

DEVELOPMENT OF PREDICTIVE MODELS FOR DISENFECTANT BY-PRODUCTS AND FILTRATION TECHNOLOGY ASSESSMENTS IN SMALL COMMUNITY WATER SUPPLY SYSTEMS

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ABSTRACT

The main objective of this study was to conduct an in-depth investigation on the formation of disinfectant-by-products in the drinking water supply systems in small communities near St. John's. This was accomplished by taking water samples from intake, and from different nodes of water supply system after chlorination (e.g., storage tanks, main transmission lines and residential taps) in communities near St. John's. For this, Torbay and Pouch Cove communities were selected for a detailed investigation. The detailed analysis on the level of Trihalomethanes and Haloacetic acids was conducted for these two communities with and without filtration. The levels of DBPs in these communities were found much higher than the Canadian guidelines. Other objective of this study was to design a cost-effective filtration system to reduce trihalomethanes (THMs) and haloacetic acids (HAAs) in the drinking water systems. To reduce the concentration of THMs and HAAs, a series of experiments were conducted on tap water from Pouch Cove using an inexpensive adsorbent. The results show more than 95% removal of THMs and a 35% of HAAs in the Pouch Cove drinking water using activated carbon. These preliminary analysis shows a great potential to develop an affordable filtration technology for small communities in the province.

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1. BACKGROUND INFORMATION

Disinfection by-products (DBP) are formed in the drinking water supply systems due to chlorination and presence of precursors such as dissolved organic carbons (DOC). Some of these DBPs are harmful to health and have shown to be carcinogenic, in animal studies. There are hundreds of different types of known DBPs associated with different forms of disinfection and it is difficult to monitor all of them. The recent focus has however been on mainly two groups of DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs) because these two groups have been identified as the largest classes of DBPs detected in the chlorinated drinking water

Chloroform, bromodichloromethane (BDCM), chlorodibromomethane (CDBM), and bromoform (CHBr_3) are four compounds within the THM group. Sum of their concentrations, known as total trihalomethane (TTHM) should not exceed 100 $\mu\text{g/l}$ as per Canadian Guidelines (Health Canada, 2008) and 80 $\mu\text{g/l}$ as per USEPA standards (US EPA, 2003).

There are nine compounds within HAA group. These are: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), and Tribromoacetic acid (TBAA) and three mixed chloro- and bromo- acetic acids which are: Bromodichloroacetic acid (BDCAA), Dibromochloroacetic acid (DBCAA) and Bromochloroacetic acid (BCAA). The total combined concentration of the five most prevalent HAAs (MCAA, DCAA, TCAA, MBAA, DBAA) known as HAA₅ should not exceed 80 $\mu\text{g/l}$ per Canadian Guidelines (Health Canada, 2008) and 80 $\mu\text{g/l}$ as per USEPA standards (US EPA, 2003).

DBPs in drinking water have received considerable interest because of their possible association with cancers especially with bladder and rectal cancers (King & Marrett 1996; National Cancer Institute 1998; Wigle 1998). Recently there has been a shift of interest from cancer to reproductive outcomes such as spontaneous abortion, stillbirth, neural tube defect, low birth weight, etc. Bladder cancer and chlorinated DBPs (CDBPs) exposure

has historically been the most strongly supported association of all the possible cancers, based on human epidemiological evidence. A positive association between the consumption of chlorinated water and bladder cancer was found by Yang et al., (1998). Further the evidence for an association between DBPs and rectal cancer is stronger than for colon cancer. Yang et al., (1998) and Hildesheim et al., (1998) both found associations between chlorinated drinking water exposure and rectal cancer. The maximum concentration levels as proposed by U.S. EPA 2003, the World Health organization (WHO), and Health Canada are listed in Table 1 (Health Canada, 2008).

Table 1 DBPs Guidelines (mg/L)

DBPs	US EPA (2003)	WHO (2004)	Health Canada (2008)
Total THMs	0.08		0.1
Chloroform		0.2	
Dibromochloromethane		0.1	
Bromodichloromethane		0.06	0.016
Bromoform		0.1	
Haloacetic acids (HAA5)	0.06		0.08
Chlorite	1.00	0.700	1.00
Chlorate			1.00
Bromate	0.01	0.01	0.01
Chlorine	4.0	5.0	
Chloramines	4.0		
Chlorine dioxide	0.080		
<i>E. coli</i>	-	0.1	0 per 100ml
<i>Cryptosporidium</i>	0	0.001	-
<i>Giardia lamblia</i>	0		
Total coliforms	0		0 per 100ml
Protazoa			-
Enteric viruses	0		-
Turbidity			1.0 NTU
Color	15 TCU		15 TCU (aesthetic)
pH	6.5-8.5 (no units)		6.5-8.5 (no units)

2. FACTORS AFFECTING DBP FORMATION

The assessment of the level of the levels of DBPs in small community drinking-water systems was initiated by Environmental Engineering Group at Memorial University in 1997. The early work was mainly based on sampling and analyzing THMs in drinking-water systems and assessing the risk to consumers in selected communities (i.e., St. John's, Clarenville, and Shoal Harbour) in the province (Kar, 2000; Sadiq et al., 2002; Chowdhury and Husain, 2005). The study showed high levels of THMs in Shoal Harbour and Clarenville, but since St. John's has a large system, the level of THMs in St. John's was found to be low. In order to find corrective measures to reduce THMs, this work was later extended to studying the mechanism of formation of THMs and HAAs in drinking water by concentrating on five communities (i.e., Keels, Clarenville, Ferryland, Bonavista, and Burin) (Boyella, 2004; Boyella et al., 2006; Boyella et al., 2009) and predictive models were developed (Husain et al., 2008). These studies indicated that the formation of DBPs is mainly due to the presence of DBP precursors, which is mainly high-level natural organic matter (NOM) represented by the total organic carbon (TOC). The study showed that an effective way to reduce THMs and HAAs in the drinking water is to remove NOM before chlorination.

