HAAs in Water Distribution Systems in Newfoundland and Labrador: Causes and Peak Location

January 2010

Newfoundland
Labrador

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Glossary

ALARA	As Low As Reasonably Achievable
BAT	Best Available Technology
BCA	Bromochloroacetic acid
BDCA	Bromodichloroacetic acid
BDCM	Bromodichloromethane
CALA	Canadian Association for Laboratory Accreditation
DBA	Dibromoacetic acid
DBCA	Dibromochloroacetic acid
DBP	Disinfection by Product
DCA	Dichloroacetic acid
DOC	Dissolved Organic Carbon
GAC	Granular Activated Carbon
GCDWQ	Guidelines for Canadian Drinking Water Quality
HAA	Haloacetic Acids
HAA5	5 regulated Haloacetic Acids
IDSE	Initial Distribution System Evaluation
LRAA	Locational Running Annual average
LTD	Less Than Detect
MAC	Maximum Acceptable Concentration
MBA	Monobromoacetic acid
MCA	Monochloroacetic acid
MCLG	Maximum Contaminant Level Goal
MRTL	Maximum Residence Time Location
NOM	Natural Organic Matter
TBA	Tribromoacetic acid
TCA	Trichloroacetic acid
THM	Trihalomethanes
TOC	Total Organic Carbon

Introduction

In July of 2008, Health Canada issued a drinking water quality guideline for Haloacetic Acids (HAAs). The guideline is as follows (Health Canada, 2008):

The maximum acceptable concentration (MAC) for total haloacetic acids in drinking water is 0.08 mg/L (80 µg/L) based on a locational running annual average (LRAA) of a minimum of quarterly samples taken in the distribution system.
Utilities should make every effort to maintain concentrations as low as reasonably achievable (or ALARA) without compromising the effectiveness of disinfection.

There is some uncertainty as to where to sample for HAAs as the guideline is locational. Generally the sampling location for disinfection by-products (DBPs) should be taken at the point of maximum formation. There has been some evidence that HAAs tend to peak in the beginning to middle of the distribution system, and not at the end of the system due to microbial degradation of HAAs from biofilms formed on the pipe wall.

The Health Canada guidance document for HAAs suggests the location of sampling be based on historical data. Where historical data is not available, HAAs should be monitored in the middle and extremities of the distribution system. Areas with extremely low or no disinfectant residual should be avoided, but areas where disinfectant residuals are significantly lower than the system average because of a long residence time (e.g., dead ends, low flow areas) should be targeted. In systems with booster chlorination stations and water tanks or reservoirs, it is expected that higher HAA concentrations would be found downstream of these components.

This technical study will look at HAA levels at different sites in 11 water distribution systems in Newfoundland and Labrador, evaluate what is causing high levels of HAAs, and make the recommendation on the preferred province wide sampling site for future HAA sampling.

Background

Haloacetic acids or HAAs are a family of organic compounds based on the acetic acid molecule (CH_3COOH) as a derivative of a benzene ring, where one or more hydrogen atoms attached to carbon atoms are replaced by a halogen (chlorine, bromine, fluorine and/or iodine- Figure 1). There are nine different species of HAAs, however, not all are regularly tested. HAAs are colourless, polar, non-volatile, dissolve easily in water and are fairly stable. When water is disinfected with chlorine, trihalomethanes (THMs) are the predominant DBP formed followed by HAAs.

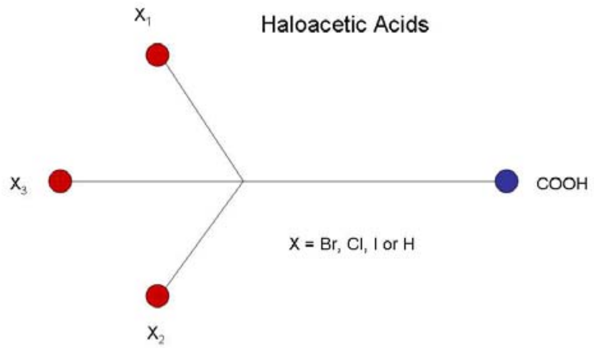

Figure 1: HAA molecule

HAA Speciation and Health Risks

The nine species of HAAs can be classified according to the number of halogens they contain as follows:

- Monohalogenated (XAA)
- Dihalogenated (X_2AA)
- Trihalogenated (X_3AA)

The most commonly measured individual haloacetic acids include the following and are referred to as HAA9:

- Monochloroacetic acid (MCA) [$ClCH_2COOH$]
- Dichloroacetic acid (DCA) [$CHCl_2COOH$]
- Trichloroacetic acid (TCA) [CCl_3COOH]
- Monobromoacetic acid (MBA) [$BrCH_2COOH$]
- Dibromoacetic acid (DBA) [$Br_2CHCOOH$]
- Bromochloroacetic acid (BCA) [$CHBrClCOOH$]
- Bromodichloroacetic acid (BDCA) [$CBrCl_2COOH$]
- Dibromochloroacetic acid (DBCA)[$CClBr_2COOH$]
- Tribromoacetic acid (TBA) [CBr_3COOH]

The HAAs present in the greatest concentrations are typically dichloroacetic and trichloroacetic acid. Looking at HAA data from 2001 to 2007 from across the province, the HAA species with the highest concentrations are trichloroacetic acid followed by dichloroacetic acid. Together they account for approximately 95 percent of total HAAs in the province. Figure 2 indicates that the ratio of regulated HAAs (HAA5) to the non-regulated portion of HAAs (HAA9) is not significant. The rate of formation of TCA is significantly favoured by low pH (Health Canada, 2008). Bromine is more reactive than chlorine in reactions that form HAAs and the HAA speciation will also depend on the ratio of bromide to chlorine (Singer, 1999).

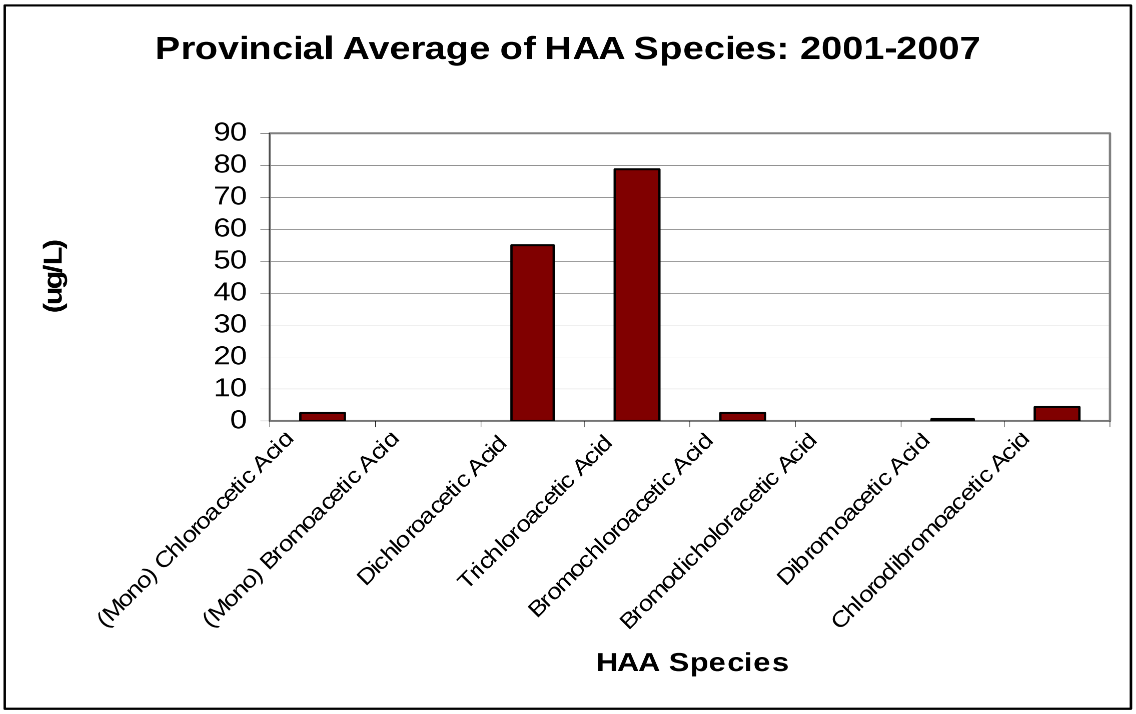

Figure 2: Average HAA Species in Newfoundland and Labrador: 2001-2007

Exposure to haloacetic acids from drinking water through inhalation and skin contact is not considered significant. The main route of exposure is through ingestion. There is sufficient scientific data available to determine the health-based effects of several of the individual HAA species as follows:

- MCA- Group IV- unlikely to be carcinogenic to humans
- DCA- Group II- probably carcinogenic to humans
- TCA- Group III- possibly carcinogenic to humans
- MBA- Group VI- unclassifiable with respect to carcinogenicity in humans
- DBA- Group II- probably carcinogenic to humans

These five HAA species make up what is commonly referred to as HAA5. The Guideline for Canadian Drinking Water Quality (GCDWQ) for HAAs is based on a comparison to HAA5. The two species that display the highest health risk, dicloroacetic acid and dibromoacetic acid, make up 39% and 0.3% of average provincial HAA totals respectively.

Table 1 summarizes known health risks of both THM and HAA species. Short term exposure above guideline levels may increase the chance of spontaneous abortions in pregnant women, however evidence is inconclusive. Long term exposure to HAAs above guideline levels may cause an increased risk of cancer.

Table 1: Health risks associated with various DBP compounds

Class of DBPs	Compound	Rating	Effects
THM	Chloroform	B2	Cancer, liver, kidney and reproductive effects
	Dibromochloromethane	C	Nervous system, liver, kidney and reproductive effects
	Bromodichloromethane	B2	Cancer, liver, kidney and reproductive effects
	Bromoform	B2	Cancer, nervous system, liver and kidney effects
HAA	Monochloroacetic acid	E	
	Dichloroacetic acid	B2	Cancer, reproductive and developmental effects
	Trichloracetic acid	C	Liver, kidney, spleen and developmental effects
	Monobromoacetic acid	D	
	Dibromoacetic acid	B2	

A: Human carcinogen; B1: Probable human carcinogen (with some epidemiological evidence); B2: Probable human carcinogen (sufficient laboratory evidence); C: Possible human carcinogen; D: Non classifiable; E: Not likely to be carcinogenic to humans.

The USEPA has a HAA5 maximum contaminant level of 0.06 mg/L (USEPA, 1998). It has also established maximum contaminant level goals (MCLG) for individual HAA species. The MCLG for DCA is 0.0 mg/L, and for TCA it is 0.3 mg/L (likely to be reduced to 0.02 mg/L in future regulations). A MCLG for MCA of 0.03 mg/L is also likely to be established in future regulations.

HAA Precursors

Regulated HAAs form when chlorine reacts with natural organic matter and/or bromide ions in raw water supplies. The process of HAA formation and decay differs somewhat from that of THMs. HAAs are a group of acetic acids that are more likely to form under low pH conditions, and peak levels observed in distribution systems do not occur at the point of maximum residence time, as with THMs, due to microbial decomposition in the network. The presence of brominated HAAs depends on the presence of bromine in the source water. The rate of formation of HAAs also increases at higher water temperature.

HAAs are formed in drinking water when chlorine disinfectants used in water treatment react with organic matter (e.g., humic or fulvic acids) and inorganic matter (e.g., bromide ion) naturally present in the raw water (IPCS, 2000). HAAs are the second most frequently occurring DBPs, after THMs. In many communities in the province, however, HAA levels have been observed to exceed THM levels. Various water treatment methods lead to the formation of chlorinated and brominated acetic acids, including chlorination, ozonation and chloramination. HAA formation during chloramination is 5-20% of that observed with chlorination (AWWARF, 2004).

In the case of chlorination, hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-) are formed, which in turn react with a bromide ions, if present, oxidizing it to hypobromous acid ($HOBr^-$) and hypobromite ion (OBr^-), respectively. Hypochlorous acid and hypobromous acid then react with natural organic matter (NOM) to form different DBPs, including HAAs. The chlorinated HAAs generally dominate; however, in high-bromide waters, the brominated HAAs may be more prevalent.

HAA formation can be appreciable when drinking water is chlorinated under conditions of slightly acidic pH (IPCS, 2000). pH is frequently sited as the most significant factor in HAA formation. Whereas THM formation increases with increasing pH, HAA formation decreases, hydrolysis likely being a significant factor. Despite the fact that HAAs and THMs have different pH dependencies, their formation appears to correlate strongly when treatment conditions are relatively uniform and when the water has a low bromide concentration.

Organic compounds are present in water from natural processes and are frequently referred to as natural organic matter (NOM). NOM is typically measured by surrogate parameters such as TOC, DOC, UV absorbance or fluorescence. DOC is the only regularly monitored surrogate in Newfoundland and Labrador drinking water supplies. DOC is indicative of the mass of material and is the result of microbial degradation of organic matter, oxidative polymerization of phenolic compounds in plants and soil, and photolytic degradation of NOM (Singer, 1999). In drinking water supplies, organic carbon compounds consist of humic and fulvic acids, polymeric carbohydrates, polysaccharides, proteins, carboxylic acids, and low molecular weight acids. Organic carbon is often considered the growth-limiting nutrient in water distribution system bacterial re-growth. Increases in DOC concentration are generally observed after heavy rainfalls, and are attributed to increased leaching from soil organic matter during high river discharges. DOC levels are significantly higher in surface water sources (average of 6.4 mg/L) in the province than in groundwater sources (average of 1.3 mg/L). NOM also displays high levels of seasonal variation.

Humic substances (see Figure 3) serve as the most important DBP precursor, with low molecular weight acids serving as biodegradable organic matter within a distribution system (AWWARF, 2006). The most problematic of the humic substances are aromatic organics– humic acids such as tannins. Aromatic organics are more reactive than other organics having a double bond ring structure that results in free electrons that are readily available to react with other molecules. Non-aromatic (aliphatic) organics, such as fulvic acids, tend to be less reactive. Increased concentrations of NOM with aromatic content (humic acids) in raw water favour formation of HAAs. NOM in the hydrophilic fraction are more reactive in forming HAAs than the hydrophobic fraction. Increased concentrations of NOM in raw water also increase the chlorine demand and favour the formation of chlorinated DBPs.

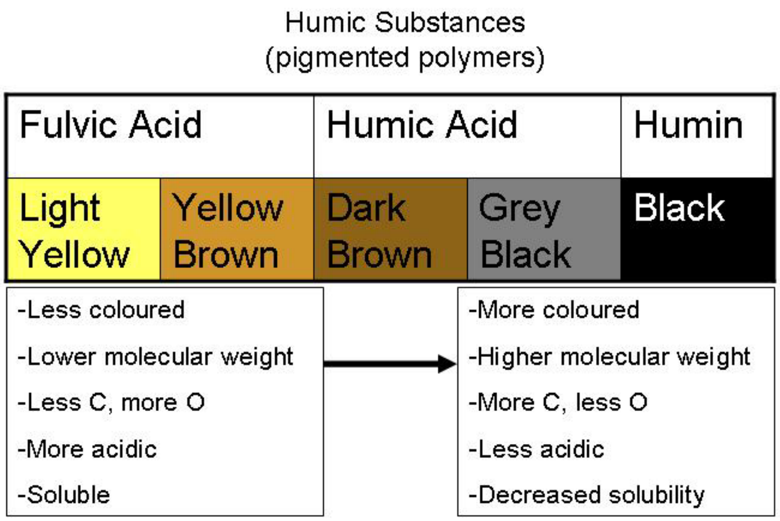

Figure 3: Chemical properties of humic substances

At higher water temperatures, chemical reaction rates are faster and chlorine demand is higher. When chlorine demand is higher more chlorine is dosed in order to maintain residuals at the end of the distribution system. Longer contact times with storage tanks and larger than necessary pipes also contribute to greater HAA formation.

