Factors Affecting Disinfection By-products from Surface Source Waters on Vancouver Island

by

Deborah Norine Epps
B.Sc., University of Victoria, 1994

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Supervisory Committee

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Abstract

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A comparison of disinfection by-product (DBP) results for 12 surface source waters on Vancouver Island, British Columbia determined that there was a distinct spatial difference in DBP production based on biogeoclimatic ecoregions. The main factors affecting the DBP production between ecoregions was source water quality, water body type (stream versus lake) and treatment strategy. Typically water bodies within an ecoregion exhibit similar water quality and produce similar DBPs. Differences in DBPs between water body types were attributed to the source of natural organic matter (NOM), allochthonous or autochthonous origin, and seasonal variability. Additional source water quality parameters such as pH, chlorophyll *a*, total phosphorus, water temperature and bromide concentrations support the spatial differences observed in DBP production between ecoregions. These results suggest that source water quality and water body type could be used as a preliminary tool to predict the amount of DBPs a community within a specific ecoregion may be exposed to.

A review of a long-term data set determined that changes in treatment strategy significantly affected the DBPs produced. The most distinct changes in DBP production were associated with booster station treatment processes in terms of annual versus seasonal re-chlorination and the decommissioning of a booster station. Sooke reservoir water quality, following an inundation project, changed significantly with respect to water temperature and NOM. The increase in TOC levels did not result in any changes to DBP production, however cooler water temperatures reduced the potential for losses of chlorine residual and for the re-growth of bacteria. The results of this research suggest that the management and protection of drinking water sources, along with treatment strategies, is the most promising way to ensure minimal risk to human health.

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Chapter 1: General Introduction

Overview and Significance

Most surface water in North America would be unpotable without some form of treatment. Water disinfection is one of the major achievements of the 20th century in the prevention of infectious diseases. Chlorine has been the most widely used disinfectant in many water treatment plants to inactivate microorganisms since it was first introduced in 1908 (Kim and Yu, 2005). Disinfectants are also used for (a) removing taste and color; (b) oxidizing iron and manganese; (c) improving coagulation and filtration efficiency, and (d) preventing algal growth in sedimentation basins and filters (Sadiq and Rodriguez, 2004). However, in the early 1970's it was discovered that the process of disinfecting drinking water itself could serve as a source of contaminants that posed risks to human health (Rook, 1974). These contaminants are called disinfection by-products (DBPs).

Disinfection by-products are formed when disinfectants (chlorine, ozone, chlorine dioxide, or chloramines) react with natural organic matter (NOM), such as humic and fulvic acids, found in the source water (Serodes *et al*., 2003; Chowdhury, 2005). Over 700 DBPs have been identified; however, only a small percent are well characterized and adequately understood, particularly with respect to toxicity (Ates *et al*., 2007). The DBPs occurring most frequently and with the highest concentration are trihalomethanes (THMs) and haloacetic acids (HAAs) (Chaiket *et al*., 2002). Total THM (TTHM) refers to the sum of four substances: chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform. While HAAs include nine substances, only the sum of five HAAs (dichloracetic acid (DCAA), trichloroacetic acid (TCAA), dibromoacetic acid (DBAA), monochloroacetic acid (MCAA) and monobromoacetic acid

(MBAA)) is regulated and generally referred to as HAA5. Emerging and unregulated DBPs are also being produced and include haloacetaldehydes, haloacetonitriles, halopropanones, halonitromethanes, cyanogens, and several inorganic ions such as chlorite and bromate (Chowdhury, 2005; Muellner *et al*., 2007; Richardson *et al*., 2007). In addition there are a number of unidentified DBPs that make up a significant contribution (more than 70%) to the total organic halides (TOX), particularly with chloramination (Hua and Reckhow, 2007). The concentration and distribution of various DBPs has been shown to vary widely as a function of source water quality and treatment process (Krasner *et al*., 2006).

The formation of DBPs is of great concern because of the potential impacts of these compounds on public health and the environment. Disinfection by-products can be ingested, inhaled or absorbed. A recent route of exposure study (Villanueva *et al*., 2007) indicated that much of the human health concerns associated with chlorinated water may be due to showering, bathing and swimming (dermal and inhalation exposures) rather than oral exposures. In fact, they found that much of the risk for bladder cancer associated with drinking water was associated with three factors: THM levels, dermal/inhalation exposure and genotype (having the GSTT1-1 gene). In addition, a number of other regulated and emerging DBPs have also been classified as potential carcinogens, based on evidence from animal studies (Richardson et al., 2007; Kitis *et al*., 2004; Nikoloau and Lekkas, 2001). DBPs are also expected to be toxic and/or mutagenic to humans if ingested over extended years. Some DPBs have acute reproductive and developmental effects with bromated organic DBPs posing more significant health risks than chlorinated analogs (Plewa *et al*., 2004a).

Balancing acute risks of water borne pathogens and chronic risks from DBP exposure has been a key issue in the process of drinking water risk assessment and management. Current standards and guidelines related to DBP levels in North America, and for that matter, the world, are limited, primarily due to lack of information (i.e. monitoring data, toxicity effects). The United States Environmental Protection Agency (USEPA) (2002) has developed more recent regulations for total THMs and HAA5 (80.0 µg/L and 60 µg/L respectively). However, in Canada these guidelines are higher, with the total THM guideline at 100.0 µg/L and in May 2008, a guideline was established for HAA5 at 80.0 µg/L (Health Canada, 2008).

To better understand the DBP formation process, a more in-depth look at the source water quality is required. Due to the complexity of natural organic matter (NOM) in terms of composition and structure, the exact mechanisms for DPB formation during disinfection still remain unclear. NOM includes a vast assemblage of large complex organic structures with varying characteristics depending on location and time of year (Singer, 1994). Natural organic matter characteristics are also known to vary from watershed to watershed and to be affected by all chemical and biological processes in the water (Kim and Yu, 2007). Management of water quality at the source, along with the appropriate treatment strategy, is the ultimate and most promising way to reduce DBP precursors as well as microbial pathogens (Wang et al., 2007)

Source Water Quality and Treatment Strategies

NOM is a complex mixture of organic compounds in dissolved, colloidal and particulate forms. It is derived from living or decomposed vegetation and microbial breakdown processes (Leenheer and Croue, 2003). Total organic carbon (TOC) and dissolved organic carbon (DOC) are widely used indirect parameters to quantify NOM levels. However, DOC tends to be the more widely selected parameter to represent NOM as 83% to 98% of the TOC in raw water sources is in the dissolved form (Chin and Berube, 2005; Karanfil et al., 2002; Owen et al., 1995).

NOM can be classified through resin adsorption into hydrophobic and hydrophilic fractions (acid, base and neutral for each) (Panyapinyopol et al., 2005; Marhaba et al., 2003; Leenheer, J.A. 1981). The fractionation of NOM allows for a more thorough investigation of the formation potential of THMs from the organic matter in the water source. The hydrophobic fraction is composed mainly of the fulvic and humic acids (Chang et al., 2001). It has also been determined that hydrophobic fractions tend to have higher THM formation reactivity than the hydrophilic fraction (Ma, 2004).

The reactivity of NOM is closely tied to its physiochemical properties such as molecular weight, aromaticity, elemental composition and functional groups content (Swietlik *et al.*, 2004). Therefore quantification and characterization of NOM is an important parameter in drinking water treatment. NOM is derived from both allochthonous (terrestrial) and autochthonous (aquatic photosynthesis) sources (Chow *et al.*, 2007). The major loading of NOM in the water column, particularly streams, tends to come from allochthonous sources such as seasonal run-off, precipitation, sediment resuspension and human activity (if present). In most cases, the allochthonous input remains relatively constant over time unless significant changes are made to the upstream land-use practices. However, in contrast, the contribution of NOM from autochthonous input, such as algae in lakes, can increase with the increase of nutrients in the water (Leenheer and Croue, 2003).

The rate of NOM transformation, mostly mediated by microbial degradation, physical photolysis or by the combined utilization processes, changes temporally and spatially (Liang and Singer, 2003). Temperature and nutrient conditions affect microbial metabolism of NOM, while UVA, UVB and photosynthetically active radiation (PAR) determines physical processes (Dabrowska *et al.*, 2004). As a result of seasonal change, NOM distribution in the water column varies with depth and water stratification (lakes).

Fluorescence and ultraviolet (UV) absorbance are spectral techniques used to broadly assess various dissolved organic matter structural characteristics. In general, the intensity of the fluorescence signal increases with increasing DOC content (the higher the UV absorbance, the higher the fluorescence emission) (Leenheer and Croule, 2003). Furthermore, ratios of fluorescence intensities determined at different wavelengths have been proposed as indicators of the allochthonous versus autochthonous origins of dissolved organic matter (DOM). UV at 254 nm (UV_{254}) can be used as an index of the aromaticity contained in humic substances. A high UV_{254} suggests a high concentration of aromatic material in the water (Sweitlik et al., 2004). DBPs can be formed from chlorination of activated aromatic rings (Korshin et al., 1997; Reckhow and Singer, 1990). Specific UV absorbance (SUVA) is the ratio of UV 254 to the concentration of DOC in the source water. SUVA appears to provide insight into the nature of NOM through an indirect quantitative measure of the aromatic content of the organic carbon in water. Strong correlations have been reported linking SUVA and DBP formation

(Karanfil et al., 2002; Kitis et al., 2004; Chang et al., 2000). Therefore, UV-NOM relationships depend not only on the origin of the NOM (i.e. specific for a given water course), but on seasonal changes and temperature variations.

Other factors can also contribute to the DBP formation potential of a particular water body such as the chemical composition, temperature, pH, chlorophyll *a,* bromide concentration and treatment variables such as type of treatment, length of distribution system and chlorination time for a particular water source (Nikoloau and Lekkas, 2001; Kitis *et al*, 2004; Plewa *et al*, 2004b; Panyapinyopol *et al*., 2005; Krasner *et al*., 2006). Various comparative, empirical and mechanistic models have been developed to identify the relative significance of water quality parameters and operational variables responsible for the formation of DBPs. Pre-treatment of the raw water appears to be one method for reducing the DBPs and includes such processes as filtration, sedimentation and granular active carbon. Kim and Yu (2005) studied the DBP formation potential after the removal of DOC and NOM fractions through various pre-treatment processes and determined that the ultrafiltration-nanofiltration combined membrane process is one of the best available methods for removing NOM. Regardless of the pre-treatment process, some form of disinfection is still required to prevent human health risks. More recently post-treatment processes such as, nanofiltration (NF) techniques have also been shown to remove THMs compounds (Uyak *et al*., 2008).

Another effective method to control chlorinated DBPs in drinking water is the use of alternative disinfectants such as ozone, chloramines, chlorine dioxide and more recently ultraviolet (UV) light, either alone or in combination with chlorine (Teksoy et al., 2008). The use of non-chlorinated disinfectants, such as ozone as a primary disinfectant, can potentially reduce the amount of chlorine that must be added as a secondary disinfectant during drinking water treatment. However, some of the non-chlorinated disinfectants can also form DBPs such as aldehydes, aldoketoacids and carboxylic acids, which are also suspected carcinogens (USEPA, 1998). Sweitlik et al (2004) found that while ozonation caused the reduction of hydrophobic compounds, the hydrophilic fractions increased. In addition, the biodegradable by-products can reduce the biological stability of a drinking water system, especially those with a long residence time in a distribution network. Guay et al (2005) found that UV radiation achieves pathogen inactivation at rates higher than chlorine, however the high cost of UV generation has hindered its application to drinking water disinfection.

Despite the work that has been done to date to investigate the NOM fractions and their potential for DBP formation, links between a particular source water quality and the type and concentrations of DBPs produced are yet to be determined. Therefore, it is unclear whether different land use activities within each watershed will change the nutrient and carbon input, thus affecting production of DBPs. It is also unclear whether DBP production is regulated by autochthonous or allochthonous drivers of DOC. Ultimately, these sources of DOC may be affected both spatially and seasonally. Furthermore, many of the DBPs have only been studied at bench scale or in limited full-scale surveys. Thus, there is significant uncertainty over the identity and levels of DBPs that people are exposed to in their drinking water (Krasner *et al*., 2006).

Thesis Objectives

My main goal in conducting this research was to perform a comparative analysis of the relationship between source water quality, treatment strategies and the DBP concentrations in tap waters. More specifically, I wanted to determine if source water quality could be used as a preliminary tool to predict the amount of DBPs the communities on Vancouver Island are exposed to. To do this, I proposed to investigate the spatial and temporal distributions of DBPs produced from 12 surface source waters on Vancouver Island. Secondly, as the source of carbon, allochthonous or autochthonous, or a combination thereof, provides the reactivity contribution to DBP formation, I wanted to test the hypothesis that water body type (stream or lake) can affect DBP production based on differing sources of carbon. Finally, a long-term DBP data set provided a unique opportunity to capture changes to source water characteristics and treatment strategies. Therefore, I wanted to observe if changes in NOM, water temperature and treatment strategies influenced the concentration and distribution of THMs and HAAs produced within a given watershed. The results of this research can be applied to the management and protection of drinking water sources, and the determination of the potential for other communities on Vancouver Island to be exposed to human health risks based on source water characteristics.

Chapter 2: An investigation of the spatial and temporal distributions of disinfection by-products in relation to biogeoclimatic zones on Vancouver Island

The relationship between NOM and DBP concentrations has been well documented. However, the exact mechanisms of this relationship still remain unclear. In addition, NOM characteristics are known to vary from watershed to watershed and are affected by all chemical and biological processes in the water (Wang and Hsieh, 2001).

In this chapter I wanted to determine if surface source waters on Vancouver Island produce similar types and concentrations of DBPs. More specifically I wanted to identify seasonal and spatial patterns of DBP production based on biogeoclimatic zones on Vancouver Island. I wanted to test the hypothesis that water body type (stream or lake) can affect DBP production based on differing sources of carbon. And finally I wanted to determine if the exposure risk from DBPs for communities change as a function of different biogeoclimatic zones?

Chapter 3: Long term trends in DBP production under changing watershed and treatment management strategies in the Greater Victoria drinking water service area

Physical and chemical treatment processes are known to alter the structure and compositions of NOM (Kim and YU, 2007). These differences in NOM have been shown to cause changes in its reactivity with disinfectants and the resulting DBPs (Dabrowska *et al*., 2004). There has been very little research conducted involving long-term DBP data sets, looking at trends over time. In this chapter, I was provided the unique opportunity to review a long-term DBP data set, which captured both changes to the source water quality and to the treatment strategies within the distribution area. The Capital Regional District (CRD), located in Victoria, British Columbia, has been collecting DBP data from the Sooke watershed and its distribution area since 1991. My goal was to identify differences in DBP production following changes to the source water quality, in terms of NOM and water temperature. I wanted to determine if changes to treatment strategies influenced the types and concentrations of DBPs formed. Finally, I wanted to provide information to the CRD to assist with the management and protection of the drinking water sources to ensure minimal risks to human health.

Chapter 2: An Investigation of the Spatial and temporal Distributions of Disinfection By-products in Relation to Biogeoclimatic Zones on Vancouver Island.

Abstract

In this study a spatial difference in DBP production was observed between ecoregions. The watersheds from the South Gulf Islands (SGI) ecoregion had the highest DBPs, correlating DBP formation to high levels of TP, chlorophyll *a*, DOC, bromide and pH in the source water. Treatment strategies were shown to reduce DBP production in the North Island ecoeregion watersheds, which had naturally occurring tannins and lignins in the source water. Both the East and West Coast ecoregions were similar in that they had low DOC concentrations and generally low DBP production. For all watersheds chloroform was the primary THM produced while dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) were the main HAAs produced. Additional brominated acetic acids were produced in watersheds with elevated bromide levels. In particular, this study showed that DBP formation was dependent on water body type (i.e. lakes versus streams), mainly as a result of differences in sources of DOC. Nutrient rich lakes tended to have the highest levels of DBPs associated with autochthonous DOC, while DBP production in streams was associated with precipitation events, when allochthonous DOC concentrations were elevated. Significant seasonal differences in DBP production were only observed in the SGI ecoeregion, likely attributed to algal bloom production in the summer and fall. Overall, these results provide evidence that source water quality and water body type within different biogeocliamtic zones can be used to predict DBP formation potential for communities on a preliminary basis.

Introduction

Disinfection of drinking water is one of the greatest advances in public health protection. However, during drinking water treatment, unintended chemical disinfection by-products (DBPs) are produced. DBPs are formed through the interaction of chlorine with natural organic matter (NOM), such as humic and fulvic acids, found in the source water (Serodes *et al*., 2003; Chowdhury, 2005). DBP research and regulatory agencies have primarily focused on chlorinated and brominated analogs of the two most abundant DBP classes: trihalomethanes (THMs) and haloacetic acids (HAAs) (Charrois and Hrudy, 2007). Emerging DBPs are increasing with advancing analytical technologies and include such compounds as haloacetaldehydes, haloacetonitriles, haloketones, cyanogens, and several inorganic ions such as chlorite and bromate (Muellner *et al*., 2007; Richardson *et al*., 2007; Jung and Son, 2008). Past research has established that levels of DBPs in chlorinated waters vary according to the levels of their precursors (NOM) present in the source water and the treatment strategy (Rodriguez *et al*., 2003).

Although the immediate need and benefits of drinking water disinfection are acknowledged, the health risks due to long-term DBP exposure are not well understood (Muellner *et al*., 2007). Several studies have demonstrated elevated risks of developing urinary bladder cancer (Villanueva *et al*., 2007) or adverse reproductive outcomes (Kitis *et al*., 2004; Nikoloau and Lekkas, 2001) from increased exposure to drinking water DBPs. While it is well known that bromated organic DBPs pose more significant health risks than chlorinated analogs (Plewa *et al*., 2004a), unregulated DBPs, such as N-Nitrosodimethylamine (NDMA), are emerging as a major human health concern (Charrois and Hrudey, 2007).

Current standards and guidelines related to DBP levels in North America, and for that matter the world, are limited, primarily due to lack of information (i.e. monitoring data, toxicity effects). The United States Environmental Protection Agency (USEPA) (2002) has developed regulations for total THMs and for the sum of five HAAs (also known as HAA5) at 80 µg/L and 60 µg/L, respectively. However, in Canada these guidelines are higher, with the THM guideline at 100.0 µg/L and HAA guideline at 80.0 µg/L (Health Canada, 2008). Balancing acute risks of water borne pathogens and risks from chronic DBP exposure has been a key issue in the process of drinking water risk assessment and management.

Due to the complexity of NOM in terms of composition and structure, the exact mechanisms for DPB formation during disinfection still remain unclear. NOM includes a vast assemblage of large complex organic structures with varying characteristics depending on location and time of year (Singer, 1994). It is derived from living or decomposed vegetation and microbial breakdown processes. Total organic carbon (TOC) and dissolved organic carbon (DOC) are widely used as indirect parameters to quantify NOM levels. However, DOC tends to be the more widely selected parameter to represent NOM as 83% to 98% of the TOC in raw water sources is in the dissolved form (Chin and Berube, 2005; Karanfil *et al*., 2002; Owen *et al*., 1995). NOM characteristics are also known to vary from watershed to watershed and to be affected by all chemical and biological processes in the water (Kim and Yu, 2007).

Other factors can also contribute to the DBP formation potential of a particular water body such as the chemical composition, temperature, pH, chlorophyll *a* levels, bromide concentration and treatment variables such as type of treatment, length of distribution system and chlorination time for a particular water source (Nikoloau and Lekkas, 2001; Kitis *et al*, 2004; Plewa *et al*, 2004b; Panyapinyopol *et al*., 2005; Krasner *et al*., 2006; Charrois and Hrudey, 2007). Various comparative, empirical and mechanistic models have been developed to identify the relative significance of water quality parameters and operational variables responsible for the formation of DBPs (Rodriguez *et al*., 2003; Sadiq and Rodriguez, 2004; Uyak *et al*., 2005; McBean *et al*., 2008). Pre-treatment of the raw water appears to be one method for reducing the DBPs and includes such processes as filtration, sedimentation and granular active carbon to name a few (Lou and Lin, 2008). Regardless of the pre-treatment process, some form of disinfection is still required to prevent human health risks.

Despite the work that has been done to date to investigate the NOM fractions and their potential for DBP formation, links between a particular source water quality and the type and concentrations of DBPs produced are yet to be determined. Different land use activities within a watershed can affect the nutrient and carbon input of the water source (Fleck et al., 2004; Chow *et al*., 2007). However, it remains unclear whether DBP production is regulated by autochthonous (aquatic photosynthesis) or allochthonous (terrestrial) drivers of DOC. Hong et al. (2008) found that algal cells are just as important as humic substances, such as humic and fulvic acids, as precursors of dichloroacetic acid. In addition, the sources of DOC can be affected both spatially and seasonally (Jung and Son, 2008). Furthermore, many of the DBPs have only been studied at bench scale or in limited full-scale surveys; thus, there is significant uncertainty over the identity and levels of DBPs that populations are exposed to in their drinking water (Krasner et al., 2006).

The goal of this study is to provide information on DBP production, in terms of source water quality, water body type and geographic location for 12 surface drinking water supplies on Vancouver Island, British Columbia, Canada. I wanted to identify which source water parameters affect the types and concentrations of DBPs produced in the community water supplies. More specifically, I wanted to test the hypothesis that water body type (stream or lake) can affect DBP production based on differing sources of carbon. In addition, I wanted to identify seasonal and spatial patterns of DBP production based on biogeoclimatic zones on Vancouver Island. This is the first DBP study to be conducted on Vancouver Island and the results will provide important information on the potential for human health concerns in relation to drinking water source and treatment.

Materials and Methods

Sampling locations

Vancouver Island, located on the west coast of British Columbia, Canada, has been divided into 3 ecoregions based on the ecosection classification developed by Demarchi (1995). These ecoregions, also referred to as biogeoclimatic zones, are based on similar climate, geology, soils, hydrology and the principle that fundamental water quality within similar geographical regions is very similar. Twelve drinking water sources were selected for this study (Figure 2.1 and Table 2.1). All water supplies are treated using chlorine as the main disinfectant-with the exception of Sooke Lake water, which is treated through a chloramination process. In addition, Sooke water is subject to ultraviolet (UV) radiation prior to chloramination. Tsulquate River and Newcastle Creek water also undergo a pre-treatment process via coagulation and filtration to remove colloids and particulate matter.

Table 2.1: Summary of 12 drinking water sources on Vancouver Island, and their respective biogeoclimatic ecoregion.

Water Source	Ecoregion	Lake or Stream	Dominant Land Use
Cusheon	Southern Gulf Islands	Lake	Rural residential
Maxwell	Southern Gulf Islands	Lake	Forest
St. Mary	Southern Gulf Islands	Lake	Rural residential
Sooke	East Coast Vancouver Island	Lake	Forest
Shawnigan	East Coast Vancouver Island	Lake	Rural residential
Nanaimo	East Coast Vancouver Island	Lake	Forest
Bainbridge	West Coast Vancouver Island	Lake	Forest
China	West Coast Vancouver Island	Stream	Forest
McKelvie	West Coast Vancouver Island	Stream	Forest
Quatse	North Vancouver Island	Lake	Forest
Newcastle	North Vancouver Island	Stream	Forest
Tsulquate	North Vancouver Island	Stream	Forest

Figure 2.1: Watershed and ecoregion locations on Vancouver Island. (North Island =NWL and NIM, West Coast =WIM, East Coast = LIM and NAL, and Southern Gulf Islands (SGI) includes SaltSpring Island (SSI)). Stars indicate water sampling sites used in this study.

Sampling and analysis

Samples were collected on a monthly basis at both the source water intake location and at 3 locations throughout the distribution system (first tap - Site 1, mid station -Site 2 and end of distribution -Site 3) from January to December 2006. Exceptions are Quatse Lake, which was sampled from July 2006 to June 2007, and Nanaimo Lake, which only had results for 2007 (January to December) with corresponding DBP and source water data. In addition, Shawnigan Lake DBP data was only collected for 2 sites (first tap and end of system) and Nanaimo DBP data was only collected at first tap. There were no re-chlorination stations associated with any of the 3 sampling sites on any system.

Source water samples were collected, following BC MOE (2003) sampling protocols, at each site, approximately 0.5 m below the water surface with an open-mouthed 1L bottle and a 1 L amber glass bottle (for chlorophyll *a* only). Water samples for DBP analysis were collected in duplicate from the tap in 50 mL amber purge vials, ensuring no headspace in the sample vial. At each tap location the chlorine residual was also recorded. Samples were kept on ice and shipped in a cooler to the University of Victoria (UVIC) Water and Aquatic Sciences Research laboratory for analysis; upon receipt, the samples were transferred to a refrigerator and kept at 4° C until analyzed.