The formation of THMs and HAAs varies according to the source of water. Surface water provides higher concentration of DBPs compared to the ground water. THMs are more stable than HAAs and the growth rate of HAAs is faster than the THMs (Singer et al., 2002). HAAs are neutralized as pH value increases even with very low concentration of disinfectant in the water supply systems (Singer et al., 2005; Baribeau et al., 2006).

Formation of DBPs in the water supply system depends on pH value, contact time of residual chlorine, water temperature, NOM and residual chlorine level (Baribeau et al., 2006). To maintain safe water quality for consumers, we should have a good knowledge of the types of microorganisms in the water and their counts, sizes and materials of the pipe and storage tank, sediments in the pipe, NOM, the disinfectant dose, and treatment technology (Singer et al., 2005; Baribeau et al., 2006).

The chemical stability of DBPs and its concentration varies in the water as the retention time increases in the water supply system. Due to biodegrading effect, long retention times, and availability of free chlorine prior to exhaustion, the concentration of HAAs and THMs increases but in some cases the HAAs values decrease to zero for long distance occupants in the water supply system but it does not have any effect on the THMs (Reckhow & Singer, 2011). The concentration of THMs and HAAs increases as the reaction time of the NOM and disinfectant increases (Xie, 2004). The level of THMs increases from the water distribution system to the first consumer but reduces towards the last consumer. This is due to longer retention time, and the concentration of HAAs is low in the beginning but very high at the end point (Rodriquez and Srodes, 2005). Due to biodegradation of chlorine, the level of HAAs decreases in the water distribution system in the summer at extreme end of the system (Baribeau et al., 2006).

As the pH increases in the water distribution system, THMs increase and HAAs decrease, but it is important to note that the value of pH has different effects on each compound of HAAs. For example DCAA does not change with the change in pH values compared to TCAA which reduces with the increase in pH (Reckhow & Singer, 2011). With the significant increase in pH value above 7 to 8, the THMs increase but HAAs reduce because HAAs are decomposed at high pH value compared to THMs (Reckhow and Singer, 1985; Liang and Singer et al., 2003).

During warmer months of the year, the concentration of total THMs (TTHMs) and total HAAs (THAAs) is at its peak in the water distribution system (Baribeau et al., 2006). The formation of TTHMs and THAAs increases as the temperature rises. Pilot study in a controlled condition shows that the concentration of chloroform increases with the increase in the temperature, but DCAA and TCAA do not show much change with the temperature. Biodegrading effect in HAAs increases as temperature increases (Reckhow and Singer, 2011). In the summer months, the efficiency of chlorine decreases with higher temperature. As a result, the amount of the chlorine dose required also increases in the water distribution systems. The reaction rate between NOM and disinfectants is higher in summer than in the winter season.

Residual chlorine is directly proportional to DBP formation (Xie, 2004). The concentration of THMs increases as dose of disinfectants increases (Reckhow and Singer, 2011). Minor changes in disinfectant in the water distribution system do not have any major impact on the formation of DBPs in the system. A study reveals that when the residual chlorine is reduced to 0.3 mg/L in the system, the formation of DBPs is also

relatively low (Reckhow and Singer, 2011). Chlorine concentration also decreases because of corrosion, biofilm and scaling in the pipelines (Rossman, 2006; Al-Jasser, 2007).

3. PREDICTIVE MODELING

As discussed earlier, the factors affecting formation of TTHM and THAA are the levels of organic matter in the raw water; chlorine dose; pH of water; water temperature; and the reaction time of residual chlorine in water. There are several models available in literature. Some of these as summarized by Boyella (2004) are listed in Table 3.

Since there was no similar modeling studies conducted for the communities in the province of Newfoundland and Labrador, Boyella (2004) made an attempt to conduct research on the formation of DBPs by analyzing both the tap water and raw water samples from selected communities of Newfoundland to find the DBPs concentration and correlated with the level of TOC, chlorine dose, contact time and pH. Five communities in the province selected were Keels, Clarenville, Ferryland, Bonavista, Burin, and St. John's. Among all the THMs studied for the communities in the province of Newfoundland, chloroform had the significant presence and highest concentration in both the drinking water and chlorinated raw water samples. Chloroform constituted more than 90% of the total THMs. Other compounds such as dichloroacetonitrile (DCAN) among the Haloacetonitriles (HAN) group and 1,1,1-trichloropropanone among the halo ketones (HK) group also had the most significant presence.