In the presence of bromide, the chlorination process may also favour the formation of brominated DBPs, depending on the physical and chemical properties of the water. High chlorine concentrations also favour the formation of higher concentrations of TCA compared with MCA and DCA. However, if bromide levels are high in source waters, the formation of brominated and chloro-brominated HAAs is more likely to occur. Bromide levels in surface water and groundwater may fluctuate seasonally and may occur as a result of saltwater intrusion or pollution, as well as from natural sources.

Levels of HAAs are highest in treated water from sources with high organic matter content, such as rivers and lakes. HAA levels are typically significantly lower when the source is groundwater. Within a single distribution system, however, HAA levels can vary greatly, depending on both water quality (e.g., HAA precursors, pH, temperature, ammonia and carbonate alkalinity) and treatment conditions (e.g., disinfectant dose, contact time, removal of NOM before the point of disinfectant application, prior addition of disinfectant).

To discover which variables played the most significant role in HAA formation, a correlation analysis was performed using data from 63 samples from different communities across the province covering the period from 2001 to 2007 (DOEC, 2009). MINITAB statistical software was used to calculate the Pearson product moment correlation coefficient between each pair of variables listed. The correlation coefficient measures the degree of linear relationship between two variables. The correlation coefficient assumes a value between -1 and +1. If one variable tends to increase as the other decreases, the correlation coefficient is negative. Conversely, if the two variables tend to increase together the correlation coefficient is positive. For this analysis DOC was used as a surrogate of natural organic material, as it is an indicator of the mass of organic substance in water.

Table 2: Correlation analysis between HAAs and HAA precursors in NL

Variable	Pearson Correlation Coefficient for HAAs	P-Value
Sample size	63	
Total THM	0.732*	0.000
DOC	0.387*	0.002
Total Chlorine	0.328*	0.012
Colour	0.264*	0.036
Iron	0.258*	0.041
Free Chlorine	0.204	0.118
Turbidity	0.158	0.216
Water Temperature	0.149	0.256
pH	-0.137	0.286
Nitrate/Nitrite	-0.134	0.295
Site Number	0.129	0.315
Bromide	-0.050	0.696

* statistically significant at $\alpha = 0.05$

HAAs were most closely correlated to THMs followed by DOC, total chlorine, colour and iron. All other correlations were not deemed significant. Although pH was not found to be significant, it did correlate negatively with HAAs. The overwhelming majority of drinking water systems in the province that display high HAAs also display pH levels below the aesthetic guideline of 6.5.

UV absorbance (typically indicated by UV absorbance at 254 nm [UV254]), which is generally related to the aromatic and unsaturated components of NOM, is considered a good predictor of the tendency of a source water to form THMs and HAAs.

HAA Behaviour in the Water Distribution System

Studies indicated that of the five HAAs, DCA and TCA are present in the highest concentrations (Health Canada, 2008). DCA and TCA levels in these studies ranged from <0.3 to 231 µg/L and from <0.1 to 473 µg/L, respectively. Generally, concentrations of both compounds peaked in the distribution system (where chlorine was used to disinfect) and decreased in the extremities of the system, were higher in summer than in winter and were higher in smaller facilities than in larger ones. Frequently, DCA peaked before TCA, indicating that the former may have a faster rate of formation and degradation. The remaining HAA5 compounds, MCA, MBA and DBA, were found at concentrations ranging from <0.01 to 18 µg/L. A comparison of HAA5 levels for the different disinfection processes indicated that levels were generally higher for plants using chlorine.

A U.S study reported unexpectedly low HAA concentrations at the maximum residence time locations in distribution systems (Health Canada, 2008). Analysis of water quality parameters revealed that water at the maximum residence time locations had low levels of free chlorine and high heterotrophic plate counts. Others have previously identified specific bacteria and haloacid dehalogenase as being capable of degrading DCA. Research on haloacid dehalogenase has shown it to have some degree of substrate selectivity, where MCA, DCA, MBA and DBA were degraded while TCA was not.

Specific bacteria observed to be effective in the degradation of various HAA species include *Burkholderia*, *Sphingomanas* and GJ-10 species (AWWRF, 2006). These bacteria were found to be effective in degrading mono and dihalogenated HAA species, however, they did not degrade trihalogenated HAAs. These bacteria also displayed selectivity for dihalogenated HAAs over monohalogenated HAAs due to enzyme affinity for active sites on the molecular chain.

Another factor that may affect the spatial variation of HAA5 in distribution systems is pH. The rate of formation of TCA is significantly favoured by low pHs (<pH 7), whereas the rate of DCA formation is only slightly higher at low pHs.

According to the USEPA (2005), the highest THM and HAA5 level often occur at different points in the distribution system. Only 52.3% of water treatment plants looked at in this USEPA study had the highest THM and HAA5 levels occur at the same location. The joint highest level location for both DBPs was found to vary throughout the distribution system from finished water coming from the water treatment plant (8.7%) to a point of average residence time in the distribution system (31.1%) to the point of maximum residence time in the distribution system (50.9%).

In AWWARF (2006), decreases in HAA concentration at the maximum residence time location (MRTL) were observed in a majority of samples. This effect was most noticeable during warmer months when chlorine residuals were low. Such conditions are preferred for biodegratation of HAAs.

HAA formation rates may increase with temperature, though the effects are less pronounced than for THMs. High temperature conditions in the distribution system promote the accelerated depletion of residual chlorine, which can mitigate DBP formation and promote biodegradation of HAAs (unless chlorine dosages are increased to maintain high residuals). For these reasons, depending on system-specific conditions, the highest THM and HAA levels may be observed during months which are warm, but not necessarily the warmest.

Seasonal trends affect where high HAA concentrations might be found. For example, when water is colder, microbial activity is typically lower and DBP formation kinetics are slower. Under these conditions, the highest HAA concentrations might appear coincident with the oldest water in the system. In warmer water, the highest HAA concentrations might appear in fresher (younger) water, which is likely to contain higher disinfectant residuals that can prevent the biodegradation of HAAs.

DBPs continue to form in drinking water as long as disinfectant residuals and reactive DBP precursors are present. Generally, the longer the contact time between disinfectant/oxidant and NOM, the greater the amount of DBPs that can be formed. In the presence of a continuing significant disinfectant residual, both THMs and HAAs have generally high chemical stabilities and will persist after formation. However, there are some chemical stability differences between THMs and HAAs which can result in differences in long term accumulations. High THM values usually occur at points in the distribution system with the longest total residence time (the "oldest" water age). In contrast, high HAAs values cannot be consistently related to water age because HAAs are known to biodegrade over time when the disinfectant residual is low. This might result in relatively low HAA concentrations in areas of the distribution system where disinfectant residuals are depleted.

In general, changes in the disinfectant dose have a great impact on DBP formation during primary disinfection because the disinfectant is typically the limiting reactant in DBP formation reactions. In the distribution system, DBP formation reactions become disinfectant-limited when the free chlorine residual drops to low levels; a free chlorine residual concentration of 0.3 mg/L has been suggested as a rule of thumb.

In many systems, booster disinfection is applied to raise disinfectant residual concentration, especially in remote areas of the distribution system or near storage tanks where water age may be high and disinfectant residuals can be low. The additional chlorine dose applied to the water at these booster facilities can result in increased formation of THMs and HAAs. Further, booster chlorination can maintain high HAA concentrations because the increased disinfection residuals can prevent the biodegradation of HAAs.

Studies indicate that the location of maximum HAA formation can vary from one distribution system to another (AWWARF, 2006).

Best Available Technology for HAA Treatment

The removal and reduction of HAAs in drinking water focuses primarily on the removal of HAA precursors (NOM and bromide), reducing the oxidant demand and therefore the overall required disinfectant dosage, source water selection, optimization of the disinfection process, and by using alternative disinfection methods.

Conventional municipal scale water treatment techniques (coagulation, sedimentation, dissolved air flotation, precipitative softening and filtration) can reduce the amount of HAA precursors (NOM), but are ineffective in removing HAAs once they are formed. Granular activated carbon (GAC), membranes and ozone–biofiltration systems can also remove organic matter from water.

The USEPA has identified several precursor removal technologies as Best Available Technologies (BAT) for controlling DBP formation including:

- Enhanced coagulation and media filtration
    - Uses conventional treatment processes of chemical addition, coagulation, sedimentation and dual media filtration.
    - Benefits: low capital costs; proven and reliable process
    - Limitations: operator care required with chemical usage; sludge disposal

- GAC filtration
    - Uses extremely porous carbon media in a process known as absorption. As water passes through media, the dissolved contaminants are attracted and held on the solid surface.
    - Benefits: well established, suitable for home use
    - Limitations: effectiveness based on contaminant type, concentration, rate of flow and type of carbon used; requires careful monitoring

- Enhanced coagulation and membrane filtration (microfiltration or ultrafiltration)
    - Uses membrane filtration for coagulated NOM.
    - Benefits: low capital costs
    - Limitations: higher operator care than for media filtration; higher O&M costs

- Membrane filtration (ultrafiltration and nanofiltration)
    - Uses membranes to physically separate the NOM from the water.
    - Benefits: less operator care; consistent low NOM water produced
    - Limitations: membrane fouling; operator care; higher O&M costs, concentrate disposal

- Reverse osmosis
    - Uses semipermeable membrane and high pressure pump to cause the water, but not the NOM to pass through the membrane.
    - Benefits: produces high quality water
    - Limitations: high cost; membrane fouling; pretreatment and feed pump requirements; concentrate disposal

- Lime softening
    - Uses $Ca(OH)_2$ to raise the pH to 10 to precipitate carbonate hardness and trap NOM in the process.
    - Benefits: lower capital costs; proven and reliable
    - Limitations: operator care required with chemical usage; sludge disposal; pH readjustment needed

The type and location of disinfection can greatly affect the amount and species of HAAs formed. Options include moving the disinfection point closer to the first user to reduce HAA formation time, chlorinating after coagulation, raising pH before disinfectant addition, or switching to an alternative disinfectant such as chloramines, chlorine dioxide, UV or ozone. HAA formation is favoured by high chlorine disinfectant residual levels in the distribution system. Reducing the chlorine dose and resulting residuals, while still maintaining secondary disinfection requirements can also reduce HAA levels.

The selection of source water can also play a significant role in reducing the formation potential of HAAs. Source water characteristics such as the quantity and type of NOM, amount of bromide and pH can all affect the quantity and species of HAAs formed. Removal of HAAs after they have formed is less common, but can be achieved using activated carbon filters and reverse osmosis. Such systems are most often point of use household treatment devices that have been certified to reduce HAAs.

Other treatment technologies that may help reduce HAAs include:

- Potassium permanganate addition
    - Used to oxidize organic precursors at the head of the treatment plant, thus minimizing the formation of by-products at the disinfection stage.

- Dissolved air floatation
    - Used to remove dissolved organics from water by dissolving air under pressure and releasing it in the water column where air bubbles adhere to suspended matter causing it to float to the surface where it can be removed.

- Ozonation
    - Used for the oxidation of precursors prior to chlorination. Ozone has been shown to be effective at reducing precursors at low pH.

- pH adjustment
    - Used to increase the pH of water and impede HAA formation. Increasing the pH of water from 7 to 9 has been shown to result in a 50% reduction in HAA levels (AWWARF, 2004).

The USEPA Stage 1 Disinfectants and Disinfection Byproducts Rule is a staged set of rules that will reduce the allowable levels of DBPs in drinking water (USEPA, 1998). The rule is designed to limit capital investments and avoid major shifts in disinfection technologies until additional information is available on the occurrence and health effects of DBPs. The rule recommends treatment techniques such as enhanced coagulation or enhanced precipitative softening to improve the removal of DBP precursors for systems using conventional filtration treatment. The rule also sets required removal percentages for TOC (or NOM). TOC removal is dependent on alkalinity as it is generally more difficult to remove in higher alkalinity waters, and source water with low TOC levels.

Extent of HAA Issues in Newfoundland and Labrador

In the Sustainable Options Report (DOEC, 2008), drinking water quality issues observed over the period from April 2003 to March 2006 were highlighted. The preparation of this report occurred before the Health Canada HAA guideline for drinking water quality was announced, and so for comparison purposes, the USEPA guideline value of 0.60 mg/L for HAA5 was used. Comparisons with the US guideline were made on individual samples, not the annual running average as HAA samples were not regularly collected or collected in all communities at the time. 536 serviced areas were examined for this report.

Table 3 lists the number of serviced areas that experienced HAA exceedances from the Sustainable Options Report. Also listed from the Sustainable Options Report is the number of serviced areas that saw HAA exceedances occur with THM and pH exceedances, and the number of serviced areas that saw HAA exceedances occur independent of any other DBP exceedance. These results indicate that more communities (serviced areas) are experiencing exceedances in HAAs than with THMs. While HAA and THM exceedances occur together 58% of the time, 42% of the time HAA exceedances occur independent of THMs. THMs are likely to exceed on their own without HAAs only 14 % of the time. 72% of the time HAA exceedances occur with pH exceedances (below 6.5).

Table 3: Number of serviced areas with different types and combined exceedances

Type of Exceedance	Sustainable Options Report (April 2003- March 2006)
Total HAA Exceedances	184 (168 if guideline was 0.8 mg/L)
Total THM Exceedances	124
HAA & THM Exceedances	107
HAA Exceedances Only	77
THM Exceedances Only	17
HAA & pH Exceedances	132

From the Sustainable Options report (DOEC, 2008), looking at tap water quality data from the period 2003-2006 (and using the USEPA guideline of 60 µg/L for HAAs), the total population impacted by HAA exceedances has gone as high as 48%.

Based on over 1500 HAA samples collected in the province from 2001 to 2007, HAA concentrations from systems across the province ranged from 0-2420 µg/L, with a median value of 94 µg/L (see Figure 4). These results are skewed towards the high end as HAA sampling in the province during this period was targeted towards drinking water systems where high HAA levels had been observed.