Source water was analyzed for the following parameters: TOC/DOC, total phosphorus, total nitrogen, pH, bromide, and chlorophyll *a*. Methods for analysis of the above mentioned parameters followed Standard Methods (BC MOE, 1994) and were conducted by laboratory staff at the UVIC Water and Aquatic Sciences Research lab, with the exception of the chlorophyll *a* samples. Samples for chlorophyll *a* were collected by MOE on a quarterly basis for lakes only; samples were collected in a 1L plastic bottle and filtered using 0.45µm filter paper. The filters were placed in petri dishes and shipped on ice to Maxxam Analytics in Burnaby, British Columbia for analysis.

Analysis of Disinfection By-products

Samples of THMs were analyzed following the EPA methods 502.2 (USEPA, 1995) and 551.1 (USEPA, 1995). The method is based on the solid phase micro extraction (SPME) procedure used for sample preparation and gas chromatography (GC) analysis with a mass spectrometer. The sample is extracted using a SPME device installed in a Varian CP-8200 autosampler. The sample components are separated in a fused-silica capillary gas chromatographic column CP-SIL8CB-MS 30 m x 0.25 mm i.d. with 0.25 um film thickness using temperature ramping and detection by a Varian Saturn 2200 mass spectrometer. The resultant chromatogram of THM compounds is collectively integrated and stored in the GC/MS computer database. Individual concentrations of target THM analytes are determined using 7- point calibration curve. Individual THMs and their respective minimum detection limits are shown in Table 2.2. Results are expressed as total THMs (addition of all four compounds shown in Table 1).

Table 2.2: List of individual THMs analyzed and their respective minimum detection limits (MDLs).

Parameter	**MDL, ug/L**
Chloroform	1.0
Bromodichloromethane (BDCM)	0.8
Dibromochloromethane (DBCM)	0.5
Bromoform-	0.6

USEPA Test Methods for Determination of trihalomethanes (THMs); Method 502.2/551.1 (1995).

HAAs were determined using the USEPA Method 552-2 (USEPA, 1995). A 40 mL volume of sample is adjusted to pH<0.5 with concentrated H_2SO_4 and extracted with 4 mL of methyl-tert-butyl-ether (MTBE). The HAAs, partitioned into the organic phase, are then converted to their methyl esters by the addition of acidic methanol followed by moderate heating at 50°C. The acidic extract is neutralized by a back extraction with a saturated solution of sodium bicarbonate ($NaHCO_3$) and measured by capillary column gas chromatography using an electron capture detector (GC/ECD). Analytes are quantified using procedural standard calibration based on 5 calibration points. Individual HAAs and their respective minimum detection limits are shown in Table 2.3. For quality control purposes, 2,3-dibromopropionic acid was used as a surrogate standard (Surr. Std).

Table 2.3: List of HAAs analyzed and their respective minimum detection limits (MDLs).

Full Name	Abbreviation	MDL, ug/L
Monochloroacetic Acid	MCAA	0.50
Monobromoacetic Acid	MBAA	0.20
Dichloroacetic Acid	DCAA	0.45
Trichloroacetic Acid	TCAA	0.20
Bromochloroacetic Acid	BCAA	0.20
Dibromoacetic Acid	DBAA	0.20
Bromodichloroacetic Acid	BDCAA	0.20
Chlorodibromoacetic Acid	CDBAA	0.50
2,3-Dibromopropionic Acid	DBPA (Surr.Std.)	0.20
Tribromoacetic Acid	TBAA	1.00

USEPA Test Method for Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatization and Gas Chromatography With Electron Capture Detection; Method 552.2 (1995).

Statistical Analysis

Multivariate analysis was conducted to differentiate and test the various contributions of the source water quality parameters collected such as: DOC/TOC, chlorophyll ‘a’, total phosphorus, pH and bromide, to the production of the DBP results (includes both individual and total results for HAAs and THMs). JMP (7.0) statistical software was used for all analyses and in all cases, $p<0.05$ was considered significant. In this study, there was no significant difference between DOC and TOC values (r=0.9927; $p<0.0001$); therefore, DOC values were used for most analyses.

To try and better understand DBP differences between watersheds, an analysis of covariance (ANCOVA) approach was used to look at the effects from seasons, ecoregions and water body type. The DBP results were separated into 4 seasons, ecoregion classifications were assigned to each watershed, and water body type was identified (lake or stream). Seasons were organized according to the time of year the samples were collected: winter = January, February and March; spring = April, May and June; summer = July, August and September; and fall = October, November and December. A general linear model was used to account for ecoregion and seasonal differences only:

(1) $Log\ (DBP) = ecoregion \times season \times (ecoregion*season) \times watershed\text{-}R$

The "ecoregion" term tests for differences among the ecoregions. The "season" term allows for season-to-season differences among the DBPs and the "ecoregion*season" term is the interaction between ecoregion and seasons (e.g. is the season effect the same for all ecoregions). The "watershed-R" accounts for multiple watersheds within each ecoregion as indicated by the random effect term (R). This equation was computed using JMP statistical software for all THM and HAA values (i.e. for sites 1, 2 and 3, respectively).

As watershed type differed, a two-sample comparison of means was conducted to compare the difference in DBP production based on water body type alone. The two-sample t-test is the simplest method to compare the means of a numerical variable between two independent groups (lake and stream) (Witlock and Schluter, 2009). However, if the assumption that the standard deviations of the two populations are different, the Welch's approximate t-test should be used. In this study, the preliminary analysis of the data suggested the standard deviations were different (*p*<0.0001), thus the Welch's t-test was used to test if THM and HAA results differ by water body type.

To determine the effects of water body type, in conjunction with season and ecoregion effects on DBP production, model (1) was altered to account for water body type, and thus a new model was used,

(2) L*og(DBP) = ecoregion* x *season* x *ecoregion*season* x *watershed(water body type)-R,* where we exchange "watershed-R" from model (1) with "watershed(water body type)-R" to account for differences between streams and lakes. This model was computed using JMP statistical software for all THM and HAA site 1, 2 and 3 results, respectively.

Results and Discussion

DBP Overview

The annual mean and range (minimum-maximum) of total THMs and HAAs produced from 12 drinking water supplies on Vancouver Island are summarized in Table 2.4. The THM annual mean results ranged from 5.97 µg/L at China Creek (Site 1) to 173.21 µg/L at Cusheon Lake (Site 3). The HAA annual mean values exhibited a similar pattern, ranging from 3.03 µg/L at China Creek (Site 1) to 144.48 µg/L usheon Lake (Site 1). Three watersheds, Cusheon Lake, Maxwell Lake and Newcastle Creek, had maximum THM values above the Canadian THM guideline of 100 µg/L at 213.4, 111.9 and 114.9 µg/L, respectively. Cusheon Lake (288.84 µg/L), Maxwell Lake (205.44 µg/L), and Newcastle Creek (92.27 µg/L) all produced maximum HAA values above the

Canadian HAA guideline of 80 µg/L. It should be noted that all the Cusheon Lake THM values and all but one HAA value (58.93 µg/L) were greater than both guidelines mentioned above. Watersheds that exceeded the guidelines tended to be lakes, with the exception of Newcastle Creek. Furthermore, when looking at the overall DBPs produced by ecoregion, SGI watersheds had the highest values of both THMs and HAAs, followed by North Island, West Coast and finally East Coast with the lowest values.

Watershed variability

There are several factors that may be contributing to the variation in DBP production observed in this study. In natural systems, factors such as DOC, pH and temperature are known to vary temporally and spatially (Chowdhury *et al*., 2008). The results from model (1), which looked at the relationship between seasonal and spatial attributes on DBP formation, found only the SGI ecoregion being statistically different ($p<0.0015$) from the other three ecoregion DBP results on Vancouver Island. This corresponds with the exceptionally high DBP values observed from the water supplies on Salt Spring Island, which are all lakes. There were no seasonal differences noted in the pooled data set for model 1. Upon further investigation it was observed that some of the ecoregions are comprised of lakes, streams or a combination of both (SGI – 3 lakes; North Island – 2 streams and 1 lake; West Coast – 2 streams and 1 lake; East Coast – 3 lakes) and that water body type may play a role in the formation of DBPs. A comparison looking at DBP production against water body type (stream versus lake) using Welch's approximate t-test showed a positive relationship for THMs ($t_{(0.05)(2),99} = 3.45$; $p<0.008$) and HAAs ($t_{(0.05)(2)101} = 2.83$; $p<0.0057$) confirming that lake source water DBPs are significantly different than stream source water DBPs.

Therefore, when accounting for water body type, ecoregion and seasonal differences in DBP production, the results from model (2) indicate that THMs from the North Island ecoregion are statistically different ($p<0.0498$) from the East and West Coast ecoregions for streams only and the SGI ecoregion THM results are significantly different ($p<0.0015$) from the three ecoregions on Vancouver Island for lakes only. Again, no seasonal differences with THM production were observed. However, when this same equation was used and THM was substituted with HAA values, only the SGI ecoregion was different ($p<0.05$) from the rest of the ecoregions for HAA production from lakes and no differences were observed for rivers. While not significant, a difference did appear for HAAs between seasons for lakes ($p>0.0772$). Ates et al. (2007) also found seasonal changes with HAA production from lakes, with lowest HAA concentrations obtained in summer, similar to the findings from this study.

Variation in DOC

The annual average DOC values ranged from 0.78 mg/L (China Creek) to 7.89 mg/L (Quatse Lake) while the TOC values ranged from 0.78 to 8.95 mg/L also for China Creek and Quatse Lake, respectively (Table 2.5). The relationship between DOC and DBP formation has been well studied (Panyapinyopol *et al*., 2005; Kitis *et al*, 2004; Chang *et al*, 2001) and among the factors affecting THM formation, such as DOC, pH, water temperature, bromide concentrations and treatment (chlorine dose and contact time), DOC is the most important (Panyapinyopol *et al*., 2005). In this study there was a significant correlation ($p<0.001$) between the DBP values per water distribution area, and their corresponding source water DOC concentration (Appendix 2.1). Overall, the East and West Coast ecoregion watershed DOC values tended to be lower than the North

Island and SGI ecoregion DOC values, and as such they tended to have lower total DBP production.

Sources of DOC

While there existed a strong correlation between DOC concentrations and DBP production, it appeared that the actual source of the DOC may be the contributing factor. The major loading of DOC in water, especially streams, tends to come from allochthonous sources such as seasonal run-off, precipitation, sediment resuspension and human activity (Wang and Hsieh, 2001; Chow *et al*., 2007). In most cases, the allochthonous input remains relatively constant over time unless significant changes are made to the upstream land-use practices. When comparing streams to lakes in this study, it appeared that most of the DOC in the streams is allochthonous in nature as it was linked to rainstorm events. During these heavy precipitation events, DOC loadings increase in the streams, which is subsequently reflected in the DBPs being produced. All the streams in this project are forested, with little human activity, with the exception of China Creek, which has active harvesting occurring in the watershed. The North Island watersheds have naturally higher color and DOC values and consequently one would expect higher DBP values. This is true for Newcastle Creek. In the past, Quatse Lake and Tsulquate River have also produced high levels of DBPs; however, this has been greatly reduced because of the updated treatment at both water plants.

Table 2.4: Annual average mean and range (minimum-maximum) DBP results for Vancouver Island watersheds. (Site 1-first tap; Site 2 – mid way; Site 3 – last tap).

			THM (ug/L)			HAA (ug/L)	
EcoRegion	Watershed	Site 1	Site 2	Site 3	Site 1	Site 2	Site 3
SGI	Cusheon	137.47 (107.6-164.3)	144.39 (100.8-183.2)	173.21 (133.9-213.4)	144.48 (78.63-229.43)	142.66 (58.93-272.41)	138.84 (80.5-288.84)
	Maxwell	51.90 (39.9-69.4)	71.80 (45.1-103.5)	84.41 (56.6-111.9)	42.43 (17.79-85.29)	85.22 (46.38-153.85)	82.64 (93.82-205.44)
	St. Mary	30.30 (18.8-44.2)	62.13 (37.4-83.2)	73.68 (50.3-87.6)	17.85 (11.28-25.59)	37.57 (15.71-78.32)	6.62 (0.66-14.15)
East Coast	Nanaimo	21.71 (2.7-47.46)			18.77 (0.35-66.83)		
	Shawnigan	29.98 (14.6-41.8)		49.14 (3.4-76.1)	25.05 (13.78-44.32)		30.89 (4.09-49.64)
	Sooke	9.13 (2.1-12)	13.52 (4.7-17.9)	13.25 (2.6-18.2)	13.27 (11.6-15)	13.75 (5.87-21.2)	8.80 (4.6-13.8)
West Coast	Bainbridge	25.14 (21.3-29)	47.58 (42.7-57.1)	71.4 (44.3-95.4)	24.25 (17.0-46.83)	64.46 (23.71-171.64)	86.15 (42.37-159.18)
	China	5.97 (3.3-14.4)	12.23 (7.3-21.3)	21.75 (11.9-33.6)	3.03 (2.23-4.18)	10.23 (5.29-22.19)	15.83 (5.97-43.64)
	McKelvie	13.91 (4.0-39.3)	14.10 (2.2-38.5)	16.26 (4.1-29.9)	12.92 (2.68-40.1)	15.87 (2.38-46.71)	17.97 (3.96-40.62)
North Island	Quatse	28.29 (15.4-40.1)	40.12 (20.1-51.3)	35.26 (24.1-45.3)	21.81 (4.41-33.45)	24.81 (4.15-43.09)	15.06 (2.33-37.56)
	Newcastle	46.03 (14.4-84.7)	51.88 (17.5-114.9)	67.23 (34-111.1)	42.43 (14.16-90.58)	55.24 (18.88-92.27)	28.37 (4.22-62.08)
	Tsulquate	21.99 (4.7-31.5)	24.31 (14.0-34.7)	54.69 (51.6-59.8)	21.05 (3.7-46.93)	22.50 (12.24-32.72)	25.65 (18.44-34.96)

Table 2.5: Source water quality parameters (2006) – annual average and range (minimum-maximum) *Nanaimo data is from 2007

EcoRegion	Watershed	DOC (mg/L)	TOC mg/L	Total P (ug/L)	Total N (ug/L)	Chlorophyll 'a' (mg/L)	pH	Bromide (ug/L)
SGI	Cusheon Lake	5.25 (3.9-6.6)	5.42 (4.0-6.6)	21.15 (9.8-40.7)	371.79 (192.5-628.3)	4.73 (0.7-6.9)	7.15 (5.8-7.8)	12.46 (3.4-21.7)
	Maxwell Lake	4.27 (3.4-5.2)	4.48 (3.7-5.6)	10.56 (6.9-24.6)	198.45 (158.1-238.6)	3.7 (2.1-7.4)	7.09 (6.0-7.5)	8.11 (5.4-10.4)
	St. Mary Lake	3.66 (3.0-4.8)	4.25 (3.8-4.4)	44.31 (18.7-73.8)	371.20 (219.2-556.5)	6.38 (1.8-12.8)	7.39 (6.1-8.1)	40.32 (8.3-56.1)
East Coast	Shawnigan Lake	3.57 (3.1-5.3)	3.72 (3.0-5.5)	5.89 (2.7-7.8)	165.26 (102.3-246.8)	1.27 (1.0-1.6)	6.98 (6.1-7.5)	6.45 (2.9-16.9)
	Sooke Lake	2.48 (2.2-2.8)	2.57 (2.2-2.8)	5.36 (0.7-8.01)	107.24 (66.07-196.69)	1.71 (0.99-2.61)	7.30 (7.1-7.5)	4.99 (1.2-10.3)
	Nanaimo Lake*	1.67 (1.3-2.3)	1.76 (1.4-2.4)	4.96 (3.81-6.51)	75.74 (45.30-133.50)	0.35 (0.07-0.94)	6.60 (6.3-7.3)	1.96 (0.29-7.43)
West Coast	Bainbridge Lake	2.34 (1.6-3.5)	2.48 (1.7-3.6)	5.58 (3.2-9.4)	76.56 (45.4-94.9)	n/a	7.04 (6.1-7.6)	2.02 (0.8-4.9)
	China Creek	0.78 (0.5-1.7)	0.78 (0.5-1.7)	2.87 (2.2-4.2)	44.48 (22.4-70.7)	n/a	7.68 (7.1-8.0)	0.96 (ND-1.8)
	McKelvie Creek	0.80 (0.3-1.5)	0.82 (0.38-1.6)	4.02 (1.0-19.4)	84.76 (26.7-186.5)	n/a	7.21 (6.55-7.5)	1.24 (0.1-2.7)
North Island	Quatse Lake	7.89 (5.7-10.6)	8.06 (6.1-10.6)	5.91 (4.6-7.9)	98.49 (81.2-125.3)	1.6 (1.0-2.3)	6.41 (5.8-6.8)	3.70 (1.1-6.2)
	Newcastle Creek	2.74 (1.0-4.2)	2.88 (1.1-4.4)	3.79 (1.1-11.0)	57.16 (20.2-101.3)	n/a	7.00 (6.56-7.3)	1.89 (ND-13.2)
	Tsulquate River 1	6.44 (3.9-12.7)	6.57 (4.0-12.8)	4.94 (1.0-10.4)	82.39 (28.6-131.1)	n/a	6.77 (6.34-7.3)	1.32 (0.3-1.9)
	Tsulquate River 2	1.71 (1.2-3.0)	1.91 (1.3-3.1)	2.32 (1.0-3.7)	40.87 (23.7-84.9)	n/a	6.44 (6.1-6.8)	8.04 (4.2-18.5)

In contrast, the lakes in this study tended to have both terrestrial and algal derived DOC. Leenheer and Croue (2003) found that the DOC concentrations not only depend on the nature of the watershed, but are also influenced by seasonal variations such as run-off or lake algal blooms. In addition, the contribution of DOC from autochthonous input can increase with the increase of nutrients in the water (Wang and Hsieh, 2001). Phosphorus levels and chlorophyll *a* values are highest in the SGI ecoregion confirming higher algal production in the lakes. Nguyen et al (2005) confirmed that autochthonous, algal-derived, DOC can be a significant source of DBP precursors. They concluded that DOC produced by green algae was more reactive in forming chloroform than the blue-green algae or diatoms, and that algae-produced DOC was more reactive to forming DCAA than TCAA (both HAAs). These three DBPs had maximum values found in the SGI lakes compared to any other lakes or streams in the study. This coincided with the known algal blooms that occur in the lakes during late summer and early fall (when DCAA values are higher then TCAA values) and the overall higher DBPs found in this ecoregion. Plummer and Edzwald (2001) also found that compared to other sources of organic matter, algae under bloom conditions contributes significantly to the DBP precursor pool. However, they also noted that the majority of the DBP precursors (70%) were attributable to cellular material, and that the removal of algal cells from a drinking water supply prior to treatment substantially reduces these DBP precursor concentrations.

Lakes in the remaining ecoregions can be classified as oligotrophic, with the exception of Shawnigan Lake, which is more mesotrophic in nature. The DBPs produced from these source waters were substantially lower than the SGI lakes. Shawnigan Lake did have some elevated THM values (end of tap), which also tended to coincide with algal bloom periods in early spring and late fall. Hong *et al*. (2008) observed similar relationships between algal-derived DOC, chlorophyll *a* values and DBP formation.

DOC and DBP Relationship

To better observe the relationship between source water DOC levels and the resulting DBPs from this study, a representative watershed from each ecoregion was selected and is illustrated in Figures 2.2 to 2.5. The McKelvie Creek watershed located in the West Coast ecoregion (Figure 2.2) clearly demonstrated the relationship between levels of DOC in the source water and the resulting DBP formation. This strong relationship was likely more pronounced in McKelvie Creek as the DOC concentrations for this watershed were quite low, ranging from 0.3 to1.6 mg/L. This correlation between DBP and low DOC has been demonstrated in other studies (Ates et al, 2007). In addition, this watershed has had little or no human influence and is completely forested. As DOC levels increase, likely due to spring and winter rain storm events, DBP concentrations rise. Consequently the opposite is true, in that as DOC levels decrease during the low flow seasons, DBP concentrations were lower. Overall, HAA production tended to be slightly higher than THMs, especially in the fall and spring. Thus on an individual watershed basis, seasonal differences in DBP production are apparent, as observed in McKelvie Creek.

The distribution area for this water supply is relatively small, with a low water residence time. Rodriguez *et al*. (2004) reported that residence time of water within the distribution system is a significant contributing variable for spatial variation of THMs. The low residence time at this site may explain the lower THM values. China Creek, which also has low DOC levels, exhibited similar patterns to McKelvie Creek with respect to the relationship between DOC and DBP production. Bainbridge Lake water did produce some higher DBPs for the West Coast ecoregion, and this is likely attributed to the source of the DOC, allochthonous versus autochthonous.

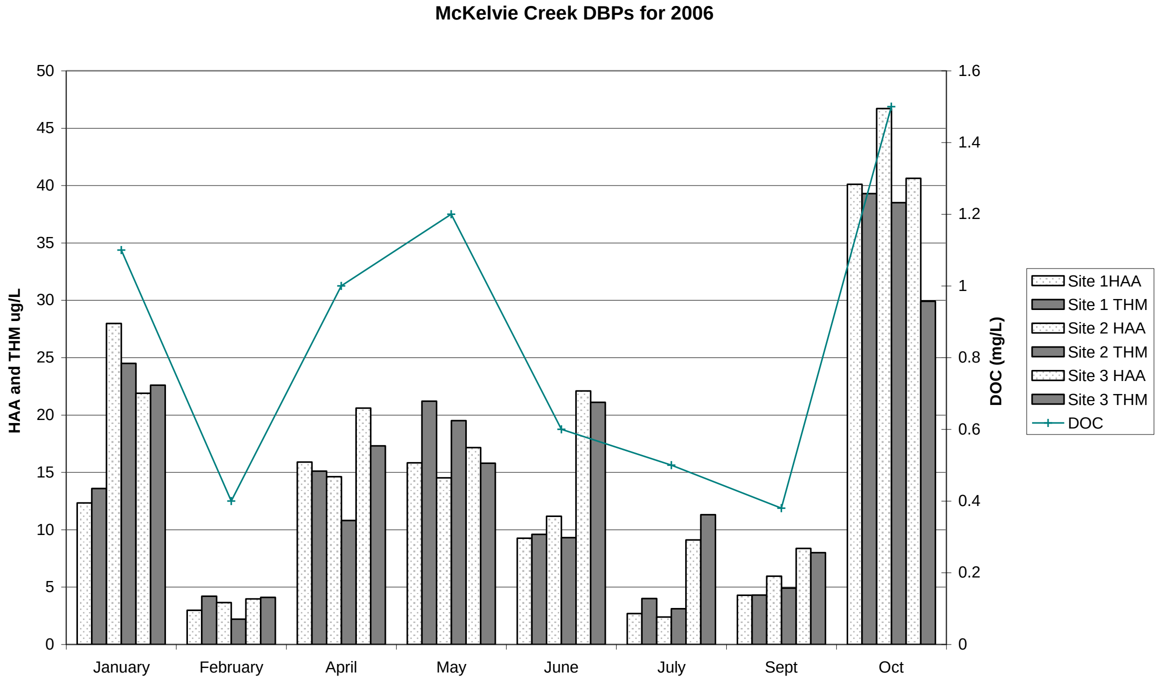


Figure 2.2: Monthly McKelvie Creek source water DOC and the corresponding DBP values after treatment for 2006. This is summarized for total HAAs and THMs for all three sample sites in the distribution system (Site 1 – first tap, Site 2 – mid way, Site 3 – end of distribution.

Cusheon Lake, located on Salt Spring Island in the SGI ecoregion, had some of the highest DOC values in this study (ranging from 3.9 mg/L to 6.6 mg/L) as well as the highest overall DBP results. This combination illustrated a more complex relationship between DOC and DBP production (Figure 2.3). While higher DOC concentrations still corresponded to higher DBP production, this association was not as clear as that shown with the McKelvie Creek watershed. HAAs appeared to be higher in January, April and December, whereas the remainder of the year was dominated by THMs, especially during May to August at all three sites. This suggested that there were other factors influencing the ultimate production of DBPs such as water temperature and the NOM characteristics, which are known to vary seasonally, especially in smaller and unprotected watersheds (Ates et al., 2007; Panyapinyopol et al., 2005). The Cusheon Lake watershed is characterized by a combination of rural and agricultural land use, which results in significant nutrient and organic inputs to the lake. An increase in nutrients can result in algal blooms, which have been found to be precursors to DBP production ((Plummer and Edzwald, 2001; Nguyen *et al*., 2005; Hong *et al*., 2008). The high DBPs observed in this watershed were likely related to the combination of both algal cells and humic substances. The remaining watersheds in the SGI ecoregion (St. Mary and Maxwell Lake) produced DBP results similar to those of Cusheon Lake.

