation, sedimentation, GAC filtration, fluoride addition, permanganate addition, post chlorination |
| Main St. Well | Wells 50 - 150 ft | 1951 - present | 1951: pH adjustment, chlorination 1973: aeration, coagulation/flocculation, sedimentation, filtration, fluoride addition, permanganate addition, post chlorination 2001: GAC filtration |
| Old Swamp River/South Cove | River | 1966 - present | 1966: coagulation/flocculation, sedimentation, filtration, pH adjustment, permanganate addition, post chlorination 1972: fluoride addition |</p>
<table>
<thead>
<tr>
<th>Location</th>
<th>Source Type</th>
<th>Dates</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whitman's Pond Lake</td>
<td>Emergency</td>
<td>1965 - present</td>
<td>No treatment</td>
</tr>
<tr>
<td>Wilmington</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldrich Road Well</td>
<td>Wells &lt;50 ft</td>
<td>1971 - 1972: closed due to Fe and Mn contamination</td>
<td>No treatment</td>
</tr>
<tr>
<td>Barrows Wellfield</td>
<td>Wells &lt;50 ft</td>
<td>1954 - present</td>
<td>1989: aeration, coagulation/flocculation, sedimentation, GAC filtration, pH adjustment, permanganate addition, post chlorination</td>
</tr>
<tr>
<td>Brown's Crossing Wellfield</td>
<td>Wells 50 - 150 ft</td>
<td>1927 - present</td>
<td>1989: aeration, coagulation/flocculation, sedimentation, GAC filtration, pH adjustment, permanganate addition, post chlorination</td>
</tr>
<tr>
<td>Butters Row Well #1</td>
<td>Wells 50 - 150 ft</td>
<td>1971 - 2002: closed due to NDMA</td>
<td>1980: coagulation/flocculation, sedimentation, GAC filtration, air stripping, pH adjustment, permanganate addition, post chlorination</td>
</tr>
<tr>
<td>Butters Row Well #2</td>
<td>Wells &lt;50 ft</td>
<td>1981 - 2002: closed due to NDMA</td>
<td>1981: coagulation/flocculation, sedimentation, GAC filtration, air stripping, pH adjustment, permanganate addition, post chlorination</td>
</tr>
<tr>
<td>Chestnut St. Well</td>
<td>Wells 50 - 150 ft</td>
<td>1961 - 2002: closed due to NDMA</td>
<td>1980: coagulation/flocculation, sedimentation, GAC filtration, pH adjustment, permanganate addition, post chlorination</td>
</tr>
<tr>
<td>Chestnut St. Well 1A</td>
<td>Wells 50 - 150 ft</td>
<td>1991 - 2002: closed due to NDMA</td>
<td>1992: coagulation/flocculation, sedimentation, GAC filtration, air stripping, pH adjustment, permanganate addition, post chlorination</td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>2001 - present: Emergency supply source</td>
<td>No additional treatment by PWS</td>
</tr>
<tr>
<td>Salem St. Well</td>
<td>Wells &lt;50 ft</td>
<td>1969 - present</td>
<td>1989: aeration, coagulation/flocculation, sedimentation, GAC filtration, pH adjustment, permanganate addition, post chlorination</td>
</tr>
<tr>
<td>Shawsheen Ave. Well</td>
<td>Wells &lt;50 ft</td>
<td>1971 - present</td>
<td>1999: coagulation/flocculation, sedimentation, GAC filtration, air stripping, pH adjustment, permanganate addition, post chlorination</td>
</tr>
</tbody>
</table>

PWS operates the Wilmington WTP and the Butters Row WTP.
<table>
<thead>
<tr>
<th>Location</th>
<th>Type</th>
<th>Age</th>
<th>History</th>
<th>Additional Treatment by PWS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Middle Reservoir</td>
<td>Reservoir</td>
<td>1891-p</td>
<td>1940: pH adjustment, chlorination 1956: fluoride addition 1996: coagulation/flocculation, GAC filtration, pH adjustment, fluoride addition, pre and post chlorination</td>
<td></td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1946-p</td>
<td>No additional treatment by PWS</td>
<td></td>
</tr>
<tr>
<td>North Reservoir</td>
<td>Reservoir</td>
<td>1874-p</td>
<td>1940: pH adjustment, chlorination 1956: fluoride addition 1996: coagulation/flocculation, GAC filtration, pH adjustment, fluoride addition, pre and post chlorination</td>
<td></td>
</tr>
<tr>
<td>Pond Brook</td>
<td>Wells &lt;50 ft</td>
<td>[1938]-p</td>
<td>[1938]: filtration</td>
<td></td>
</tr>
<tr>
<td>Tubular Wells</td>
<td>Wells &lt;50 ft</td>
<td>[1938]-p</td>
<td>[1938]: filtration</td>
<td></td>
</tr>
<tr>
<td>South Reservoir</td>
<td>Reservoir</td>
<td>1894-p</td>
<td>1940: pH adjustment, chlorination 1956: fluoride addition 1996: coagulation/flocculation, GAC filtration, pH adjustment, fluoride addition, pre and post chlorination</td>
<td></td>
</tr>
<tr>
<td>Winthrop</td>
<td>See separate entry</td>
<td>1895-p</td>
<td>No additional treatment by PWS</td>
<td></td>
</tr>
<tr>
<td>Horn Pond Dug</td>
<td>Wells &lt;50 ft</td>
<td>1908-1937</td>
<td>[1908]: chlorination</td>
<td></td>
</tr>
<tr>
<td>Horn Pond Filter</td>
<td>Wells &lt;50 ft and 50-150 ft</td>
<td>1872-1987</td>
<td>[1872]: filtration 1933: chlorination</td>
<td></td>
</tr>
<tr>
<td>Horn Pond Well B</td>
<td>Wells 50 - 150 ft</td>
<td>1931-p</td>
<td>[1978]: pH adjustment, fluoride addition, chlorination 2002: GAC filtration, permanganate addition</td>
<td></td>
</tr>
<tr>
<td>Horn Pond Well C2</td>
<td>Wells 50 - 150 ft</td>
<td>1931-p</td>
<td>[1978]: pH adjustment, fluoride addition, chlorination 2002: GAC filtration, permanganate addition</td>
<td></td>
</tr>
<tr>
<td>Horn Pond Well D</td>
<td>Wells 50 - 150 ft</td>
<td>1931-p</td>
<td>[1978]: pH adjustment, fluoride addition, chlorination 2002: GAC filtration, permanganate addition</td>
<td></td>
</tr>
<tr>
<td>Horn Pond Well E</td>
<td>Wells 50 - 150 ft</td>
<td>1937-1979</td>
<td>[1978]: pH adjustment, fluoride addition, chlorination</td>
<td></td>
</tr>
<tr>
<td>Horn Pond Well F</td>
<td>Wells 50 - 150 ft</td>
<td>1937-1979</td>
<td>[1978]: pH adjustment, fluoride addition, chlorination</td>
<td></td>
</tr>
</tbody>
</table>