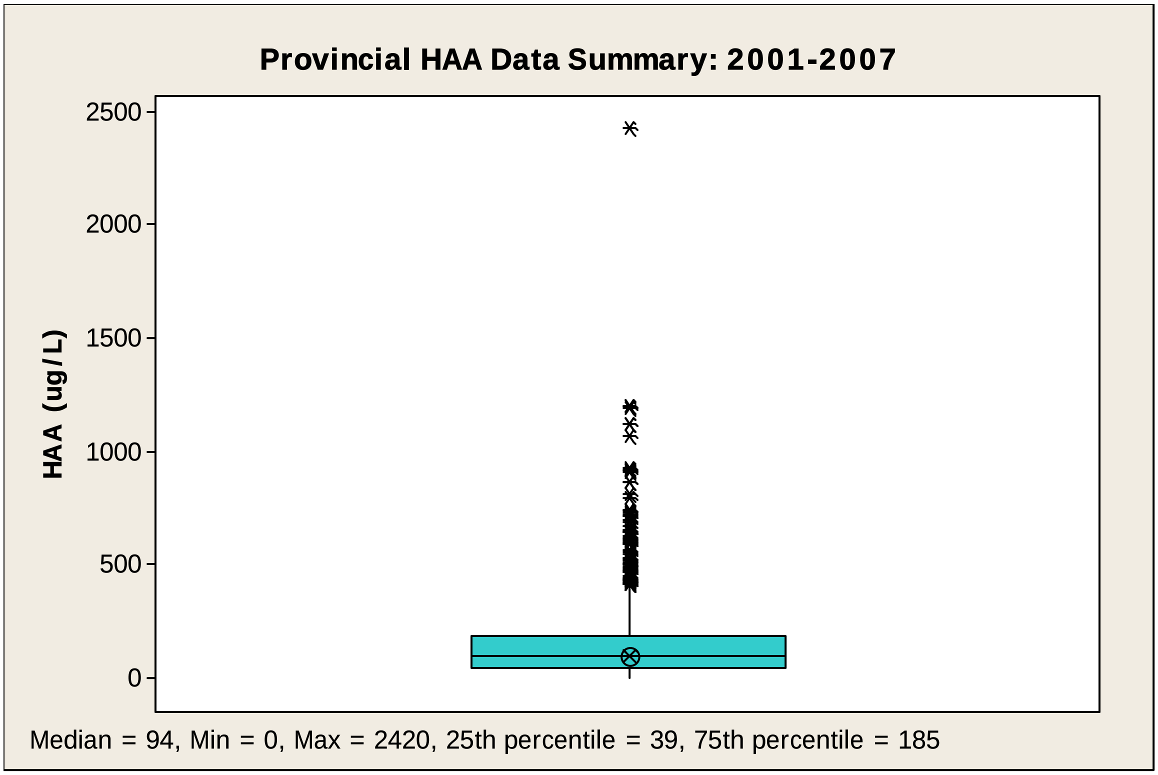

Figure 4: Provincial HAA data summary: 2001-2007

Communities with HAA Issues

Prior to the spring of 2008, HAAs had been handled as an emerging or special parameter by the DOEC and therefore sampling was on a site-specific basis, and the extent and frequency of sample collection was decided annually. A guideline of 80 µg/L for total HAAs (or HAA5) has since come into effect, and with it more regular sampling.

HAA data from the spring 2008 to winter 2009, using both annual running and simple averages (for communities without 4 consecutive quarterly samples), was compared with the HAA guideline of 80 µg/L. HAA exceedances have been broken down into the following descriptive categories and are displayed in Table 4:

- Minor– average level is between 80-100 µg/L
- Moderate – average level is between 100-150 µg/L
- Major– average level is between 150-250 µg/L
- Very Major– average level is above 250 µg/L with some extremely elevated values

Out of 426 public water supplies with chlorination, 162 communities have HAAs above the GCDWQ. 28 communities have very major HAA issues, 64 communities have major HAA issues, 48 have moderate HAA issues, and 22 have minor HAA issues. For this same period of record, out of these 426 public water supplies, 136 had THM exceedances (either running or simple average based).

Table 4: Public water supplies with HAA issues

Very Major HAA Issues	Major HAA Issues	Moderate HAA Issues	Minor HAA Issues
Keels	Fogo	Upper Island Cove	Long Harbour-Mount Arlington Heights
New-Wes-Valley	Millertown	Hawke's Bay	Port Albert
New-Wes-Valley	Massey Drive	Merritt's Harbour	New Perlican
Hermitage	Happy Adventure	Charlottetown (Labrador)	Hant's Harbour
Burlington	Purcell's Harbour	Hare Bay	Clarke's Beach
Salvage	Pleasantview	Rose Blanche-Harbour Le Cou	Garnish
Burgeo	Lewin's Cove	Joe Batt's Arm-Barr'd Islands-Shoal Bay	Heart's Delight-Islington
Brighton	Trinity	Little Bay	Gambo
Parkers Cove	St. Lawrence	Fairbanks-Hillgrade	Glovertown
St. George's	South River	Triton	Ming's Bight
Cartwright	Centreville-Wareham-Trinity	Garden Cove	Beaches
St. Lunaire-Griquet	Baie Verte	Irishtown-Summerside	Northern Arm
Little Bay Islands	Isle aux Morts	Southern Harbour	Old Perlican
Postville	Placentia	Trepassey	Bishop's Falls
Rigolet	Twillingate	Reidville	Springdale
Centreville-Wareham-Trinity	Port Blandford	St. Anthony	Gander
Bonavista	St. Lewis	Conche	Glenwood
Birchy Bay	Burin	King's Point	Avondale
Mary's Harbour	Goobies	Channel-Port aux Basques	Cottrell's Cove
Sunnyside (T.B.)	Leading Tickles	Howley	Hopedale
Pouch Cove	Arnold's Cove	George's Brook-Milton	Main Brook
Ferryland	Cupids	Robert's Arm	Port au Choix
St. Pauls	Lourdes	Corner Brook	
Queen's Cove	Dover	Embree	
Cottlesville	Pasadena	Mount Moriah	
Summerford	Smith's Harbour	Peterview	
St. Lunaire-Griquet	Lamaline	West St. Modeste	
Gander Bay South	Whitbourne	Seal Cove (WB)	
	Little Catalina	Corner Brook	
	Norman's Cove-Long Cove	Come By Chance	
	Whiteway	Bay L'Argent	
	Corner Brook	George's Brook-Milton	
	Terrenceville	Grand Falls-Windsor	
	Dildo	Lumsden	
	Steady Brook	Fortune	
	Tizzard's Harbour	Placentia	
	Tilting	Harbour Grace	

	Miles Cove	Gaskiers	
	Greenspond	Wooddale	
	Point Leamington	Spaniard's Bay	
	Marystown	Harbour Main-Chapel's Cove-Lakeview	
	Norris Arm	Botwood	
	Rocky Harbour	Buchans	
	Milltown-Head of Bay D'Espoir	Benton	
	Musgrave Harbour	Burin	
	West Bay	Appleton	
	Harbour Breton	South Dildo	
	Comfort Cove-Newstead	Jackson's Arm	
	Port Hope Simpson		
	Fermeuse		
	Brigus		
	Torbay		
	Cow Head		
	Lushes Bight-Beaumont-Beaumont North		
	Deadman's Bay		
	Rattling Brook		
	St. Shott's		
	Trinity Bay North		
	Bellevue		
	Trinity Bay North		
	Point of Bay		
	Gillams		
	Conne River		
	Makkovik		

Empirical Models

Empirical models for predicting HAA formation as a result of chlorination have been reported by the AWWA Research Foundation. The following are the reported empirical equations for various HAA species (Singer, 1999):

$$MCAA = 1.634(TOC)^{0.753}(Br+0.01)^{-0.085}(pH)^{-1.124}(Cl_2Dose)^{0.509}t^{0.3}$$

$$DCAA = 0.605(TOC)^{0.291}(UV)^{0.726}(Br+0.01)^{-0.568}(Cl_2Dose)^{0.48}(Temp)^{0.665}t^{0.239}$$

$$TCAA = 87.182(TOC)^{0.355}(UV)^{0.901}(Br+0.01)^{-0.679}(pH)^{-1.732}(Cl_2Dose)^{0.881}t^{0.264}$$

$$MBAA = 0.176(TOC)^{0.1.664}(UV)^{-0.624}(Br)^{0.795}(pH)^{-0.927}(Temp)^{0.45}t^{0.145}$$

$$DBAA = 84.94(TOC)^{-0.62}(UV)^{0.651}(Br)^{1.073}(Cl_2Dose)^{-0.2}(Temp)^{0.657}t^{0.12}$$

The database for developing these equations included:

- TOC values ranging from 2.8 to 11 mg/L
- Reaction time ranged from 0.1 to 105 hours
- Temperature ranged from 13 to 20 ºC
- pH ranged from 5.6 to 9.0
- UV absorbance ranged from 0.05 to 0.38 cm-1
- Bromide levels ranged from 0.005 to 0.430 mg/L
- Chlorine dosages ranged from 3.0 to 25.0 mg/L

The parameters used in these equations to predict HAA species levels are of interest in this study for comparison purposes with what parameters are most significant in promoting HAA growth in the province.

These equations were incorporated into the Water Treatment Plant Simulation computer program developed for the USEPA. These equations are based on raw water chlorination, and only represent the central tendency of the database from which they were developed.

Communities

Eleven communities were selected for this study comprising of a variety of different types of water distribution systems (long linear system, system with tank, system with fish plant demand). The communities selected include:

- Arnold's Cove- Eastern
- Brighton- Central
- Channel- Port aux Basque- Western
- Grand Bank- Eastern
- Keels- Eastern
- Norris Arm- Central
- Point of Bay- Central
- St. Paul's- Western
- St. George's- Western
- Steady Brook- Western
- Sunnyside- Eastern

HAA samples were taken at 4 different sites in the distribution system representing the beginning (1), beginning to middle (2), middle to end (3), and end (4) of the distribution system. Samples were collected for each season (spring, summer, fall, winter) over the 2008-09 drinking water sampling year.

All communities selected have a surface water source. Table 5 provides average values for the main HAA precursors in all surface water sources in Newfoundland and Labrador from winter 2001 to spring 2009. DOC, pH and bromide are regularly sampled for as part of the drinking water quality monitoring program. Average pH was 6.43 and average DOC was 6.30 mg/L.

Table 5: Surface water quality characteristics, winter 2001 to spring 2009

	pH	DOC (mg/L)	Bromide (mg/L)
Mean	6.43	6.30	0.013
Minimum	4.09	0	0
Maximum	8.58	27.9	0.43

Arnolds Cove

The Arnolds Cove water distribution system is a linear system approximately 9.4 km long. Source water quality is typical of the province. Water demand in the system varies greatly with the operation of the fish plant.

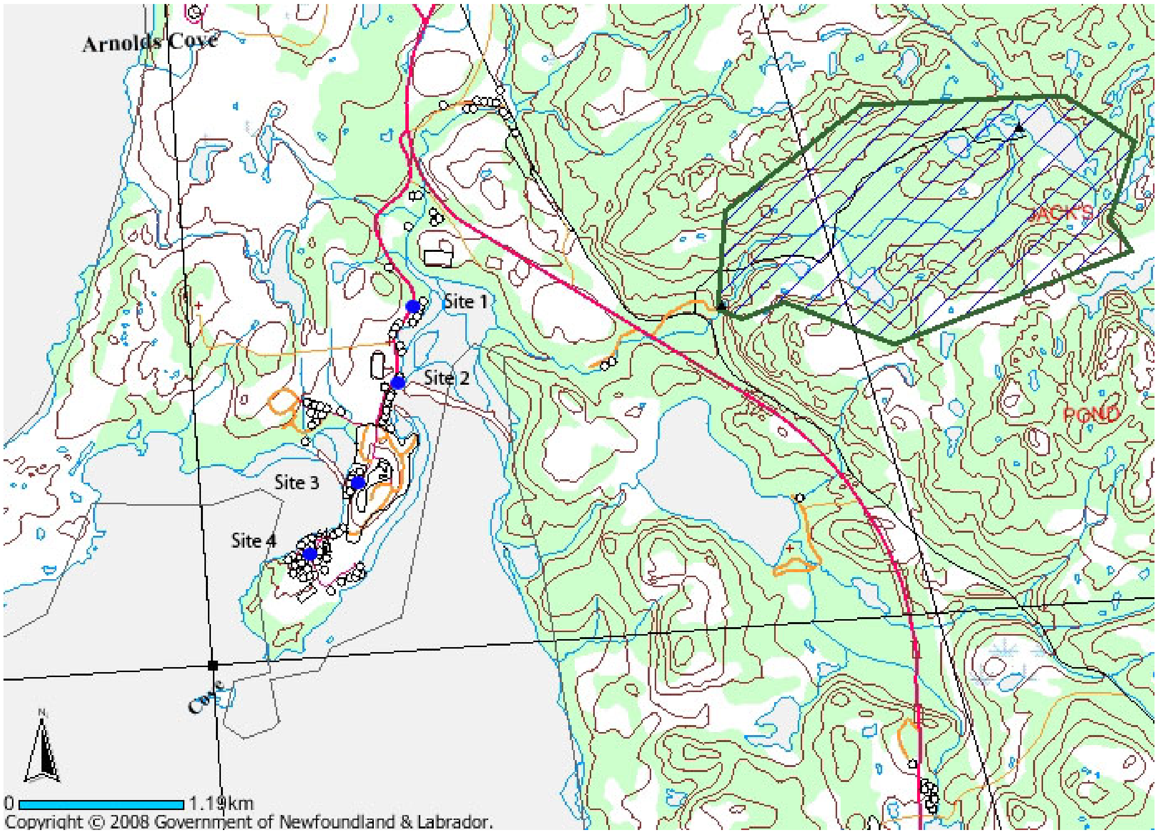

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Figure 5: Arnolds Cove

Table 6: Arnolds Cove distribution system characteristics

Treatment	gas
Pop	1003
Fishplant	yes
Type	linear
Tank	no
Booster	no
Q (m^3/d)	1090-5996
Retention Time (h)	9.8-53
Peak HAA Location	2,3,4
Average HAA5 (ug/L)	151
Average Free Cl (mg/L)	0.62
Cl dose (mg/L)	4.17
DOC (mg/L)	5.29
pH	6.41

Brighton

Brighton has a linear distribution system approximately 3.1 km in length. When the pump is working, water is pumped to the town and tank, otherwise water to the town is fed from the tank. The tank takes approximately 6 hours to fill and 30 hours to empty. The tank is at the beginning of the system, has a single inlet/outlet, and 25% of the tank volume is inactive. Source water displays above average DOC.