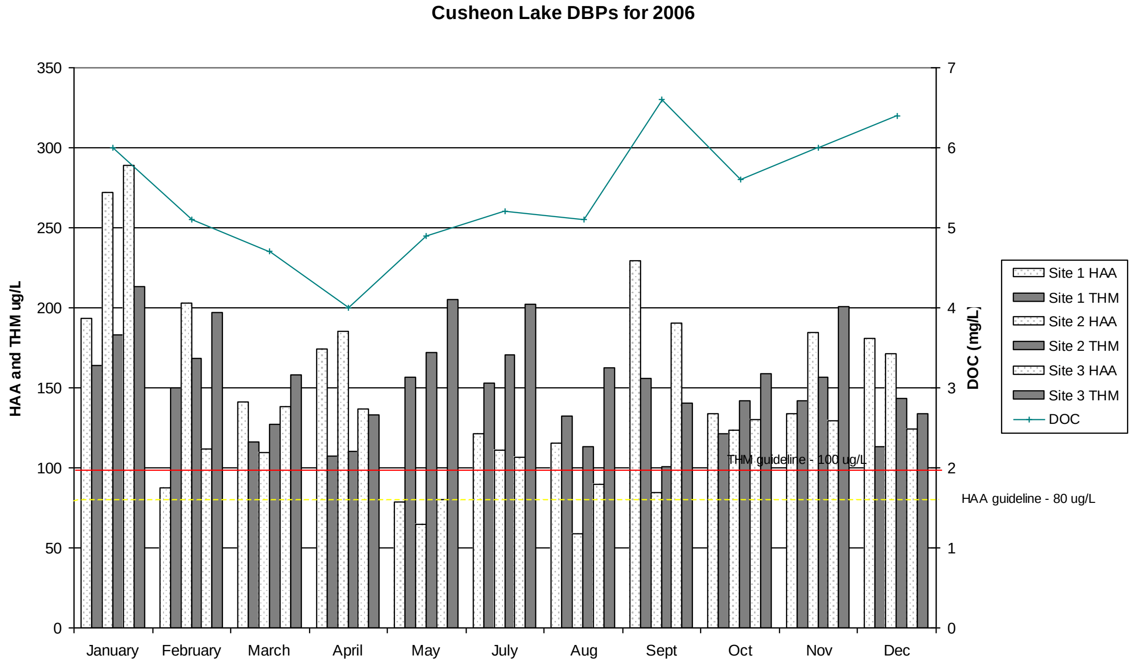


Figure 2.3: Monthly Cusheon Lake source water DOC and the corresponding DBP values after treatment for 2006. This is summarized for total HAAs and THMs for all three sample sites in the distribution system (Site 1 – first tap, Site 2 – mid way, Site 3 – end of distribution). The Canadian Drinking water guidelines for both THM (100 ug/L) and HAA (80 ug/L) are shown in solid and dashed lines, respectively.

The North Island watersheds (Tsulquate, Quatse and Newcastle) had a high amount of naturally occurring tannins and lignins in the water and are often referred to as "tea colored" (Nordin and Phippen, 1997). These watersheds are forested and have little or no human activity above the water supply intake. To reduce DBP formation potential, both Tsulquate and Quatse water treatment plants have a pre-treatment process to remove organics prior to disinfection. Two sets of analyses were conducted on Tsulquate River water: the first on the actual source water, and the second taken after pre-treatment (filtration and flocculation), prior to chlorination.

Figure 2.4 illustrates the reduction in DOC after pre-treatment and the resulting DBP production (both THMs and HAAs for all three site) for Tsulquate River water. Prior to removal, DOC monthly values ranged from 3.9-12.7 mg/L, the highest in the study, however, after the pre-treatment process DOC monthly values decreased ranging from 1.2-3.0 mg/L. The relationship between level of DOC and amount of DBP being produced was still observed; however, overall DBPs tended not to fluctuate as much throughout the year due to the pre-treatment removal of organics. Higher DBP values were found during the fall period (September and November) when DOC levels are elevated due to rainstorm events. More importantly the Tsulquate River DBP data showed consistently higher THMs at the end of distribution (site 3), approximately 2 times higher than site 1 and 2 THM values. As reported in previous investigations, the increase in THM production at site 3 was likely linked to residence time and chlorine residual values within the distribution system (Rodriguez *et al*., 2003; Chowdhury *et al*., 2008).

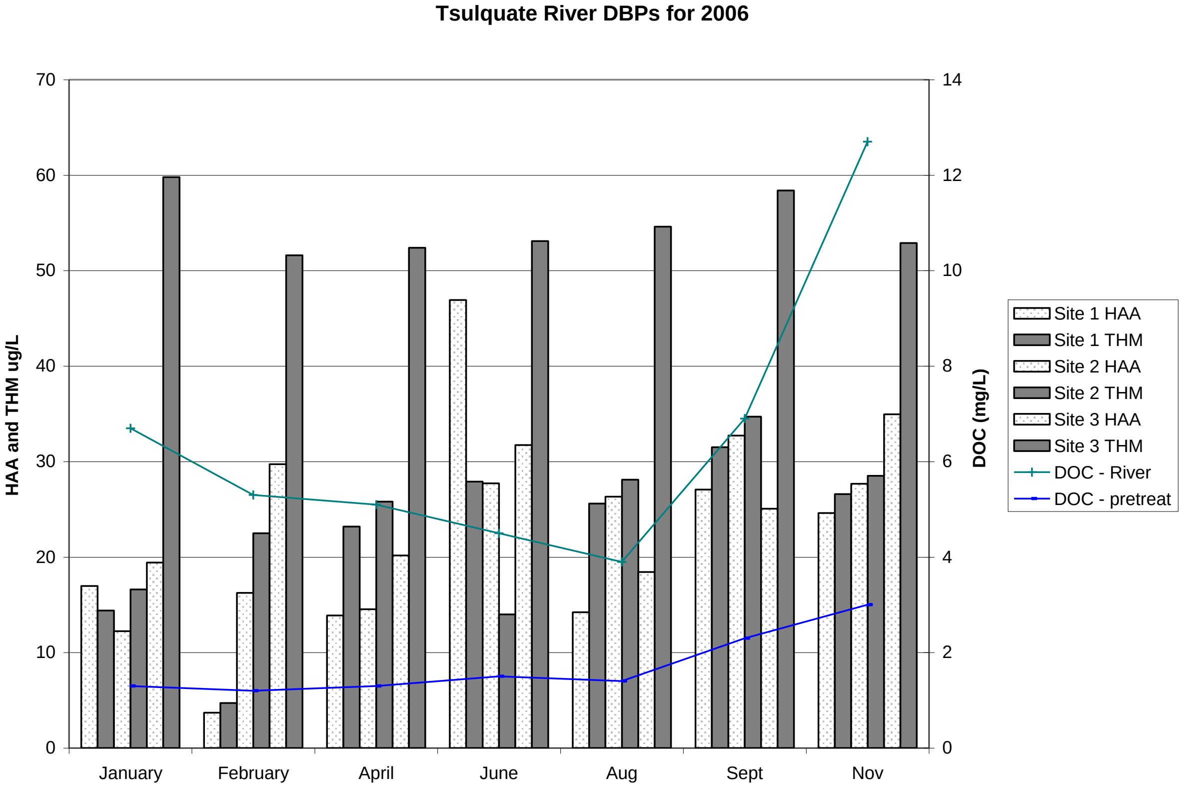


Figure 2.4: Monthly Tsulquate River source water DOC, pretreatment DOC (after filtration and coagulation and prior to disinfection) and the corresponding DBP values after treatment for 2006. This is summarized for total HAAs and THMs for all three sample sites in the distribution system (Site 1 – first tap, Site 2 – mid way, Site 3 – end of distribution).

If the organics were not removed from this water supply prior to disinfection the resulting DBPs would likely be comparable to those found in Cusheon Lake or possibly higher. This is also similar for Quatse Lake, however samples were not collected after pre-treatment so we were unable to record the reduction in DOC values. A water quality assessment and objectives report, developed for Quatse Lake in 1997 (Nordin and Phippen), found THMs taken from samples of treated water (after chlorination) were relatively high (ranging from 102 µg/L to 162 µg/L). The report suggested the high THMs were due to the high amounts of natural organic material in the water (measured as TOC and colour). In response to this assessment, the water purveyors for both these systems upgraded the water treatment systems for both communities (2001 for Tsulquate and 2006 for Quatse). While Tsulquate River and Quatse Lake exhibited similar DBP results, as a result of pre-treatment, Newcastle Creek water is not pre-treated prior to chlorination and thus the DBPs were elevated for this eco-region.

Shawnigan Lake, found in the East Coast ecoregion, was unique in that it appeared DBPs decreased with increased DOC levels (Figure 2.5). During the winter (January to March) when DOC levels were at their highest, the corresponding DBPs were at their lowest. From April to September, DOC levels tended to drop off and remain constant around 3.5 mg/L, but DBPs, especially THMs at Site 3, were at their highest (approximately 2-3 times higher than at site 1). Similar to Cusheon Lake, HAA's tended to be produced more than THMs in November, December and January. Shawnigan Lake is highly developed with numerous homes and rural properties around the entire lake. There are many factors in this watershed that may have influenced the formation of DBPs; however, they still remained substantially lower than the SGI lakes, and below the Canadian drinking water guidelines. Lake stratification, NOM input and output, and NOM decay by various means are all affected by seasonal changes (Ates et al., 2007). These complex and water-specific interactions appeared to affect DBP formations in Shawnigan Lake. The larger size of Shawnigan Lake (537 ha) may also help to protect the water quality of this source water as compared to Cusheon Lake (26.9 ha), which is much smaller. Sooke and Nanaimo Lake are also large watersheds, however, they are forested with little or no anthropogenic activity. The DOC and the corresponding DBP results were low for these watersheds.

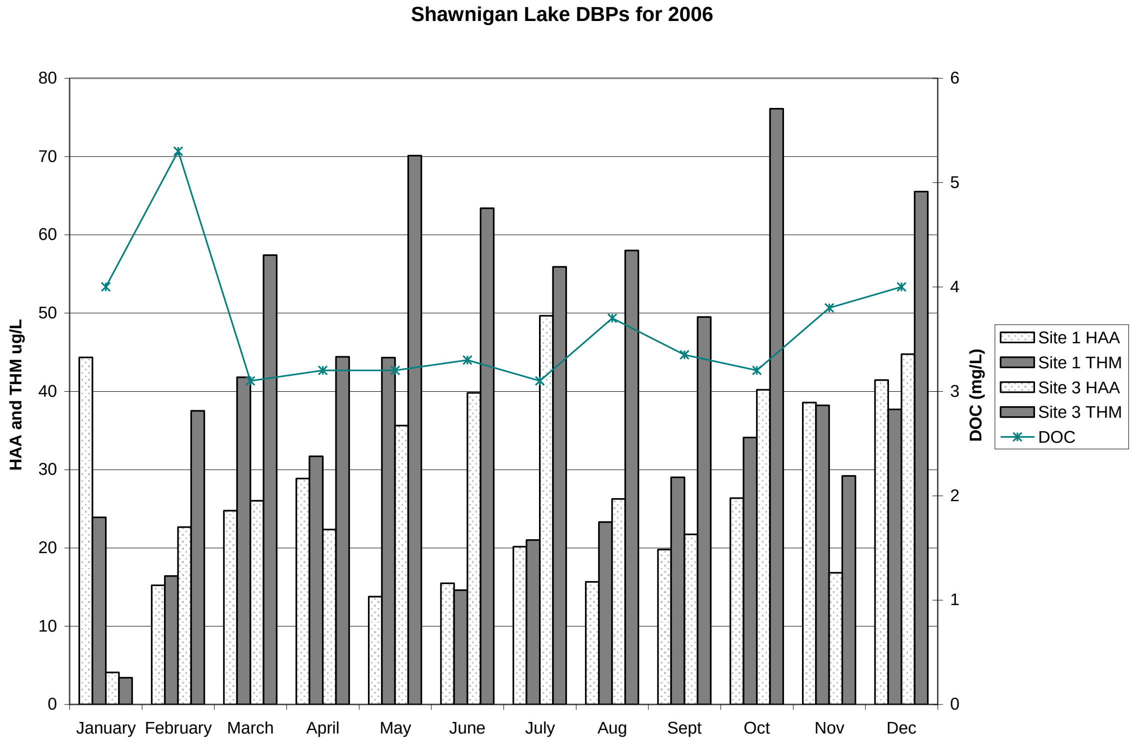


Figure 2.5: Monthly Shawnigan Lake source water DOC and the corresponding DBP values after treatment for 2006. This is summarized for total HAAs and THMs for two sample sites in the distribution system (Site 1 – first tap and Site 3 – end of distribution). There is no Site 2 for this watershed.

DOC concentrations are just one of many analytical tools used to provide some insight into the quantity and /or characteristics of NOM in source waters and the tendency of these source waters to form DBPs. In this study, the levels of DOC were used to provide a general overview or correlation for the amount of DBPs produced from each water supply. Further work should be conducted in this area, using additional tools such as ultraviolet absorbance at 254nm (UV_{254}), specific UV adsorption (SUVA), fluorescence spectroscopy, size exclusion chromatography, and size and polar fractionation, to try and confirm the sources for DOC. Recent work by Chowdhury et al. (2008) found that SUVA was a good overall indicator of the DBP formation potential for a given water source, when they were investigating the characteristics of NOM in two different raw surface water sources. However, they also reaffirmed that NOM is very complex, and in fact NOM from different sources cannot be simply treated as one entity and compared with one another.

Additional Source Water Parameters – Nutrients, bromide and pH

A summary of additional source water parameters is found in Table 2.5. When looking at nutrient levels in the watersheds, the SGI watersheds had the highest annual average total phosphorus (TP) (44.31 µg/L) and chlorophyll *a* (6.38 mg/L) values both at St. Mary Lake. These SGI results were consistent with other studies (Nordin *et al*, 1983; McPherson, 2004), both of which supported the eutrophic status of these lakes. Overall the lake watersheds tended to have higher TP values than streams. Eutrophic lakes tended to have higher algal biomass than nutrient poor lakes. Algae cells and their excreted metabolic products are known to contribute to the DBP precursor pool, producing both THMs and haloacetonitriles upon chlorination (Plummer and Edzwald, 2001). Correlations have been found between algal activity and THM formation potential concentrations in open surface waters, with the highest levels coinciding with peak extracellular production time (Karimi and Singer, 1991).

Bromide average annual results ranged from 0.96 µg/L (China Creek) to 40.32 µg/L (St. Mary Lake). Again, the SGI ecoregion had the highest bromide values while the rest of Vancouver Island had comparatively lower values overall. This may be a result of saltwater intrusion as previously noted by Richardson *et al*. (2003). The higher natural bromide values found in the SGI source waters were reflected in the amount and type of brominated DBPs being produced; making this ecoregion unique. Several studies confirm that when bromide is naturally present in the source water, an increase in bromide-containing DBPs results after disinfection with chlorine (Richardson *et al*, 2003; Plewa *et al*, 2004a). Westerhoff *et al*. (2004) found that aqueous bromine reacts faster with NOM than with corresponding aqueous chlorine reactions by a factor of approximately 10. Richardson et al. (2003) also found that coastal areas, where the ground and surface waters can be impacted by saltwater intrusion, are susceptible to natural elevations of bromide and iodide. This may reflect why SGI lakes had higher natural bromide levels but this would have to be confirmed in a future study.

Bromide levels in the Tsulquate River increased in the source water after pre-treatment and prior to chlorination. This increase in bromide has resulted in the formation of DBAA and BDCAA in the fall, when bromide levels were at their highest. This was specific only to Tsulquate River in the North Island ecoregion and is a result of pre-treatment rather than natural occurring bromide. This was likely due to some factors within the pre-treatment process possibly from bromide traces in the soda ash used in the coagulation process, but would have to be further investigated for confirmation.

More recent studies have focused on other parameters, such as pH for determining DBP formation (Chowdhury and Champagne, 2008; Navalon et al, 2008; Garcia and Moreno, 2006). Average annual pH values ranged from 6.41 (Quatse River) to 7.68 (China Creek). Watersheds in the North Island ecoregion are known to have lower pH values, primarily during the rainy season, associated with low alkalinity and hardness (Nordin and Phippen, 1997). The formation and distribution of THMs and HAAs are strongly dependent on the pH values of the source water during chlorination (Bo et al, 2008). When analyzing the DBPs against the water source parameters, there was a moderate correlation with DOC and pH ($r=-0.3362$; $p=0.0012$) (Appendix 2.2).

THM production, especially BDCM and DBCM, in the presence of bromide, increased with increasing pH values (Bo *et al*, 2008). This information, along with the fact the SGI lakes have the highest pH and bromide levels, are consistent with the high production of THMs from this ecoregion. Conversely, the lower pH levels found in the North Island ecoregion may have helped to keep THM concentrations lower than one would expect given the high DOC and color values.

In the East and West Coast ecoregions, the DOC and bromide levels were relatively low and pH is consistently neutral. The DBPs produced from these water sources were all well below guidelines for the protection of human health, with the exception of Bainbridge Lake during winter where both HAAs (December to February) and THMs (December) were substantially higher. Elevated HAAs at this time of year were also noted in both Cusheon and Shawnigan lakes.

Individual DBPs

Some of the seasonal differences between HAA and THM production may be due to the individual types of DBPs being produced. The speciation of DBPs depends on several factors: the nature and concentrations of NOM; the bromide ion concentration; chlorine/DOC ration; bromide/DOC ration; background water chemistry; and chlorination conditions (Ates *et al*., 2008; Panyapinyopol *et al*. 2005). The majority of THMs for all watersheds in this study were comprised of chloroform (approximately 90%), with a small portion of BDCM, although THMs in Cusheon and St. Mary lakes also included small amounts of CDBM. For HAAs there was more diversity in the types of individual HAAs being formed. In all watersheds, for the majority of the year, DCAA and TCAA were the main HAAs produced, followed by small amounts of BCAA. The

DCAA and TCAA values were similar among watersheds but may have varied between sites within the distribution system. For example, Bainbridge Lake had higher DCAA at Site 1 and higher TCAA at Site 3. Cusheon Lake was opposite to this in that TCAA was higher at Site 1 with DCAA higher at Site 3.

Hypoclorous acid (HOCl), the dominant chemical form of active aqueous chlorine, or other oxidants can oxidize bromide to hypobromous acid (HOBr), which is not only a stronger oxidant but also a stronger halogenating agent than chlorine species (Ates et al., 2007). A mixture of HOCl/HOBr leads to the formation of various brominated and chlorinated DBP species. As the amount of bromide increases in source waters, a shift toward brominated DBPs generally occurs. As expected from the bromide results, SGI watersheds and the Tsulquate River all had an increase in the brominated acetic acids over the remaining watersheds. St. Mary and Cusheon Lakes produced MBAA, BCAA, and DBAA in small amounts throughout the year. Maxwell produced MBAA from October to December only, while Cusheon also produced BDCAA during this time period. Tsulquate River had a minor increase in the brominated HAAs, producing both DBAA and BDCAA in the fall. Bromide may become more available during the fall and winter periods when it is transported into the water column through rainstorm events or through limnological processes.

Water Treatment

Another important component to DBP production is related to the treatment process, more specifically the chlorine dosage, reaction or contact time, length of distribution system, rechlorination stations and chlorine residual values (Singer, 1994; Nikolaou *et al*., 2004; Krasner *et al*., 2006). There were no rechlorination stations located prior to any sites sampled for DBPs in this study. Table 2.6 provides a summary of the treatment, chlorine dose and residual values for the 12 study water supplies. With the exception of Sooke Lake, which uses chloramination, the 8 water systems on Vancouver Island use a chlorine injection process, while the 3 water supplies on Salt Spring Island use a combination of sodium hypchlorite and granular chlorine in 1% solution. This difference in treatment may be part of the explanation as to why the SGI ecoregion had higher DBPs than the rest of Vancouver Island study water sources. Only three watersheds (Sooke, Quatse and Tsulquate) had a pre-treatment process prior to chlorination. This was an important component to the North Island watersheds (Quatse and Tsulquate) for reducing the DOC and corresponding DBP levels.

Maintenance of adequate chlorine residuals and control of DBPs throughout water distribution systems is an important issue. The majority of water purveyors in this study tend to base the chlorine dose on the chlorine residual from the first tap. Chlorine residual values at Site 1 (first tap) on average tended to vary around 1.0 mg/L or just below. However by the end of the system, or Site 3, chlorine residual values on average were around 0.25 mg/L. Speight and Singer (2005) found that under conditions of low residual chlorine, HAA concentrations were low, even at locations with long residence time. In contrast, THM concentrations were generally high at these same locations. This may explain the consistently higher THM values found at site 3 (end of distribution system) for both Shawnigan and Tsulquate. Both of these systems had the lowest chlorine residual values at these extreme sites at 0.10 and 0.18 mg/L, respectively, and considerably lower HAA values. It has also been suggested that this decrease in HAA concentrations (in particular DCAA) near the extremities is a phenomenon probably related to microbiological degradation of these substances (Rodriguez et al, 2004). This can lead to implications for human health concerns at which time a risk trade-off analysis between microbial and chemical risks becomes necessary (Sadiq and Rodriguez, 2004). A more detailed investigation is required to fully understand the relationship between treatment strategies and DBP formation for these watersheds on Vancouver Island.

Table 2.6: Summary of water treatment, chlorine dose and residual values for 12 water supply systems.

			Chlorine Residual - average and range (mg/L)			
Watershed	Treatment	Chlorine Dosage	Site 1 (first tap)	Site 2 (mid way)	Site 3 (last tap)	Site Locations
Cusheon	1% solution using 12% sodium hypochlorite	5.3 mg/L monthly/annual average based on residual values	0.95 (0.5-1.2)	0.65 (0.21-2.11)	0.24 (0.02-0.44)	Site 1 - Lautman (first tap), Site 2 - 144 Creekside (mid way), Site 3 - Samual Cres (end of system)
Maxwell	1-1.3% solution using 65% HTH granular chlorine	3.5 mg/L daily average. Dosage varies depending on the demand at different times of the day. As flow increases the initial does decreases.	1.09 (0.6-1.53)	0.54 (0.2-1.16)	0.20 (0.03-0.40)	Site 1 - Shepherd Hills (first tap), Site 2 - Building Inspectors Office (mid way), Site 3 - Churchill Air Valve station (end of system)
St. Mary	Use three metering pumps and a series of barrels to mix a 1% solution using 65% HTH granular chlorine	5 mg/L daily average. Dosage control is through residual monitoring	1.38 (0.07-2.07)	0.32 (0.03-0.64)	0.19 (0.01-1.73)	Site 1 - Parminter bulk Chamber (first tap), Site 2 - Southey Point Standpipe (mid way), Site 3 - Channel Ridge pump station (end
Nanaimo	Chlorine gas injection	Based on chlorine residual (target 1.0-1.2 mg/L) monitored 20 min	1.10 (0.88-1.30)			Site 1 -1071 College Drive (first tap)
Shawnigan	Chlorine gas injection	Based on chlorine residual - manual adjustment	0.74 (0.3-2.0)		0.10 (0.10)	Site 1 - first tap, Site 2 - end of system
Sooke	Three step process: UV disinfection, addition of free chlorine (10 minute contact time), followed by addition of ammonia (5 pt chlorine to 1 pt ammonia)	1.5-1.7 mg/L free chlorine - annual range	1.19 (1.1-1.34)	1.02 (0.89-1.23)	0.37 (0.10-0.59)	Site 1 - JGO-TR-01 Lakehurst PRV (first tap), Site 2 - San-CB-02 Dooley meter vault (midway), Site 3 - SID - SI-03 Sidney, Bowden, Allbay furthest tap not subjected to rechlorination
Bainbridge	Chlorine gas injection	Dosage varies from 35-82 lbs/day based on water flow/demand (11454-17376 m3)	1.21 (0.86-1.62)	0.65 (0.37-0.84)	0.24 (0.16-0.34)	Site 1 - Anderson Ave (first tap), Site 2 - Wallace St (mid way), Site 3 - Falls Rd (end of system)
China	Chlorine gas injection	Dosage varies from 27-40 lbs/day based on water flow/demand (9374-16393 m3)	0.76 (0.6-0.88)	0.56 (0.43-0.63)	0.46 (0.34-0.64)	Site 1 - Anderson Ave (first tap), Site 2 - Wallace St (mid way), Site 3 - Falls Rd (end of system)
McKelvie	Chlorine gas injection	1.0 mg/L - Dosage varies depending on residual levels	0.49 (0.06-0.66)	0.47 (0.12-0.73)	0.37 (0.07-0.55)	Site 1 - public works yard (first tap), Site 2 - Village of Tahsis rec center (midway), Site 3 - Village
Quatse	Pretreat - floculation, filtration followed by chlorine gas injection	Chlorine added after pretreatment. Varies from 1.1-1.8 mg/L				Site 1 - first tap, Site 2 - mid way through distribution system, Site 3 - end of distribution system
Newcastle	Chlorine gas injection	0.05-1.0 mg/L chlorine adjusted to residual values, flow varies from 390-600 cubic meters per	0.81 (0.4-1.2)			Site 1 - Village office (first tap), Site 2 - 210 Sayward Hts (midway), Site 3 - Hemlock St (end of
Tsulquate	Three parallel train process with floc tanks and DAF (Dissolved Air Flotation) tanks. Color removed using ISOPAC 6 coagulant with soda ash addition for alkalinity.	Chlorine added after pretreatment as water is pumped to the reserviors. Varies from 1.1-1.8 mg/L	0.83 (0.68-1.0)	0.69 (0.52-0.87)	0.18 (0.08-0.24)	Site 1 - reservoir, Site 2 - public works yard (first tap), Site 3 - Chatham Ave (end of system)

Conclusions

This study documented a spatial difference in DBP production with respect to biogeoclimatic ecoregions on Vancouver Island. For the 12 watersheds under review, THM and HAA concentrations varied considerably and were linked to DOC levels found in the source waters, with higher DOC concentrations generally correlating to higher DBP production. The watersheds from the SGI ecoregion had the highest DBPs, linking DBP formation to high levels of TP, chlorophyll *a*, DOC, bromide and pH in the source water. Treatment strategies were shown to reduce DBP production in the North Island ecoeregion watersheds, which had naturally occurring tannins and lignins in the source water. Both the East and West Coast ecoregions were similar in that they had low DOC concentrations and generally low DBP production.