Table 2 Overview of different THMs predictive models (Boyella, 2004)

Authors	Source of data	Data generation approach for THM	Model equation	r ²
Arizona State university (Amy et al., 1987)	Raw waters from different utilities across the US	Laboratory scale with variable chlorine dose, temperature and contact time	$TTHM^{**} = 0.031 (UV * TOC)^{0.440} * (D)^{0.409} * (t)^{0.265} * (T)^{1.06} * (pH-2.6)^{0.715} * (Br+1)^{0.0358}$	0.90
Lou & Chiang (1994)	Water from the Taipei (Taiwan) distribution system	Eighteen points sampled twice over a 6 month period	$TTHM = (TTHM_0) + 7.01 (pH-2.3)^{0.11} (NVTOC)^{1.06} (t)^{0.748} (D)^{0.764} (\beta)$	NP
Ibarluzea et al., (1994)	Water from the treatment plant of Sebastian (Spain)	Sampling at the treatment plant and the finished water	$CHCl_3 = 10.8 + 0.04(Flu) + 1.16(ph) + 0.12(T) + 1.91 (Co)$	0.98
US Geological Survey (Rathbun 1996)	Waters collected at different locations along the Mississippi river and two affluents	Laboratory scale with variable chlorine doses, pH and contact time. Temperature kept constant	$TTHM = 14.69 (pH-3.8)^{1.01} (D)^{0.206} (UV)^{0.849} (t)^{0.306}$	0.94
Chang et al., (1996)	Water samples from raw water at a utility in Taiwan	Laboratory scale with variable chlorine dose and contact time	$TTHM = 12.7 (TOC)^{0.291} (t)^{0.271} (D)^{-0.072}$	0.82
Clark & Sivaganesan (1998)	Prepared synthetic waters with solution of humic acid	Laboratory scale with variable chlorine dose, temperature, pH and contact time	$TTHM = A \left(C_1 - \left(\frac{C_1(1-K)}{1 - Ke^{ut}} \right) \right)$	0.71 & 0.78 for A & K
Golfinopoulos et al., (1998)	Water from the utility of Athens (Greece)	Sampling at four points in the treatment plant (one at the finished water outlet)	$TTHM = 13.5 \ln(Chla) - 14.5(pH) + 230(Br) - 140(Br)^2 - 25.3(S) + 11.06(Sp) - 6.6(T*Sp) + 1.48(T*D)$	0.98
Rodriguez et al., 2000		Laboratory	$TTHM = 0.044(DOC)^{1.030} (t)^{0.262} (pH)^{1.149} (D)^{0.277} (T)^{0.968}$	0.9

NP: value not presented by authors; **in $\mu\text{mol/L}$

Nomenclature: TTHM: total trihalomethanes($\mu\text{g/l}$); TTHM₀: TTHM at the finished water before chlorination($\mu\text{g/l}$); UV: absorbance at 254nm(cm^{-1}); TOC: total organic carbon(mg/l); NVTOC: non-volatile TOC(mg/l); Br: bromide($\mu\text{g/l}$); Chla: chlorophyll a(mg/m^3); T: water temperature($^{\circ}\text{C}$); Flu: fluorescence of the raw water(%); d :chlorine dose(mg/l); t: contact time(h); Co: residual chlorine at the treatment plant after chlorination(mg/l); C₁: initial residual chlorine(mg/l); β : parameter depending on water dispersion within distribution system; e: random error; K: dimensionless parameter; u: reaction rate constant(min); S: dummy variable indicating summer season; Sp: dummy variable indicating spring season;

The non-linear regression model developed by Boyella (2004) for THMs for the above five communities for raw water is as follows:

$$\text{THMs} = 0.001(D)^{3.14} (\text{pH})^{1.56} (\text{TOC})^{0.69} (t)^{0.175} \quad (1)$$

Where t is the reaction time in hours after chlorination; D the chlorine dosage in mg/L; and TOC is the total organic carbon in mg/L; pH is the pH value of water

The linear regression model for the formation THM in tap water is mainly dependent on TOC and pH although it also depends on temperature of the water. Since all the samples were collected in winter season, temperature fluctuation was not studied. The model developed for THM formation in tap water is as follows:

$$\text{THMs} = 173.64 - 30.31(\text{pH}) + 22.53(\text{TOC}) \quad (2)$$

Where TOC is the total organic carbon in mg/L.

The models developed by Boyella (2004) were dependent on the quality of water source and were very much site specific based on samples collected in winter seasons only. However, for any decision-making purposes further sampling covering all seasons of the years are required. The analysis for the HAAs is not performed in this study. It would be useful in future to continue work on the formation of DBPs due to presence of HAA in raw and treated water in Newfoundland communities.

4. DPBS IN CANADIAN WATER SUPPLY SYSTEMS

In urban areas, 75% of Canadians use drinking water supplied by a municipal water supply system (Statistics Canada, 2008). Canadians are exposed to DBPs in their life time through municipal water supply system (Health Canada, 2008).

Table 2 lists mean standard deviation and concentration range of THMs and HAAs in the drinking water supply systems in Canadian provinces. As demonstrated in Table 3, highest mean THMs are found in the Manitoba as 164.9 $\mu\text{g/L}$ and Nova Scotia as the second highest as 110.2 $\mu\text{g/L}$ while British Columbia has the lowest mean value of 38.9 $\mu\text{g/L}$. In terms of mean HAAs, Nova Scotia has the highest value as 116.2 $\mu\text{g/L}$, while Newfoundland has the second highest values as 104 $\mu\text{g/L}$.

Mean values of TTHMs and THAAs are also plotted in Figure 1, As shown in the Figure, Manitoba has the highest mean value of THMs while Nova Scotia has the highest mean value of HAAs.