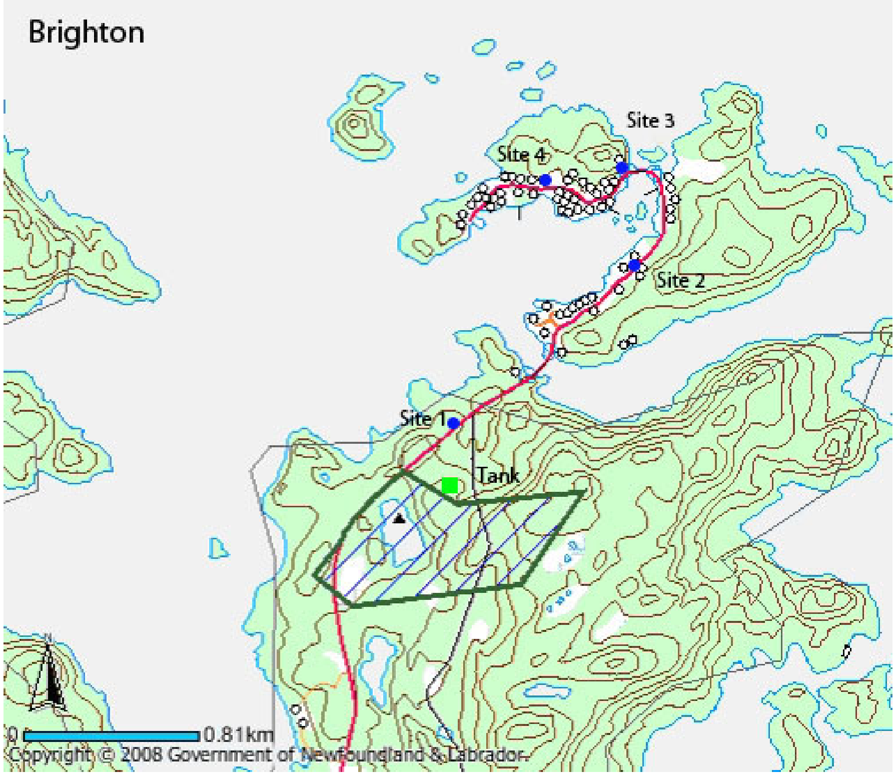

Figure 6: Brighton

Table 7: Bright distribution system characteristics

Treatment	liquid
Pop	203
Fishplant	no
Type	linear
Tank	yes
Booster	no
Q (m^3/d)	115
Retention Time (h)	102
Peak HAA Location	1,3,4
Average HAA5 (ug/L)	382
Average Free Cl (mg/L)	0.47
Cl dose (mg/L)	6.28
DOC (mg/L)	6.59
pH	6.99

Channel- Port aux Basques

Channel-Port aux Basques has a branched system with multiple dead ends. The distance from the intake to the end of the system is approximately 5 km. Source water quality displays low pH and high DOC. The town has a water treatment plant that treats water near the intake. There is also fishplant demand on this system.

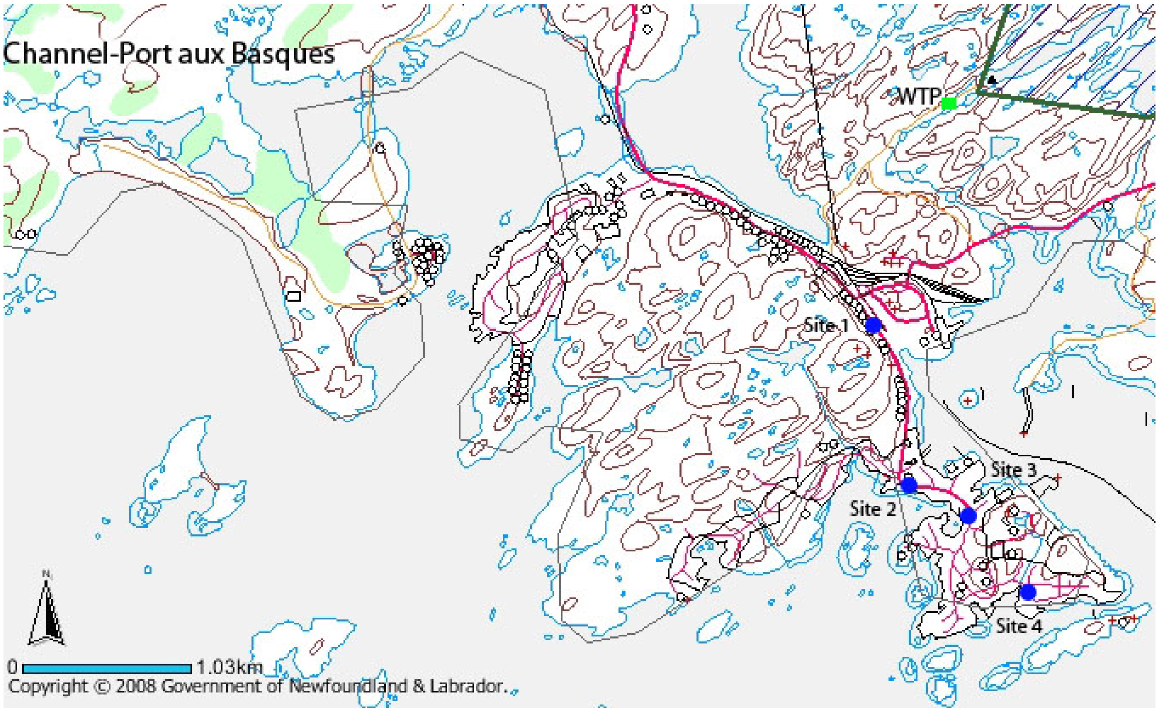

Figure 7: Channel- Port aux Basques

Table 8: Channel-Port aux Basques distribution system characteristics

Treatment	gas, WTP-Degremont
Pop	4319
Fishplant	yes
Type	branched
Tank	yes
Booster	no
Q (m^3/d)	2160
Retention Time (h)	
Peak HAA Location	1,3,4
Average HAA5 (ug/L)	106
Average Free Cl (mg/L)	0.42
Cl dose (mg/L)	
DOC (mg/L)	7.06
pH	5.32

Grand Bank

The Grand Bank distribution system is branched with multiple dead ends. The system has a tank and fishplant demand. Source water quality is slightly above average for the province.

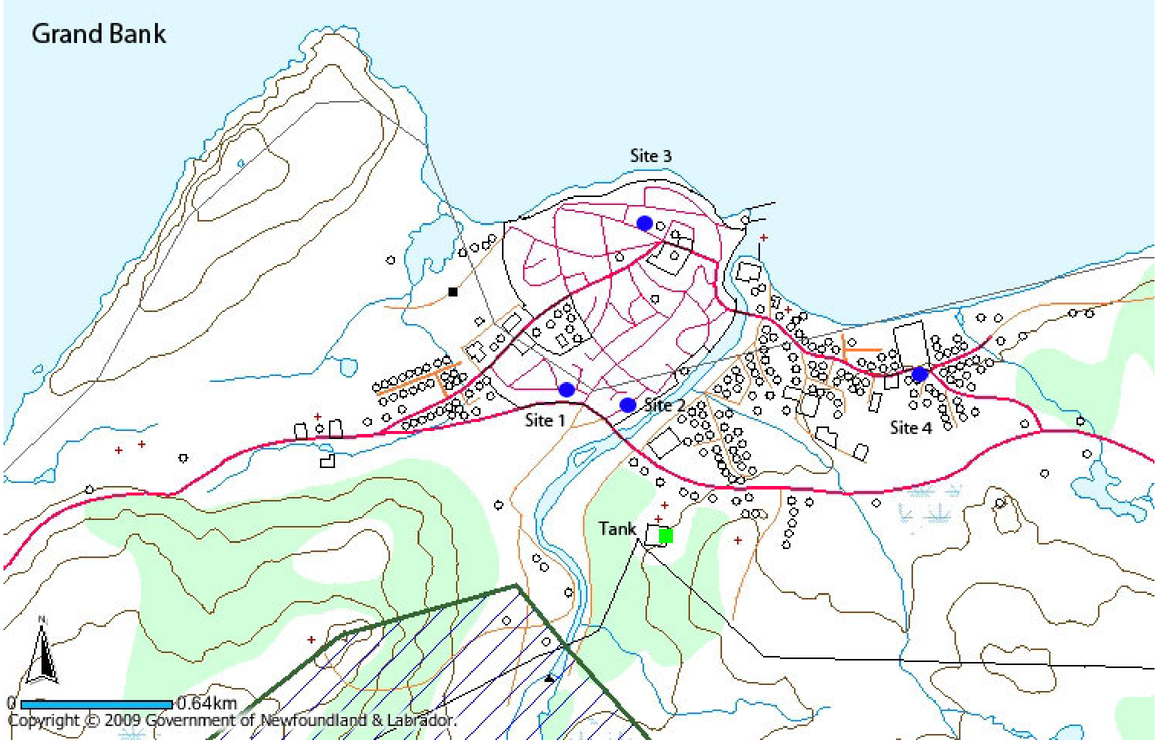

Figure 8: Grand Bank

Table 9: Grand Bank distribution system characteristics

Treatment	gas, multi-media pressure filter
Pop	2580
Fishplant	yes
Type	branched
Tank	yes
Booster	no
Q (m^3/d)	1,609
Retention Time (h)	
Peak HAA Location	2,3,4
Average HAA5 (ug/L)	116
Average Free Cl (mg/L)	0.19
Cl dose (mg/L)	
DOC (mg/L)	4.43
pH	6.51

Keels

The Keels water distribution system is a small branched system approximately 2 km in length from the intake to the last user. Source water quality has low pH and high DOC.

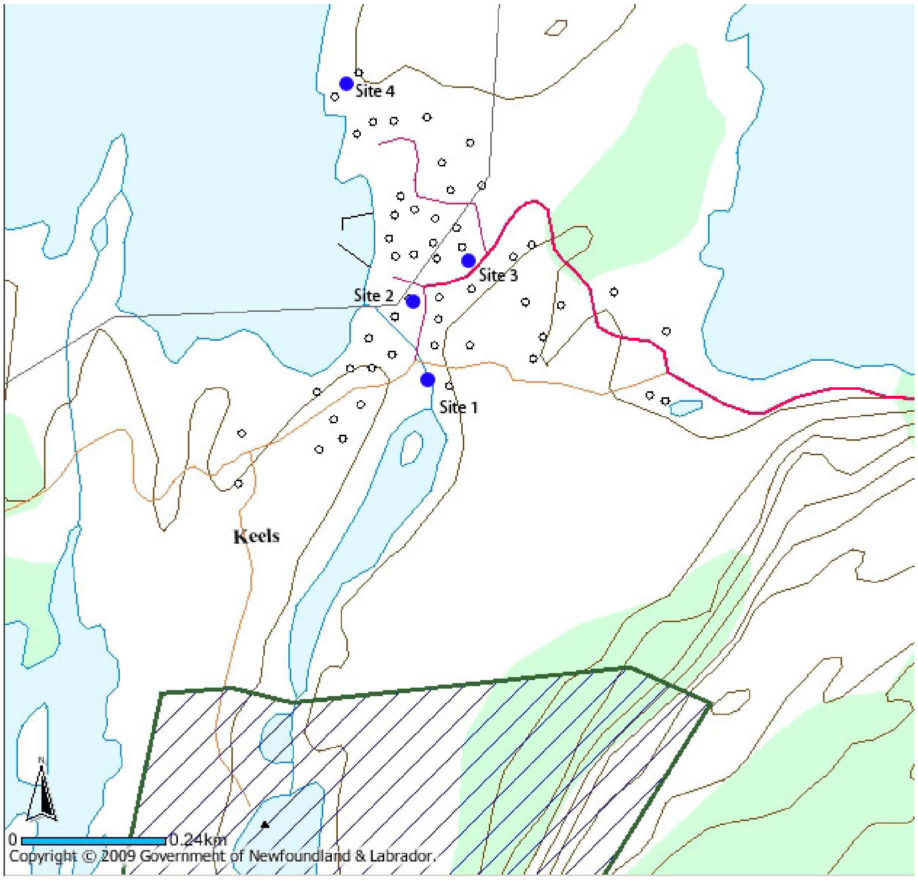

Figure 9: Keels

Table 10: Keels distribution system characteristics

Treatment	liquid
Pop	73
Fishplant	no
Type	branched
Tank	no
Booster	no
Q (m^3/d)	26
Retention Time (h)	
Peak HAA Location	1,3
Average HAA5 (ug/L)	624
Average Free Cl (mg/L)	0.48
Cl dose (mg/L)	
DOC (mg/L)	8.73
pH	5.14

Norris Arm

The Norris Arm distribution system is a linear system approximately 6.5 km long from the intake to the end of the system. Source water quality is slightly above average for the province.

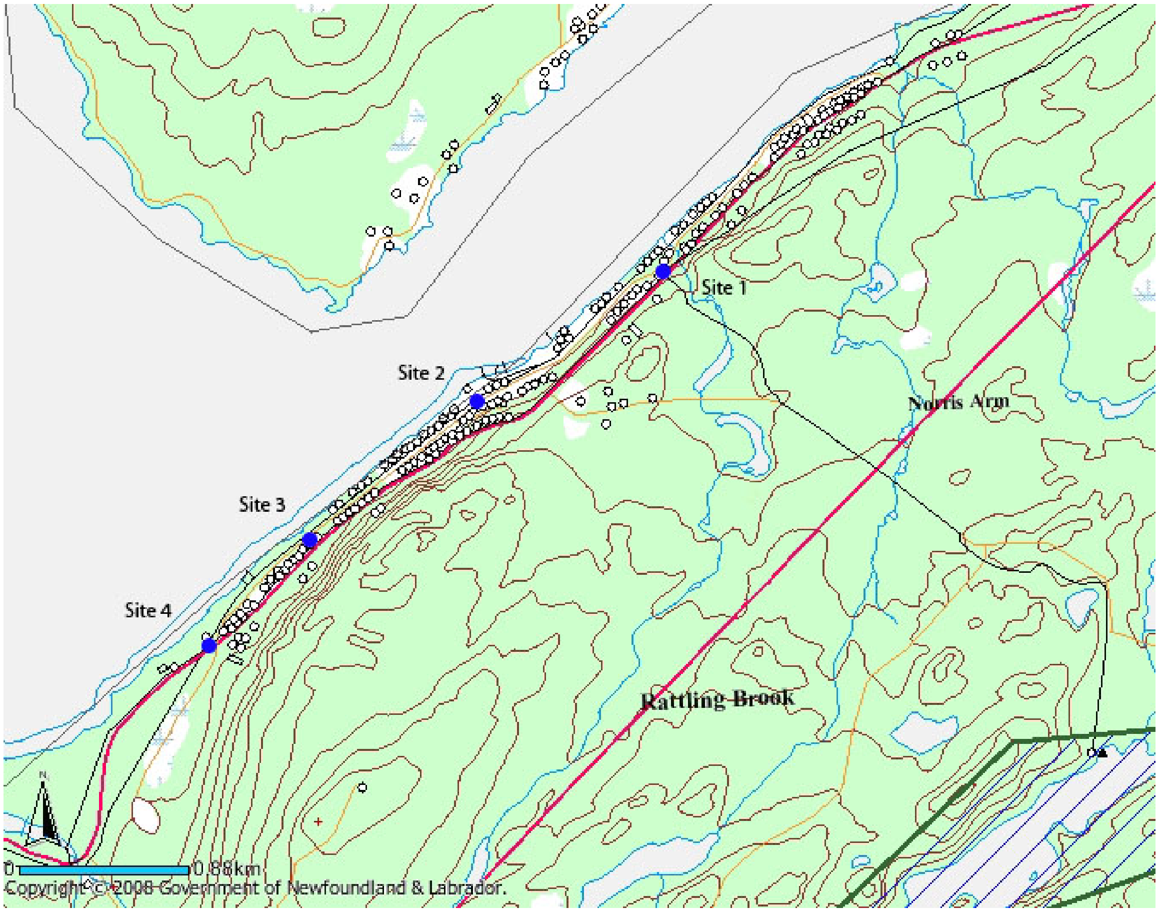

Figure 10: Norris Arm

Table 11: Norris Arm distribution system characteristics

Treatment	gas
Pop	843
Fishplant	no
Type	linear
Tank	no
Booster	no
Q (m^3/d)	654
Retention Time (h)	
Peak HAA Location	3
Average HAA5 (ug/L)	130
Average Free Cl (mg/L)	0.25
Cl dose (mg/L)	
DOC (mg/L)	4.43
pH	6.69

Point of Bay

Point of Bay has a linear distribution system approximately 6 km long. There is a tank on the distribution system. Source water quality is slightly above average for the province.

