AFFORABLE WATER FILTRATION TECHNOLOGY FOR SMALL RURAL COMMUNITIES

HE ZHANG, HODA TAFVIZI,
TAHIR HUSAIN & YUAN CHEN
MAY 2017

2015-16 HARRIS CENTRE RBC WATER
RESEARCH AND OUTREACH FUND

THE HARRIS CENTRE
Memorial University

Acknowledgements

The support provided by the Harris Centre at Memorial University in the form of the Harris Centre RBC Water Research and Outreach Fund is highly appreciated. Appreciation is also extended to the Water Resources Management Division of the Department of Environment and Conservation for providing technical support and arranging for water sampling. Special thanks go to the mayors, town clerks and town hall staffs from the Towns of Sunnyside, New-Wes-Valley and Salvage for the coordination and arrangement in the water sample collection. Last but not least, many thanks go to our research team members, Mr. Jingjing Ling and Mr. Jiabin Liu, for the help and assistance during the water sample collection.

Executive Summary

Chlorine has been commonly used as disinfectant and oxidant in the drinking water supply systems due to its germicidal potency, efficiency, and low cost. Chlorination process not only removes odour, color, and certain metals, but also kills pathogens that usually grow in the pipelines. However, chlorine can react with natural organic matter (NOM) and produce compounds known as disinfection by-products (DBPs). Different water treatment processes have been applied to remove NOM before it reacts with chlorine to form DBPs. However, traditional water treatment methods showed limited capability in NOM removal. Activated carbon is identified as the best available technology and has been applied for NOM removal because of its high affinity to organic matters even at low concentrations. In this study, a column filtration technology utilizing activated carbon as a barrier was developed and applied in the treatment of source waters collected from three local communities. TOC, as a NOM indicator, is identified more reliable than UV since the UV reading can only reflect the amount of light-sensitive organic matters. Batch test results demonstrate the use of 0.5 g (AC) /L (water) has the highest adsorption effectiveness and lowest cost of AC. Meanwhile, column filtration results indicate the activated carbon barrier is effective to remove 64, 77 and 74 percent of NOM from the source water of Sunnyside, New-Wes-Valley and Salvage, respectively. The follow-up chlorination experiment illustrates that the formation of THMs and HAAs can be considerably reduced after the water passed through the column. NOM fractionation of Sunnyside and New-Wes-Valley source water were also discovered; it is found the New-Wes-Valley source water contains higher amount of hydrophobic fraction which can result in the higher concentrations of THMs and HAAs in the disinfection process. This is proved in the chlorination experiments by assessing the formation potential of THMs and HAAs. The fractionation result can help to predict that the concentration of low molecular size NOM in New-Wes-Valley is higher than that in Sunnyside. Above all, the cost-effective carbon filtration technology developed in this study can be potentially applied as a pre-treatment technology for intake source waters for the local communities.

Table of Contents

List of Figures

List of Tables

1 Background Information

1.1 DBPs formation and impacts

Chlorine has been commonly used as disinfectant and oxidant in the world’s drinking water supply system due to its germicidal potency, efficiency, and low cost. Chlorination process not only removes odour, color, and some unwanted metals, but also kills disease-causing pathogens, such as bacteria and viruses which commonly grow in water distribution systems. However, chlorine can react with natural organic matter (NOM) in the drinking water supply system to produce compounds known as disinfection by-products (DBPs). NOM refers to a complex combination of organic compounds (Cheng et al., 2005) with varying molecular size and properties, and different functional groups such as phenolic, hydroxylic and carboxylic (Zularisama et al., 2006). NOM is derived from the decomposition of living organisms such as animals and plant residues (Schreiber et al., 2005). It can contain humic acids, fulvic acids, carbohydrates, carboxylic acids, proteins, lipids, amino acids and polysaccharides depending on the characteristics of the water basins (Cheng et al., 2005; Schreiber et al., 2005; Zularisama et al., 2006), it can also be grouped into hydrophobic, with humic high molecular substance, and hydrophilic, with non-humic low molecular organic matter (Imai et al., 2001).

Since DBPs were first identified in 1970s, DBPs have been actively investigated. Significant research efforts have been directed toward increasing understanding of DBPs formation, occurrence, and health effects of chronic exposure (Richardson et al., 2002). Research studies show that there is an association between long-term exposures to high levels of DBPs and increased incidents of cancers of liver, kidney, bladder, and colon, as well as other health impacts (ENVC, 2009; Health Canada, 2017).

Due to the potential carcinogenicity and other health impacts of DBPs, drinking water regulations across the world require regular monitoring of the concentrations of DBPs in the water supply systems. There are hundreds of different types of known DBPs produced from the reaction between NOM and the residual chorine, and it is difficult to monitor all of them. Recent focus has, however, been on two groups of DBPs - trihalomethanes (THMs) and haloacetic acids

(HAAs) - as these have been identified as the largest class of DBPs detected on a weight basis in chlorinated drinking water. The THMs group includes four compounds: chlorodibromomethane, chloroform, bromodichloromethane and bromoform. Although the HAAs group includes a total of nine compounds, five most prevalent HAAs, known as HAA_5, are regulated including monochloroacetic acid (MCA), dichloroacetic acid (DCA), trichloroacetic acid (TCA), monobromoacetic acid (MBA) and dibromoacetic acid (DBA). Water quality guidelines or standards in most jurisdictions establish the maximum concentration levels for total THMs (TTHMs) and HHA_5. For example, the Guidelines for Canadian Drinking Water Quality (GCDWQ) recommend a maximum acceptable concentration of 100 μg/L for TTHMs and 80 μg/L for HAA_5 (Health Canada, 2017). United States Environmental Protection Agency (USEPA) developed the Stage 1 Disinfectants and Disinfection Byproducts Rule which prescribes the maximum concentration levels of TTHMs and HAA_5 should not exceed 80 μg/L and 60 μg/L, respectively.

It is important to note, however, that although the long-term exposure of disinfectants and DBPs can cause adverse health effects, the risk from illness and death resulting from exposure to pathogens in drinking water is much greater. As concluded by the World Health Organization (WHO, 2004), disinfection remains the most important treatment for drinking water, and should receive priority over any other considerations in relation to drinking-water treatment including DBPs formation.