The majority of THMs for all watersheds were comprised of chloroform (approximately 90%), with a small portion of BDCM, while HAAs, for the majority of the year, DCAA and TCAA were the main HAAs produced, followed by small amounts of BCAA. Elevated levels of bromide in the SGI watersheds and Tsulquate River treated water, resulted in the production of brominated acetic acids such as, MBAA, BCAA and DBAA.

In particular this study has shown that DBP formation was dependent on water body type, lakes versus streams, with eutrophic lakes having the highest levels of DBPs. Previous studies have shown that these elevated DBPs in lakes are likely derived from autochthonous DOC sources, produced during algal blooms in the spring and fall (Hong *et al*., 2008). DBP production in streams is largely tied to precipitation events, occurring during fall and winter, which increases allochthonous DOC concentrations in the watershed (Chow *et al*., 2007). However, further work is required in this area to characterize and confirm the sources of DOC. In addition, as shown by Hong *et al*. (2008), linking the types of algae in the lakes with the types of DBPs produced may also explain the variation in individual THMs and HAAs. Significant seasonal differences in DBP production were only observed in the SGI ecoeregion, likely attributed to algal bloom production in the summer and fall.

This study also provided a brief summary of the water treatment processes used for the 12 water supplies. Due to the inconsistencies in treatment, such as disinfectant dose, reaction time, length of distribution system, and in some cases lack of data, the treatment strategies were not included in the analyses. However, treatment strategies are an important component in the production of DBPs (Singer, 1994; Nikolaou *et al*., 2004; Krasner *et al*., 2006) and should be considered for future research.

This study presents evidence that on a preliminary basis source water quality and water body type could be used to predict the DBP formation potential within different biogeoclimatic zones. Thus, communities within an ecoregion would be able to identify the potential exposure risk from DBPs for a particular water source and provide adequate measures to address this issue, such as treatment strategies. Ultimately, the type and effectiveness of the treatment process remains a key first line of defence in the protection of human health.

Chapter 3: Long Term Trends in DBP Production Under Changing Watershed and Treatment Management Strategies In the Greater Victoria Drinking Water Service Area

Abstract

In reviewing a long-term disinfection by-product (DBP) data set, collected from 1991 to 2008, it was determined that changes to treatment strategies significantly altered the types and concentrations of DBPs formed. These differences in DBP production were associated with changes in disinfection process, sampling location within the distribution system, re-chlorination stations and chlorine residuals. Typically trihalomethanes (THMs) increased with longer residence time, while haloacetic acids (HAAs) tended to degrade over time. While the main treatment plant provided indirect benefits to extremity sites, through chlorine residuals, the DBPs produced following booster site locations were influenced significantly by changes to the booster stations (e.g. seasonal versus annual re-chlorination and decommissioning of booster stations). For all sites, THMs were comprised primarily of chloroform (90% or greater) and bromodichloromethane (BDCM), while HAAs consist of dichloroacetic acid (DCAA), trichloroacetic acid (TCAA) and small amounts of bromochloroacetic acid (BCAA). Overall there was a significant reduction in the formation of DBPs for the Greater Victoria water supply area following changes to treatment strategies.

The reservoir inundation project (2002-2005) was a success in that summer water temperatures were reduced. Total organic carbon (TOC) concentrations increased in the Sooke reservoir and are likely attributed to an increase in algal production (e.g. higher chlorophyll a levels). However, there was no significant difference in overall DBP production during and following the reservoir inundation period. Bacteriological quality

of the disinfected water at the first customer site improved substantially following the changes to treatment strategies. With the increased use of alternative disinfectants, such as chloramines, water utilities need to assess the risk trade-offs between potential adverse human health effects and formation of regulated and unregulated DBP species.

Introduction

Chemical disinfection of drinking water sources has been widely used to eliminate pathogens and protect human health against waterborne diseases. Chlorine has traditionally been the preferred disinfection agent because of its proven effectiveness and low cost (Rodriguez and Serodes, 2000). However, the process of disinfection produces another group of contaminants referred to as disinfection by-products (DBPs) (Rook, 1974). The formation of DBPs is of great concern because of the potential carcinogenic impacts of these compounds (Koivusalo *et al*., 1994; Bull *et al*., 1995; Richardson *et al*., 2007; Villanueva *et al*., 2007). In order to control DBPs in drinking water systems, the use of alternative disinfectants, notably chloramination, has been pursued, leading to the reduction of concentrations of some regulated DBPs (Roccaro and Vagliasindi, 2009). Balancing acute risks of water borne pathogens and chronic risks from DBP exposure has been a key issue in the process of drinking water risk assessment and management.

The DBPs occurring most frequently and with the highest concentration are trihalomethanes (THMs) and haloacetic acids (HAAs) (Chaiket *et al*., 2002). THM refers to the sum of four substances chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM) and bromoform. While HAAs include nine substances, only the sum of five HAAs (dichloracetic acid (DCAA), trichloroacetic acid (TCAA), dibromoacetic acid (DBAA), monochloroacetic acid (MCAA) and monobromoacetic acid

(MBAA)) is regulated and generally referred to as HAA5. Additional DBPs have also been identified, including compounds such as haloacetonitriles (HANs), haloketones (HKs), short chain carboxylic acids, acetones, chlorinated phenols, phenolic acids, chlorinated quinones, benzoic acids, iodoacids, and heterocyclic compounds (Richardson, 2003; Ates *et al*., 2007). Current standards and guidelines related to DBP levels in North America, and even the world, are limited, primarily due to lack of information (i.e. monitoring data, toxicity effects). The United States Environmental Protection Agency (US EPA) (2002) has developed regulations for THMs and HAA5 (sum of 5 HAAs) of 80 µg/L and 60 µg/L, respectively. However, in Canada these guidelines are higher, with the THM guideline at 100 µg/L and HAA5 guideline at 80 µg/L (Health Canada, 2008).

The main factors affecting overall DBP formation and speciation are the physical/chemical/biological characteristics of the source water and the treatment strategy provided. Key parameters in the source water include water temperature, pH, concentration and properties of natural organic matter (NOM), chlorophyll *a*, and bromide concentration (Nikoloau and Lekkas, 2001; Kitis *et al*, 2004; Plewa *et al*, 2004; Panyapinyopol *et al*., 2005; Krasner *et al*., 2006). Organic compounds in the source waters, including both terrestrial and algal derived NOM, are the principal DBP precursors in surface drinking water sources (Chang et al., 2000; Hong *et al*., 2008). In fact Plummer and Edzwald (2001) found algae under varying stages of growth yield higher chloroform production than from humates. Variations in temperature, both short and long term, is found to strongly affect the kinetics of chlorine consumption and DBP formation (Serodes *et al*., 2003; Toroz and Uyak, 2005; Roccaaro *et al*., 2008). During warmer seasons, more chlorine is required to ensure acceptable levels of residual disinfectant.

While source water quality plays a role in DBP formation, the treatment type, disinfectant contact time and dose, length of distribution system and chlorine residuals throughout the water system also influence the types and amounts of DBPs produced (Singer, 1994; Nikolaou *et al*., 2004; Krasner *et al*., 2006). The disinfectant used must achieve an adequate inactivation of microbial organisms before the treated water reaches the first customer (primary disinfection) and must be large enough to ensure an adequate residual at the periphery of the distribution system to inhibit microbial re-growth (secondary disinfection) (Boccelli *et al*., 2003). Several studies have shown that HAAs are biodegradable, particularly in the absence of a disinfectant residual (Baribeau et al., 2000; Speight and Singer, 2005). Lu *et al (*2009) found the yields of THMs and HAAs increased more significantly in chlorination than in chloramination with the increase of disinfectant dosage, contact time and NOM content.

Modern water supply systems tend to be large and interconnected with longer retention times that can result in poor maintenance of chlorine residual and high concentrations of THMs (Lee et al, 2007). In these larger distribution systems, re-chlorination or booster stations are required to maintain adequate chlorine residuals and control microbial re-growth throughout the water system. The reactive material characteristics at the time of re-chlorination would be different from those at the time of the first dose or treatment, resulting in a change of DBPs being formed (Tryby *et al*., 1999). Hence the DBP precursor molecules present in the water at the booster stations has been chemically altered by the first treatment and may give rise to a different concentration or distribution of DBPS. Hernandez-Castro (2007) developed a two-stage stochastic approach to optimize the location of booster disinfection stations. The model minimizes the expected total cost involved in the booster stations and the mass of disinfectant needed to satisfy the residual concentration constraints within the network. Ultimately a balance is required between microbial and chemical risk to human health concerns.

There has been very little research involving long term DBP data sets, looking at trends over time, areas of concerns within a distribution system and documenting improvements to the distribution systems following upgrades or changes to the treatment process. The Water Services Department of the Capital Regional District (CRD), located in Victoria, British Columbia, has been collecting DBP data from the Greater Victoria Water Supply Area since 1990. There have been many sampling stations established throughout this time period; however, sampling has been relatively consistent at only a few sites. The distribution system is relatively large and has re-chlorination or booster stations located in some of the outer distribution areas. One of the unique opportunities provided by the CRD long-term data on DBPs is capturing the changes in the quality of source water following the raising of the dam in the Sooke Reservoir and the subsequent inundation of 134 hectares of new land over a three-year period (2003-2005). The data set also captures changes that have occurred to the disinfection treatment system throughout this period, including the main treatment plant (Japan Gulch) and booster stations throughout the distribution area.

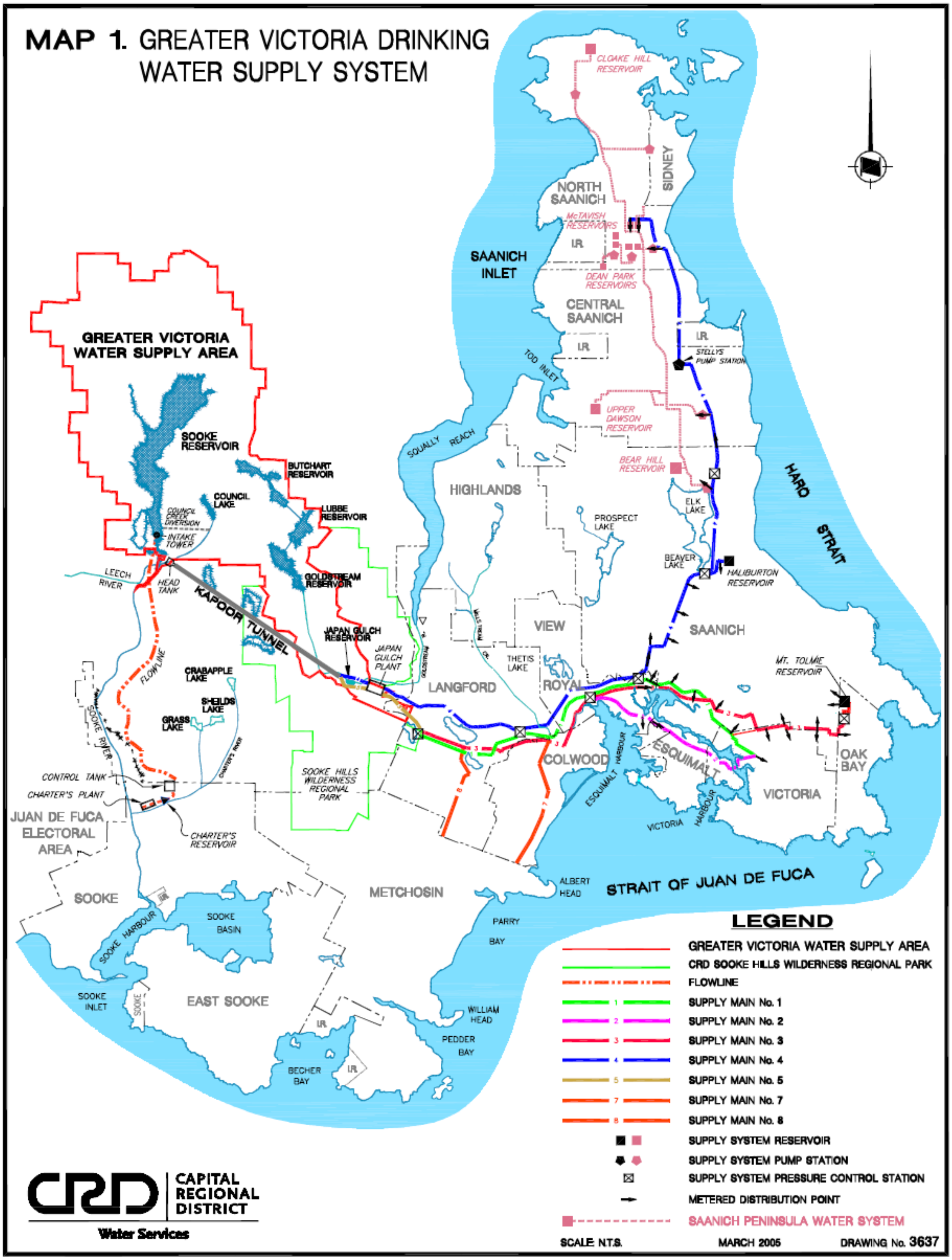
The goal of this study is to test if and how the changes in source water quality in terms of NOM and temperature, in addition to changes to treatment strategies, influences the types and concentrations of DBPs formed. More specifically, after the raising of the dam and inundation of the surrounding land, were there any notable changes to NOM concentrations in the source water, and consequently the types and concentrations of DBPs produced. Furthermore, did the increase in reservoir depth, provide lower water temperatures for a longer period during summer and fall. Finally, did the changes to treatment strategies either at the main plant or at the booster stations alter the type and quantity of DBPs produced. The results from this study will enhance our understanding of environmental and treatment processes influencing DBP formation and assist water departments with the management and protection of the drinking water sources to ensure minimal risks to human health.

Materials and Methods

Greater Victoria Water Supply Area

The drinking water for Greater Victoria, British Columbia comes from a protected watershed called the Greater Victoria Water Supply Area (GVWSA), which is managed by the CRD. The water supply area is approximately 11,000 ha and is located about 30 km northwest of Victoria, British Columbia, Canada (Figure 3.1). The water supply area is comprised of five reservoirs, which have been used since the early 1900's (CRD, 2006). Sooke Lake Reservoir, the largest of the reservoirs, is the primary water source, supplying approximately 98% of Greater Victoria's drinking water. The other four reservoirs are Butchart, Lubbe, Goldstream and Japan Gulch, which typically remain off-line and are used only as a backup water supply.

Figure 3.1: Map of the Greater Victoria drinking water supply area (CRD, 2009).



Water at the southern end of Sooke Reservoir enters the intake tower and is screened through stainless steel screens. From the intake tower, the water passes through two 1,200 mm diameter pipelines to the Head Tank, then flows through the 8.8 km long, 2,300 mm Kapoor Tunnel, to the Japan Gulch Water Treatment Plant. Water for the community of Sooke is also supplied from the Sooke Reservoir but travels a different route to the Charters Water Treatment Plant.

The Sooke watershed area has been protected from public access since 1999. Historically the watershed had been actively logged. At present, commercial logging, farming, mining, recreation, or use of herbicides, pesticides and fertilizers is no longer allowed in this area. This barrier eliminates many of the organic and inorganic chemicals that can contaminate the source water and virtually eliminates the potential for human disease agents being present. Very few drinking water utilities in Canada and the Unites States can claim this type of protection (CRD, 2006).

Sooke Reservoir Expansion Project

The Sooke reservoir expansion project commenced in 2002 with the raising of the dam by 6 meters and the clearing of vegetation (134 hectares) around the perimeter of the reservoir area (i.e. the area expected to be inundated). Vegetation removal prior to inundation greatly reduced any organic carbon input to the water supply during flooding. The inundation phase of the project took place between 2003 and 2005. The Sooke reservoir was allowed to fill 1.9 meters above the old full pool level in 2003, an additional 2.5 meters in 2004 and in 2005 the remaining meter to obtain the new full pool level in the reservoir (CRD, 2009) (Figure 3.2). The goal of the Sooke reservoir expansion project was to provide more water storage to prevent severe water restrictions in times of drought weather cycles and a deeper, colder water supply (CRD, 2005). The cooler water in the summer months would help to reduce the potential for losses of chlorine residual, control the re-growth of bacteria and help to meet the British Columbia (BC) drinking water temperature guideline of less than 15 degrees Celcius (BC MOE, 2006).

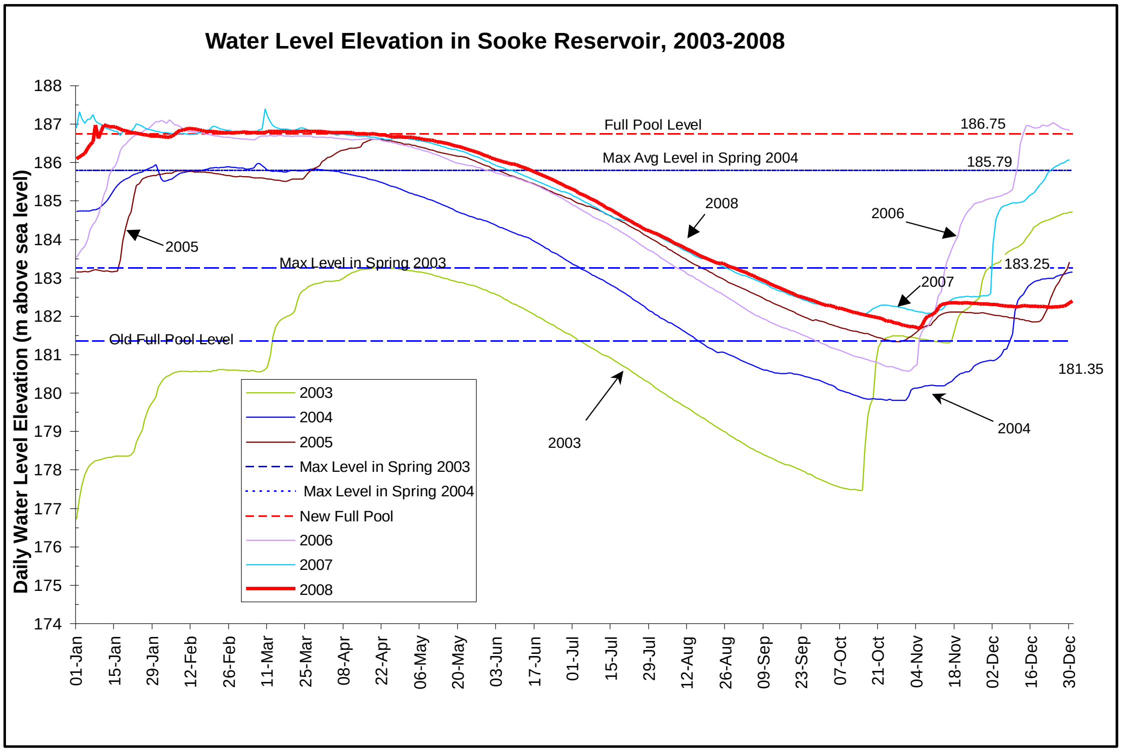


Figure 3.2: Water level elevation in Sooke Reservoir, 2003-2008 (CRD, 2009).

Distribution System

The Greater Victoria drinking water distribution system is comprised of nine individual distribution systems (Figure 3.1). Six of the systems are separately owned and operated by the municipalities of Central Saanich, North Saanich, Oak Bay, Saanich, Sidney and Victoria. The Victoria municipality also owns and operates the Esquimalt distribution system. The last two distribution systems are owned by the CRD and operated by the Environmental Services Department. These latter two systems include the combined distribution system in the Western Communities (comprised of Colwood, Langford, Metchosin, and View Royal) and a separate system in Sooke.

Treatment Process

The Greater Victoria Drinking Water System (GVDWS) is an unfiltered drinking water system. The disinfection treatment process in the GVDWS is comprised of two treatment plants. The Japan Gulch Treatment Plant disinfects all of the water in the GVDWS except for the Sooke distribution area, which receives treated water from the Charters Creek Plant. At the Japan Gulch Treatment Plant, the water passes sequentially through a three-part disinfection process consisting of two primary disinfection steps followed by a secondary disinfectant step (CRD, 2006):

1. *UV Disinfection*. Ultraviolet (UV) disinfection, which began in 2004, is the first step in the primary disinfection process and inactivates parasites such as *Giardia* and *Cryptosporidium* as well as reducing bacteria levels in the water.
2. *Free Chlorine Disinfection.* The second step, which began in 2001, involves a free chlorine dosage of approximately 1.7 mg/L, using approximately 10 minutes (depending on flow) of contact time between the free chlorine and the

water. This step kills bacteria and provides a 4-log (99.99%) kill of viruses (CRD, 2006).

3. *Ammonia Addition*. Ammonia, at a ratio of approximately 5 parts chlorine to 1 part ammonia, is added at a point downstream where the water has been in contact with the free chlorine for approximately 10 minutes or more. In the water, these chemicals combine to produce a chloramine residual. This residual remains in the water and continues to protect the water from bacterial contamination (secondary disinfection) as it travels throughout the pipelines of the distribution system. This treatment process was also initiated in 2001.

Chloramination has been practiced in the Greater Victoria area since the 1940s; however, the chlorine and ammonia were added within 10 meters of each other, inside the Japan Gulch treatment plant. From 1996 to 2001, seasonal increases in the chlorine dosage in summer months provided better disinfection and chlorine residuals to the far end of the distribution system. The change to free chlorine contact time occurred in 2001 at the request of the Public Health Office. Similar to the Japan Gulch treatment plant, the Charters Creek treatment plant process undergoes UV disinfection followed by chlorination and the downstream addition of ammonia, which allows for some free chlorine contact time (approximately 10 minutes) prior to forming chloramines. This study focuses on the Japan Gulch treatment plant and distribution system.

Re-Chlorination Stations

There are a number of booster stations through out the Greater Victoria drinking water distribution system. The following section provides information on the stations that pertain to this study, which are located in the North Saanich, Metchosin and Central Saanich distribution areas. To control bacterial regrowth in the Cloake Hill pressure zone of the North Saanich distribution system the CRD Environmental Services Department adds additional chlorine using sodium hypchlorite at the Deep Cove pumphouse (since the early 1990's), when the chlorine residual drops below 0.3 mg/l at the outlet of Cloake Hill Reservoir. In the early years, the re-chlorination station was operated periodically and only more recently (since 2003) has the re-chlorination been virtually continuous (CRD, 2007a). This pump house provides a direct feed of water containing the higher chlorine residuals to Cloake Hill Reservoir (CLR-01-01), which in turn, supplies water to part of the North Saanich Distribution System (reflected by site NOS-CP-01 after 2001). In response to elevated DBP results observed in this distribution area in February 2007 the re-chlorination station at the Deep Cove Pumphouse was decommissioned in April 2007. The Upper Dean Park Reservoir in N. Saanich has also been re-chlorinated with sodium hypchlorite since its construction (late 1990's).