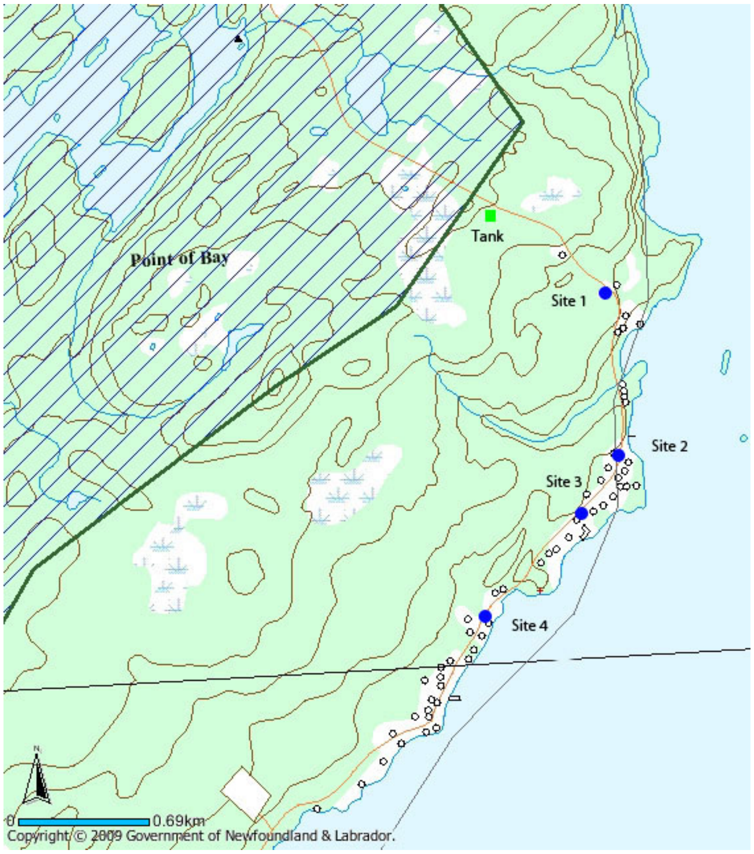

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Figure 11: Point of Bay

Table 12: Point of Bay distribution system characteristics

Treatment	liquid
Pop	153
Fishplant	no
Type	linear
Tank	yes
Booster	no
Q (m^3/d)	68
Retention Time (h)	
Peak HAA Location	1,2,4
Average HAA (ug/L)	134
Average Free Cl (mg/L)	0.82
Cl dose (mg/L)	
DOC (mg/L)	4.92
pH	6.92

St. Paul's

St. Paul's has a branched, linear system approximately 6 km in length from the intake to the end. Water is pumped directly to a tank at the beginning of the system where chlorine is injected and controlled by a residual analyzer. All water to the town goes through the tank which takes 4 hours to fill and 4 hours to empty. The tank has a separate inlet and outlet, and 86% of the tank volume is inactive. Source water quality DOC is typical for the province.

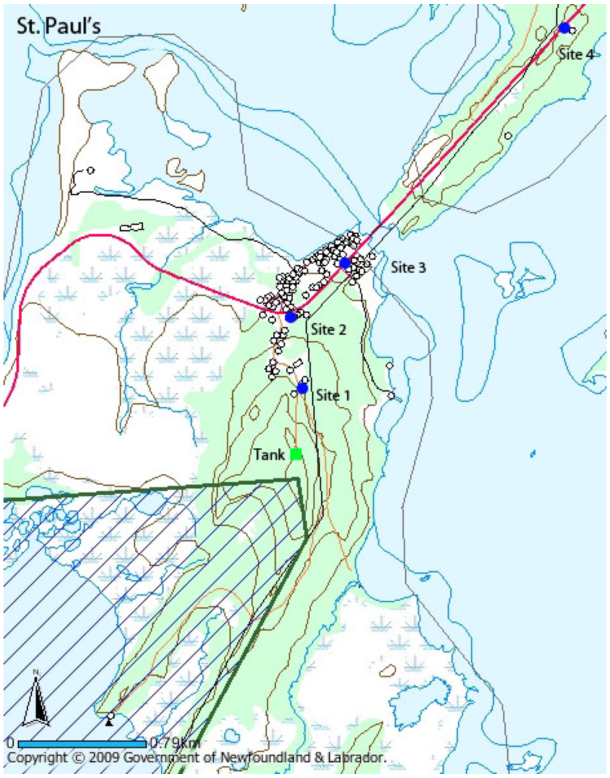

Figure 12: St. Paul's

Table 13: St. Paul's distribution system characteristics

Treatment	gas
Pop	309
Fishplant	no
Type	branched
Tank	yes
Booster	no
Q (m^3/d)	220
Retention Time (h)	59
Peak HAA Location	2,3
Average HAA (ug/L)	279
Average Free Cl (mg/L)	0.43
Cl dose (mg/L)	12.6
DOC (mg/L)	6.16
pH	7.33

St. George's

The St. George's distribution system is a long, branched system approximately 9.2 km from the intake to the end of the system. There is a tank on the system. Source water quality is high in DOC.

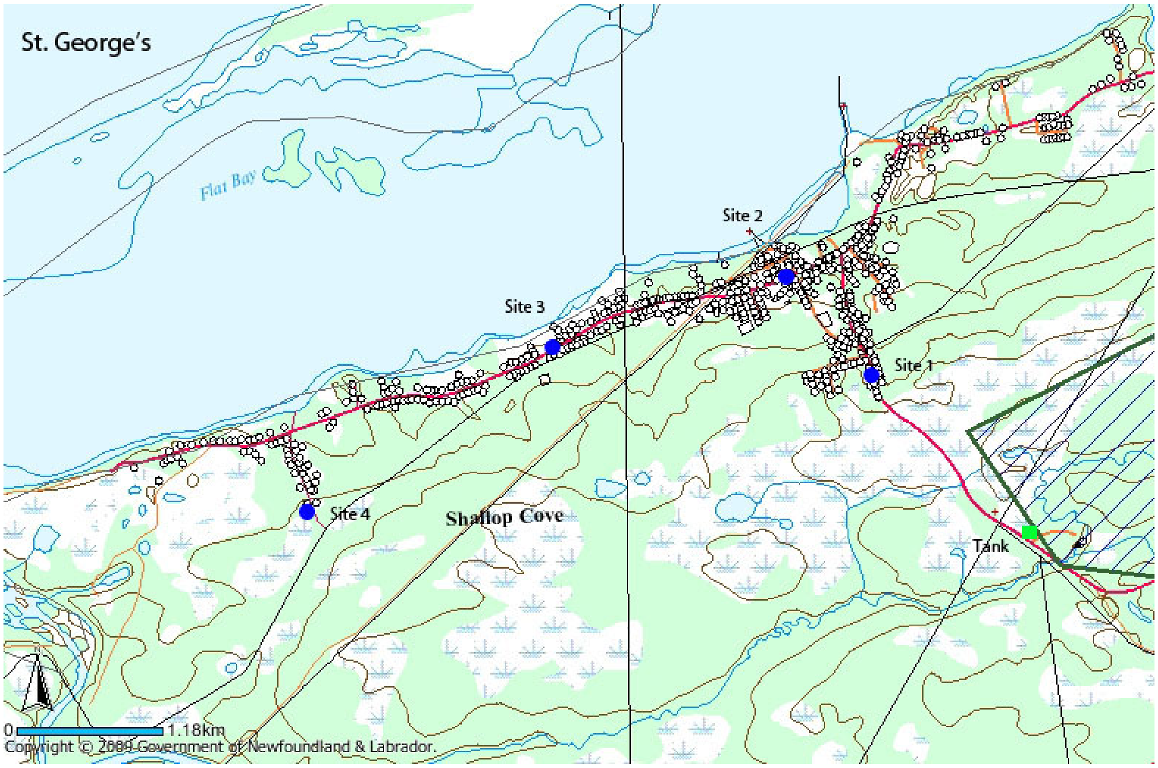

Figure 13: St. George's

Table 14: St. George's distribution system characteristics

Treatment	gas
Pop	1246
Fishplant	no
Type	branched
Tank	yes
Booster	no
Q (m^3/d)	623
Retention Time (h)	
Peak HAA Location	1,2
Average HAA (ug/L)	365
Average Free Cl (ug/L)	0.90
Cl dose (mg/L)	
DOC (mg/L)	8.51
pH	6.96

Steady Brook

The Steady Brook distribution system is a branched system that runs approximately 4.5 km from the intake to the end of the system. Source water quality has low pH and high DOC.

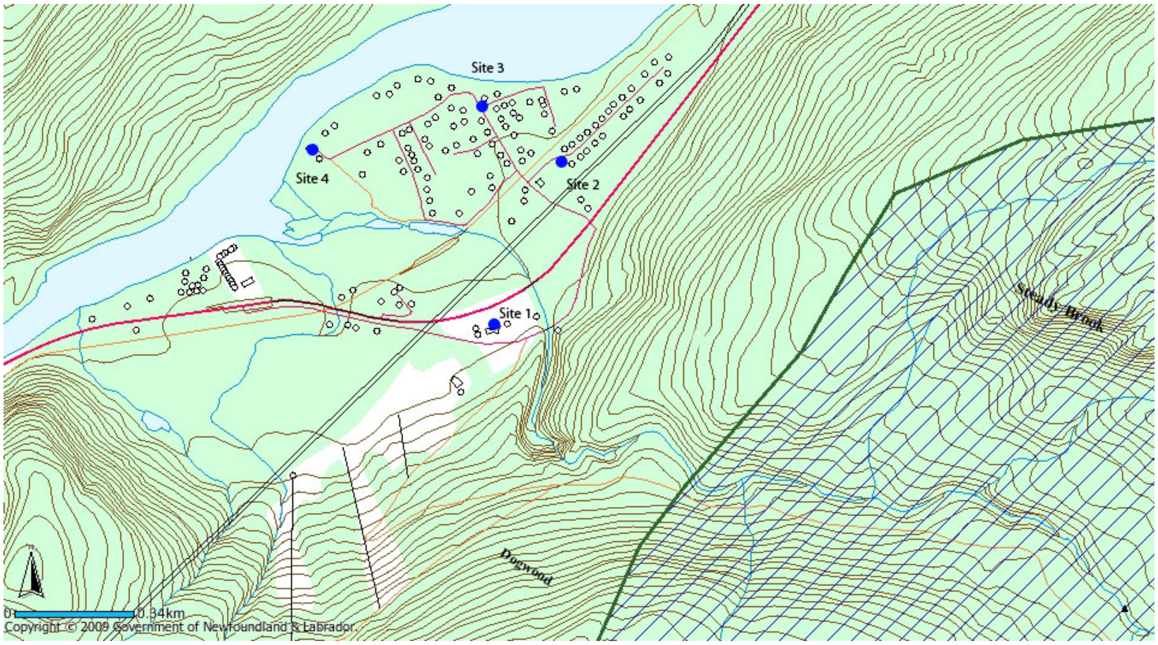

Figure 14: Steady Brook

Table 15: Steady Brook distribution system characteristics

Treatment	gas, filtration
Pop	394
Fishplant	no
Type	branched
Tank	no
Booster	no
Q (m^3/d)	142
Retention Time (h)	22.4
Peak HAA Location	2,3,4
Average HAA (ug/L)	188
Average Free Cl (mg/L)	0.40
Cl dose (mg/L)	
DOC (mg/L)	6.73
pH	5.94

Sunnyside

The Sunnyside distribution system is a linear system approximately 7.5 km long. Source water quality has below average pH.

Figure 15: Sunnyside

Table 16: Sunnyside distribution system characteristics

Treatment	liquid
Pop	450
Fishplant	no
Type	linear
Tank	no
Booster	no
Q (m^3/d)	790
Retention Time (h)	
Peak HAA Location	1,3
Average HAA (ug/L)	211
Average Free Cl (mg/L)	0.19
Cl dose (mg/L)	
DOC (mg/L)	6.06
pH	6.07

Results

HAA samples have only been collected regularly on all water distribution systems in the province since the spring of 2008 with the introduction of the new Health Canada guideline of 80 µg/L for HAA5. Prior to this, HAA samples were collected at least once for each distribution system that was chlorinating, and more regularly for systems servicing large populations or that displayed high HAA levels.

The Canadian Association for Laboratory Accreditation (CALA) has set a fixed error acceptance limit of 40% for each HAA species within a concentration range of 10-50 µg/L. The minimum detection limit for either HAA species is also 5 µg/L. Every season the DOEC performs QA/QC tests on drinking water quality samples. Table 17 indicates the relative error for MCA, DCA and TCA for samples taken in winter 2009. All HAA samples are within the allowable error range. The error range for DCA and TCA is less than that for MCA as values for these HAA species tend to exceed the concentration range for the fixed error limit. The values for MCA tend to be less than the concentration range for the fixed error limit.

Table 17: Error ranges for winter 2009 DOEC HAA samples

HAA Species	Error Range (%)	Number of Samples not in 10-50 µg/L Concentration Range
MCA	0-35.3	14 out of 15 less then
DCA	0-14.3	11 out of 15 exceed
TCA	0-11.4	9 out of 15 exceed

HAA Precursors

Correlation analysis was performed on related source, tap, THM and HAA samples for each of the 11 communities involved in the study as summarized in Table 18. The sample size for the correlation analysis varied from 66 to 123. Results were similar to what was observed in a previous study (DOEC, 2009); however, there were slight differences. There was a significant positive correlation between HAA levels and total THMs (and bromodichloromethane- BDCM); source water DOC, colour and water temperature; and tap water total and free chlorine. The correlation between HAAs and pH was not significant although it was negative (ie. as pH decreased, HAAs increased). HAAs also displayed a negative correlation with site number, indicating that HAAs tended to decrease towards the end of the distribution system. In the previous analysis the correlation with iron was significant and that of water temperature and free chlorine was not.

Table 18: HAA-water quality correlation analysis of 11 study communities

Variable	Pearson Correlation Coefficient for HAAs	P-Value	Sample Size
Total THM	0.726*	0.000	123
Source DOC	0.554*	0.000	72
BDCM	0.331*	0.000	123
Total Chlorine	0.269*	0.003	122
Source Water Temperature	0.358*	0.003	66
Source Colour	0.328*	0.005	72
Free Chlorine	0.208*	0.021	122
Source Iron	0.218	0.066	72
Site Number	-0.072	0.226	285
Source Bromide	-0.083	0.487	72
Source pH	-0.057	0.633	72
Source Manganese	-0.035	0.767	72
Source Turbidity	0.012	0.917	72

statistically significant at α = 0.05

Seasonal averages of HAA values from spring 2008 to winter 2009 for the 11 communities studied indicate that HAA levels peak in the summer, and are lowest in the fall as indicated in Figure 16.