1.2 Preventing DBP formation using activated carbon

Where it is possible, without comprising the microbiological quality of drinking water, proactive actions should be taken to minimize the concentrations of DBPs caused by the employment of disinfectant. One effective strategy to control DBPs formation in drinking water supplies is to remove the organic precursors of DBPs (WHO, 2004). Different water treatment processes have been researched and/or applied to remove NOM before it reacts with chlorine to form DBPs, including coagulation-based process, oxidation process using ozonation, high pressure membrane filtration processes, and adsorption processes using activated carbon or various resins (CBCL, 2011). Some of the traditional water treatment methods showed low capability in the removal of NOM (Xia and Ni, 2015). It leads to the necessity of equipping water treatment plants with additional treatment stages in order to decrease disinfection by-products (DBPs) after chlorination (Liua et al., 2016) and reduce the chlorine demand for preventing bacterial growth in the pipeline (Chow et al., 2004). Among these treatment methods, enhanced coagulation and activated carbon adsorption are identified as the best available technology for NOM removal (USPEA, 2003). Nevertheless, the effectiveness of both treatment methods largely depends on the dosage of coagulant and/or activated carbon, and the characteristics of NOM in the water (Uyak et al., 2007). Activated carbon has been used in many water treatment plants for organic matter removal due to its high affinity to organic matters even at low concentrations (Babi et al., 2007).

All water treatment processes to remove NOM have their advantages and drawbacks. Despite there are many advantages of using activated carbon for removal of organic and inorganic contaminants in water treatment industry, activated carbon adsorption technology has some drawbacks. One major drawback associated with the use of activated carbon for NOM removal is the natural variability of the raw material, which causes differences in the adsorptive capacity. The other drawback is that the quantity and composition of NOM varies seasonally in most surface water sources, including Newfoundland and Labrador. Both drawbacks create challenges to determine the NOM removal capability and the frequency with which the activated carbon filter should be replaced (CBCL, 2011). Addressing these challenges will require both extensive laboratory research and field pilot studies to evaluate the effectiveness of the treatment process and the seasonal variations of NOM levels through the year, which are also the purposes of the study.

The commercial activated carbons on the market can be made from various raw material such as wood products, bituminous and lignite coal, coconut shells, and petroleum coke. Those commercial activated carbons have high removal efficiency, but due to the high cost of the raw materials, using commercial activated carbon filters manufactured from these materials in small communities is not economically feasible. This has led to the need to find a low-cost adsorbent by extracting unburned carbon from fly ash (FA). This waste is abundant, with millions of tons being generated annually (Mofarrah, 2014).

As mentioned above, the effective removal of DBPs precursors requires the proper characterization of the NOM levels in the intake water. The surface water in NL is generally characterized by low pH, low alkalinities, and high concentration of NOM (CBCL, 2011). However, each intake source has different characteristics, and the hydrophilic and hydrophobic constituents in the watersheds need to be better understood through laboratory analysis. To effectively assess the DBPs formation potential and control efficiency, the characteristics of NOMs at each drinking water source should be investigated, such as the molecular size, polarity (hydrophobic and hydrophilic characteristics), and seasonal variations in acid, base, and neutral forms.

1.3 DBPs level in Newfoundland’s water supply systems

In the province of Newfoundland and Labrador (NL), over 90% of water treatment plants use chlorine as primary disinfectant. According to a comprehensive report prepared for water supply system in NL, chlorinated water supply systems service a population base of approximately 449,000, which represents 97.8% of the serviced population of the province (DOE, 2001). Specific and effective actions have been taken by the provincial government to improve drinking water quality and safety, such as the source-to-tap source water protection program, operator education and training program, provincial drinking water quality monitoring program.

Tap water samples, connected to water supply sources, have been collected on a regular basis and analyzed for various organic and inorganic parameters. All of the chemical analysis results (e.g., organic, inorganic, THMs, HAAs) for water samples across the province, including surface water sources, groundwater wells and tap water, taken under the monitoring program are stored in a provincial database (DOE, 2001). Along with other physical and chemical parameters, the summaries of the THMs and HAAs levels for water supplies of all communities are provided to the public on a regular basis. The statistics for THMs and HAAs analysis show that, as of September 2016 the averaged concentrations of THM in 136 of 497 province’s water supplies exceeded guideline, and the HAAs levels in 161 of 499 water supplies exceeded guideline (ENVC, 2017a).

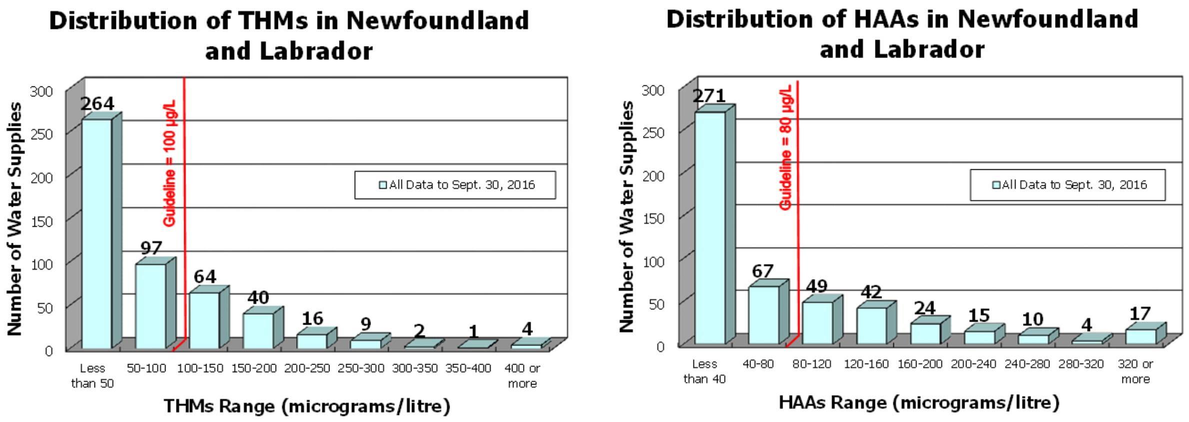

Figure 1-1 The distribution of THMs and HAAs in Newfoundland and Labrador (Source: ENVC, 2017a)