Table 3 TTHMs and THAAs in Canadians drinking water systems ($\mu\text{g/L}$)

Province	Period	Number of water treatment plants (WTP)	TTHMs			THAAs		
			Mean	Range	SD	Mean	Range	SD
Ontario(ON)	2000-04	179	40.9	.5-343	39.9	28.6	.4-244	28.9
Quebec(QC)	2002-06	622	42.5	0-565	53.3	41.2	3.9-166	36.2
Manitoba(MB)	2001-06	74	164.9	.7-640.	110.9	72.4	12-249	76.1
Saskatchewan(SK)	2002-06	204	95.3	4-445	71.8	51.8	1-238	70.8
Alberta(AB)	2000-05	449	61.5	.6-447	66.0	38.4	3-141	39
British Columbia(BC)	2001-05	13	38.4	9-116	22.7	54.4	11-117	21
Nova Scotia (NS)	1999-04	24	110.2	2-640	84.9	116.2	8-602	119
Newfoundland and Labrador(NL)	2001-07	467	77.3	0-470	79.5	107.8	0-507.5	103
New Brunswick(NB)	1993	4	62.1	4.1-146	45	85.7	10-398	96.1
Prince Edwards Island(PEI)	2003-06	-	3.5	1.4-5.9	.96	N/A	N/A	N/A

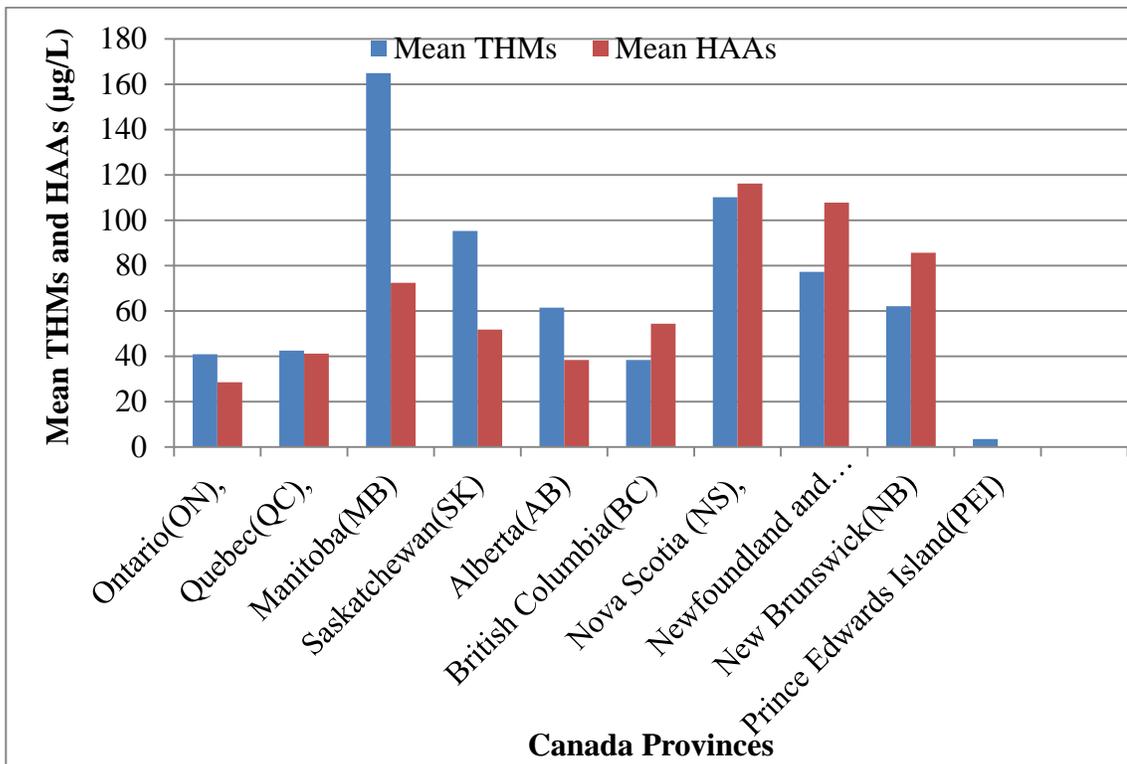


Figure 1 THMs and HAAs in different provinces in Canada

The Department of Environment and Conservation in Newfoundland regularly monitors THMs and HAAs in the water supply systems (MOENL, 2011) in the province. The results are plotted in Figure 2 and Figure 3. As demonstrated in these Figures, THMs and HAAs in various communities in the province are higher than the Health Canada guidelines of 100 µg/L for THMs and 80 µg/L for HAAs; the THMs level in few communities even exceeds 400 µg/L. More than one third communities in the province have higher HAAs level than Health Canada guidelines, and 27 communities have even higher than 300 µg/L HAAs in the water supply systems.