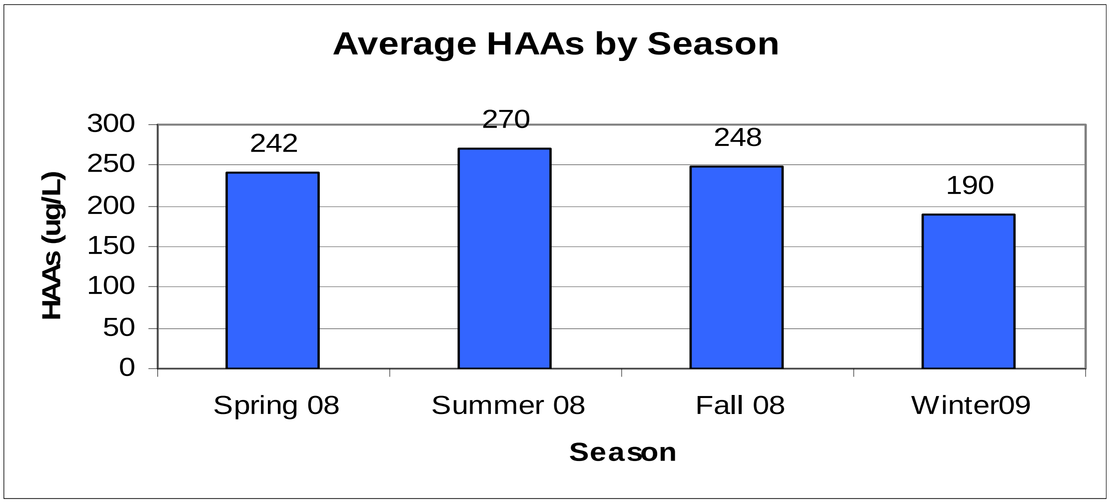

Figure 16: Average HAAs by season

A correlation analysis was performed on average HAA levels and system characteristics for each of the 11 communities in the study as summarized in Table 19. The only significant result was the correlation between HAAs and DOC which has already been identified. Of interest is the fact that smaller systems with smaller populations and flows tend to have higher HAA levels.

Table 19: HAA-distribution system characteristics correlation analysis of 11 study communities

Variable	Pearson Correlation Coefficient for HAAs	P-Value	Sample Size
Population	-0.461	0.153	11
Q (m^3/s)	-0.554	0.077	11
Retention Time (h)	0.842	0.158	4
Average Free Chlorine (mg/L)	0.219	0.517	11
Chlorine Dose (mg/L)	0.301	0.806	3
DOC (mg/L)	0.772*	0.005	11
pH	-0.193	0.569	11

statistically significant at α = 0.05

An analysis of variance (ANOVA) statistical test was carried out to see if there was any difference in HAA levels from distribution systems with tanks and without, with fishplants and without, and between systems that are linear versus branched as summarized in Table 20. Results indicate there is no significant difference in mean HAA levels in either case. However, systems with tanks, systems without fishplants, and systems that were branched all displayed higher mean HAA levels.

Table 20: ANOVA of mean community HAAs with system characteristics as analysis factor

Status of Watershed	Number of Watersheds	Mean HAA (Standard Deviation)	p-value
With Tank	6	260.8 (± 205.5)	0.770
Without Tank	5	230.3 (± 127.5)	
Linear	5	201.6 (± 105.9)	0.447
Branched	6	279.7 (± 195.5)	
Fishplant	3	124.3 (± 23.6)	0.131
No Fishplant	8	289.1 (± 165.8)	

statistically significant at α = 0.05

HAA Speciation

From the 11 communities studied, average DCA (123 ug/L) and TCA (120 ug/L) over the period of record were roughly equivalent. A previous study indicated that TCA was the predominant HAA species (DOEC, 2009) in the province. Average values for the other species that make up HAA5 were comparatively insignificant: MCA (4.43 ug/L), MBA (0 ug/L), and DBA (0.03 ug/L). Figure 17 indicates average DCA and TCA over the period of record in the 11 communities studied. DCA was the predominant HAA species in 7 out of 11 communities.

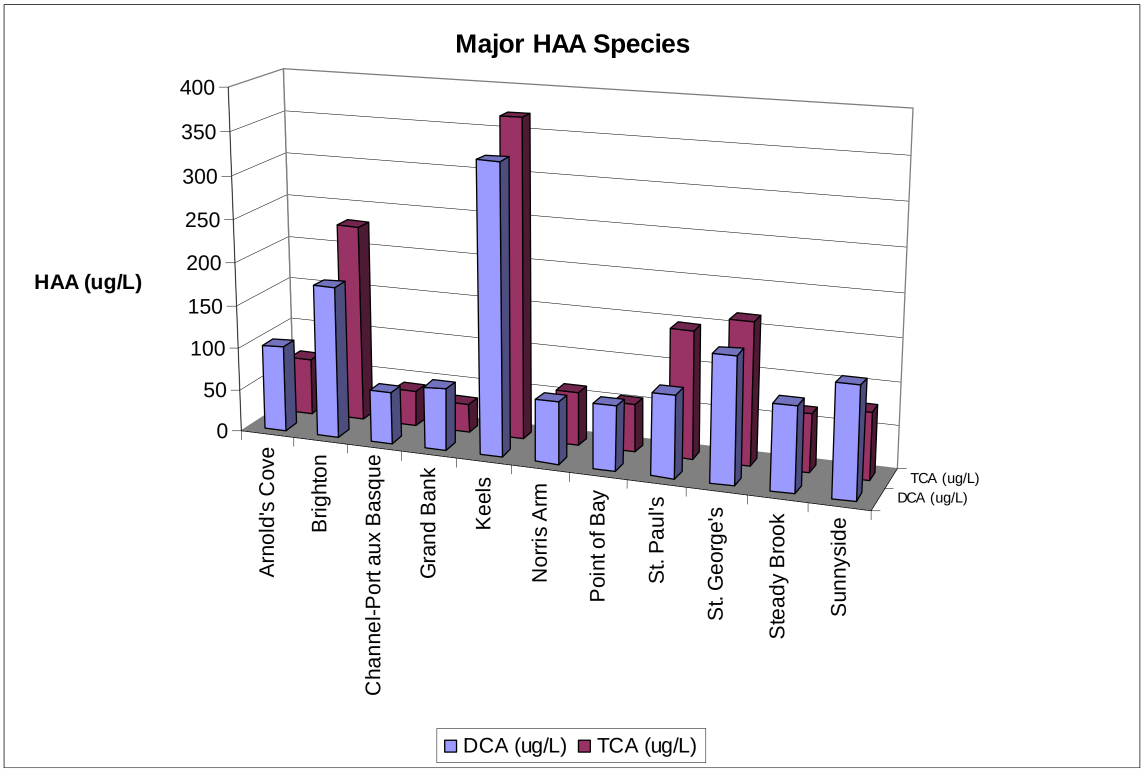

Figure 17: Major HAA species averages in 11 study communities

From the 11 communities studied, DCA and TCA make up the majority of HAA5, 50% and 48% respectively as shown in Figure 18. Brominated HAAs are barely present in most communities.

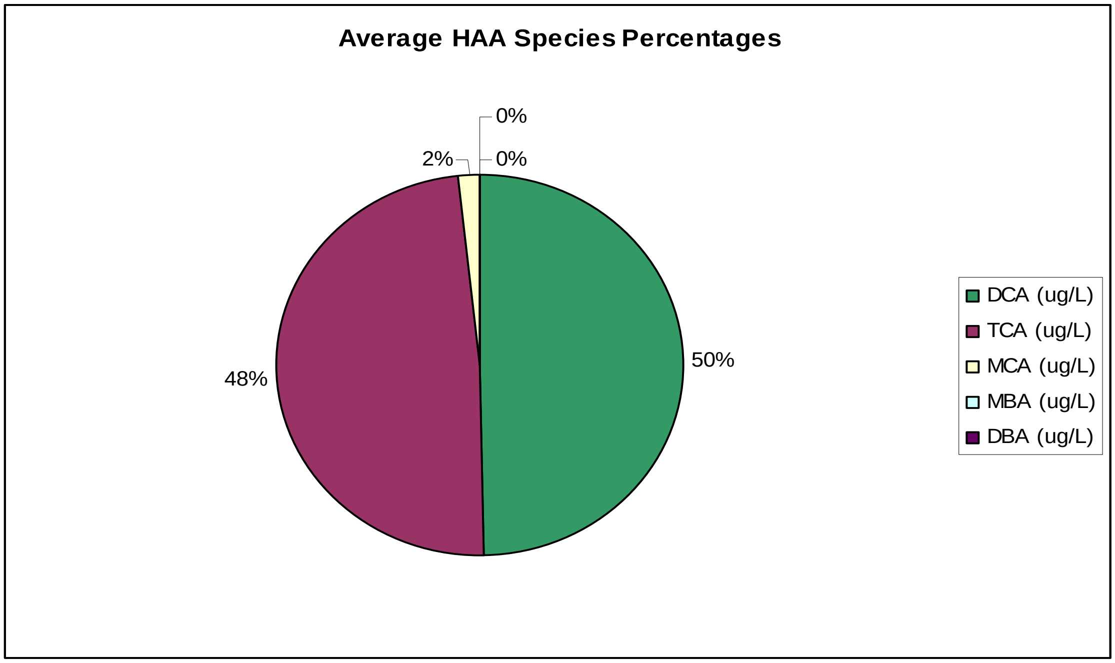

Figure 18: Makeup of average HAA5

A correlation analysis was performed for DCA and TCA and various precursors of interest as shown in Table 21. DOC, total chlorine, free chlorine and water temperature were all significantly and positively correlated with both HAA species. The major difference observed between DCA and TCA was that the correlation between site number for DCA was very close to being significant, whereas it was no where near to being significant for TCA. This seems to indicate that DCA values tend to peak earlier in the distribution system and then decay as compared with TCA.

Table 21: DCA and TCA-water quality correlation analysis of 11 study communities

Variable	Pearson Correlation Coefficient for DCA	P-Value	Pearson Correlation Coefficient for TCA	P-Value	Sample Size
Source DOC	0.546*	0.000	0.511*	0.000	72
Total Chlorine	0.271*	0.003	0.234*	0.010	122
Source Water Temperature	0.262*	0.034	0.403*	0.001	66
Free Chlorine	0.204*	0.024	0.183*	0.043	122
Site Number	-0.113	0.057	-0.034	0.565	285
Source Bromide	-0.130	0.276	-0.038	0.752	72
Source pH	-0.147	0.218	0.013	0.915	72

statistically significant at $\alpha = 0.05$

Appendix A contains graphs of the variation of HAAs at different monitoring sites from spring 2008 to winter 2009 for each of the 11 communities in the study. Generally speaking the trend for HAAs over the 4 sites in the summer is one of decline, and either flat-lined or increasing in the winter. This would seem to indicate that HAA species tend to peak earlier in the distribution system in the summer and with warmer water temperatures.

Point of Maximum HAA Concentration

Appendix A contains graphs of free chlorine residual variation at different sites in the water distribution for each of the 11 communities in this study for the period from spring 2008 to winter 2009. Free chlorine residuals at the end of the distribution system are practically nonexistent for all seasons in 7 out of 11 of the communities studied. Where chlorine residual values were fairly consistent throughout the distribution system, HAA values tended to be more stable. Where there was a decrease in the free chlorine residual towards the end of the distribution system, HAA levels also tended to decrease.

Average HAA values from site 1 to 4 for this period indicate that HAAs tend to peak at site 3, however, there was little variation in the averages from site 2 and 3 as indicated in Figure 19. The lowest observed HAA average was at site 4.

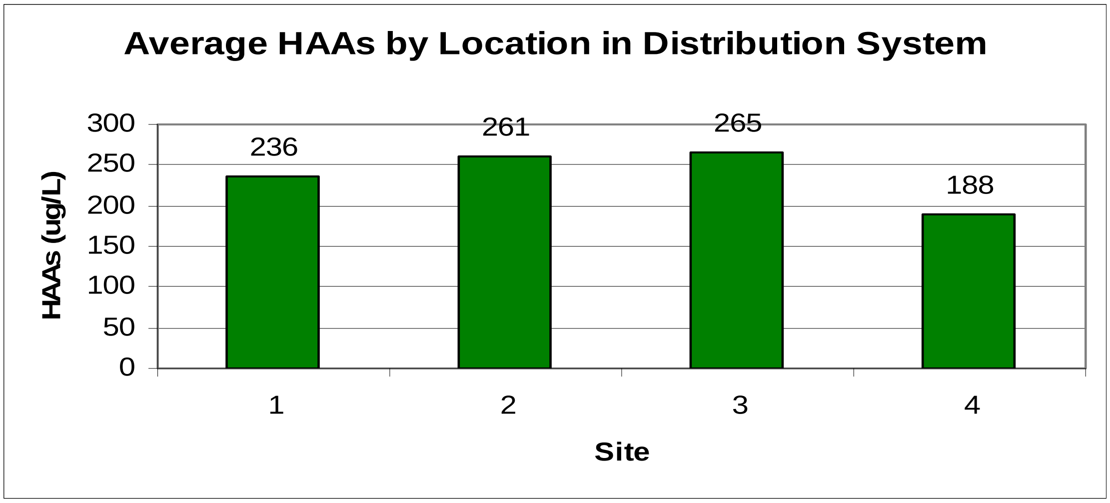

Figure 19: Average HAAs by location in distribution system

During the entire period of observation for the 11 communities, site 3 displayed the largest number of maximum HAA values as indicated in Figure 20.

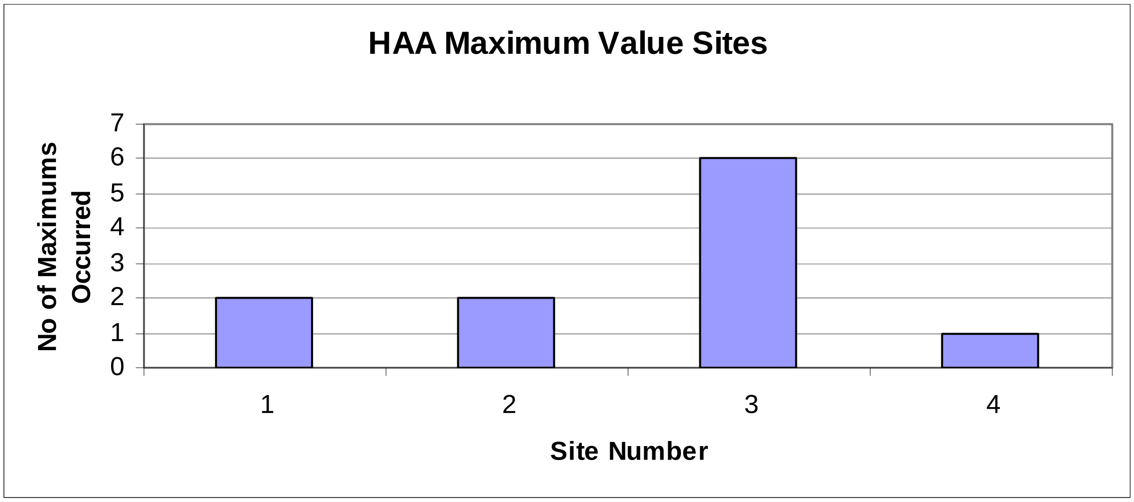

Figure 20: Location of maximum HAAs

Under USEPA Stage 2 DBP Rules, sampling sites are identified under the Initial Distribution System Evaluation (IDSE) based on areas of highest risk in the distribution system that represent the highest levels of DBPs. For regulatory compliance, systems must report the highest locational running annual average (LRAA) for HAA5 and the range of individual sample results for all monitoring locations. If more than one location exceeds the HAA5 guideline, the system must include the locational running annual averages for all locations that exceed the maximum contaminant level. Of the communities studies, Site 3 had the highest occurrence of maximum LRAAs as indicated in Figure 21. All communities had all sampling sites with LRAAs above the HAA5 guideline value with the exception of site 4 at Grand Bank. St. Paul’s and St. George’s also had significantly lower LRAA values at site 4.