PWS operates the Winchester Lake Street WTP

PWS operates the Horn Pond WTP
<table>
<thead>
<tr>
<th>Well Name</th>
<th>Wells</th>
<th>Years</th>
<th>History</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horn Pond Well G</td>
<td>50 - 150 ft</td>
<td>1964 - 1979 closed</td>
<td>closed due to TCE 1968: chlorination</td>
</tr>
<tr>
<td>Horn Pond Well H</td>
<td>50 - 150 ft</td>
<td>1967 - 1979 closed</td>
<td>closed due to TCE 1968: chlorination</td>
</tr>
<tr>
<td>Horn Pond Well I</td>
<td>50 - 150 ft</td>
<td>1985 - present</td>
<td>[1978]: pH adjustment, fluoride addition, chlorination 2002: GAC filtration, permanganate addition</td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1972 - present: 30% of current supply purchased year-round</td>
<td>No additional treatment by PWS</td>
</tr>
<tr>
<td>Worcester</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Holden Reservoir #1</td>
<td>Reservoir</td>
<td>[1900] - present</td>
<td>1970: chlorination 1997: aeration, coagulation/flocculation, filtration, pH adjustment, chemical softening, fluoride addition, pre and post chlorination, ozone</td>
</tr>
<tr>
<td>Holden Reservoir #2</td>
<td>Reservoir</td>
<td>[1900] - present</td>
<td>1970: chlorination 1997: aeration, coagulation/flocculation, filtration, pH adjustment, chemical softening, fluoride addition, pre and post chlorination, ozone</td>
</tr>
<tr>
<td>Kendall Reservoir</td>
<td>Reservoir</td>
<td>[1924] - present</td>
<td>1970: chlorination 1997: aeration, coagulation/flocculation, filtration, pH adjustment, chemical softening, fluoride addition, pre and post chlorination, ozone</td>
</tr>
<tr>
<td>Kettle Reservoir #1</td>
<td>Reservoir</td>
<td>[1880] - present</td>
<td>1970: chlorination 1997: aeration, coagulation/flocculation, filtration, pH adjustment, chemical softening, fluoride addition, pre and post chlorination, ozone</td>
</tr>
<tr>
<td>Kettle Reservoir #2</td>
<td>Reservoir</td>
<td>[1880] - present</td>
<td>1970: chlorination 1997: aeration, coagulation/flocculation, filtration, pH adjustment, chemical softening, fluoride addition, pre and post chlorination, ozone</td>
</tr>
<tr>
<td>Kettle Reservoir #3</td>
<td>Reservoir</td>
<td>[1880] - present</td>
<td>1970: chlorination 1997: aeration, coagulation/flocculation, filtration, pH adjustment, chemical softening, fluoride addition, pre and post chlorination, ozone</td>
</tr>
<tr>
<td>Kettle Reservoir #4</td>
<td>Reservoir</td>
<td>[1880] - present</td>
<td>1970: chlorination 1997: aeration, coagulation/flocculation, filtration, pH adjustment, chemical softening, fluoride addition, pre and post chlorination, ozone</td>
</tr>
<tr>
<td>Lynde Brook Reservoir</td>
<td>Reservoir</td>
<td>1864 - present</td>
<td>1970: chlorination 1997: aeration, coagulation/flocculation, filtration, pH adjustment, chemical softening, fluoride addition, pre and post chlorination, ozone</td>
</tr>
<tr>
<td>MWRA System</td>
<td>See separate entry</td>
<td>1949 - present: Emergency supply source</td>
<td>No additional treatment by PWS</td>
</tr>
<tr>
<td>Pine Hill Reservoir</td>
<td>Reservoir</td>
<td>[1924] - present</td>
<td>1970: chlorination 1997: aeration, coagulation/flocculation, filtration, pH adjustment, chemical softening, fluoride addition, pre and post chlorination, ozone</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

PWS operates the Worcester WTP
| Quinnapoxet Reservoir | Reservoir | 1952 - present | 1970: chlorination 1997: aeration, coagulation/flocculation, filtration, pH adjustment, chemical softening, fluoride addition, pre and post chlorination, ozone |
REFERENCES


Bryan, Darleen P. (2005). Investigation of Disinfection Byproduct Precursors in the Wachusett Reservoir Watershed, Master’s of Science Environmental Engineering Project, Department of Civil and Environmental Engineering at the University of Massachusetts, Amherst.