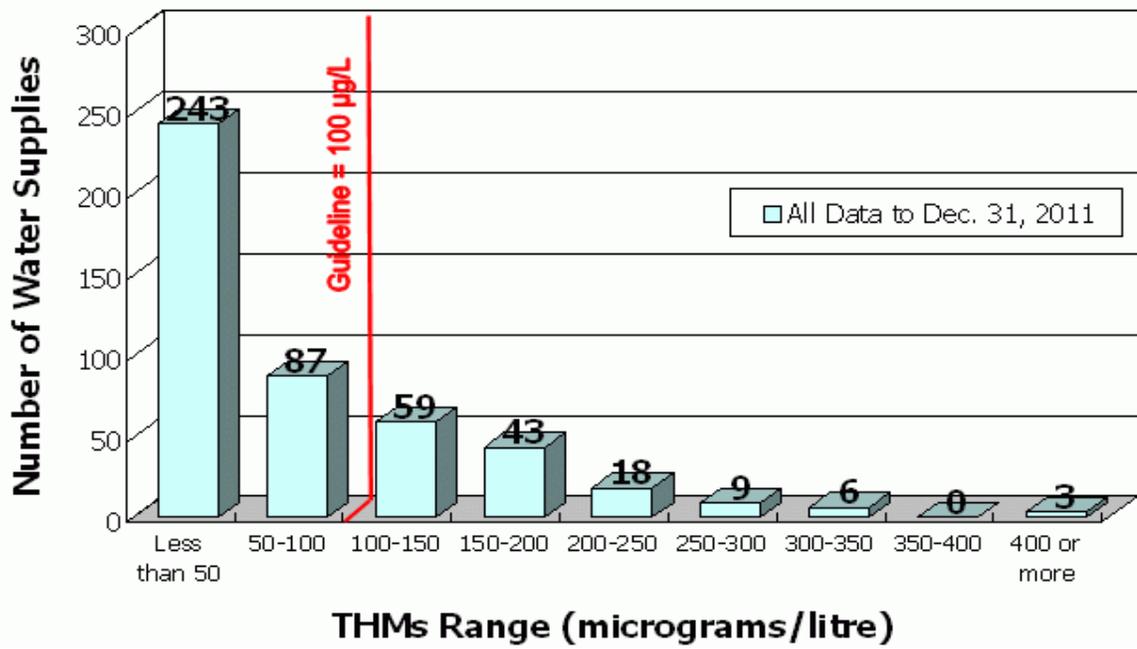


Figure 2 Distribution of THMs in NL Communities (MOENL,2011)

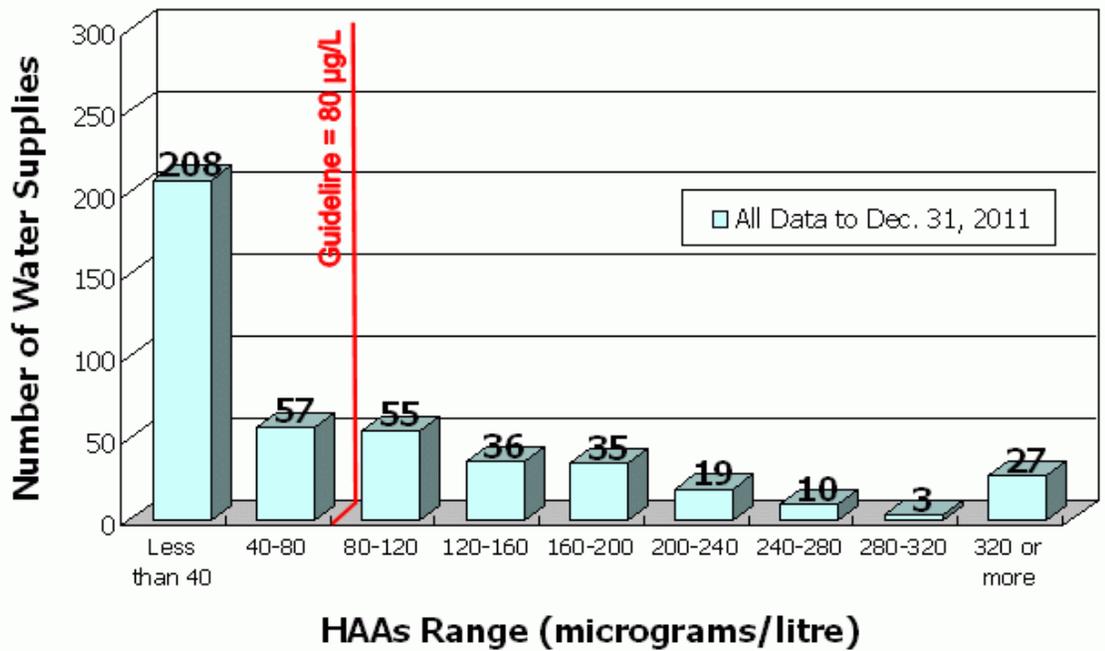


Figure 3 Distribution of HAAs in NL Communities (MOENL, 2011)

In the province of Newfoundland and Labrador, chlorine is the most commonly used form of disinfection. Out of 536 public water supply systems, 459 utilities use chlorine. The province started monitoring THMs and HAAs in in 1998 and found that 124 water systems in the have high level of THMs and 184 had high level of HAAs above specified guidelines used in Canada Most of these exceedances occur in small and rural drinking water systems.

5. ANALYSIS OF THMS AND HAAS IN POUCH AND TORBAY TAP WATER

As discussed earlier, the province of Newfoundland and Labrador has a number of smaller communities. This research focuses on two small communities, i.e., Torbay and Pouch Cove, close to the capital city; these communities have high concentration of THMs and HAAs in the drinking water.

Torbay is located 15 km north of St. John's. According to the 2011 census, the total population of Torbay is 7,397 which has considerably increased since 2006, when the population was recorded as 6,281. The community is served by a municipal water supply system. The main source of raw water in the community is from North Pond.

The population of Pouch Cove community is 1,866 and it is located about 30km northeast of St. John's. The main source of raw water is North Three Island Pond and it is chlorinated by gas and the pH is adjusted with Soda ash between 6.5 and 8.5 as per Canadian guidelines.

The above two communities do not have water treatment plants and just rely solely on the chlorination of intake water and pH adjustments.

Tap water samples from the communities were collected from different locations such as the Post Office, Town Hall and Convenience stores at different times of the day (morning, afternoon and evening) and raw water samples were collected from the intake sources before chlorination.