Table 1-1 THMs and HAAs levels in drinking water source in NL communities

Community Name	Population (2006)	Source Name	No. of HAA samples	HAAs Average (µg/L)	THMs Average (µg/L)	No. of THM samples	Last sampled month
New-Wes-Valley	500	Carter's Pond	41	707.05	191.75	78	Jan 2016
Salvage	174	Wild Cove Pond	39	486.75	344.50	70	Feb 2016
Sunnyside	260	Center Cove River	64	200.57	105.03	51	Feb 2016

(Source: ENVC, 2017a)

It was found that many communities with high THMs and HAAs levels in water supplies are located in rural area of NL with very low residential population. A recent study shows that small rural communities with low population generally cannot afford the high cost of a comprehensive water treatment system, and also lack highly skilled, certified operators to maintain a residual level of chlorine and to address other technical challenges during water treatment process. Due to the limited provincial resources, small rural communities are given a great deal of responsibilities in providing sustainable and safe drinking water to their residents at affordable cost, but it is virtually impossible for them to meet such responsibilities (Minnes et al., 2014). Considering the above challenges and financial constraints faced by these communities, there is a need to develop an affordable and easy-to-operate filtration technology to provide safe and sustainable drinking water to the residents.

There are many rural communities in NL with low population having both high THMs and HAAs levels in their water supplies. It is ideal if all communities can be covered in this study, but due to limited time and resources available to conduct this study, three communities were selected considering their community sizes, DBPs levels, proximity to St. John's, and accessibility to sampling sites.

1) Sunnyside (150 km from St. John's),
2) New-Wes-Valley (375 km from St. John's),
3) Salvage (300 km from St. John's).

1.4 Objectives of the study

The ultimate goal of the research is to introduce a simple filtration barrier of activated carbon to reduce DBP-causing precursors before chlorination thus improving drinking water safety for small, rural communities in NL. To achieve the goal, the objectives of this study are to:

1) fully characterize water quality and NOM levels of drinking water source in the three communities,

2) conduct batch tests to study the adsorption kinetics and equilibrium, and develop isotherm curves which can help to determine the optimal carbon dose to treat source waters,

3) develop column filtration technology and evaluate the performance of carbon barrier on NOM removal, and

4) investigate the THMs and HAAs formation potential in raw and filtered water with variable residence time and residual chlorine.

2 Characterization of Source and Drinking Water Samples

According to Guidelines for Canadian Drinking Water Qualities (GCDWQ), the maximum acceptable concentration (MAC) for THMs and HAAs in drinking water are 100 and 80 µg/L, respectively. As of September 2016, it was found that 121 out of 495 serviced areas have THM levels above MAC, and 139 out of 470 serviced areas are with HAA levels above MAC (ENVC, 2017b, c). Due to limited time and resources available to conduct this study, it is not possible to cover all the communities in this research project. Hence, only Sunnyside, New-Wes-Valley and Salvage, which are close to St. John’s and convenient for water sampling, are selected to conduct research in this study.

Figure 2-1 displays the location of three communities on the island of Newfoundland. According to the Statistics Canada Census Profile (2016), Sunnyside, located on the Isthmus of Avalon, has an area of 39.66 km^2 and a population of 396 residents; New-Wes-Valley is a combination of eight original coastal villages which has an area of 133.59 km^2 and 2172 residents; the population of Salvage is 124 by the year of 2016, and the town is in Division No.7 with an area of 15.86 km^2.

2.1 Methodology

The source and drinking water samples were collected from Towns of Sunnyside, New-Wes-Valley, and Salvage in the summer of 2016. The intake source water samples were characterized by color, turbidity, pH, UV at a wave length of 254 nm, Total organic carbon (TOC), alkalinity, total dissolved solids (TDS) and metals. Results of color, turbidity, alkalinity, TDS were obtained from the Newfoundland and Labrador Water Resources Portal. UV$_{254}$ and pH were measured by using a UV/Vis spectrophotometer (Thermo Scientific Genesys) and an education series EL20 benchtop pH meter (METTLER TOLEDO®), respectively, in the environmental laboratory of Engineering Department. TOC was determined by a Shimadzu TOC-V series TOC analyzer in the Biogeochemistry of Boreal Ecosystem Research Group (BBERG) laboratory of Earth Science Department. Before TOC analysis, the source water samples from all the communities were passed through a 0.45 µm membrane filter in order to remove the suspended solids. The major and trace metals were analyzed for both source and drinking water samples by a Perkin – Elmer ELAN DRC II Mass Spectrometer in TERRA facilities under CREAIT Network. Besides metals, the TOC of the drinking water samples were also measured. The analytical results of THMs and HAAs in the drinking water samples in the past few seasons were extracted from the Newfoundland and Labrador Water Resources Portal.

2.2 Results and discussion

The characteristics of color, turbidity, pH, UV_{254}, TOC, alkalinity and TDS in source water samples from three communities are listed in Table 2-1. The pH, turbidity and TDS of the analyzed source water are all within the Canadian drinking water quality guidelines. Only the level of color exceeds that in the guideline. Color is prevalent in natural source waters especially surface waters. The higher level of color indicates more organic matter in the water.

Table 2-2 listed the TOC of all the drinking water samples collected from all the three towns. At Town of Sunnyside, Resident A is close to the water treatment station, while Resident B is located at almost the end of pipeline. The Town Hall is near the middle of the pipeline. It is noticed that the TOC is higher at Resident A than that at Resident B, which implies there might be some corrosion or leaking problems at the interior of the pipeline. Among all the three towns, Salvage has higher level of TOC in its drinking water samples. Therefore, it can lead to the existence of a significant amount of THMs and HAAs in the same water samples. Town of New-Wes-Valley uses water from two sources for drinking water supply. One is Carter’s pond, it serves the Newtown and Templeman area. The other is Little Northwest Pond, which serves Wesleyville, Badger’s Quay, Pool’s Island, Brookfield, Pound Cove and Valleyfield. The drinking water samples of WTS-1, MP-1, Town Hall, Booster station, and End of pipeline belongs to the service area of the Little Northwest Pond, while WTS-2 and MP-2 are within the Carter’s pond service area. The source water of Carter’s pond and the associated drinking water contain more organic matter than that of Little Northwest Pond, hence can result in more serious DBP problems in the Newtown and Templeman area. This is also proved by the amount of THM and HAA in the drinking water. As summarized in Table 2-3, the THM concentration of drinking water in Carter’s Pond service area is similar to that in Little Northwest Pond service area. However, the HAA amount in the same drinking water in Carter’s Pond service area is significantly higher than that in Little Northwest Pond service area in the past four seasons. Although other DBP compounds were not counted in the analysis, it is not difficult to imagine that the situation of DBP problems in Carter's Pond service area could be more serious.