In the Metchosin distribution system, the CRD Environmental Services Department established a re-chloramination station in 2002 at Rocky Point Reservoir to boost the chlorine residuals near the extremity of that system. The installation was intended to boost chloramine residuals within the reservoir before water moves south to the Deer Park Reservoir pressure zone and the Becher Bay First Nations Reserve. The system was typically operated in the summer months when residuals were low and the water temperature was high, a combination that often leads to bacterial growth. However, during 2004, the service area of this reservoir was increased and the booster station is now kept in full service throughout the year. In 2006, the chlorine dosage was increased to provide a target total chlorine residual of 1.0 mg/L at the outlet of Rocky Point Reservoir (CRD, 2007). The target chlorine to ammonia dosage ratio is 5:1.

Small amounts of free chlorine can also be added, but rarely used, at the Upper Dawson Reservoir and McTavish Reservoir, located in Central Saanich, to enhance the chlorine residual in these reservoirs and reduce the potential for bacterial regrowth.

Sampling Locations

Over the study period, 1990 to 2008, the sampling stations have evolved to better reflect the conditions through out the distribution system. Table 3.1 provides a list of the sample locations, identifies which distribution system they come from, indicates if the stations have been subject to re-chlorination, and where they are in relation to the larger GVWSA (i.e. first tap, mid-point contact or extremity). It should be noted that the JGO-TR-01 station replaced the JGO-TR-00 station effective January 2001, and the NOS-SB-03 station at Swartz Bay replaced the NOS-SB-02 station effective March 2001. These replacement sites are virtually identical to the original site, with samples being collected in adjacent or nearby buildings. Site NOS-SB-03 at Swartz Bay ferry terminal was discontinued from sampling in June 2005 as the data from site NOS-CP-01 currently represents the last user in the system with influence from re-chlorination.

Table 3.1: Sampling locations within the GVWSA.

Distribution Area	Site Code	Site Description	Years Sampled	Location in Distribution System
Non-Rechlorinated Locations				
Japan Gulch	JGO-TR-01	PRV-2818 Lakehurst Dr. (replaces JGO-TR-00)*	Dec 1990 - Dec 2008	First Tap
Saanich	SAN-CB-02	Dooley meter vault - mid way through system	Apr 1991 - Dec 2007	Mid-point
Sidney	SID-SI-03	Bowden and Allbay pumphouse	Mar 2003 - Dec 2007	Extremity
Rechlorinated Locations				
Metchosin	MET-PB-01	E. Sooke Road at Rocky Point Road	Sept 2002 - Dec 2007	Extremity
Central Saanich	CES-BR-06	Amwell and Aston SE corner, QC in meter box	Aug 1999 - Aug 2005	Extremity
North Saanich	CLR-01-01	Cloake Hill Reservoir	May 2000 - Dec 2008	Extremity
North Saanich	NOS-CP-01	Lot N of 10943 Boas Rd.	June 1995 - Dec 2008	Extremity
North Saanich	NOS-SB-03	Swartz bay - meter bldg (replaces NOS-SB-02)**	Aug 1997 - June 2005	Extremity
* includes data from JGO-TR-00				
** includes data from NOS-SB-03				

Sampling Methods

DBP samples were collected, following standard sampling protocols (BC MOE, 2003), by the CRD staff. Since 2005 samples were taken every second month (February, April, June, August, October and December) on an annual basis. Samples collected prior to this time were either collected at a minimum on a quarterly basis or up to 9 times per year. Samples were collected and then placed on ice and shipped in a cooler to the appropriate lab for analysis. Prior to 2003, DBP samples were sent to two labs, Cantest, in Burnaby, British Columbia for THM analysis only and Montgomery Watson in California, for both THM and HAA analysis. Since 2003, the DBP samples were analyzed by the University of Victoria (UVIC) Water and Aquatic Sciences Research laboratory. THM samples were analyzed following USEPA methods 502.2 (USEPA, 1995) and 551.1 (USEPA, 1995). The method detection limits for chloroform, BDCM, DBCM, and bromoform were 1.0, 0.8, 0.5 and 0.6 µg/L, respectively. HAAs were determined using USEPA Method 552-2 (USEPA, 1995). The method detection limits (µg/L) were as follows: MCAA (0.50), DCAA (0.45), TCAA (0.20), MBAA (0.20), DBAA (0.20), BCAA (0.20), BDCAA (0.20), CDBAA (0.50), and TBAA (1.00). Only those individual DBPs (THM or HAA) results with values above detection limits were used for this report, all others were not discussed.

For the purposes of this report, THM data from December 1990 up to and including December 2008 (if available) were used. HAA data was not available prior to 1997 due to analysis constraints in the laboratories, and from 1997 to 2002 was collected on a limited basis. Since 2002, HAAs were collected on a more consistent basis.

Water chemistry samples were collected on a monthly basis from the raw source water entering the Japan Gulch treatment plant by the CRD staff. Parameters included TOC, DOC, total phosphorus, chlorophyll *a*, water temperature and bacteriological samples.

Statistical Analysis

The TTHM and HAA5 data results were plotted by date for each sample location to identify different "treatment" periods. A treatment period is described as a change to the disinfection treatment process either at the Japan Gulch plant or at booster stations. . To calculate the differences to both TTHM and HAA5 production, the results for most sites were separated into the following sampling periods: prior to 2001, from 2002-2004 and post 2004. These time periods represent the different disinfection treatment processes that occurred at the Japan Gulch Plant: chloramination, free chlorine followed by addition of ammonia approximately 10 minutes downstream and UV disinfection prior to chlorination, respectively. Exceptions to these time periods and treatment processes are found in three re-chlorination stations, MET-PB-01, CLR-01-01 and NOS-CP-01, where changes were made to the re-chlorination process (MET-PB-01) or the booster station was discontinued (CLR-01-01 and NOS-CP-01). A log (natural log) transformation of the DBP data was then conducted to smooth out the variability within each treatment period, as well as identify outliers.

An analysis of variance (ANOVA) approach was used to identify if changes to DBP production occurred between each treatment period. Sample means and standard deviations were calculated for each treatment period per location for both TTHMs and HAA5s. The null hypothesis is that there is no difference in DBP production between each treatment period (equal means). If there was strong evidence (p value less that 0.05) that the means were not all the same, then a multiple comparison (Tukey's) test was conducted to see which means could differ from each other. This process was conducted for all TTHM and HAA5 results for all sample locations using JMP (7.0) statistical software.

Results and Discussion

TTHM and HAA5 Results - Non Re-chlorinated Sites

The DBP results for the non re-chlorinated sites were consistently low and were well below the Canadian drinking water guidelines (Table 3.2). The mean TTHM values ranged from 8.69 µg/L (JGO-TR-01, first tap) to 13.81 µg/L (SID-SI-03, end of distribution system) and HAA5 mean values ranged from 9.62 µg/L (SID-SI-03, end of distribution system) to 14.48 µg/L (SAN-CB-02, mid-point). In these non re-chlorinated sites TTHM values were lower at the first tap after treatment and higher at the end of the distribution systems, while HAA5 values decreased with the longer residence time. Similar studies looking at locational values of DBPs in distribution systems have also reported the degradation of HAA5s over time following chlorination, which may be associated with microbial activity (Rodriguez *et al*., 2004; Baribeau, *et al*., 2000). Rodriguez *et al*. (2004) also determined that residence time of water within the distribution system is a significant contributing variable for spatial variation of TTHMs. Their study found that the most notable increase in TTHMs was at the 5 hour mark, but between the 5 hour and 14 hour mark of residence time the concentrations of TTHMs remained stable.

Table 3.2: Summary of TTHM and HAA5 results for CRD sample locations, including both non re-chlorinated sites and those sites subject to re-chlorination/re-chloramination**.**

	THM (ug/L)						HAA5 (ug/L)					
Site	Mean	SD	Minimum	Maximum	CL (95%)	n	Mean	SD	Minimum	Maximum	CL (95%)	n
Non Rechlorinated Sites												
JGO-TR-01	8.69	5.41	1	21.9	1.09	96	13.85	4.21	1	30.19	1.16	53
SAN-CB-02	10.41	7.25	2.5	44.2	1.54	88	14.48	4.21	5.87	26.82	1.25	46
SID-SI-03	13.81	3.87	2.6	22	1.29	37	9.62	2.92	3.22	15.74	0.97	37
Rechlorinated Sites												
MET-PB-01	13.64	4.52	3.4	25.2	1.58	34	9.93	5.33	2.79	31.1	1.83	35
CES-BR-06	21.34	22.23	3.9	114.9	7.11	40	13.68	4.44	5.98	22.16	2.02	21
CLR-01-01	32.44	16.43	3.7	68.5	4.4	56	41.43	25.46	8.31	145.8	8.25	39
NOS-CP-01	46.9	2.395	3.5	104.7	5.88	71	41.69	29.51	5.73	177.5	9.2	42
NOS-SB-03	30.01	20.91	2.6	74.9	6.43	43	45.53	26.23	4	86.36	9.8	30

TTHM and HAA5 Results - Re-chlorinated/re-chloraminated sites

The HAA5 mean values for the re-chlorinated sites were all within the Canadian drinking water guidelines ranging from 9.93 µg/L (MET-PB-01) to 45.53 µg/L (NOS-SB-03) (Table 3.2). The lower HAA5 values observed at MET-PB-01 site were likely a result of seasonal re-chloramination, i.e. during periods when re-chloramination was not in operation. At that time HAA5s could be degraded through microbial breakdown processes (Rodriguez *et al.*, 2004). Maximum values at MET-PB-01 and CES-BR-06 were also below the Canadian guidelines. The two North Saanich re-chlorinated sites, CLR-01-01 and NOS-CP-01 had maximum HAA5 values of 145.8 µg/L and 177.5 µg/L respectively, both of which occurred during the winter of 2006/07 and were above the Canadian guidelines. The re-chlorination sites were all located at the extremity of the drinking water distribution system and were located after booster stations. As observed in other studies, DBPs are expected to be higher immediately following re-chlorination (Lee et al., 2007). The observed elevated HAA5 values prompted the CRD to make changes to the booster station supplying water to these areas. In the spring of 2007 the booster station was decommissioned and as a result, maximum HAA5 values in these distribution areas were substantially lower at 30.19 µg/L (CLR-01-01) and 25.39 µg/L (NOS-CP-01). Chowdhury and Champagne (2008) also noted that chloramination tends to produce relatively low concentrations of halogenated DBPs.

The mean TTHM values at the re-chlorinated/re-chloraminated sites were approximately 1.5 to 3.5 times higher than the non re-chlorinated sites, ranging from 13.64 µg/L (MET-PB-01) to 46.9 µg/L (NOS-CP-01), but were all below the Canadian drinking water guidelines. However, maximum TTHM values exceeded these guidelines on occasion for sites CES-BR-06 (114.9 µg/L) and NOS-CP-01 (104.7 µg/L), both of which are extremity sites. The higher values occurred during the summer/fall period of 1999 and are a direct result of re-chlorination done by CRD Environmental Services at the Upper Dawson Reservoir site during the summer period. After 2001, the maximum TTHM value for CES-BR-06 was observed on July 29th, 2003 at 19.8 µg/L. This was a substantial overall decrease and was attributed to the termination of re-chlorination at the Upper Dawson Reservoir. In 2001, site NOS-CP-01 was removed from the Lower McTavish Pressure zone and added to the Cloake Hill Pressure Zone, which receives re-chlorinated water from the Deep Cove pump station. TTHM values at this site fluctuated between 13.1 and 84.0 µg/L due to the re-chlorination at the Deep Cove pump house in response to seasonal variability and chlorine residual values as noted by CRD (2007b).

After 2007, when the re-chlorination process was stopped, the maximum TTHM value noted at NOS-CP-01 was 21.0 µg/L in October 2007.

Changes in Treatment Strategies

Of the eight GVWSA monitoring sites mentioned above, six were considered long term datasets, with results from the 1990's to 2008. These sites captured the effects from the change in disinfection treatment at Japan Gulch treatment plant in 2001, the Sooke Reservoir inundation period (2003-2005), and any subsequent changes that occurred to either the treatment process at Japan Gulch treatment plant or booster stations. The two remaining extremity stations (MET-PB-01 and SID-SI-03) only had data sets from 2003 to 2007 inclusive, which does not capture the initial change to treatment at the Japan Gulch plant. Table 3.3 provides a summary of treatment period means and the differences ($p<0.05$) between treatment types (Tukey's multiple comparison test) for all sites.

Non-Rechlorination Sites

Changes to DBP production after the subsequent changes to disinfection treatment were observed and are shown in Figures 3.3 and 3.4, for sites JGO-TR-01 (first tap) and SAN-CB-02 (mid point), respectively. There was a significant difference in TTHM production observed in both of these sites following reconfiguration of the disinfection method at the Japan Gulch water treatment plant in 2001 ($p<0.0001$) (Figure 3.3; Table 3.3). In this situation, TTHM mean values increased approximately 3 to 4 times, following the free chlorine plus addition of ammonia treatment, in 2001, at sites JGO-TR-01 and SAN-CB-02, respectively. This increase in TTHMs was likely a result of the NOM in the source water reacting with the free chlorine molecules prior to the addition of the ammonia (Carlson and Hardy, 1998; Lu *et al*, 2009). Following the addition of UV in 2004, only the SAN-CB-02 TTHM results showed a slight decrease in mean TTHM production (p=0.01) with no difference occurring for TTHMs at site JGO-TR-01.

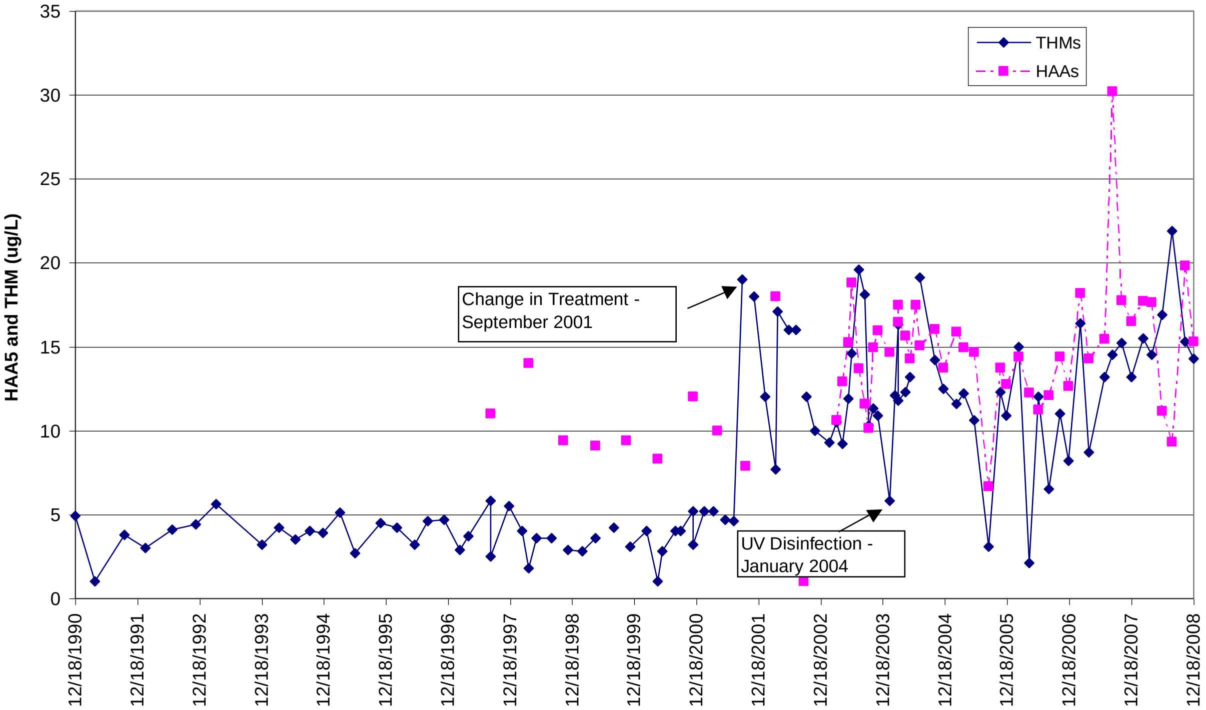


Figure 3.3: DBP results from 1990 to 2008 for Site JGO-TR-01, first tap after treatment at Japan Gulch plant. Treatment changes occurred at the Japan Gulch main plant.

In contrast, the HAA5 results for these two sites suggested that there was no significant change in HAA5 production, regardless of the changes to the disinfection treatment process at the Japan Gulch treatment plant. Lu *et al.* (2009) found a similar trend with chloramination, in that TTHMs increased more than HAA5s within the first 36 hours of contact time and significant differences were not observed between 48 and 72 hours. It should also be noted that while there was an increase in TTHM production following changes to the disinfection process, the TTHM mean values at JGO-TR-01 (13.34 µg/L) and SAN-CB-02 (17.15 µg/L) were still very low, at 5 to7 times lower than the Canadian drinking water guideline of 100 µg/L. The benefit of switching to chloramination is that it can provide a longer-term residual disinfection, when a sufficient contact period is allowed, inhibiting the growth of microbes in the distribution system (Chowdhury and Champagne, 2008).

Table 3.3: Summary of the treatment period means for both THM and HAA results and the corresponding differences (Tukey's test), if observed, for each sampling location. Note: if a difference was observed the corresponding *p*-value is shown. * Data only collected until June 2005.

		Sample Period - mean values (µg/L)				
Site Location	DBP Type	P1 = Prior to July 2001	P2 = Sept 2001 to Dec 2003	P3 = Jan 2004 to Dec 2008		Summary
Non-rechlorinated Stations						
JGO -TR-01	HAA	10.68	13.13	12.56		P1=P2=P3
	THM	4	13.34	11.02		P1<P2=P3 $p<0.0001$
SAN-CB-02	HAA	10.36	13.56	13.51		P1=P2=P3
	THM	4.5	17.15	12.92		P1<P2>P3 $p<0.0001$; $p=0.01$
SID-SI-03	HAA	na	9.92	8.92		P2=P3
	THM	na	10.08	8.92		P2=P3
P1= Prior to free chlorine, followed by ammonia treatment at JGP P2 = Free chlorine followed by addition of ammonia at JGP P3 = Ultraviolet treatment at JGP						
Re-chlorinated Stations						
NOS-SB-03	HAA	16.32	61.94	65.66*		P1<P2=P3 $p<0.0001$
	THM	15.53	21.96	45.25*		P1<P2<P3 $p=0.03$; $p=0.0004$
Site Location	DBP Type	P1 = Prior to Sept 2000	P2 = Sept 2000 to Sept 2001	P3 = Sept 2001 to Dec 2003	P4 = Jan 2004 to Dec 2005	Summary
CES-BR-06	HAA	na	14.65	14.04		P2=P3
	THM	73.68	5.16	17.63	12.89	P1>P2<P3>P4 $p=0.002$;$p=0.05$;$p=0.01$
P1= Seasonal re-chlorination P2 = Re-chlorination stopped P3 = Free chlorine followed by addition of ammonia at JGP P3 = Ultraviolet treatment at JGP						
Site Location	DBP Type	P1 = Prior to July 2001	P2 = Sept 2001 to Apr 2003	P3 = May 2003 to Dec 2003	P4 = Jan 2004 to June 2005	Summary
NOS-SB-03	HAA	8.16	46.98	54.38	63.06	P1<P2=P3=P4 $p<0.001$
	THM	6.73	23.74	50.72	45.79	P1<P2<P3=P4 $p<0.01$; $p<0.02$
P1= Prior to free chlorine, followed by ammonia treatment at JGP P2 = Free chlorine followed by addition of ammonia at JGP; seasonal rechlorination P3 = Continuous reclorination P3 = Ultraviolet treatment JGP; continuous reclorination						
Site Location	DBP Type	Not sampled prior to 2003	P2 = Jan 2003 to Dec 2003	P3 = Jan 2004 to Dec 2005	P4 = Jan 2006 to Dec 2007	Summary
MET-PB-01	HAA	na	6.13	11.63	12.87	P2<P3=P4 $p=0.05$
	THM	na	13.05	14.31	15.93	P2=P3=P4
P1= Not sampled P2 = Free chlorine followed by addition of ammonia at JGP; seasonal rechloramination P3 = Ultraviolet treatment at JGP; continuous rechloramination P4 = Increase chlorine dosage at booster station						
Site Location	DBP Type	P1 = Prior to July 2001	P2 = Sept 2001 to Dec 2003	P3 = Jan 2004 to Feb 2007	P4 = Apr 2007 to Dec 2008	Summary
CLR-01-01	HAA	na	na	51.75	15.76	P3>P4 $p<0.0001$
	THM	20.06	42.36	40.89	17.76	P1<P2=P3>P4 $p=0.01$; $p<0.0001$
NOS-CP-01	HAA	na	na	39.91	11.77	P3>P4 $p=0.004$
	THM	69.06	71.67	32.9	17.07	P1=P2>P3>P4 $p=0.001$; $p=0.01$
P1= Prior to free chlorine, followed by ammonia treatment at JGP; rechlorination P2 = Free chlorine followed by addition of ammonia at JGP; rechlorination P3 = Ultraviolet treatment at JGP; rechlorination P4= Discontinuation of rechlorination						

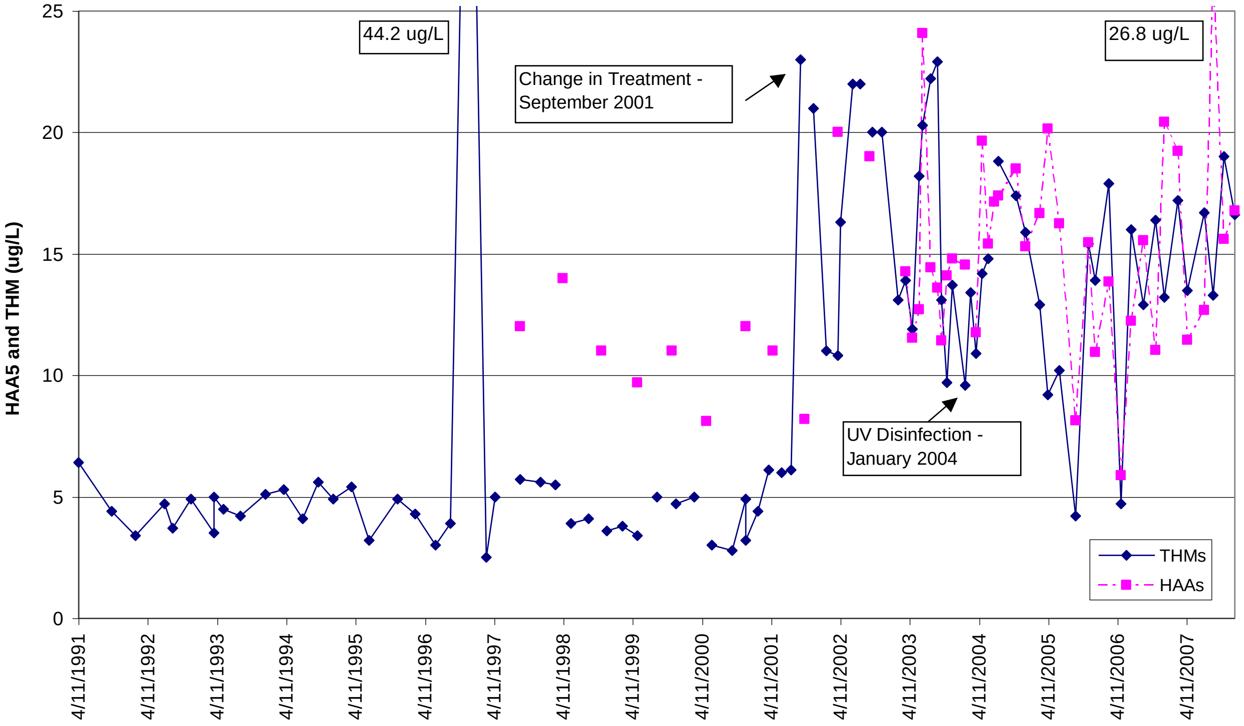


Figure 3.4: DBP results from 1991 to 2007 for Site SAN-CB-02, mid point in the GVWSA. Treatment changes occurred at the Japan Gulch main plant.