Tap water collected from Torbay and Pouch Cove were analysed using GC-ECD to determine levels of THMs and HAAs at different times of the day. Such analysis contributes to our understanding of the residence time on the formation of

these DBPs in the drinking water supply system. This analysis, to the best of the author's knowledge, is first to be conducted for small communities in the province. The findings of this study are presented in the following sections.

These results on HAA analysis are presented in Table 4 for Pouch Cove and in Table 5 in Torbay tap water. As listed in these Tables,, the concentrations of all HAAs were found high in the water supply system. By closely observing the daily trends, seven compounds of HAAs have been identified in the water supply system. However at noon and in the evening, three compounds in the system reduced to negligible levels but the concentration of four other major compounds (DBAA, BCAA, DCAA and MCAA) were consistently high throughout the day. The results show that the levels of HAAs were much higher in the Pouch Cove community water supply system than in the Torbay water system. In both communities, the concentration levels of HAAs were much higher than the specified US EPA and Canadian guidelines.

The concentration trend of THM compounds in Pouch Cove tap water is shown in Table 6 while in Torbay Tap water is listed in Table 7. We observed that the chloroform contribution to the total THMs was above 90%, which means that if chloroform is controlled, the total THMs level will be significantly reduced. According to the US EPA recommendations, the concentration of chloroform should be less than or equal to 70 µg/L, DBCM should be less than or equal to 60µg/L but for bromoform and BDCM, there is no published guidelines. These compounds should not exceed these values but the trend shows much higher values for individual THM compounds on daily basis.

Table 4 Concentrations of HAAs in Pouch Cove tap water (µg/L)

Time	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	THAA	EPA THAAs	Canadian THAAs
Morning	58.85	0	91.17	6.67	113.70	30.06	37.58	31.02	0	375.08	60	80
Noon	60.36	0	104.88	8.57	138.54	37.27	39.85	0	0	451.50	60	80
evening	61.97	0	104.50	6.39	138.14	34.33	37.92	0	0	348.95	60	80
Morning	0	0	64.09	12.18	62.71	44.55	36.31	0	0	254.92	60	80
Noon	30.63	0	59.22	0	63.63	45.62	35.97	0	0	235.07	60	80

Table 5 Concentration HAAs in tap waters in Torbay water system (µg/L)

Time	MCAA	MBAA	DCAA	TCAA	BCAA	BDCAA	DBAA	CDBAA	TBAA	THAA	EPA THAAs	Canadian THAAs
Morning	31.02	0	67.18	7.941	80.54	34.77	40.22	53.04	0	314.74	60	80
Noon	39.54	0	61.59	9.33	73.58	38.19	39.21	0	0	261.46	60	80
Morning	0	0	66.80	6.25	56.23	0	35.99	0	0	165.29	60	80
Noon	0	0	58.96	6.25	66.90	34.77	38.01	0	0	204.91	60	80
Evening	27.45	0	56.79	6.00	59.88	0	37.57	0	0	187.72	60	80

Table 6 THMs with time in the drinking water- Pouch Cove (µg/L)

Time	Chloroform	BDCM	DCBM	Bromoform	TTHMs
Morning	98.36	3.84	0.29	0.19	102.70
Noon	77.09	3.55	0.25	0.09	81.00
Morning	384.75	3.40	0.19	0.05	388.41
Noon	66.86	5.07	1.23	0.11	72.06
Evening	132.50	9.89	2.10	0.22	144.73

Table 7 THMs with time in Toray community tap water(µg/L)

Time	Chloroform	DCBM	DBCM	Bromoform
Morning	43.47	7.57	1.05	0.04
Noon	43.32	7.60	1.13	0.11
Morning	254.74	35.50	5.88	1.25
Noon	4.34	9.16	0.63	0.12
Evening	45.48	7.37	0.58	0.11

6. FILTRATION TECHNOLOGY TO REMOVE THMs AND HAAs

The analysis of tap water from the two communities indicates that the mean HAAs and THMs were found higher than the acceptable limits as outlined by the Health Canada. To reduce the concentration of these compounds to an acceptable levels, a series of experiments using activated carbon with batch and column tests were conducted. For each test, 15 gm activated carbon extracted from heavy oil fly ash was used for the batch test.

In this study, extracted carbon from heavy oil fly ash (HOFA) was used as a filter media. HOFA was collected directly from the electrostatic precipitator of the power plants which use heavy fuel oil as a fuel source. The impurities from HOFA were removed using distilled water and aqueous acidic solutions. The extracted carbon was then activated at high temperature using a programmable Lindberg/Blue M tube furnace. The furnace temperature was programmed up to 900°C with increment of 5°C/ min and then remained at this 900°C temperature for 30 to 60 minutes. During this period the constant flow rate of the ultra pure compressed air and nitrogen was set to 5ml/min.

The objective of this experiment was to assess the removal of THMS and HAAs from the drinking water using activated carbon. The design parameters considered for this experiment included activated carbon dose, temperature, and pH values.