Table 2-4 lists the metal contents analyzed for all the source and drinking water samples. As can be seen, most of the metals analyzed have concentrations that fall below the MAC. The drinking water samples collected at the water treatment station of Sunnyside is found rich in aluminum, iron and manganese. Aluminum can naturally exist in source waters, its salts are commonly utilized as coagulants in drinking water treatment process. Although the MAC of aluminum is not listed in the GCDWQ, an operational guidance value is considered based on some operational considerations. The operational guidance value of aluminum should remain below 100 ppb for conventional treatment, and below 200 ppb for the other types of treatment. Until now, there is still lack of consistent and convincing evidence showing that the aluminum in drinking water can cause adverse health effects in humans. The iron and manganese can get into the water bodies through erosion and weathering of rocks and minerals. Currently, there is no proof indicating that the iron or manganese in drinking water will bring about health-related issues. From the aesthetic point of view, the concentration of iron and manganese should not exceed 300 ppb and 50 ppb, respectively. Besides the drinking water sample from the water treatment station in Sunnyside, the source water sample of New-Wes-Valley and all the water samples collected from Salvage is also noticed having iron concentrations over 300 ppb.

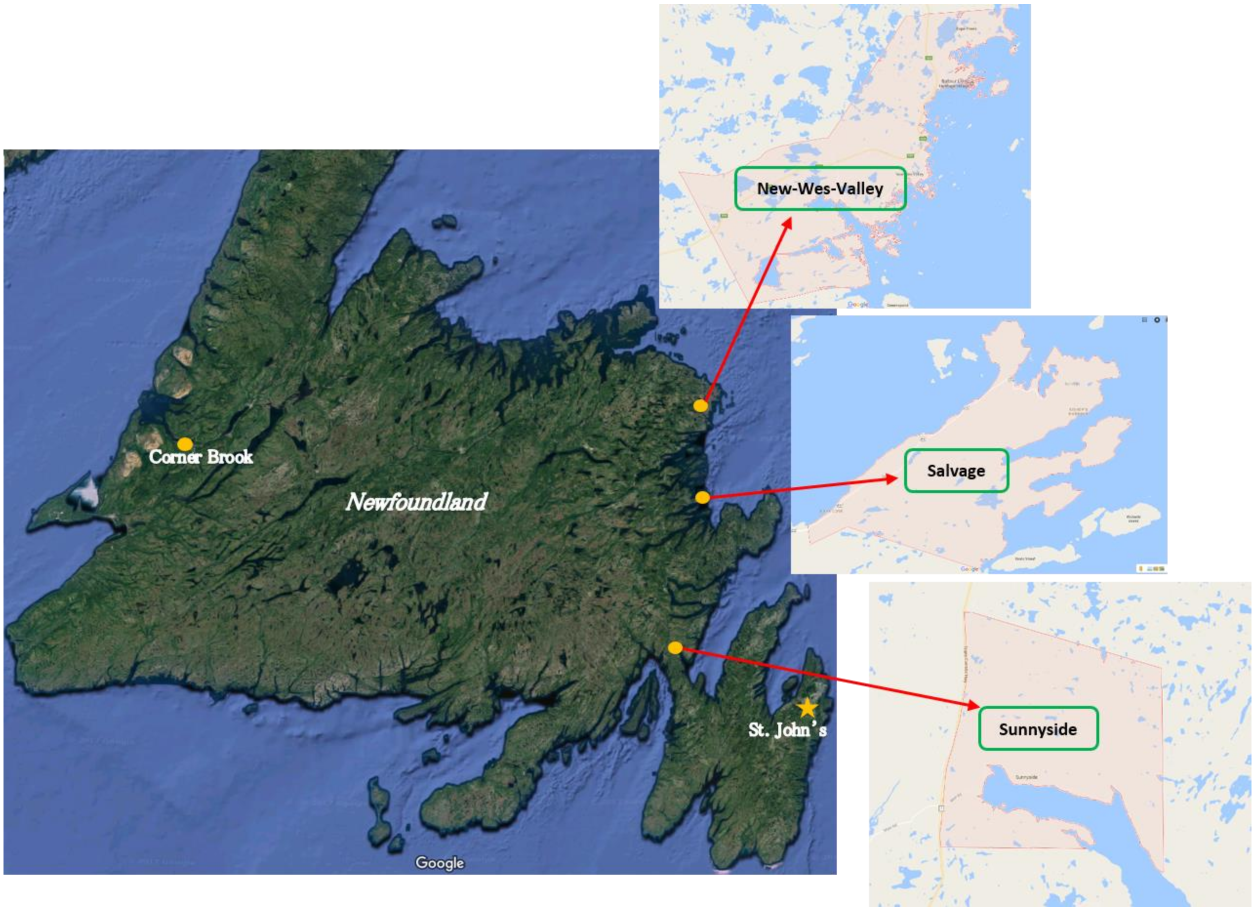

Figure 2-1 Location of three communities on the island
(Source: google map)

Table 2-1 Characteristics of source water from three local communities

Parameters	Alkalinity* (mg/L)	Color* (TCU)	pH	UV_{254} (A)	Turbidity* (NYU)	TDS * (mg/L)	TOC (mg/L)
GCDWQ	NA	15	6.5 ~ 8.5	NA	1.0	500	NA
Sunnyside	7.00	31	6.67	0.307	0.30	21	8.86
New-Wes-Valley	0.00	121	5.03	0.679	0.50	25	13.08
Salvage	6.00	80	6.58	0.643	0.80	62	14.92

(*Source: Newfoundland and Labrador Water Resources Portal; NA: not available.)