The Sidney sampling site (SID-SI-03) is located in the northeast corner of the Sidney distribution system and is the furthest location from the Japan Gulch Plant with no re-chlorination. The only change in treatment to occur during this monitoring period (2003-2007) for the SID-SI-03 sample site was the addition of UV treatment at Japan Gulch in 2004 (Figure 3.5). In comparing the pre and post UV treatment DBP results no significant differences were observed for both TTHMs and HAA5s (Table 3). The THMs and HAAs fluctuate seasonally (CRD, 2007) but both tended to average at 9.0 µg/L to10 µg/L. Lu *et al*. (2009) suggest that with longer residence time, the DBP precursors become almost exhausted and the TTHM and HAA5 yields remain relatively stable. This likely explains the lack of differences in DBPs following changes to treatment and the overall low DBP values observed at this site.

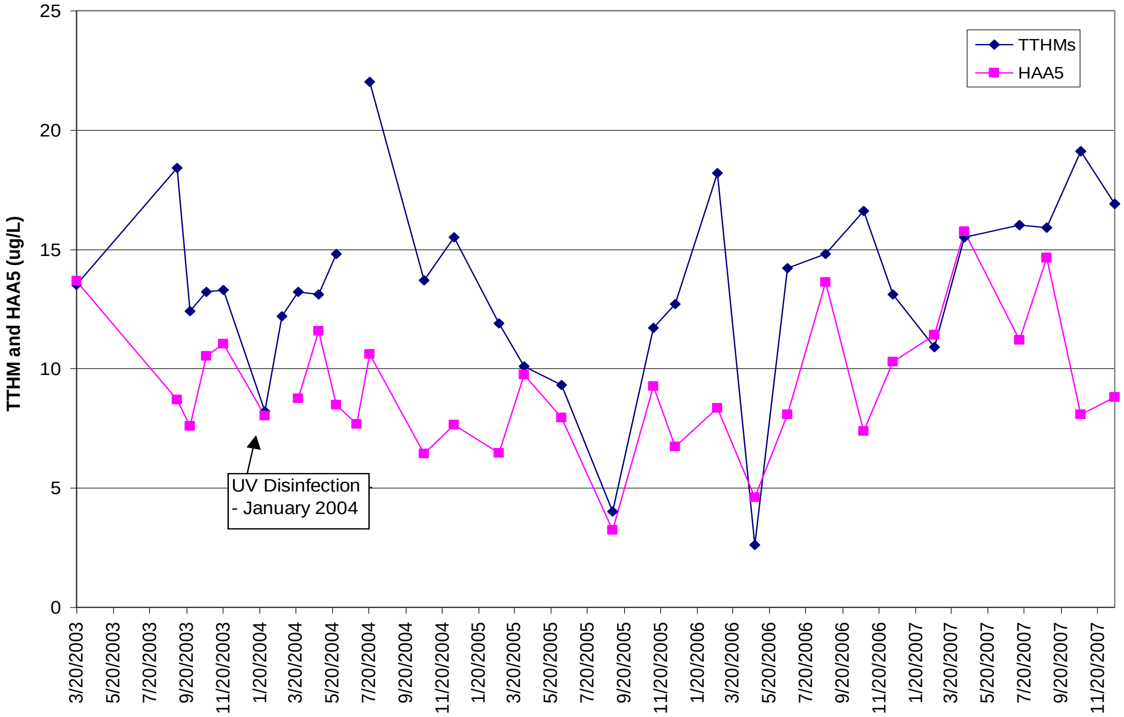


Figure 3.5: DBP results from 2003-2007 for site SID-SI-03, the farthest site from Japan Gulch treatment plant that does not receive any re-chlorination. Changes to treatment for this site only occurred at the Japan Gulch main plant.

Re-chlorinated Stations

Site CES-BR-06 is located in a small high elevation pressure zone fed by the Upper Dawson Reservoir in Central Saanich. Historically, this reservoir received small amounts of additional chlorine from time to time; site CES-BR-06 provides information on that process. There was no information in the CRD annual reports as to how often and how much chlorine was added at this site. However, this site typically had a low chlorine residual and low flow area (CRD, 2003). THM's collected in late 1999 and early 2000 were consistently high ranging from 47.6 µg/L to 114.9 µg/L (Figure 3.6). However, after September 2000, the re-chlorination process was stopped and the TTHM values decreased substantially (*p*=0.002) (Table 3.3). Following the change to treatment at the Japan Gulch Plant there was an increase (*p*<0.0001) in TTHM values, however they remained generally below 20 µg/L. There was a further small reduction (*p*=0.01) in

TTHMs subsequent to the addition of UV disinfection at the main Japan Gulch plant. HAAs were not collected until 2003 at this site and the results remain generally below 15 µg/L. It appeared that no changes were observed for HAA5 after the addition of UV treatment. Site CES-BR-06 exhibited similar DBP production patterns as the non re-chlorinated sites, with respect to changes at Japan Gulch plant. This is consistent with the decommissioning of the re-chlorination station in 2000.

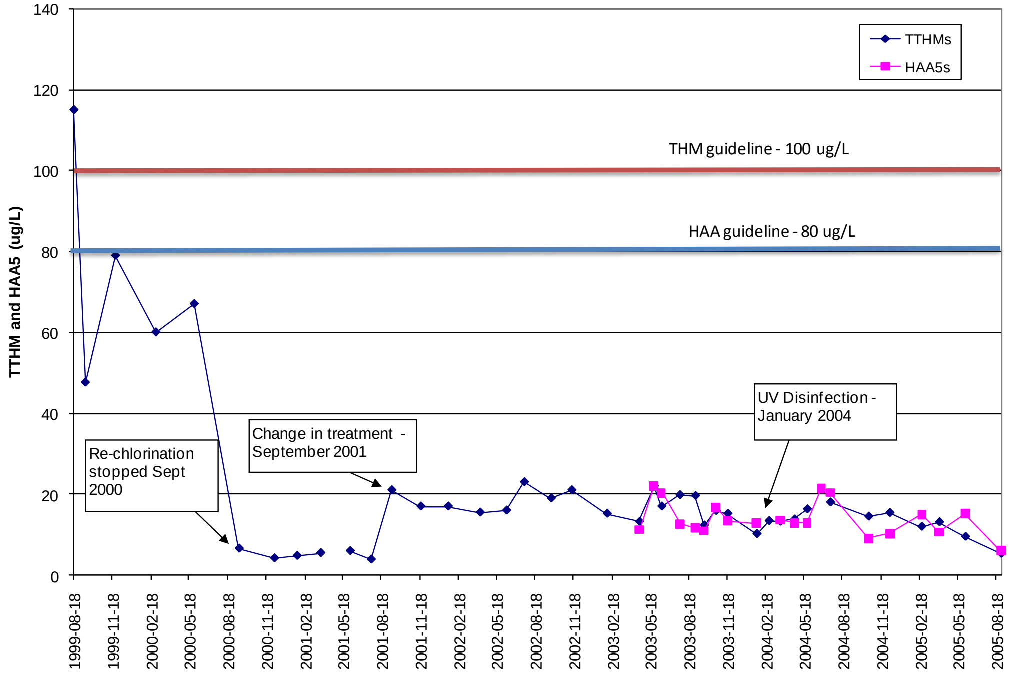


Figure 3.6: DBP results from 1999 to 2005 for site CES-BR-06, extremity site. Re-chlorination was stopped in 2000, followed by subsequent changes to the Japan Gulch plant.

Data was collected for the Swartz Bay area (site NOS-SB-03) from 1997 to 2005 (Figure 3.7). This sampling point is located at an extremity of the North Saanich distribution system. Prior to the changes to the treatment system at Japan Gulch Plant, this site had relatively low TTHM and HAA5 values, with an average of 15.53 µg/L and 8.35 µg/L respectively. However, chlorine residual values were also quite low at this site and there were some concerns over bacterial regrowth in this area. As a result, from 2001 to mid 2003, this distribution area was subject to seasonal re-chlorination, which resulted in a significant increase in DBPs ($p<0.0001$ for HAA5 and $p=0.03$ for TTHM). TTHM and HAA5 results observed during this time period (2001-2003) fluctuated from 3.8 to 49.1 µg/L and 12.79 to 86.0 µg/L, respectively. This was likely due to the influence of re-chlorination, with high values associated with the booster station being in operation. Lu et al. (2009) found that HAA yields are higher than THMs when the chlorine or chloramines dosage is initially increased.

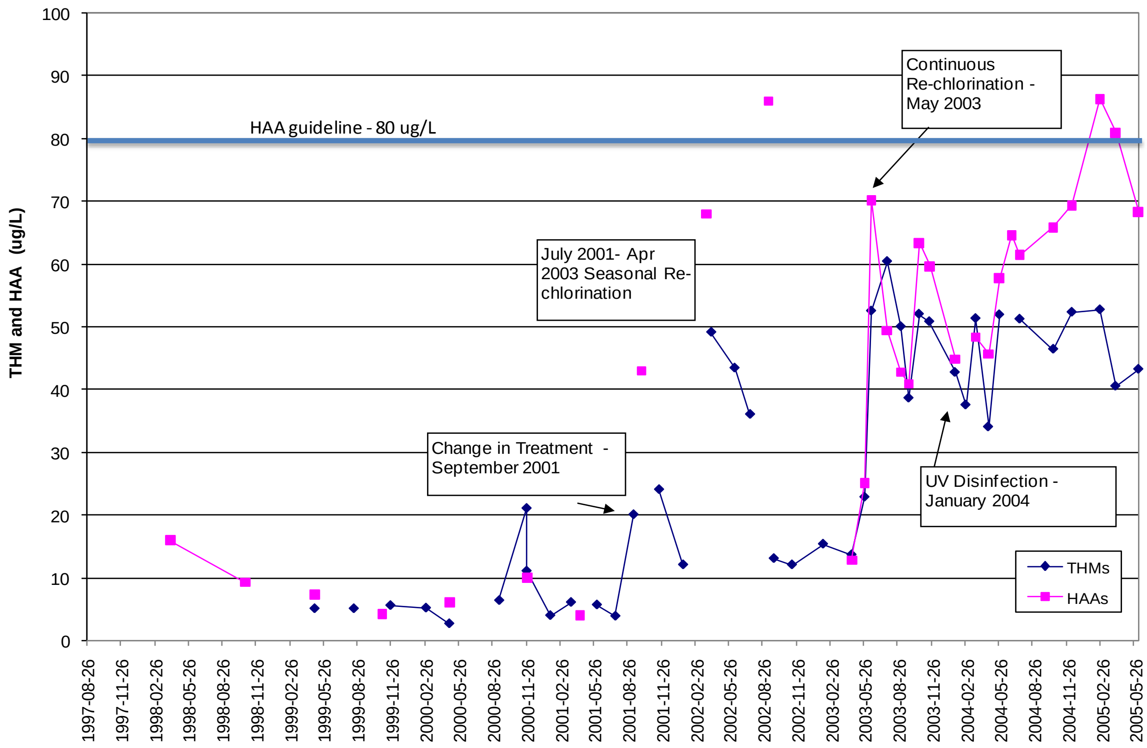


Figure 3.7: DBP results from 1997 to 2005 for Site NOS-SB-03, extremity location. Changes to treatment occur both at Japan Gulch plant (2001 and 2004) and to the re-chlorination station (seasonal versus continuous).

After mid 2003, the Swartz Bay site became part of the pressure zone of Cloake Hill reservoir and received re-chlorinated water virtually all year round. This resulted in more consistent DBP values. While there was little change to the average HAA5 values, the TTHM average value between seasonal (26.27 µg/l) and constant (45.25 µg/l) re-chlorination showed a significant increase (p=0.0004). The NOS-SB-03 site was discontinued in 2005, once re-chlorination became more constant, as the sampling station at Boas Road (NOS-CP-01) now represented the maximum potential for THM production in an extremity North Saanich booster sample station.

Site MET-PB-01 is located at the extremity of the Metchosin water distribution system on Rocky Point Road and reflects the re-chloraminated water from the Rocky Point booster station (2003 to 2007) (Figure 3.8). Water at this location was re-chloraminated on a seasonal basis until 2004, when the booster station was kept in service throughout the year (CRD, 2006). This also coincided with the time period when UV treatment was added to the Japan Gulch plant (2004). Furthermore, the chlorine dosage at the booster station was increased commencing in 2006 to provide a target total chlorine residual of 1.0 mg/L at the outlet of Rocky point reservoir (CRD, 2007). Overall there appeared to be no difference in TTHM production between sample periods. The HAA5 results showed a slight increase (p=0.05) following the change from seasonal to annual re-chloramination (Table 3) with mean HAA5 values increasing from 6.13 µg/L to 11.63 µg/L, likely a result of the increase in disinfectant dose (Lu *et al.*, 2009). However, this station generally had low DBPs (CRD, 2006).

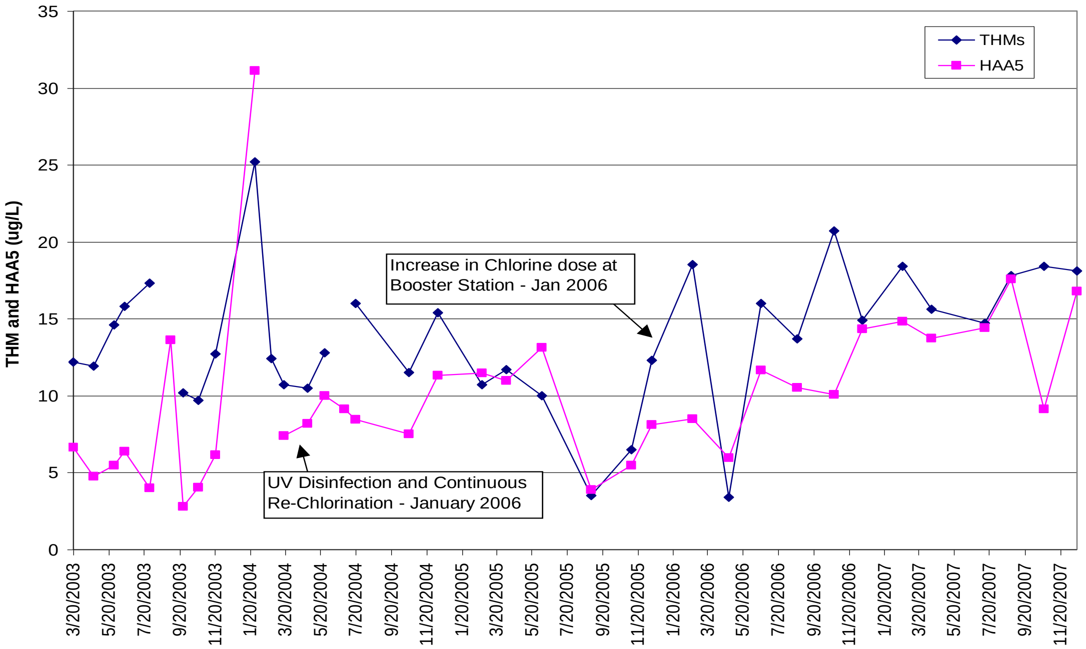
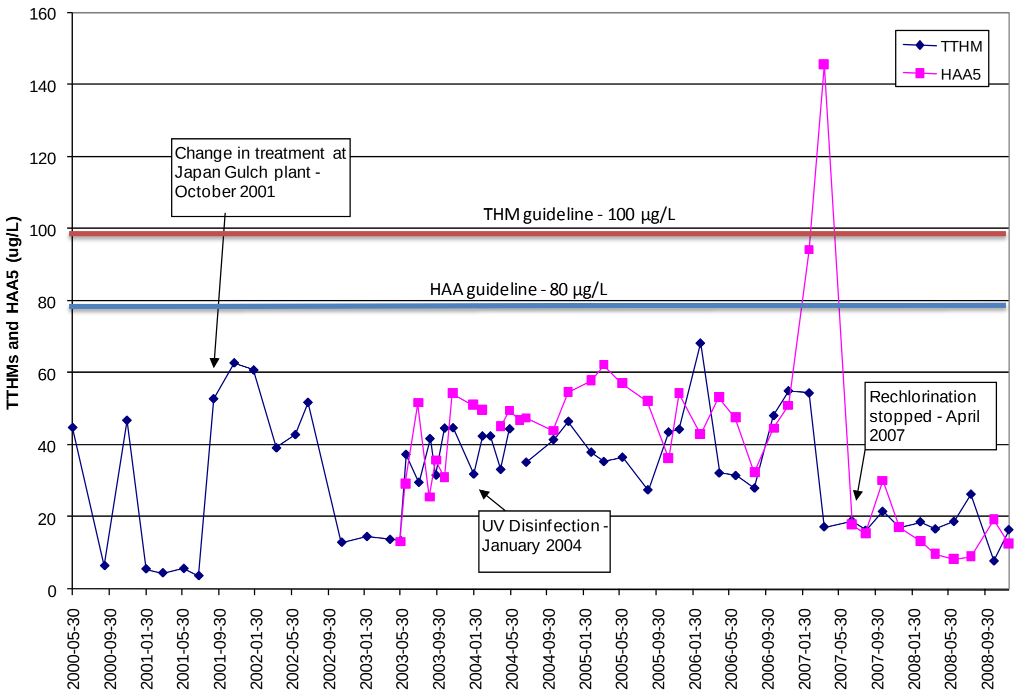


Figure 3.8: DBP results from 2003 to 2007 for Site MET-PB-01, extremity location.

Site CLR-01-01 is located just downstream of the Cloake Hill Reservoir, which receives re-chlorinated water from the Deep Cove pump house. DBPs at this site (2000 to 2008) reflect the water received by the first customers in the North Saanich distribution system. Mean TTHM values doubled (20.06 µg/L to 42.36 µg/L) following the changes to the disinfection treatment process at the Japan Gulch Plant in 2001 (Figure 3.9). HAAs were not sampled during this time period (2000-2003). However, prior to mid 2003, re-chlorination only occurred when chlorine residual values at the Cloake Hill Reservoir dropped below 0.3 mg/L, and as such the 2000-2003 TTHM results were highly variable ranging from 3.7 µg/L to 63 µg/L. The higher TTHM values seen prior to 2003 were likely a result of the seasonal re-chlorination process at Deep Cove pump house rather than any influence from the changes made to the disinfection treatment at

Japan Gulch plant. After 2003 the system was re-chlorinated virtually throughout the entire year using a chlorine dosage in the range of 3-4 mg/L (CRD, 2004). Consequently, the TTHM and HAA5 values remained more constant, averaging approximately 40.89 µg/L and 51.75 µg/L, respectively. However, there were some extreme HAA5 results in December 2006 and February 2007 (94.2 and 145.8 µg/L, respectively). In an attempt to reduce the level of DBPs, especially the HAAs, in the North Saanich distribution system, re-chlorination was stopped at the Deep Cove pump house in April 2007. This resulted in a significant difference (*p*<0.0001) in both TTHM and HAA5 production, a reduction of more than fifty percent.



Change in treatment at Japan Gulch plant - October 2001

UV Disinfection - January 2004

Rechlorination stopped - April 2007

Figure 3.9: DBP results from 2000 to 2008 for Site CLR-01-01, extremity site subject to rechlorination until April 2007.

Site NOS-CP-01, located at the northeast extremity of the North Saanich distribution system, was sampled from June 1995 to December 2008 (Figure 3.10). From 1995 to July 2001, the TTHM results tended to be quite high, averaging 69 µg/L. Even after the change to disinfection at the Japan Gulch treatment plant, mean TTHMs remained similar at 71.67 µg/l. Speight and Singer (2005) found that under conditions of low chlorine residual and longer contact time the THM concentrations were generally higher at the extremity locations. After 2003, the re-chlorination process at Deep Cove pump house became more constant, reducing the mean TTHM values by approximately 50% (32.9 µg/L; p=0.001). Adequate maintenance of chlorine residual, especially at extremity sites, can control the THM formation (Lee et al. 2007). These results indicate that changes to the treatment process at Japan Gulch plant do not necessarily affect the DBP production at the extremity sites. It appears that in most cases any significant changes to DBP production in the extremity sites was a result of changes to the booster station systems.

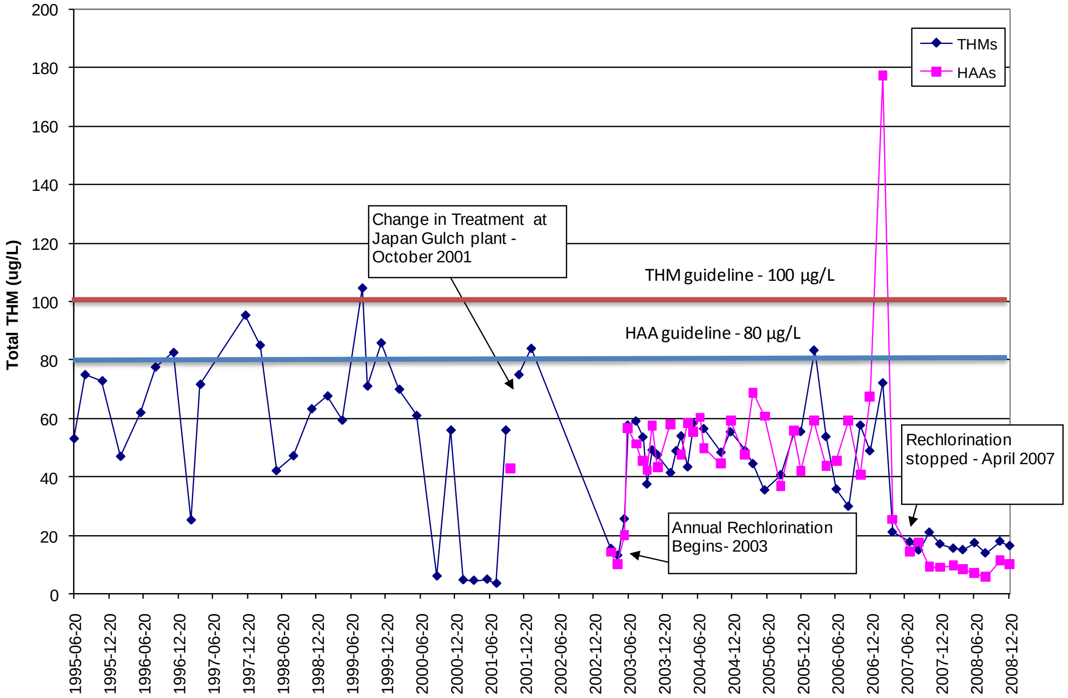


Figure 3.10: DBP results from 1995 to 2008 for Site NOS-CP-01, extremity site subject to rechlorination.

Similar to the other North Saanich Site (CLR-01-01), some high HAA5 values were observed in December 2006 (67.34 µg/L) and February 2007 (177.5 µg/L) at NOS-CP-01. Once the re-chlorination was stopped and this area received chloraminated water from Japan Gulch plant, the DBPs at this site were reduced even further, with mean values for HAA5 and TTHMs at 11.77 µg/L (*p*=0.004) and 17.01 µg/L (*p*=0.01), respectively. While the reason for the lower DBP production from chloramination was not entirely clear, it is consistent with the results of other studies (Carlson and Hardy, 1998; Chowdhury and Champagne, 2008b; Lu et al., 2009). Cowman and Singer (1996) proposed that chloramination might be a special case of chlorination with very low free chlorine formed from monochloramine hydrolysis.

Individual DBPs

The speciation of DBPs may depend on several factors: the nature and concentrations of NOM, the bromide ion concentration, chlorine/DOC ration, bromide/DOC ration, background water chemistry and disinfection conditions (Ates et al., 2008; Panyapinyopol et al. 2005). The majority of THMs for all sites in this study were comprised of chloroform (90% or greater), with a small portion of bromodichloromethane (BDCM). These findings were similar to other studies (Hong *et al*., 2008; Lu *et al*., 2009). As a result, chloroform values tended to show similar trends as total THMs, i.e. were lower in non re-chlorinated stations and higher in the booster sites in the extremity of the distribution system (Table 2). After changes occurred at the Japan Gulch treatment plant in 2001, there was a slight increase to chloroform values at most sites, as reflected in the increase in THM values in Table 3.3.

The HAA values for the CRD monitoring sites were comprised primarily of dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), followed by small amounts of bromochloroacetic acid (BCAA). All sites had the DCAA values slightly higher than the TCAA values with the exception of site NOS-CP-01, which had TCAA results higher than DCAA results. Lu et al. (2009) also noted that more DCAA was formed than TCAA for both chlorination and chloramination. However, Reckhow and Singer (1990) observed that higher TCAA formation through chlorination was related to high $SUVA_{254}$ of the water. This may explain the higher TCAA values at this site as it was subject to re-chlorination; however, $SUVA_{254}$ values were not analyzed in this study. This oddity was not observed at other re-chlorination stations. After the re-chlorination station was decommissioned in April 2007 at Deep Cove, and this site received chloraminated water from Japan Gulch plant, the DCAA results became slightly elevated over the TCAA values, similar to the other stations.