To evaluate the removal efficiency of THMs and HAAs from the tap water collected from the Pouch Cove community, batch test was conducted by taking different doses of AC samples in 125 mL of tap water with known initial concentrations of THMs and HAAs. To run the experiment in batch mode, 125 mL of water was taken in eight 250 mL Erlenmeyer flasks

and AC was added with ratio as shown in Table 8 and was agitated with magnetic stirrer at the 10 rpm for 24 hours. To avoid the evaporation of water from the flask it was sealed with a stopper. To reduce the pH value of contaminated water, sulfuric acid of a known concentration and amount was added to obtain a desired value of pH as listed in Table 9. In Table 8 range and levels (coded as -1 and +1) were designed for selected variables that play a major role in the adsorption processes. The percentage removal of THMs and HAAs was calculated on the basis of initial and final concentration of THMs and HAAs using the formula $R = \frac{[C_0 - C_f] * 100}{C_0}$ as shown in Table 9 where C_0 is reference tap water concentration and C_f is the concentration in the water after batch test

Table 8 Design parameter for experiment

Sample name	Coded values			Actual		
	A	B	C	Temperatures°C	Activated carbon(gm)	pH
B1	-	-	-	22	1	2
B2	+	-	-	30	1	2
B3	-	+	-	22	2	2
B4	+	+	-	30	2	2
B5	-	-	+	22	1	6.6
B6	+	-	+	30	1	6.6
B7	-	+	+	22	2	6.6
B8	+	+	+	30	2	6.6

Table 9 Experimental design of the batch test

Variables	Factor	Coded Level	
		-	+
AC dose(mg)	A	1	2
Temperature	B	22	30
pH	C	2	6.6

HAA Removal

The removal efficiency of HAAs after batch test is shown below in Table 10. Review of the data shows that the highest removal of HAAs occurred when the temperature and pH values were low and activated carbon with high dose. The removal efficiency was 35.56%. For experimental design and to optimize parameters, Design Expert Software version 8.07 was used (Design Expert, 2012).

The analysis of variance (ANOVA) shows that the results were significant for $p < .05$, which means that there is a significant effect on the removal of HAAs from the given batch test; in this case activated carbon and interactions of temperature and pH have significant effects with correlation co-efficient $R^2 = .9646$. The main effect of the adsorption of HAAs on each parameters analysis listed in Table 11 shows the sensitivity analysis and Figure 4 shows the contribution of different parameters. The regression relationship of HAAs removal with various combinations of parameters was developed as listed in Equation 3 below.

$$\% \text{ HAAs removal} = +32.82 - .41*A + 1.05*B - 0.58*C + 1.0*A*C \quad (3)$$

Where A, B, and C are temperature, activated carbon dose, and pH respectively. Equation 5.2 below shows % HAAs removal in term of actual code factors.

$$\begin{aligned} \% \text{ HAAs removal} = & +32.82005 - .40502 * \text{temperature} + 1.04681 * \text{activated carbon} - \\ & .58015 * \text{pH} + 1.05643 * \text{temperature} * \text{pH} \end{aligned} \quad (5.2)$$

Table 10 Experimental data and percentage removal of HAAs

A: Temperature, B: Activated Carbon C: pH

Sample name	Coded values			Actual			% HAAs Removal
	A	B	C	Temperatures ^o	Activated carbon(gm)	pH	
B1	-	-	-	22	1	2	34.59
B2	+	-	-	30	1	2	33.10
B3	-	+	-	22	2	2	35.56
B4	+	+	-	30	2	2	30.77
B5	-	-	+	22	1	6.6	30.77
B6	+	-	+	30	1	6.6	31.38
B7	-	+	+	22	2	6.6	32.4
B8	+	+	+	30	2	6.6	34.40

Table 11 Contribution of different parameters on removal of HAAs

A: Temperature, B: Activated Carbon C: pH

Parameters	% Contribution for HAAS adsorption
A- Temp	5.83
B-act carbon	38.96
C-pH	11.96
Effects of AC	39.68

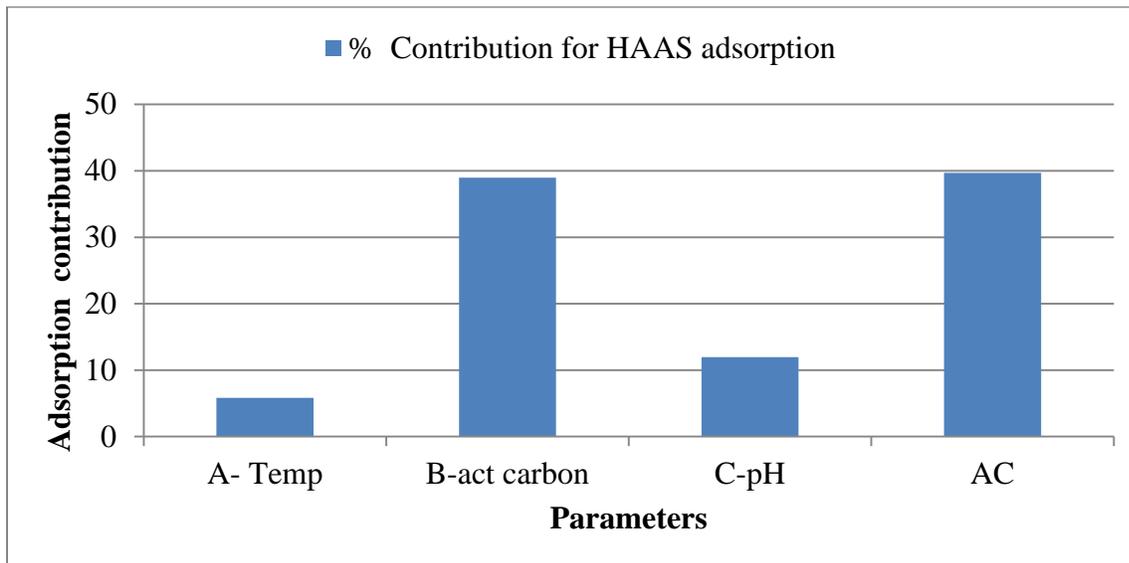


Figure 4 Contribution of different paramters on removal of HAAs,

As shown in the Figure, the interactions between factor C (pH) and factor A(temperature) also have a significant effect on HAAs removal. The dose of activated carbon B also has impact on the removal of HAAs.