Table 2-2 TOC of drinking water samples from three towns

	Town of Sunnyside				**Town of Salvage**		
	WTS	Resident A	Town Hall	Resident B	WTS	MP	Town Hall
TOC (mg/L)	8.91	8.70	9.48	10.54	14.88	15.78	15.47
	Town of New-Wes-Valley						
	Litter Northwest Pond					Carter's Pond	
	WTS-1	MP-1	Town Hall	Booster station	End of pipeline	WTS-2	MP-2
TOC (mg/L)	8.49	8.74	7.94	8.12	8.30	14.44	14.54

Notes:
WTS: water treatment station; MP: middle of pipeline.

Table 2-3 THM and HAA summary of tap water samples in the past few seasons

Season sampled	**Winter 2016**		**Fall 2015**		**Summer 2015**		**Spring 2015**	
Average	THMs (µg/L)	HAAs (µg/L)	THMs (µg/L)	HAAs (µg/L)	THMs (µg/L)	HAAs (µg/L)	THMs (µg/L)	HAAs (µg/L)
Sunnyside	105.03	200.57	130.90	248.95	165.43	231.60	118.57	258.13
New-Wes-Valley (Carter's Pond)	191.75	707.05	183.50	541.95	172.75	542.20	168.75	622.97
New-Wes-Valley (Little Northwest Pond)	206.25	360.67	182.25	358.52	186.50	374.85	218.25	420.67
Salvage	344.50	486.75	357.00	451.35	337.00	448.98	292.75	351.50

(Source: Newfoundland and Labrador Water Resources Portal.)

Table 2-4 Elemental analysis of metal in source and drinking water samples

Metal Element	**Li**	**Mg**	**Al**	**Ca**	**Cr**	**Mn**	**Fe**	**Cu**	**Zn**	**As**	**Cd**	**Sn**	**Ba**	**Pb**	**U**
Concentration in:	ppb	ppm	ppb	ppm	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb	ppb
GCDWQ	NA	NA	NA	NA	50	50	300	1000	5000	10	5	NA	1000	10	20
Town of Sunnyside															
Source water	0.3	0.4	143.6	1.7	BDL	11.4	103.3	BDL	BDL	BDL	BDL	BDL	5.4	BDL	0.0
WTS	2.5	0.5	2,806.7	7.5	0.6	4,932.1	553.6	58.2	89.2	BDL	0.4	BDL	81.2	6.8	0.1
Resident A	0.3	0.4	171.0	1.9	BDL	21.9	89.8	60.1	BDL	BDL	BDL	BDL	5.4	0.8	BDL
Town Hall	0.4	0.4	175.5	2.2	BDL	12.7	119.1	176.0	BDL	BDL	BDL	BDL	5.6	1.6	0.0
Resident B	0.4	0.4	218.9	2.7	BDL	15.7	163.9	1.4	BDL	BDL	BDL	BDL	6.8	BDL	0.0
Town of New-Wes-Valley															
Source water (Little Northwest Pond)	1.1	0.4	190.0	0.8	BDL	9.2	348.2	BDL	BDL	BDL	BDL	BDL	BDL	0.1	0.1
Town Hall	0.9	0.3	131.9	0.6	0.7	1.4	101.9	8.2	16.8	BDL	BDL	BDL	BDL	0.6	0.1
MP	1.6	0.6	210.9	1.1	BDL	3.3	131.5	204.4	15.8	BDL	0.2	0.3	1.6	0.6	0.1
Booster station	1.5	0.5	182.9	1.1	0.7	2.5	116.3	261.0	12.8	BDL	0.2	0.4	3.1	0.5	0.1
Source water (Carter's Pond)	0.4	0.4	144.6	0.5	BDL	6.2	172.9	BDL	BDL	BDL	BDL	BDL	BDL	0.2	0.0
MP	0.6	0.7	258.3	1.1	1.0	9.9	288.8	86.7	75.3	BDL	BDL	3.6	1.9	7.2	0.1
WTS	0.7	0.5	179.5	0.8	1.7	10.7	289.4	48.7	140.0	BDL	0.2	22.4	1.9	3.7	0.1
Town of Salvage															
Source water	0.5	0.9	273.8	4.0	BDL	45.7	576.4	0.9	BDL	BDL	BDL	BDL	3.3	0.2	BDL
WTS	0.5	0.8	262.0	3.6	2.5	10.1	592	5.9	17.4	0.8	0.6	BDL	3.2	1.0	BDL
MP	0.5	0.9	286.3	3.8	2.6	10.5	620.3	84.4	17.4	0.7	0.5	BDL	3.2	1.1	BDL
Town Hall	0.6	0.9	245.4	4.0	0.7	8.8	567.4	156	11.5	BDL	BDL	0.8	4.3	0.6	BDL

Notes:

BDL: below detection limit; WTS: water treatment station; MP: middle of pipeline; NA: not available.

3 Characterization and Fractionation of NOM

NOM in surface waters is formed of hydrophobic and hydrophilic compounds (Matilainen et al., 2011). These compounds are different in molecular weights and sizes (Zularisama et al., 2006). The portion of NOM that permeates a 0.45µm filtering paper is called dissolved organic matter (DOM) which consists of the refractory organic matter that cannot easily be removed (Cheng et al., 2005). The particulate organic matter that remains on the filter in most of the water samples is less than 10% of TOC (Leenheer and Croue, 2003). The molecular size of NOM affects the treatability of the type of DBPs that are produced for instance Trihalomethanes (THMs) are generated by intermediate and small molecules of humic acids (Nissinen et al., 2001). Therefore, differences in DOM characteristics affect its potential capacity of reaction with disinfectants (Chow et al., 2005).

UV_{254} is one of the indicators of DBPs precursors. Although UV measurement is compatible with NOM concentration, it is not an indicator of the hydrophobicity and reactivity of NOM (Leenheer and Croue, 2003). Various aromatic hydrocarbons have specific reactivity potential with dissinfectants (Vieira et al., 2012). Therefore, applying a method for characterization of NOM to find its most reactive part is vital, but the most significant complication for NOM characterization is to find the most suitable fractionation procedure (Matilainen et al., 2011).