The North Saanich distribution area sites (NOS-SB-03, CLR-01-01 and NOS-CP-01) showed some occasional traces of bromodichloroacetic acid (BDCAA) and monobromoacetic acid (MBAA), primarily in the fall and winter, likely associated with rainstorm events. At this time, bromide concentrations in the TOC fractions may have become available and reacted with the disinfectant to produce brominated DBPs (Bo *et al.*, 2008). However, the source waters in the Sooke reservoir typically had low concentrations of bromide (mean 1.96mg/l with a range of 0.29-7.43 mg/L (CRD, 2008) and as such brominated DBPs would be minimal.

Potential Effects From Reservoir Inundation

It is widely known that the amount of TOC present in the source water can affect the concentrations of DBPs (Karanfil et al., 2002; Kitis et al., 2001; Chang et al., 2000). To compare the pre and post inundation period, the mean TOC values from 2000 to 2006 were examined (Figure 3.11). There was a significant difference in TOC (p<0.03) noted between the pre and post inundation TOC values. In 2003 there were three higher than normal individual TOC values recorded (4.8 mg/L in March, 4.6 mg/L in August, and 9.6 mg/L in October) and one slightly higher value in 2005 (3.7 mg/L in June). Furthermore the high TOC value from October 2003 coincided with a 100- year storm event that occurred in late October (CRD, 2004). As noted, there was an increase in TOC levels immediately following the first year of inundation; however, annual TOC values now appear to be on the decline.

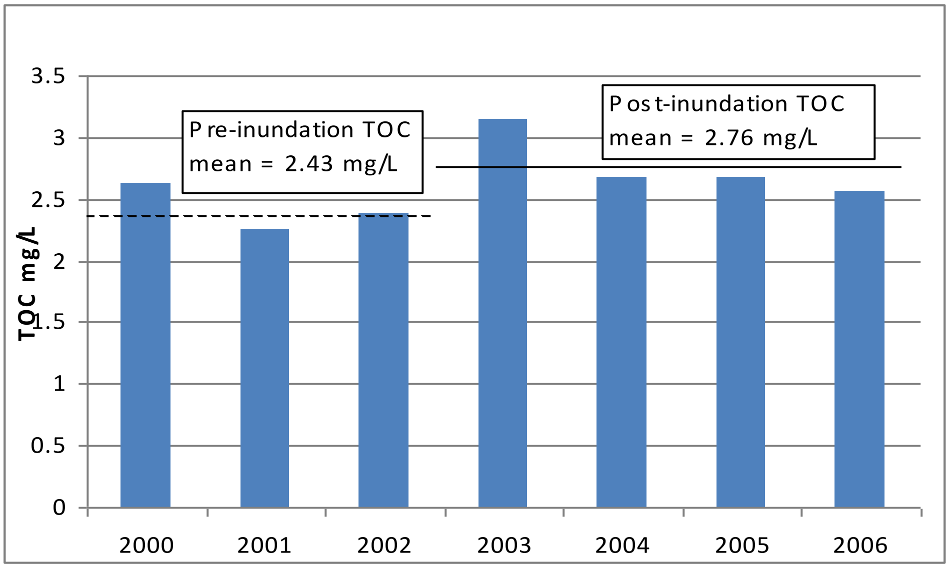


Figure 3.11: Mean TOC levels in the Sooke Reservoir prior to, during and after the inundation period (2000-2006).

Algal activity has also been associated with DBP production (Plummer and Edzward, 2001; Hguyen et al., 2005; Hong et al., 2008). Algal activity in a lake or reservoir can be correlated to total phosphorus levels, the nutrient required for algae to grow, and chlorophyll *a*, a component of all algal cells. Annual median total phosphorus values from 2003-2007 were approximately 70% higher than in the years prior to raising the water level (CRD, 2009) (Figure 3.12). Consequently, the annual median chlorophyll *a* values also increased by approximately 65% in the 5 years following the initial raising of the water level in the Sooke Reservoir (CRD, 2009)(Figure 3.13). While total phosphorus concentrations remained constantly elevated compared to pre-inundation values, the chlorophyll *a* values peaked in 2004 and, showed a declining trend towards the end of the study period. Although there was a notable increase in both median total phosphorus and chlorophyll *a* results following the inundation period, overall these values were low (5.61 µg/L and 1.63 µg/L, respectively) and were reflective of an oligotrophic (or nutrient poor) lake (Nordin, 1985).

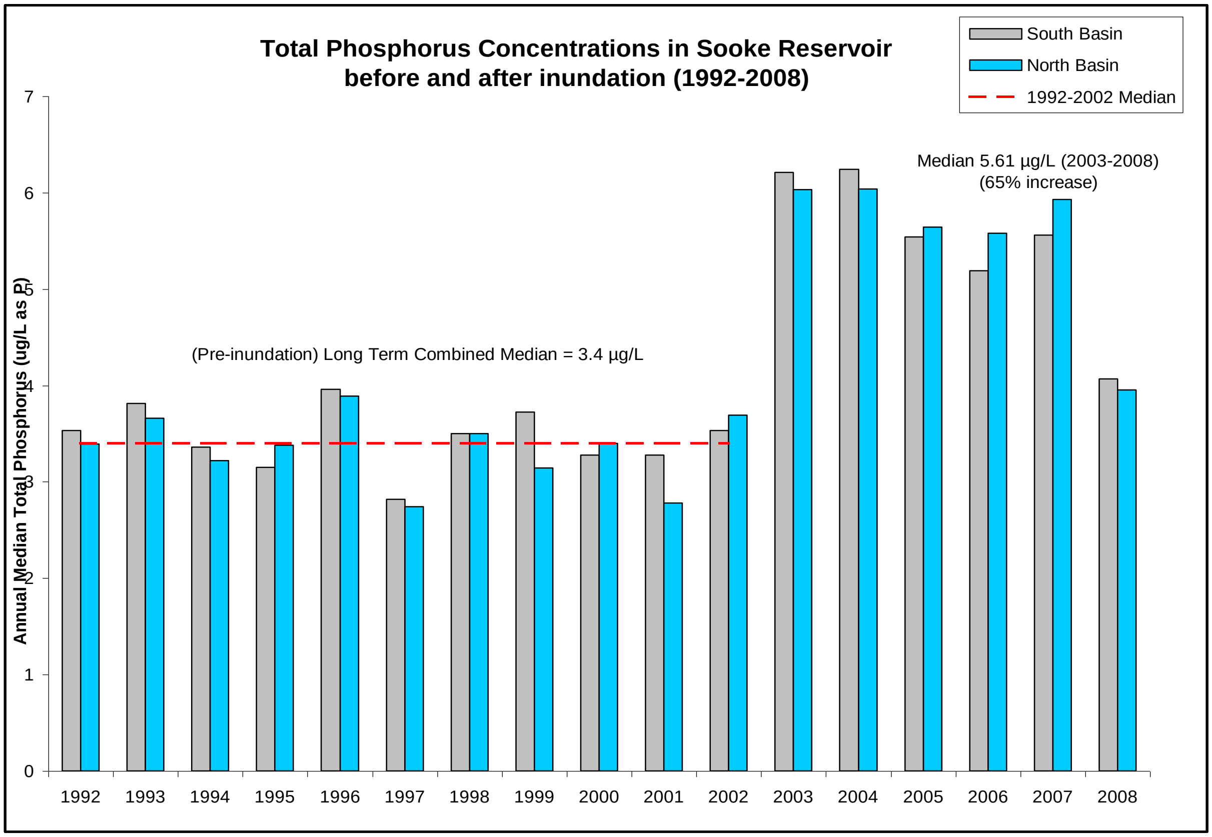


Figure 3.12: Total phosphorus concentrations in Sooke Reservoir before and after inundation (1992-2008) (CRD, 2009).

Regardless of the increase in algal activity and occasional spikes of TOC observed in the Sooke reservoir, there appeared to be no significant difference in DBP production as observed from Table 3 and Figures 3 to10 with respect to pre and post inundation TOC values. However, both TOC and algal activity are seasonally driven and were likely reflected in the seasonal variability of the DBPs that was noted in all the sampling locations (CRD, 2008). There were changes noted in DBP production in two of the North Saanich distribution sites (NOS-SB-03 and NOS-CP-01) after 2003 but these were attributed to changes in the booster station process.

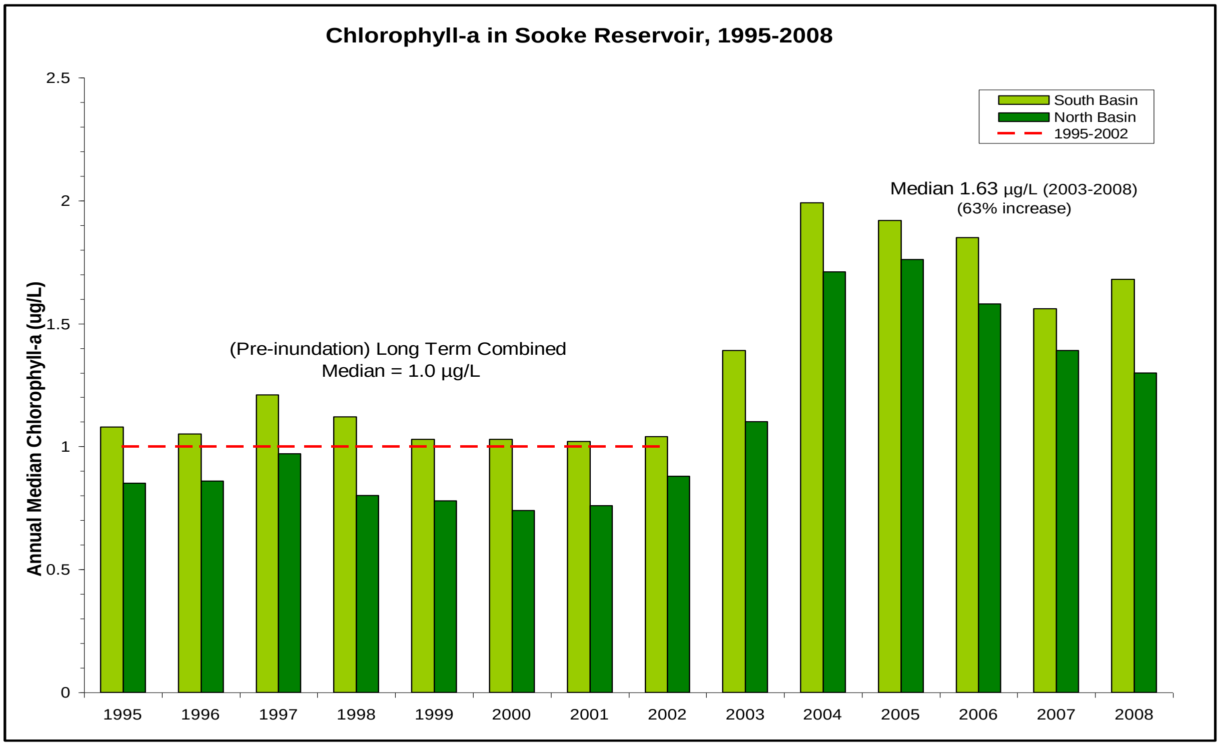


Figure 3.13: Chlorophyll *a* in Sooke reservoir, 1995-2008 (CRD, 2009).

In temperate environments, considerable seasonal changes in water temperature may produce important changes in THM levels (Rodriguez *et al*., 2003). Cooler water is beneficial in a distribution system because it reduces the potential for losses of chlorine residual and for the re-growth of bacteria (Hong *et al*., 2008). Summer water temperatures prior to the inundation project were above the 15 degree Celsius BC drinking water guideline (BC MOE, 2006) for at least 4 months each year. However, since 2005 water temperature above 15 degrees occurred for only 2 months, typically from early August to early October (Figure 3.14), and overall the water was colder by at least 2 degrees. In this respect, the Sooke Reservoir inundation project was a success.

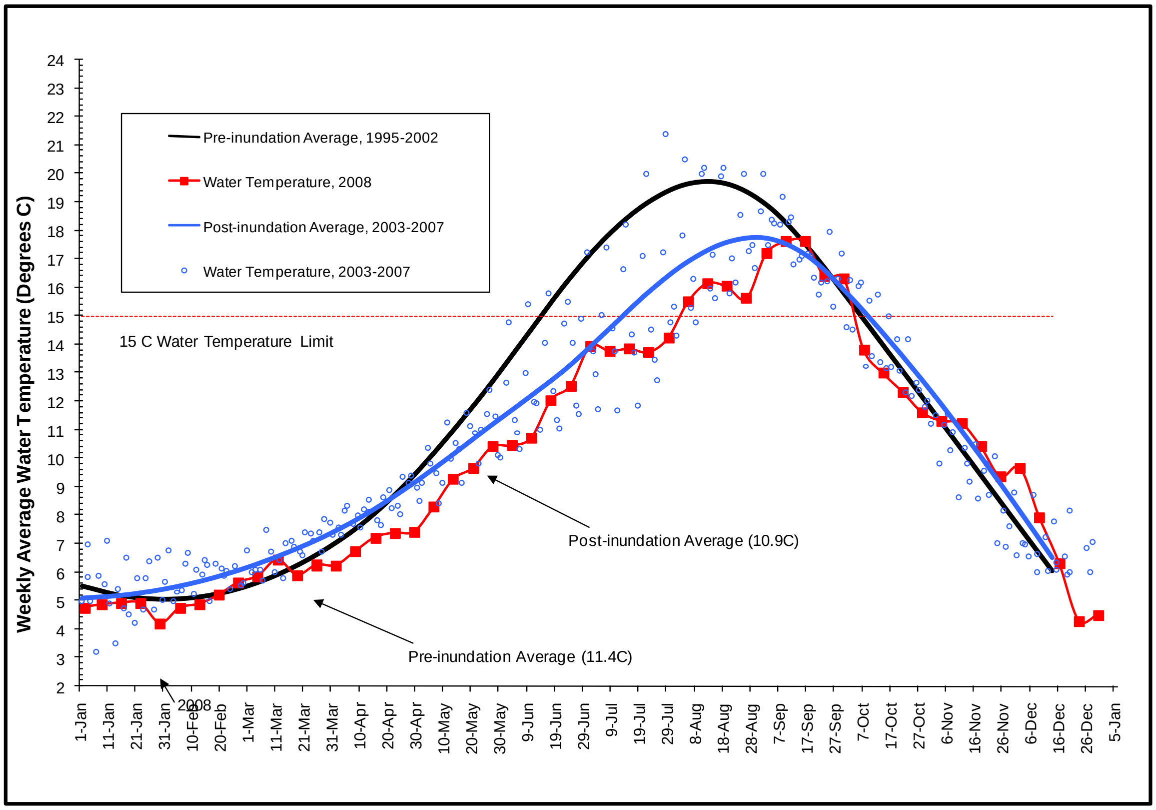


Figure 3.14: Temperature of raw water entering Japan Gulch Plant before and after inundation (CRD, 2009).

Seasonal Influences on DBP production

The extent of formation and speciation of DBPs vary greatly by season and water source (Ates *et al*., 2007). In particular, the DOC concentrations of the source water are influenced by seasonal variations such as run-off, or in the case of lakes, algal blooms (Leenheer and Croue, 2003), which impact the DBP formation potential. For the non re-chlorinated stations, seasonal average THMs were lowest in spring (3.2 µg/L) and highest in the fall (16.2 µg/L) and winter (14.9 µg/L)(CRD, 2007). These higher THM values likely corresponded to higher allochthonous (terrestrial) TOC values during rainstorm events (Wang and Hsieh, 2001). For the re-chlorinated locations, the summer season had the lowest average THM values (31.4 µg/L) and the winter had the highest average THM values (64.0 µg/L) (CRD, 2007). This was likely explained by seasonal re-chlorination, residence time and chlorine/chloramine residual levels (Speight and Singer, 2005; Lee *et al*., 2007).

For the HAA results, both non re-chlorination and booster stations sites tended to have the lowest results in the spring/winter and the highest in the summer/fall. Hong *et al*. (2008) suggest that during the summer months, the autochthonous NOM tended to be the important precursors of HAA production, especially DCAA, whereas in the fall/winter seasons the humic substances, such as humic and fulvic acids, tended to contribute to the overall DBP production. Recent research has shown that distributions of individual THM and HAA compounds are influenced by different algal species and also between cells and extracellular organic matter (Huang, et al., 2009). Further research could be conducted in this area, using additional tools such as ultraviolet absorbance at 254nm (UV_{254}), specific UV adsorption (SUVA), fluorescence spectroscopy, size exclusion chromatography, and size and polar fractionation, to try and confirm the sources for TOC (Chowdhury *et al*., 2008).

Speight and Singer (2005) also found that under conditions of low residual chlorine or chloramine concentrations, HAA values were low. Chlorine dosage tended to be higher during the summer and fall periods to deal with bacterial re-growth and elevated TOC in the source water. This may result in higher chlorine residual values, and thus explain the greater HAA concentrations in the CRD distribution system as noted.

Bacteria and chlorine residuals

Microorganisms have been shown to survive drinking water disinfection and remain viable in disinfected waters despite the presence of disinfectant residuals (Wojcicka *et al*., 2008). The presence of viable microorganisms is attributed to sublethal levels of disinfectant residuals, microbial resistance to the disinfectant (LeChevallier *et al*., 1984) or protection of microorganisms by interfering substances such as particulates (Stewart et al., 1990; Lee and Newman, 2003.). Survival or re-growth of microorganisms in distributed water is a cause for concern due to the pathogenic potential for these organisms. For this reason, CRD monitors bacteria levels in the raw water (Sooke reservoir), the treated water at first customer (JGO-TR-01) and throughout the remaining distribution systems. Total coliforms and *E.coli* are measured as their presence in the water may indicate that disease-causing organisms are also present.

Since 2001, relatively high (above 200 CFU/100ml) concentrations of total coliform bacteria were found in the raw source water entering the Japan Gulch treatment plant during the summer months (CRD, 2009). More than a decade of monitoring bacteria within the GVWS found that virtually 100% of the fecal coliform bacteria detected in the source water and the distribution system were *E. coli*. Annually, only about 11% of the samples collected from the raw source water contained *E.coli* and those that are positive for *E.coli* had levels below 20CFU/100ml (USEPA limit for surface water treatment rule to remain an unfiltered drinking water supply) more than 99% of the time (Figure 3.15). Furthermore, the data collected from the treated water sampling location near the first customer (JGO-TR-01) for 2008 indicated that the bacteriological quality of the disinfected water met the provincial guidelines in all months of the year (CRD, 2009). The 2008 annual total coliform positive rate of 0.4% at JGO-TR-01 was similar to the previous six years and much better than earlier years before the use of UV and free chlorine as primary disinfectants.

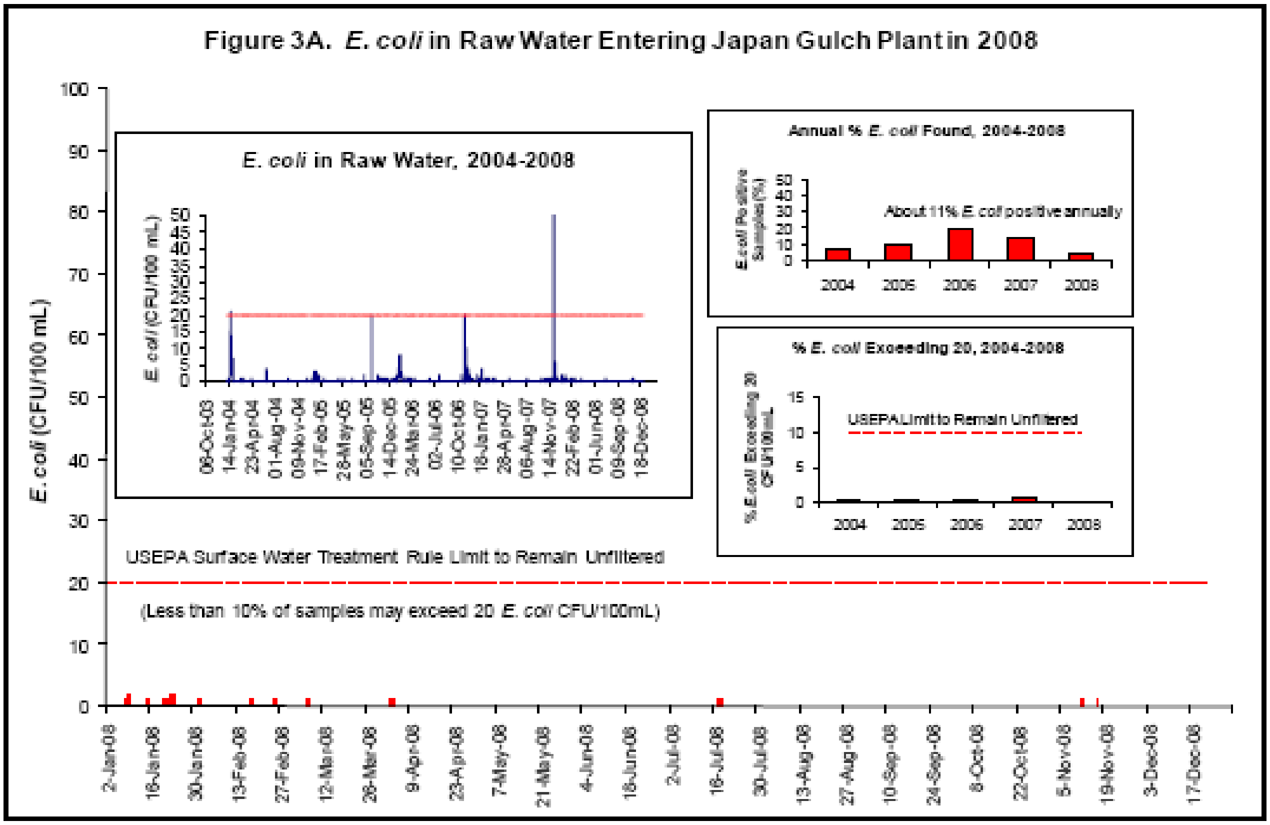


Figure 3.15: *E.coli* in raw water entering Japan Gulch plant (CRD, 2009).

The CRD reports out on the distribution system bacteriological data by considering all of the individual municipal distribution systems together as a single entity called the Greater Victoria Distribution System (GVDS). During 2008, total coliform bacteria were detected during eight months of the year; however, the percentage of positive total coliform samples did not exceed the 10% total coliform limit during any month and was therefore in compliance with the BC Drinking Water Protection Regulation (CRD, 2009). Figure 3.16 illustrates that these results were similar to the past several years (2000 onwards) and lower than in the 1990s.

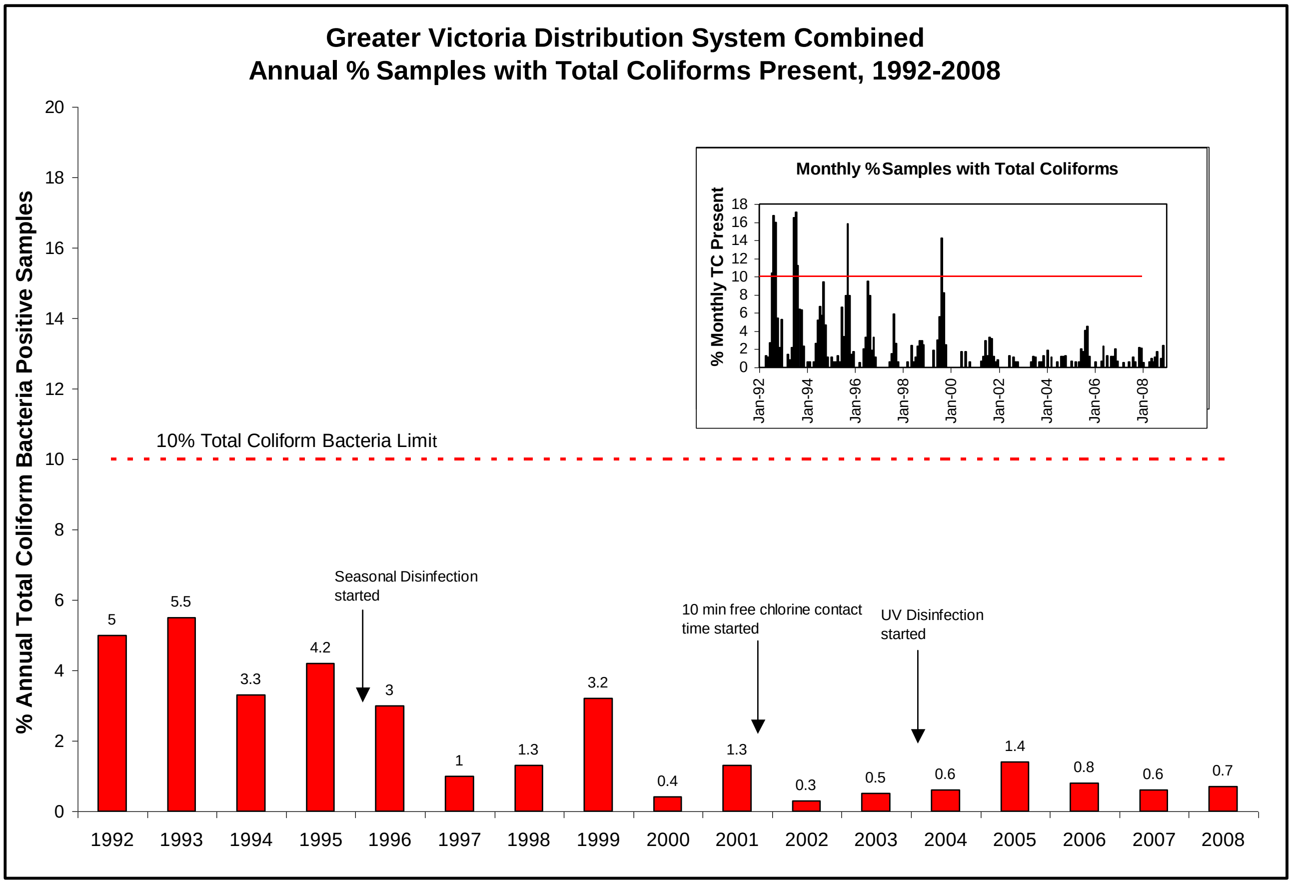


Figure 3.16: Greater Victoria distribution system combined annual % samples with total coliforms present, 1992-2008 (CRD, 2009).