THM Removal

The percentage of THM removal by batch test is shown in the Table 12. As demonstrated in the table, the activated carbon dose (AC) at B4 shows the highest removal percentage of THMs (95.56%) when considering the temperature factor and AC factor on higher side and pH on lower end B1 and B5 show very little recovery. Analysis of variance (ANOVA) shows significant correlation ($p < .05$) on the removal of THMs from the given batch test. In this case parameters are amount of activated carbon used and temperature variations. These two parameters have significant effects on the removal of THMs with correlation co-efficient R^2 as

0.90. The main effect on each parameter on the analysis of THMs adsorption is provided in Table 13 and Figure 5.

The following regression relationship is developed to predict % THM removal:

$$\% \text{ THMs remove} = 4.64 + 69.01 * A + 87.23 * B - 66.00 AB \quad (4)$$

Where A, B and C shows temperature, activated carbon and pH respectively.

Table 12 Experimental data and percentage removal of THMs

A: Temperature, B: Activated Carbon C: pH

Sample name	Coded values			Actual			% THMs Recovery
	A	B	C	Temperature °C	Activated carbon(gm)	pH	
B1	-	-	-	22	1	2	94.29
B2	+	-	-	30	1	2	6.51
B3	-	+	-	22	2	2	89.90
B4	+	+	-	30	2	2	95.56
B5	-	-	+	22	1	6.6	44.90
B6	+	-	+	30	1	6.6	94.06
B7	-	+	+	22	2	6.6	87.80
B8	+	+	+	30	2	6.6	92.69

Table 13 Contribution of different parameters on reoval of THMs

Parameters	% THMs Contribution
A- Temp	25.63
B-act carbon	40.95
C-pH	0.18
AB	23.44

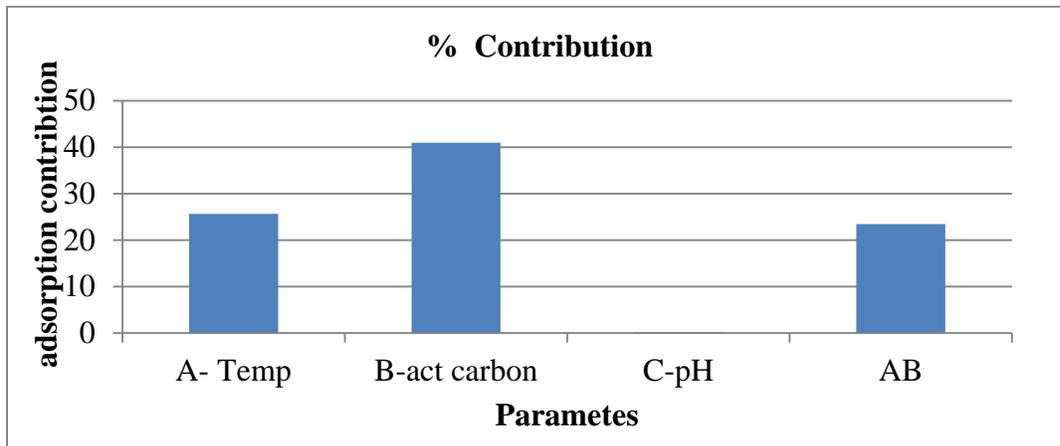


Figure 5 Contribution of different paramters in THM removal

7. CONCLUSIONS AND RECOMMENDATIONS

Although there are different types of treatment methods such as membrane filtration, coagulation, reverse osmosis and other adsorption processes available to reduce THMs and HAAs in the drinking water systems but most of these methods require trained personnel to operate and maintain the system and requires high capital investment. Due to lack of skilled personnel to operate and maintain water systems and also high capital cost, it is not feasible to install such systems in small communities. The main objective of this study was to identify a cost effective adsorbent to remove DBPs from drinking water supply systems in small communities in the province. The adsorbent developed from ash residues used in this study can be easily installed and operated at very low incremental cost. In this research, the extracted adsorbent was tested with a series of experiments using treated water from the Pouch Cove community near St. John's. The results show a significant removal of DBPs. This study also shows that the developed product can be used as an effective and inexpensive filtration media for the removal of THMs and HAAs in the water supply system. This adsorbent has also a great potential in providing safe drinking water to the rural communities.

Although the adsorbent used for this research has potential to remove DBPs from drinking water supply systems but the results reported in this work is based on limited data and requires an in-depth investigation before its use as a filtration media. Some of the limitations are highlighted in this section with a summary for future research as follows.

1. Our analysis is based on very limited number of samples. In order to have a better understanding on the variation of THMs and HAAs in the tap water more samples should be collected and analyzed covering different seasons and times covering weekend and

weekdays. Sample collection should also be done at different locations in the water distribution systems and records should be maintained on the type of pipe materials and size of pipes at the point of sampling.

2. The activated carbon used in this study was based on very preliminary work and limited samples. It is recommended to improve its adsorption capacity by micro-sieving of extracted carbon and using different physical and activation processes. Further research work on the preparation of activated carbon with chemical impregnation and homogenization is recommended.
3. The regeneration and backwashing of the adsorbent was not conducted in this study. It would be useful to develop feasibility of regeneration of adsorbent.

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