Various methods for NOM fractionation have been developed including size exclusion chromatography, resin chromatography, solvent extraction, ultrafiltration and electrophoresis (Chow et al., 2005; Matilainen et al., 2011; Kent et al., 2014). But most of these methods are complicated and need experienced experts.

The method that is used in this research is a resin fractionation technique. Although in the current approach, applying severe pH conditions can influence the structure of DOM, the time-saving process based on the DOC concentrations of different fractions of NOM are making it one of the most popular fractionation methods. Moreover, this technique helps us with grasping the type of DOM that is removed by the treatment (Chow et al., 2004).

Resin fractionation is the most popular technique for categorizing NOM components to Hydrophobic, hydrophilic and transphilic groups and acid, base, and neutral subcategories (Figure 3-1) based on their absorptivity to XAD amberlite resins (Leenheer and Croue, 2003). The synthetic resin fractionation first was used by at US Geological Survey, but many researchers expanded the method based on their needs in the experiments (Matilainen et al., 2011).

3.1 Methodology

3.1.1 Water sources

Raw water was taken from the intake points of New-Wes-Valley and Sunnyside. The water samples generally belong to high colour and high dissolved organic carbon sources. Same water samples were used for the following batch and column experiments.

3.1.2 Materials and apparatus

For NOM fractionation, Amberlite XAD-4, Supelite DAX-8 and Amberlite IRA-958 Chloride form resins were supplied by Sigma-Aldrich, Ontario, Canada. DAX resin previously was known as XAD resins. Methanol (purchased from Sigma-Aldrich), deionized water (produced in NRPOP lab), acetonitrile with purity of 99.9% (purchased from VWR) were used for preparation of resins. Three chromatography columns were made of borosilicate glass (Provided by VWR, Canada). Columns had dimensions of 25 x 150 mm (ID x L) and the capacity of 74 mL. Flow adaptors for chromatography (produced by Kimble Chase) were used to keep the level of resins and flow constant. Whatman 0.45 µm nylon membrane (purchased from Sigma-Aldrich, Canada) was used for removing particulate organic matter and filtering water before fractionation. Concentrated phosphoric acid and sodium hydroxide were used for pH adjustment. Fisher band variable-flow peristaltic pump (manufactured by Fisher Scientific) was used for maintaining a steady flow.

3.1.3 Experimental Procedure

The method is the same as the process that was described by Chow et al. (2004). It is a rapid method for characterization of NOM. NOM is separated into four fractions including Very Hydrophobic Acids that is adsorbed to DAX-8 resin, Slightly Hydrophobic Acids, adsorbed by

XAD-4, Charged Hydrophilic Acids (adsorbed to IRA-958) and Neutral Hydrophilics that is not adsorbed to the resins.

Preparation and conditioning of resins were performed according to the method was suggested for the first time by Croue et al. in 1994 (Chow et al., 2004). Preparation of DAX-8 and XAD-4 was done by soaking resin in methanol for 1 hour. Methanol was then decanted carefully and was replaced by 500 mL of water. Three consecutive washing with 500 mL deionized water was done and the last portion was left overnight. After that three successive rinses with deionized water on the next day were performed. For IRA-958, the procedure had an extra step of washing with acetonitrile for 1 minute and settling for 15 minutes; then rinsing with total 3000 mL of water as indicated for XAD-4 and DAX-8.

For the fractionation, three chromatography columns were set up in series containing 25 mL of DAX-8, XAD-4 and IRA-958 resins. Particulate TOC of water samples were removed by passing 700 mL of the sample through a 0.45 μm nylon filtering paper. The filtered water was acidified with concentrated phosphoric acid to pH of 2. Then the sample was passed through the first column containing DAX-8 at 5 mL/min. The selected flow was 0.2 bed volume per minute as recommended by Chow et al (2004). The first 50 mL, two bed volumes, of water sample from each of the columns were disposed. DOC samples were taken in duplicate from the effluent of each column. After passing water sample through DAX-8 and taking DOC samples, the remaining was passed through XAD-4 column. NaOH was added to the effluent of the second column to reach pH of 8 and then was pumped to the third column. The setup columns is shown in Figure 3-2.

3.2 Results and Discussion

The calculation of the concentration of each fraction of natural organic matter is based on the following equations (Vieira et al., 2012; Chow et al., 2004):

[1] Very Hydrophobic Acid (VHA) = Raw – (DAX-8 effluent)
[2] Slightly Hydrophobic Acid (SHA) = (DAX-8 effluent) - (XAD-4 effluent)
[3] Charged Hydrophilic Acid (CHA) = (XAD-4 effluent) – (IRA-958 effluent)
[4] Neutral Hydrophilic (NEU) = (IRA-958 effluent).

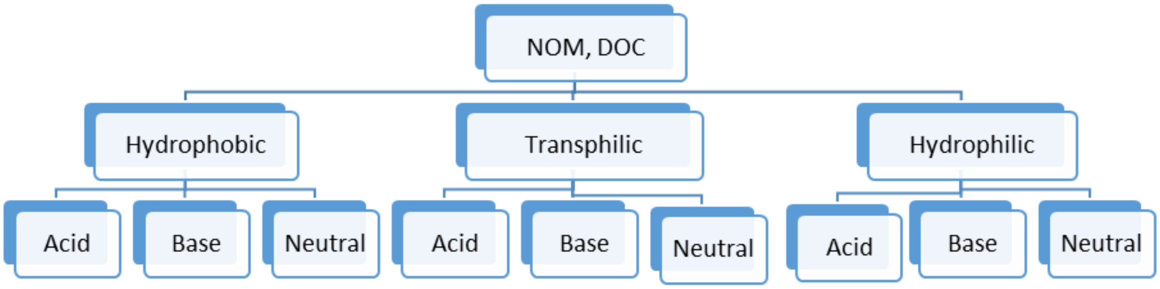

Figure 3-1 Classification of Dissolved Organic Carbon (DOC)
(Source: Leenheer and Croue, 2003)