In addition to being enough to inhibit microbial re-growth at the periphery of the distribution system, the disinfectant (chlorine or chloramines) concentration must be maintained at a level to avoid consumer complaints of disinfectant taste and odor. Chlorine (chloramines) residuals were also monitored by the CRD. The chlorine dosage level is typically maintained at 1.6-1.7 mg/L throughout the year. This dosage level resulted in a monthly median total chlorine (chloramine) residual ranging from 1.09 to 1.24 mg/l at the entry point (JGO-TR-01) to the distribution system (CRD, 2009). These values fell well within the disinfectant Canadian guideline limit of 3.0 mg/L for chloramines (Health Canada, 2008). Approximately 75% of the chloramines occurred as monochloramine (CRD, 2009). It is generally accepted that monochloramine dominated, especially at the chlorine to ammonia-nitrogen mass ratio of 4:1 and the pH range of 7.0 to 8.5 (Lu et al., 2009). Monochloramine is the most desirable form of this disinfectant as the free chlorine from the monochloramine hydrolysis can react with both ammonia and NOM, resulting in lower DBP concentrations (Duirk et al., 2005).

Chlorine residuals were relatively low (0.215 mg/L (NOS-CP-01) at the extremity locations in the early 2000's, which prompted the installation or change in treatment strategy of booster stations (2003) and the commencement of UV disinfection at Japan Gulch in 2004. In an attempt to reduce the levels of DBPs in the North Saanich distribution system, the re-chlorination station at Deep Cove pump house was decommissioned in 2007. Since 2008 median annual chlorine residual values within the distribution system were maintained at 0.64 mg/L (CRD, 2009) and bacterial re-growth did not tend to be a major concern

Ultimately the efforts to reduce potential health risks from DBPs must not compromise pathogen control. While the multiple barrier approach has shown great benefits against microbial contamination, there must also be a balance in DBP production. In a risk analysis of drinking water microbial contamination versus DBPs, Ashbolt (2004) illustrated the higher public health risks come from pathogens. However, there are over 700 potential DBPs in drinking water and while human health studies have been conducted on THMs and HAAs, very little is known about the remaining DBPs. In fact, recent evidence points to brominated compounds and nitrosamines (e.g. nitrosodimethylamine, NDMA) as the higher carcinogenic DBPs of concern (Plewa et al., 2004). Charrois and Hrudey (2007) reported that NDMA has a drinking water unit risk two to three orders of magnitude greater than currently regulated halogenated DBPs.

Many agencies have changed from chlorination to chloramination in an effort to reduce THM/HAA concentrations. If DBPs such as NDMA prove to be the carcinogens in drinking water it could have major ramifications for the water industry as NDMA is generated during chloramination of drinking water (Najm and Trussell, 2001). Hua and Reckhow (2007) also found that chloramines produced a higher percentage of unknown total organic halogen (UTOX), iodoform and total organic iodine (TOI) in the presence of iodide, than from free chlorine. Moreover, switching from chlorine only to chloramination can result in the release of lead into drinking water from distribution system pipes, solder and brass fittings (Edwards and Dudi, 2004). These chloramination risk trade-offs must be considered by CRD in managing the water supply. It is strongly recommended that NDMA monitoring should be incorporated into the CRD drinking water program. Ultimately, drinking water management must balance the human health risks from both biological and chemical contaminants.

Summary and Conclusions

Following the changes to treatment strategies for the Greater Victoria water supply area there has been a significant reduction in the formation of DBPs. While there was a slight increase to DBPs in the non re-chlorinated sites, both THMs and HAAs remained quite low and were well within the Canadian drinking water guidelines. THMs followed the typical pattern of increasing with longer residence time while the HAAs tended to degrade over time, likely due to reduced chlorine residual levels and microbial activity.

The re-chlorinated sites did not follow typical patterns of DBP production as observed in the non re-chlorinated sites. Boccelli et al. (2003) explains that in addition to re-chlorination at engineered booster stations, re-chlorination also occurred in the distribution system through mixing of waters traveling along different paths with different average residence times. This resulted in different chlorine concentrations and reactive species characteristics in the system with varying DBP formation potential. In this study the re-chlorinated sites were limited to extremity sites and had the greatest fluctuations in DBP results, especially during periods of seasonal re-chlorination.

As expected based on available literature, the DBPs were higher after re-chlorination (Speight and Singer, 2005; Lee *et al*., 2007), with mean THM and HAA values approximately 1.5 to 3.5 and 2.5 to 5 times higher, respectively, than at non re-chlorinated sites. Even after changes to the treatment plant, the North Saanich distribution area still had HAA exceedances in 2006/07, which prompted CRD to make changes to booster stations in this area. This significantly reduced the DBPs (a 50% reduction or greater). This emphasized that changes to treatment at the main disinfectant plant does not necessarily impact DBP production directly at the booster site locations.

The DBPs produced at these booster sites were influenced significantly by changes to the re-chlorination process (i.e. seasonal versus annual re-chlorination and decommission of booster station).

For all stations THMs were comprised primarily of chloroform (90% or greater) and BDCM, while HAAs consisted of DCAA, TCAA and small amounts of BCAA. North Saanich sites also had some occasional traces of BDCAA and MBAA, primarily in the fall/winter when rainstorm events occur and bromide levels within the source water are shown to increase.

The reservoir inundation project was a success in that summer water temperatures were lower and only exceeded guidelines for a two-month period (August-September), rather than four months. In addition, while TOC mean values increased post inundation, especially in 2003, there did not appear to be any significant change to overall DBP production. However, TOC composition may have been altered with an increase in algal productivity following the inundation period. This algal activity was associated with higher HAAs in the summer, while terrestrial TOC tended to drive THM formation in the fall/winter. This area needs further research to characterize and confirm sources of TOC.

Bacteriological quality of the disinfected water at the first customer site improved substantially since the use of UV and free chlorine plus ammonia disinfectants. While bacteria were still detected in the distribution system, the levels did not exceed the BC drinking water protection limits. Chlorine residuals still tended to be low in the extremity sites; however, through the addition of chlorine booster stations, management of chlorine dosages, changes to booster stations from chlorine to chloramine and even the decommissioning of booster stations, DBP levels at these extremity locations have improved.

The selection of monitoring locations and review of the data is very important for the management of a water distribution system. In addition, many drinking water utilities are increasingly incorporating alternative disinfectants, such as chloramines, in order to comply with specific DBP regulations. Chloramination also has associated human health risks such as the formation of NDMA and several iodinated DBPs.. These emerging contaminants also warrant scrutiny, thus it is recommended that CRD incorporate them into their current monitoring programs. Source water and treatment plant processes are location dependent and water utilities need to assess the risk trade-offs between potential adverse human health effects and formation of regulated and unregulated DBP species.

Chapter 4: General Conclusions

My goal in this research was to determine the factors affecting the production of DBPs in surface source waters on Vancouver Island. Previous studies have shown that DBPs are a function of source water characteristics and treatment strategy (Nikoloau and Lekkas, 2001; Kitis *et al*, 2004; Plewa *et al*, 2004b; Panyapinyopol *et al*., 2005; Krasner *et al*., 2006). Source water quality is derived from the physical, chemical and biological characteristics within a watershed (Jung and Son, 2008). With respect to DBP formation, key source water parameters include water temperature, pH, concentrations and properties of natural organic matter (NOM), chlorophyll *a*, and bromide concentration. The concentration and characteristics of NOM, the primary precursor of DBPs, tends to vary from watershed to watershed and is affected seasonally (Chang *et al*., 2001). However, based on Demarchi's (1995) ecoregion classification system, watersheds in similar biogeoclimatic zones should have similar water quality. If this principle is valid, then one would expect the DBP formation potential to be similar for all watersheds within an ecoregion. Thus, source water quality could be used as a preliminary tool to predict community DBP exposure on an ecoregion basis.

In Chapter 2, a comparison of THM and HAA results on Vancouver Island determined that there was a distinct spatial difference in DBP production between ecoregions. These differences in DBP production were attributed to source water quality and water body type (stream or lake). Key source water quality parameters affecting DBP production included levels of DOC, chlorophyll *a*, bromide and pH. Watersheds with higher concentrations of these parameters typically increased the quantity and individual type of THM or HAA produced. When accounting for water body type, streams and lakes both within and between ecoregions also differed by the type of DBPs produced, THMs or HAAs. While treatment strategies were not accounted for in Chapter 2, it was observed that pre-treatment processes to remove organics reduced DBP production in the North Island ecoregion watersheds.

To determine what was influencing the observed difference in DBP production between water bodies, I investigated the variability in DOC concentrations between both lakes and streams (Chapter 2). I determined that streams generally had low levels of DOC, with the exception of the North Island ecoregion streams. In addition, most of the studied streams had little or no anthropogenic activity within their watersheds, with the exception of China Creek, which is influenced by timber harvesting. This suggested that the majority of mainstem DOC is allochthonous, is derived from external sources within the watershed, such as the surrounding soils and terrestrial vegetation (Chow *et al*., 2007), and fluctuates due to precipitation events. Jung and Son (2008) also reported that THM formation per unit DOC concentration varied with the type of DOC as follows: humic acid>fulvic acid>hydrophilic organic matter. This likely explains the differences observed in THM production in the North Island streams, which contain naturally high levels of tannins and lignins, and resulted in higher DBP production.

Eutrophic lakes in this study, tended to have higher levels of DOC, suggesting that carbon sources, were autochthonous in nature, derived from dead organisms, phytoplankton, exudates, etc. (Chow *et al*., 2007). Nguyen et al (2005) reported that autochthonous, algal-derived, DOC can be a significant source of DBP precursors. The SGI lakes had elevated HAA results associated with peak algal bloom periods. However, during rainstorm events, DOC in the lakes could result from a combination of both allochthonous and autochthonous sources, which likely explains both the elevated THM and HAA values reported for the SGI lakes and its uniqueness as an ecoregion. Oligotrophic lakes tended to have lower concentrations of DOC and typically lower DBP production. In addition, if the actual source water DOC levels in Quatse Lake were used instead of pre-treated DOC levels, it is likely that the North Island lakes would produce THM levels similar to North Island streams. Quatse Lake is a low nutrient lake with high color values; thus, DOC sources are likely more allochthonous in nature

In Chapter 3, TOC levels in the Sooke Reservoir increased significantly following a three-year inundation project. The vegetation around the reservoir was removed prior to raising the water levels, in an attempt to reduce allochthonous TOC inputs. However, similar to the SGI lakes, elevated TOC levels in the reservoir were likely associated with an increase in algal growth, as both total phosphorus and chlorophyll *a* values increased post-inundation. Regardless of the increase in TOC levels, there was no significant difference in DBP production from the Sooke source water following the inundation period. The Sooke reservoir is a large oligotrohic lake, and while phosphorus and chlorophyll *a* values did increase substantially, they were still reflective of a nutrient poor lake.

In similar studies, DBP variation, in both THM and HAA production, was shown to be dependent on seasonal characteristics of the raw water, DOC in particular (Jung and Son, 2008). From Chapter 2, only the SGI lakes exhibited a seasonal correlation with HAA production. Again this seasonal difference is likely a result of the increased productivity of these lakes. From my experience, the lakes in the other ecoregions also experience algal blooms but not significant enough to increase HAA levels substantially.

While THM production is strongly correlated with DOC levels in this study, there was no seasonal correlation for THM production in either lakes or streams. In lakes this is likely attributed to the influence from HAA production. As allochthonous DOC levels produce both THMs and HAAs, there was likely not enough difference in their production, respectively, to warrant seasonal differences in streams.

In Chapter 3, fluctuations in DBP production at the extremity sites, was associated with seasonal chlorination. During times of the year when TOC levels were expected to increase, such as winter rains or warmer water in the summer, chlorination was either turned on or increased, resulting in elevated DBPs.

In addition to DOC levels in the source water, past research has established that levels of DBPs in chlorinated waters vary according to pH, water temperature, and bromide concentrations (Rodriquez *et al*., 2003). In general, higher values of these parameters result in higher levels of DBPs. There was no significant correlation observed between these parameters and the total DBPs produced in the 12 watersheds studied; however, an association was observed with individual THM or HAA results. SGI lakes and pre-treated Tsulquate River water, both had higher levels of bromide, which resulted in the production of brominated DBPs (DBAA, BDCAA, BDCM and DBCM). Bo *et al*. (2008) noted that THM production, in the presence of bromide, increases with increasing pH values. This effect was observed in the SGI lakes, which had both high pH and bromide concentrations. In addition, my results showed a moderate correlation between pH and DOC levels. This relationship was unique for the North Island watersheds where pH levels were low and DOC levels were high. These lower pH levels may help to keep THM concentrations lower than one would expect given the high DOC levels. These results further supported the spatial differences observed in both the SGI and North Island ecoregions, and the link between source water quality and DBP production.

With regards to temperature, cooler water is beneficial in a distribution system because it reduces the potential for losses of chlorine residual and for the re-growth of bacteria (Hong *et al*., 2008). In this regard, the Sooke Reservoir inundation project described in Chapter 3 was successful, with cooler water temperatures observed in the summer and a substantial improvement noted in the bacteriological quality of the disinfected water through out the distribution system. The SGI lakes tend to have warmer water temperatures throughout the summer and early fall. The location of the water intake in these lakes would be essential, with deeper intakes providing cooler waters, to reduce the potential for losses of chlorine residual and control the regrowth of bacteria. The intake depth for the lakes is at approximately five meters or shallower, which during the summer can equate to warmer water. Furthermore, chlorine residual values for these water supplies are extremely low at the extremity sites (Site 3) ranging from 0.01 mg/L to 0.24 mg/L, which combined with the warmer water temperatures during the summer, could result in bacterial re-growth. While there is no direct link with regards to water temperature and DBP production, indirectly water temperature affects chlorine residuals, which can alter DBP production.

Having a proper understanding of the source water quality is essential for the management of DBP formation potential. In addition, the treatment type, disinfectant contact time and dose, length of distribution system and chlorine residuals throughout the water system also influence the types and amounts of DBPs produced (Singer, 1994; Nikolaou *et al*., 2004; Krasner *et al*., 2006). I had the unique opportunity to review a long-term DBP data set that incorporated both changes to the source water quality, as noted above, and to the treatment strategy. In Chapter 3, I determined that changes to treatment type significantly affected the DBPs produced. While there was a slight increase to DBPs in non re-chlorinated sites following changes at the main treatment plant, a higher chlorine residual was maintained throughout the system, including the extremity locations. However, changes at the main treatment plant did not affect the DBPs at the extremity sites. The DBPs produced following booster site locations are influenced significantly by changes to the booster stations (e.g. seasonal versus annual re-chlorination and decommission of booster stations).

It is recognized that there are several aspects that may have strengthened this work. First, it would have been beneficial to have an equal number of lakes and streams per ecoregion. This information may have helped explain the variation that was observed in THM and HAA production by water body for each ecoregion. With respect to DOC, further work is required in this area to characterize and confirm the sources of DOC. In this study, broad references were made to autochthonous and allochthonous sources of DOC based on previous research. It would have been useful to have SUVA values, or an equivalent, to provide insight into the nature of NOM and to further help explain seasonal variability. Of the 12 surface source waters sampled in Chapter 12, nine were forested and only three, all lakes, had residential/rural development. It would have been useful to include watersheds, both streams and lakes, with different land use activities to determine if DBP production would alter. Finally, in Chapter 2, treatment factors were not incorporated in the overall analysis of DBP production. Each water treatment system was unique in how they operated, from the disinfection process to the size of the distribution system, and it is possible this information may have provided more insight into the results observed.

Findings from this research have provided a preliminary basis for predicting DBP production based on water body type, source water quality and ecoregion classifications. Furthermore, a good understanding of the source water is paramount to properly manage drinking water sources. Typically watersheds with low DOC as characterized in the East and West Coast ecoregions should result in lower DBPs. Watersheds in the North Island ecoregion and small eutrophic lakes, as shown in the SGI ecoregion, tended to produce higher DBPs, illustrating the need to remove organics prior to disinfection. When combined with other information such as land use and treatment strategy, water managers may be able to balance the risks between microbial and chemical effects to human health. Furthermore, this research supports the need for long term monitoring and review of DBP data throughout the distribution system as DBP production has been shown to change as a result to changes in treatment strategies. With many water purveyors incorporating alternative disinfectants, not only is it essential to monitor regulated DBPs, emerging contaminants, such as nitrogen based DBPs, also warrant scrutiny. Ultimately the management and protection of water quality at the source is the most promising way to reduce DBP precursors as well as microbial pathogens.

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Appendix

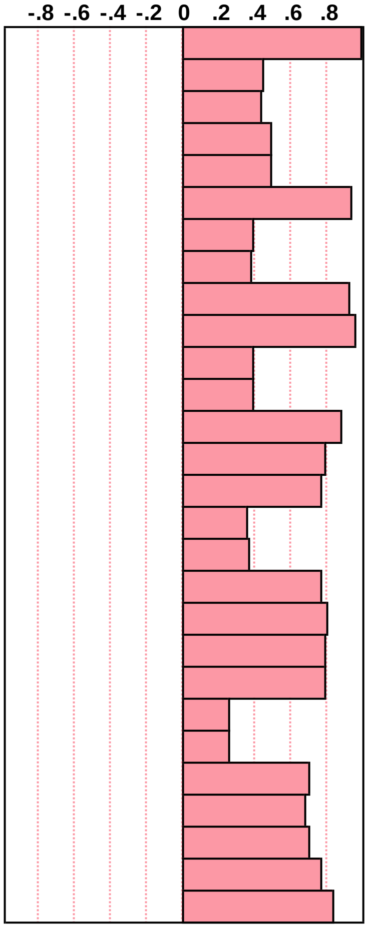
Appendix 2.1: Correlation results for TOC/DOC and DBPs.

a) Multivariate correlations for monthly TOC/DOC source water concentrations and the corresponding THM and HAA results (pooled for each sample site).

	TOC mg/L	DOC mg/L	THM Site 1	THM Site 2	THM Site 3	HAA Site 1	HAA Site 2	HAA Site 3
TOC mg/L	1.0000	0.9925	0.4600	0.5092	0.4064	0.3928	0.3705	0.2852
DOC mg/L	0.9925	1.0000	0.4692	0.5036	0.4005	0.4047	0.3740	0.2895
THM Site 1	0.4600	0.4692	1.0000	0.9409	0.9379	0.8868	0.7690	0.7109
THM Site 2	0.5092	0.5036	0.9409	1.0000	0.9579	0.7954	0.8020	0.6783
THM Site 3	0.4064	0.4005	0.9379	0.9579	1.0000	0.7892	0.7916	0.7054
HAA Site 1	0.3928	0.4047	0.8868	0.7954	0.7892	1.0000	0.7915	0.7797
HAA Site 2	0.3705	0.3740	0.7690	0.8020	0.7916	0.7915	1.0000	0.8425
HAA Site 3	0.2852	0.2895	0.7109	0.6783	0.7054	0.7797	0.8425	1.0000

b) Pairwise correlations for DOC/DOC and DBP results for the 12 watersheds.

Variable	by Variable	Correlation	Count	Signif Prob
DOC mg/L	TOC mg/L	0.9927	96	<.0001*
THM Site 1	TOC mg/L	0.4480	105	<.0001*
THM Site 1	DOC mg/L	0.4395	96	<.0001*
THM Site 2	TOC mg/L	0.4940	84	<.0001*
THM Site 2	DOC mg/L	0.4876	84	<.0001*
THM Site 2	THM Site 1	0.9385	84	<.0001*
THM Site 3	TOC mg/L	0.3867	95	0.0001*
THM Site 3	DOC mg/L	0.3801	95	0.0001*
THM Site 3	THM Site 1	0.9260	95	<.0001*
THM Site 3	THM Site 2	0.9580	83	<.0001*
HAA Site 1	TOC mg/L	0.3903	104	<.0001*
HAA Site 1	DOC mg/L	0.3860	95	0.0001*
HAA Site 1	THM Site 1	0.8851	106	<.0001*
HAA Site 1	THM Site 2	0.7955	83	<.0001*
HAA Site 1	THM Site 3	0.7743	94	<.0001*
HAA Site 2	TOC mg/L	0.3607	83	0.0008*
HAA Site 2	DOC mg/L	0.3634	83	0.0007*
HAA Site 2	THM Site 1	0.7690	83	<.0001*
HAA Site 2	THM Site 2	0.8020	83	<.0001*
HAA Site 2	THM Site 3	0.7916	82	<.0001*
HAA Site 2	HAA Site 1	0.7916	83	<.0001*
HAA Site 3	TOC mg/L	0.2555	95	0.0124*
HAA Site 3	DOC mg/L	0.2584	95	0.0115*
HAA Site 3	THM Site 1	0.7091	95	<.0001*
HAA Site 3	THM Site 2	0.6786	83	<.0001*
HAA Site 3	THM Site 3	0.7066	94	<.0001*
HAA Site 3	HAA Site 1	0.7723	95	<.0001*
HAA Site 3	HAA Site 2	0.8409	83	<.0001*



Appendix 2.2: Correlation results for source water parameters and DBPs.

a) Multivariate correlations for four source water parameters and the corresponding THM and HAA results. (Only Site 1 DBP results were analyzed, as there was a strong correlation among sites for DBP results (Appendix 2.1).

	DOC mg/L	THM Site 1	HAA Site 1	Total P (ug/L)	Bromide (ug/L)	pH
DOC mg/L	1.0000	0.4486	0.3924	-0.0034	-0.0104	-0.3372
THM Site 1	0.4486	1.0000	0.8951	-0.0835	0.0823	0.0574
HAA Site 1	0.3924	0.8951	1.0000	-0.0352	0.0234	-0.0560
Total P (ug/L)	-0.0034	-0.0835	-0.0352	1.0000	-0.0305	0.1925
Bromide (ug/L)	-0.0104	0.0823	0.0234	-0.0305	1.0000	-0.0054
pH	-0.3372	0.0574	-0.0560	0.1925	-0.0054	1.0000

b) Pairwise correlations for four source water parameters and the corresponding THM and HAA results.

Variable	**by Variable**	**Correlation**	**Count**	**Signif Prob**
THM Site 1	DOC mg/L	0.4395	96	<.0001*
HAA Site 1	DOC mg/L	0.3860	95	0.0001*
HAA Site 1	THM Site 1	0.8851	106	<.0001*
Total P (ug/L)	DOC mg/L	-0.0082	96	0.9370
Total P (ug/L)	THM Site 1	-0.0536	96	0.6037
Total P (ug/L)	HAA Site 1	-0.0301	95	0.7723
Bromide (ug/L)	DOC mg/L	-0.0099	96	0.9237
Bromide (ug/L)	THM Site 1	0.0769	96	0.4563
Bromide (ug/L)	HAA Site 1	0.0255	95	0.8061
Bromide (ug/L)	Total P (ug/L)	-0.0320	96	0.7570
pH	DOC mg/L	-0.3362	90	0.0012*
pH	THM Site 1	0.0569	90	0.5946
pH	HAA Site 1	-0.0560	89	0.6022
pH	Total P (ug/L)	0.1927	90	0.0688
pH	Bromide (ug/L)	-0.0045	90	0.9667