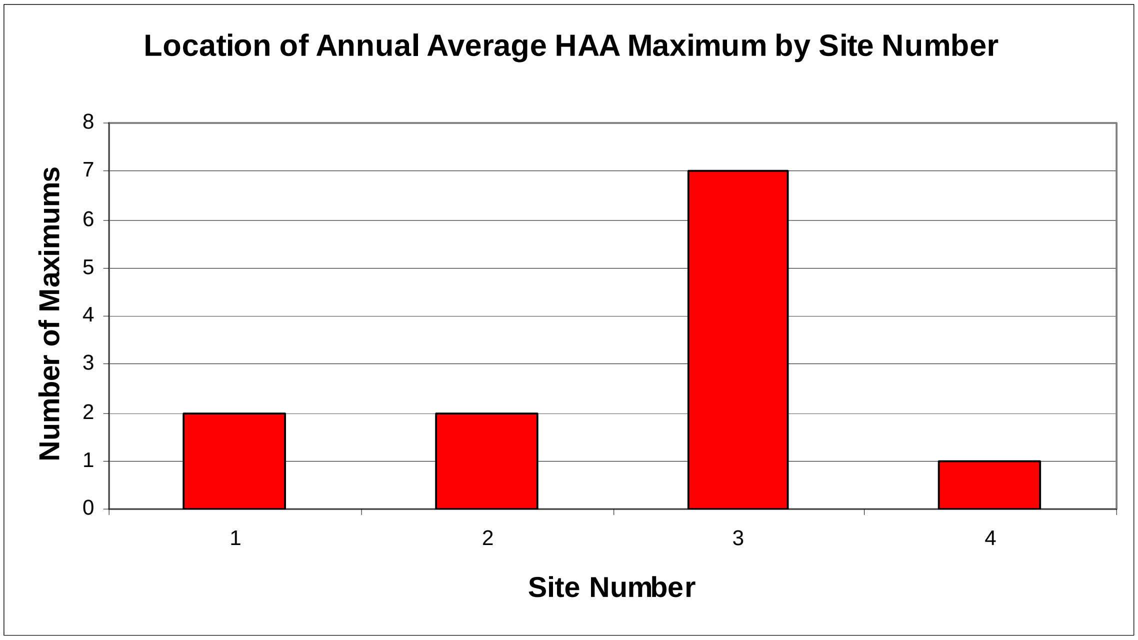

Figure 21: Location of maximum annual average HAA

Seasonal maximum HAA values are indicated in Figure 22 (there were multiple observed maximum HAA values observed in some communities in some seasons). Site 3 observed the most number of maximum HAA values in summer, fall and winter, and tied for the most number of maximum HAA values in the spring with site 2. There were more maximum HAA values observed at site 4 in the winter than for any other season. This indicates there may be less decay of HAAs in the distribution system in the winter when water temperatures are lower.

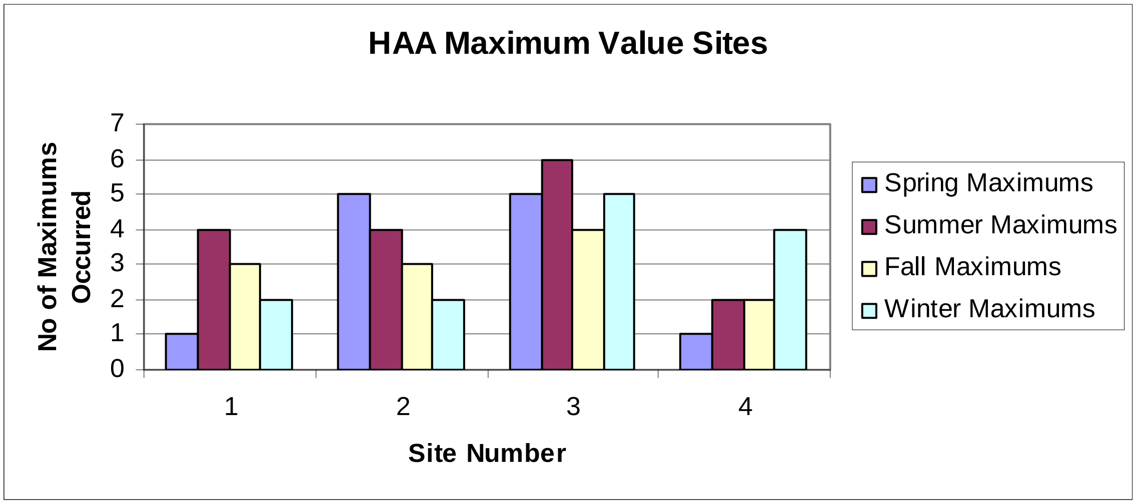

Figure 22: Location of seasonal HAA maximums

The location of the maximum average HAA value differed throughout the seasons as indicated in Figure 23. In winter and spring the average HAA value for the 11 communities was highest at site 3. In summer and fall the average HAA value for the 11 communities was highest at site 2. These results seem to indicate that the location of peak HAA values in the distribution system changes throughout the year. It also indicates that HAAs peak later in the distribution system in the winter and spring when water temperatures are colder and DOC is generally lower. HAA peaking earlier in the distribution system in the summer and fall would indicate the occurrence of HAA degradation most likely due to microbial activity in the pipe biofilm during warmer water temperatures, increased availability of DOC, and lack of chlorine residual towards the end of the distribution system.

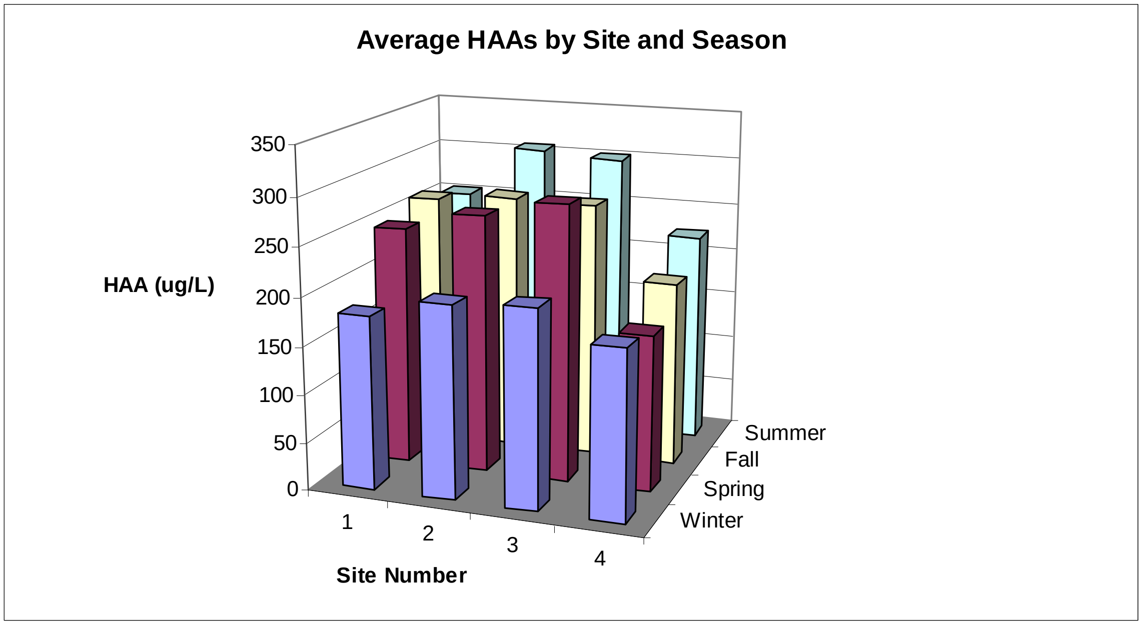

Figure 23: Average HAAs by site and season

Conclusions and Recommendations

This study has highlighted a number of issues relating to the monitoring and management of HAAs in drinking water in the province of Newfoundland and Labrador. Some observations are similar to what has been observed in other jurisdictions and in other studies specific to the province. Answers to the main questions of what is causing HAAs in the province, and where the DOEC should be sampling for HAAs have been addressed as best as possible.

The following conclusions can be made:

- There are more drinking water systems in the province experiencing HAA exceedances than THM exceedances.
- DCA and TCA are the primary HAA species observed in the province.
- DOC is significantly and positively correlated with HAA levels.
- Higher mean HAA levels were observed in systems with tanks, systems without fishplants, and branched distribution systems.

- In the majority of communities, the highest HAA levels were observed at site 3 or at three quarters of the length of the distribution system. This result was not universal or statistically significant.
- In the majority of communities, the lowest HAA levels were observed at site 4 or at the end of the distribution system.
- HAA levels peak in the summer.
- The location of peak HAA values in the distribution system tends to changes throughout the year, occurring earlier in the distribution system in summer and fall, and later in the distribution system in winter and spring.

A part of this study the following recommendations can be made:

- All distribution systems in the province should be sampled for HAAs at site 3 on the distribution system. In the absence of more conclusive information, the LRAA guideline for HAAs is most appropriate for comparison with HAA levels at site 3.

- The parameter bromide plays an important role in the formation of different HAA (and THM) species. The minimum detection limit for bromide is 0.05 mg/L. The record of data for the province of Newfoundland and Labrador indicates that bromide data is highly censored with most values less than the detection (LTD) limit. Up until spring 2004, bromide values that were LTD were recorded as half the detection limit. After this they were recorded as 0. LTD values should be recorded in a uniform manner for the entire period of record.

- For the next drinking water laboratory contract, DOEC should investigate lowering the minimum detection limit for bromide samples with the laboratory. DOEC should also include TOC and UV254 in the list of parameters regularly monitored for drinking water quality and analyzed by the chosen laboratory.

- CALA should examine what the fixed error acceptance limit should be for HAA species, particularly DCA and TCA, in a concentration range greater than 10-50 ug/L.

- More study is required to fully understand the dynamics of HAA formation potential in the province. Particularly the role of pH and organic carbon speciation.

- More study is required to fully understand the degradation of HAAs in the water distribution systems of communities in this province.

- The time of year or season of sampling may need to be considered when determining the location of HAA sampling. The HAA guideline is to be compared with a locational running annual average. This sampling location is fixed, however the location of HAA maximums is not and tends to occur earlier in the distribution system in the summer and fall.

- The period of record (spring 2008- winter 2009) was a slightly above average year for annual precipitation across the province. Precipitation and runoff events can distort DBP data. The effect of climatic variation on DBP levels should be investigated.

- Under USEPA Stage 2 DBP Rules, sampling sites for each community are identified under the IDSE, and systems must report the highest LRAA for HAA5 and the range of individual sample results for all monitoring locations. If more than one location exceeds the HAA5 guideline, the system must include the locational running annual averages for all locations that exceed the MCL. The IDSE focuses on identifying areas of highest risk in the distribution system that represent each systems highest levels of DBPs. Such an assessment may need to be considered for each community in the province, and a LRAA sampling site designated for each community at the site with the highest annual HAA average.

- While overall positively correlated, it has been observed that some communities have high HAAs but not high THMs, and vice versa. Also, some communities with low DOC have high HAAs and THMs, and vice versa. Reasons for these deviations from normal expected behaviour should be investigated as it could lead to a better understanding on the formation behaviour of these DBPs. It could also lead to improvements in precursor removal or treatment options such as targeted removal of the more problematic spectrum of NOM, optimized pH adjustment levels, optimized coagulant addition, etc.

- Removal of HAA precursors through treatment should be the preferred corrective measure for dealing with HAA levels above drinking water quality guidelines over use of alternative disinfectants. Until additional information is available on the occurrence and health effects of DBPs, precursor removal is the safer option.

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Appendix A:

HAA Data and Graphs

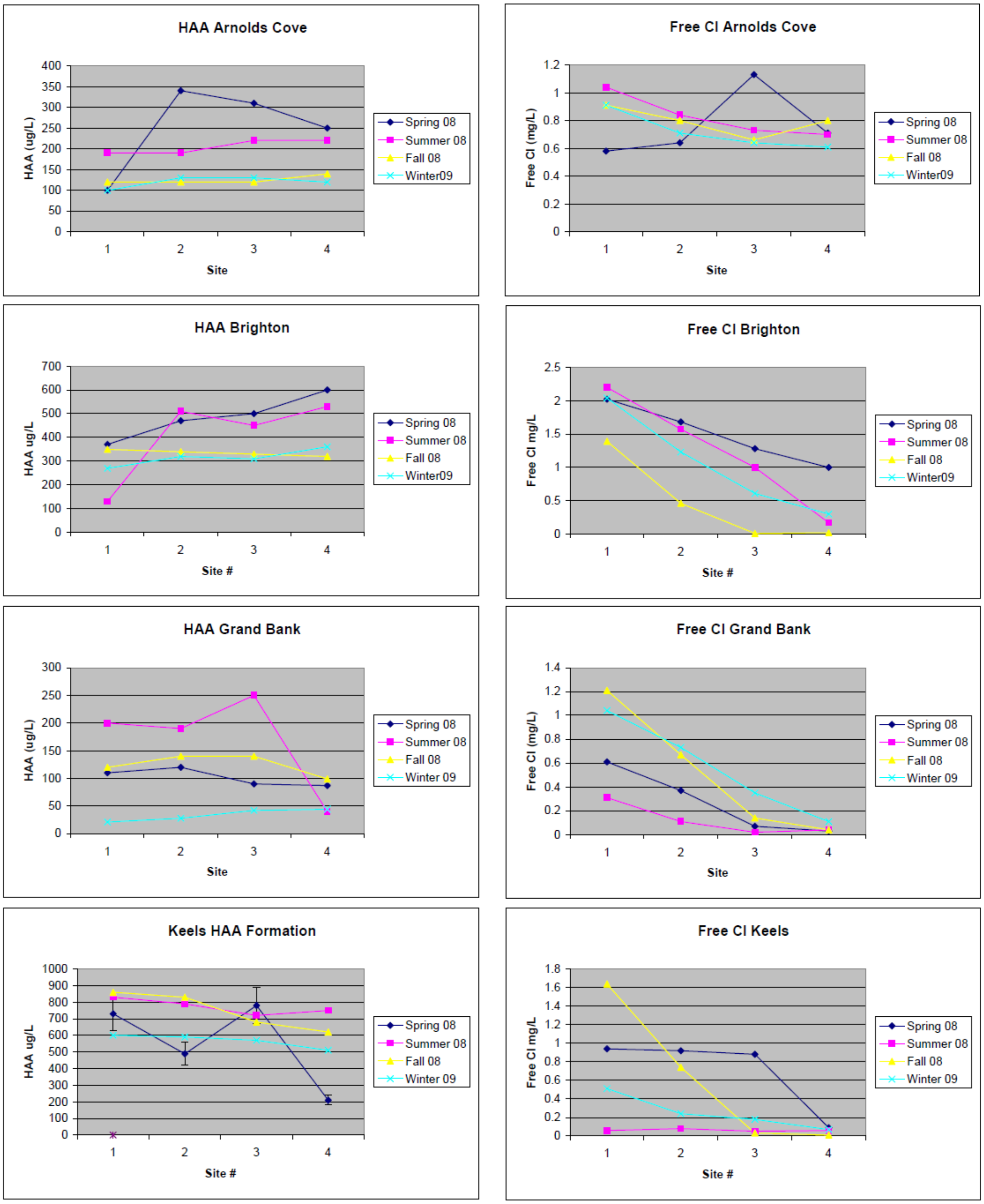
Table 1: HAA5 values in µg/L

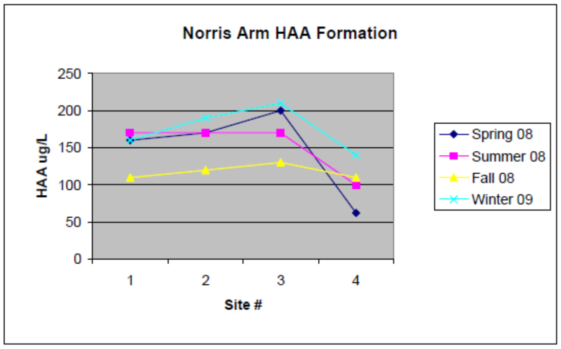
Town	Site #	Spring 08	Summer 08	Fall 08	Winter09	Average
Arnolds Cove	1	100	190	120	100	128
	2	340	190	120	130	195
	3	310	220	120	130	195
	4	250	220	140	120	183
Brighton	1	370	130	350	270	280
	2	470	510	340	320	410
	3	500	450	330	310	398
	4	600	530	320	360	453
Grand Bank	1	110	200	120	21	113
	2	120	190	140	28	120
	3	90	250	140	42	131
	4	87	40	99	44	68
Keels	1	730	830	860	600	755
	2	490	790	830	590	675
	3	780	720	680	570	688
	4	210	750	620	510	523
Norris Arm	1	160	170	110	160	150
	2	170	170	120	190	163
	3	200	170	130	210	178
	4	62	100	110	140	103
Point of Bay	1	110	230	90	110	135
	2	150	190	120	150	153
	3	130	84	110	130	114
	4	150	86	120	160	129
Port au Basques	1	76	260	120	28	121
	2	76	270	130	26	126
	3	86	290	120	25	130
	4	10	280	140	27	114
Steady Brook	1	190	87	170	180	157
	2	180	94	190	180	161
	3	220	80	230	190	180
	4	140	82	180	210	153
St. Georges	1	480	280	610	120	373
	2	540	280	530	130	370
	3	400	220	600	130	338
	4	130	8	120	64	81
St. Paul's	1	200	62	180	300	186
	2	240	320	250	300	278
	3	250	320	230	350	288
	4	39	91	110	130	93
Sunnyside	1	210	330	160	95	199
	2	180	360	200	150	223
	3	190	500	260	170	280
	4	110	260	160	160	173

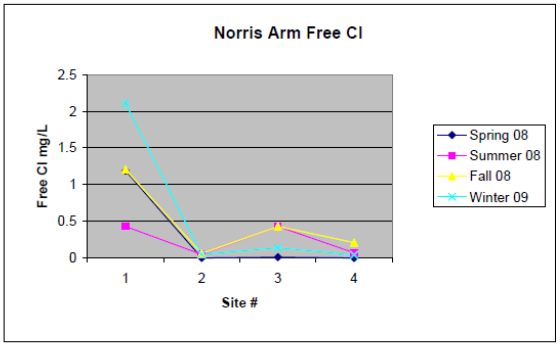
Table 2: Average HAA5 species values

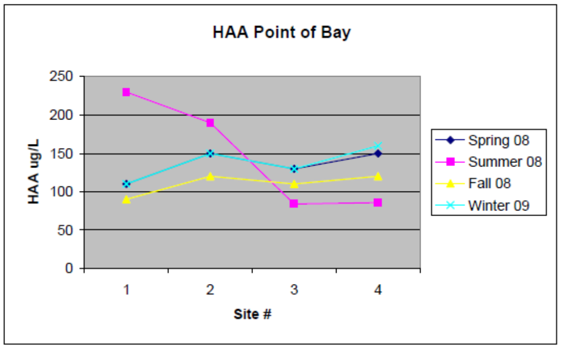
Town	DCA (ug/L)	TCA (ug/L)	MCA (ug/L)	MBA (ug/L)	DBA (ug/L)
Arnold's Cove	100	66.3	3.65	0	0
Brighton	177	231	7.65	0	0
Channel-Port aux Basque	60	42	1.1	0	0
Grand Bank	71.7	33.1	3.1	0	0
Keels	335	371	12.8	0	0
Norris Arm	72	62	0.4	0	0
Point of Bay	75	56	2.69	0	0
St. Paul's	95.2	148	4.4	0	0.3
St. George's	146	165	5.45	0	0
Steady Brook	98	68	3.7	0	0
Sunnyside	128	78	3.75	0	0

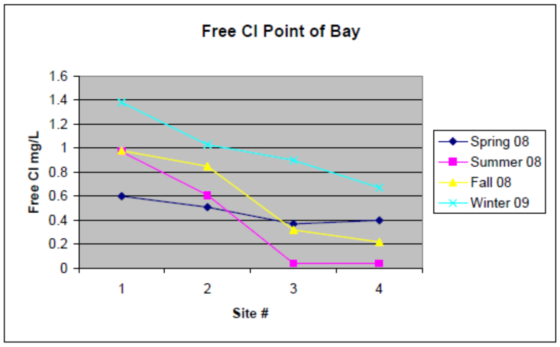
Figure 1: HAA and Free chlorine residual variation over season and site number

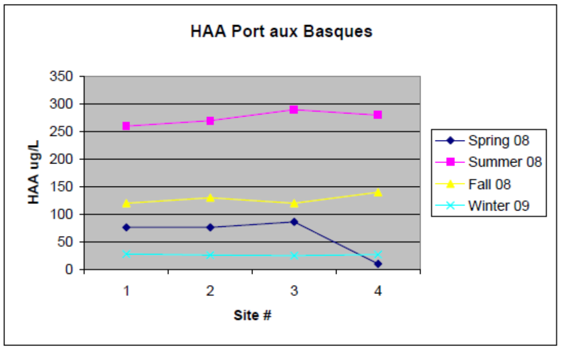


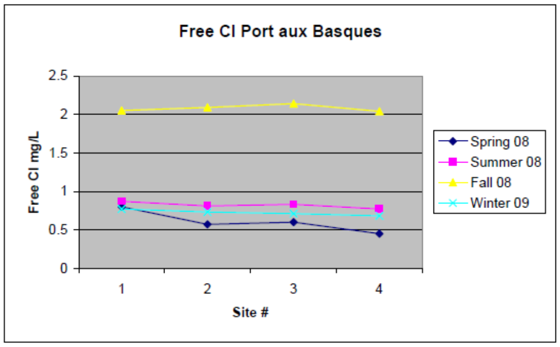

Norris Arm HAA Formation
HAA ug/L
250
200
150
100
50
0
1
2
3
4
Site #
Spring 08
Summer 08
Fall 08
Winter 09

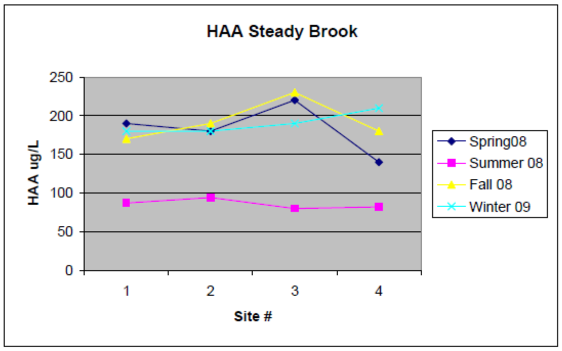

Norris Arm Free Cl
Free Cl mg/L
2.5
2
1.5
1
0.5
0
1
2
3
4
Site #
Spring 08
Summer 08
Fall 08
Winter 09

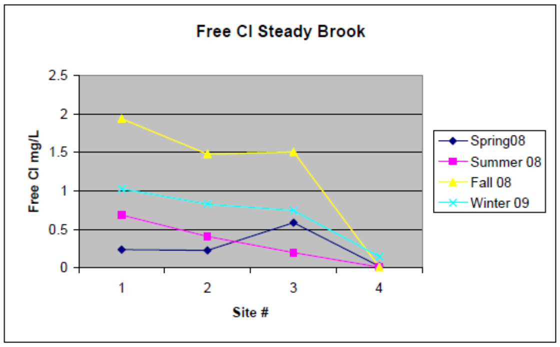

HAA Point of Bay
HAA ug/L
250
200
150
100
50
0
1
2
3
4
Site #
Spring 08
Summer 08
Fall 08
Winter 09

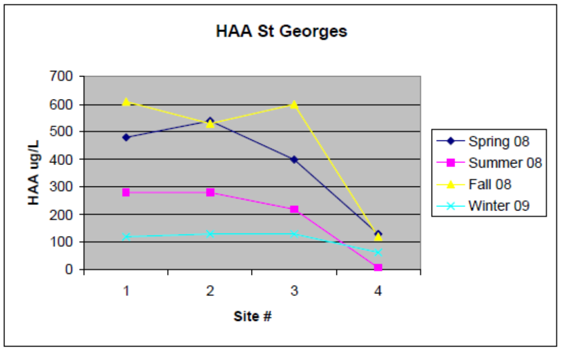

Free Cl Point of Bay
Free Cl mg/L
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
Site #
Spring 08
Summer 08
Fall 08
Winter 09

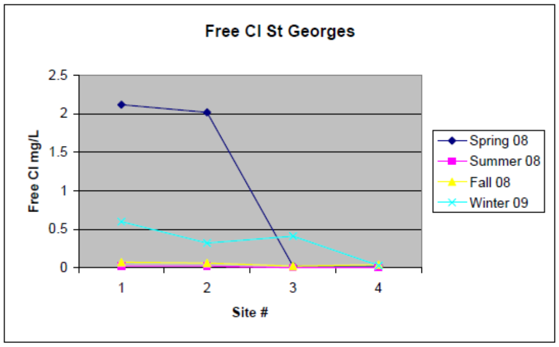

HAA Port aux Basques
HAA ug/L
350
300
250
200
150
100
50
0
1
2
3
4
Site #
Spring 08
Summer 08
Fall 08
Winter 09

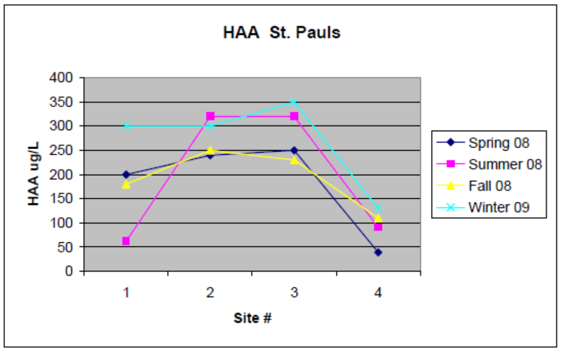

Free Cl Port aux Basques
Free Cl mg/L
2.5
2
1.5
1
0.5
0
1
2
3
4
Site #
Spring 08
Summer 08
Fall 08
Winter 09

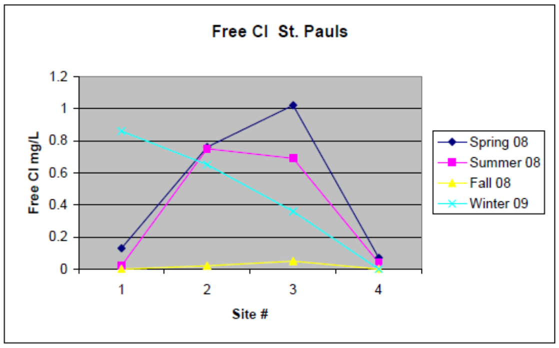

HAA Steady Brook
HAA ug/L
250
200
150
100
50
0
1
2
3
4
Site #
Spring08
Summer 08
Fall 08
Winter 09

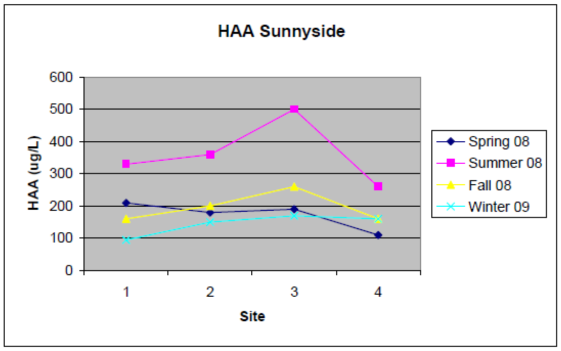

Free Cl Steady Brook
Free Cl mg/L
2.5
2
1.5
1
0.5
0
1
2
3
4
Site #
Spring08
Summer 08
Fall 08
Winter 09

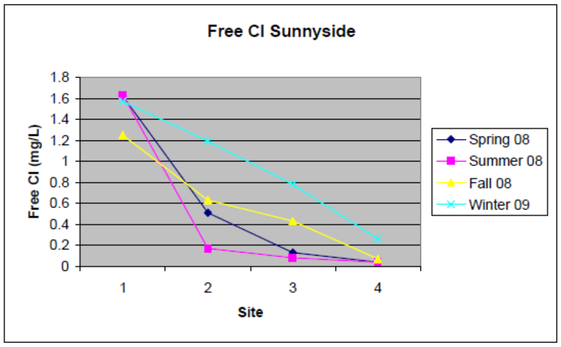

HAA St Georges
HAA ug/L
700
600
500
400
300
200
100
0
1
2
3
4
Site #
Spring 08
Summer 08
Fall 08
Winter 09


Free Cl St Georges
Free Cl mg/L
2.5
2
1.5
1
0.5
0
1
2
3
4
Site #
Spring 08
Summer 08
Fall 08
Winter 09


HAA St. Pauls
HAA ug/L
400
350
300
250
200
150
100
50
0
1
2
3
4
Site #
Spring 08
Summer 08
Fall 08
Winter 09


Free Cl St. Pauls
Free Cl mg/L
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
Site #
Spring 08
Summer 08
Fall 08
Winter 09


HAA Sunnyside
HAA (ug/L)
600
500
400
300
200
100
0
1
2
3
4
Site
Spring 08
Summer 08
Fall 08
Winter 09


Free Cl Sunnyside
Free Cl (mg/L)
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
1
2
3
4
Site
Spring 08
Summer 08
Fall 08
Winter 09