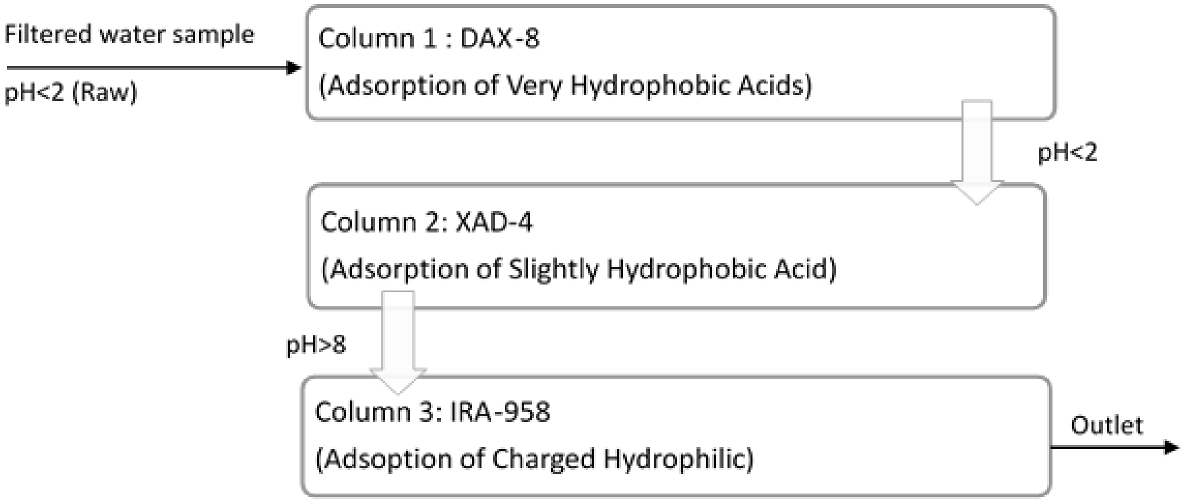

Figure 3-2 Schematic of the columns setup for NOM fractionation

Table 3-1 Natural organic matter fractionation for Sunnyside source water sample

Town of Sunnyside				
Sample name	Raw	DAX-8 effluent	XAD-4 effluent	IRA-958 effluent
DOC (mg/L)	10.39	6.252	5.250	4.194
Sample name	VHA	SHA	CHA	NEU
NOM fractions	39.82%	9.62%	10.18%	40.36%

Small amount of water sample is the most significant factor for the mentioned procedure. The use of small columns decreases the required volume of water small and guarantees the precision of the results (Chow et al., 2004).

Results are indicated in both mg/L and percentage of DOC in

Table 3-1 for Sunnyside water sample and the counterpart data for New-Wes-Valley water sample is presented in Table 3-2.

A comparative chart is presented in Figure 3-3, which indicates that the dominant fraction in New-Wes-Valley water sample is VHA with 58.11% of the total NOM. The second significant share is 35.57% which is related to NEU. Moreover, SHA and CHA had small portions with 1.99% and 4.32%, respectively. On the other hand, the most important fraction in Sunnyside water sample is related to NEU and with a slight difference, VHA stands in the second place. Their fractions were measured 40.36% and 39.82% respectively. SHA and CHA had the least portions of 1.99% and 4.32%.

According to the results of chlorination tests, it is obvious that the higher amount of hydrophobic fraction in New-Wes-Valley resulted in the higher amount of DBPs including THMs and HAAs with the concentrations of 1310 mg/L and 666 mg/L. On the other hand, lower concentration of hydrophobics in Sunnyside water sample was along with the 935 mg/L and 360 mg/L for THMs and HAAs, respectively. The result is in agreement with the research of Leenheer and Croue (2003). Also it was found by Nissinen et al. (2001) that THMs are mostly related to the low and medium molecular sized of NOM. Therefore, it can be concluded that the concentration of low molecular size NOM in New-Wes-Valley is higher.

Generally, hydrophobics can be better removed by coagulation and sedimentation (Vieira et al., 2012) . Moreover, activated carbons are more successful in removing low molecular size NOM. Therefore, it is recommended to conduct experiments using coagulation for New-Wes-Valley for removing high molecular size hydrophobics and applying activated carbon for removing lower molecular sizes such as hydrophilic neutrals. It is also indicated in the activated carbon treated water samples, the method was more successful in decreasing THMs in comparison with HAAs for the first hour of experiment, which strengthens the previous studies about the relationship of THMs and low molecular size NOM.

Table 3-2 Natural organic matter fractionation for New-Wes-Valley source water sample

Town of New-Wes-Valley				
Sample name	Raw	DAX-8 effluent	XAD-4 effluent	IRA-958 effluent
DOC (mg/L)	13.08	5.479	5.218	4.653
Sample name	VHA	SHA	CHA	NEU
NOM fractions	58.11%	1.99%	4.32%	35.57%

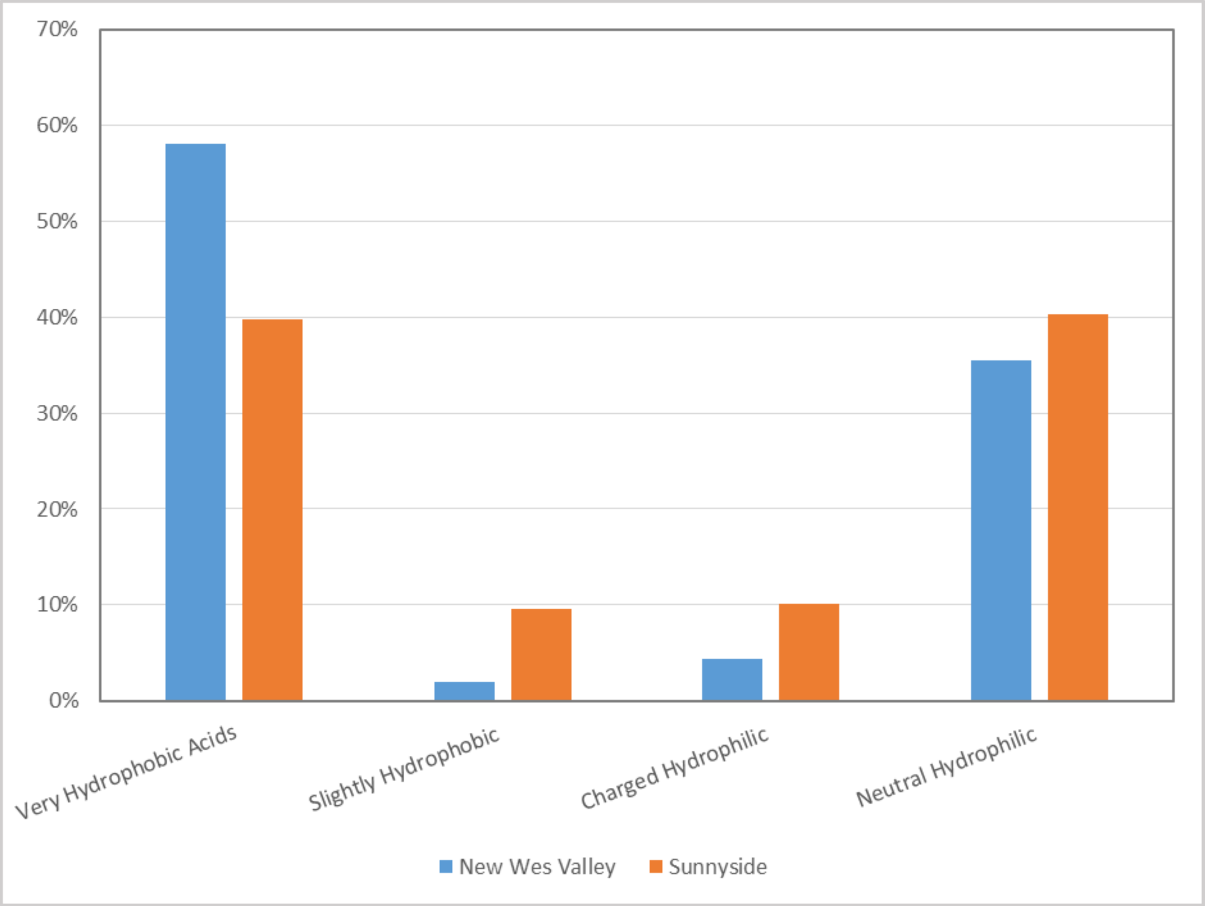

Figure 3-3 A comparison on natural organic matter fractionation of New-Wes-Valley and Sunnyside

4 Evaluation of Adsorbent Performance in Batch Test

4.1 Adsorbent generation and characterization

Corner Brook Pulp and Paper (CBPP) Ltd. is the pillar of local economy in western Newfoundland. It produces almost 700 tons of newsprint every day through a thermo-mechanical pulping process, and approximate 10,000 metric tons of fly ash waste is generated from the mill boilers annually. It has been proved by many researchers that the fly ash is able to be transformed into activated carbon, which can be further applied in the areas of air pollution control and water treatment (Davini, 2002; Aslam et al., 2015; Jegadeesan et al., 2015; Salehin et al., 2016).

To help CBPP Ltd. with their waste management strategies, our previous research mainly investigated the feasibility of converting their fly ash waste into activated carbon. The unburnt carbon in the fly ash was extracted and physically activated in a high temperature tube furnace. Effects of two factors including activation temperature and activation time were explored. Iodine number (IN), methylene blue value (MBV), surface microstructure, surface area and pore volume were all used to characterize different carbon samples, and results are shown in Table 4-

1 and

Figure 4-1. It is identified that the carbon activated under 850 °C for 2 hours exhibits good adsorption capacity on iodine and methylene blue. This activation process can help develop relative high surface area and pore volumes on the carbon surface but without great energy consumption. Hence, it is selected to conduct both batch and column tests in this study; and source water from all the three towns were applied in the experiment. More details are provided in the following sections.

4.2 Batch test

4.2.1 Methodology

Batch tests were conducted to evaluate the adsorption of natural organic matter by different AC dose and for different contact/adsorption times. In this experiment, different amount of the CBPP AC-850°C-2hr sample was mixed with a series of 500 mL source water from Sunnyside at ratios of 0.5 g/L, 1 g/L and 2 g/L. The mixtures were thoroughly mixed on magnetic stirrers for adsorption time of 15 mins, 30 mins and 60 mins, respectively. The mixtures were filtered by 0.45 μm membrane filters and the filtrates were analyzed for TOC and UV. The adsorption kinetics and isotherm were also developed, and appropriate AC dose were figured out for the following experiment. Since natural organic matter is commonly measured as TOC, it is used to quantify the natural organic matter in the water samples. It is believed that some natural organic matter compounds have certain chemical structures that can absorb UV light especially at the wavelength of 254 nm (ENVC, 2011). Hence, UV_{254} is also applied in the quantification of the natural organic matters. Besides AC dose and contact time, temperature and pH can have influences on the adsorption of organic matter as well. However, the adsorption tests in real cases were usually conducted at room temperature, and the pH of the source water does not have much fluctuation in different seasons. Alkalinity could have some impacts on the removal of NOM only when inorganic coagulants are employed in the water treatment process (Chow et al., 2004; Krasner and Amy, 1995; Owen et al., 1995). Nonetheless, the majority of the communities in NL do not utilize coagulation as pretreatment. The effects of temperature, pH and alkalinity are therefore not considered in this study.

4.2.2 Results and discussion

The adsorption capacity of CBPP AC was examined through batch tests. TOC removal and UV deduction were investigated and shown in

Figure 4-2 and

Figure 4-4. As can be seen in

Figure 4-2, 75% of TOC was removed after 60 mins adsorption at a dose of 0.5 g/L. The trend of TOC removal at dose of 1 g/L is similar to that at 2 g/L from 15 mins to 60 mins. About 85% of

TOC removal was found from 30 mins to 60 mins at both doses, which indicates that the maximum adsorption of TOC is around 85% and it can occur within 30 mins of adsorption. As shown in

Figure 4-4, a 72% of UV_{254} deduction was observed after 15 mins adsorption at the dose of 0.5 g/L, meanwhile a 95% of UV_{254} deduction was obtained after 60 mins at the same dose. For the doses of 1 g/L and 2 g/L, the UV_{254} was dramatically decreased to zero within 15 mins of adsorption, which illustrates the CBPP AC is extremely effective in UV_{254} deduction in the adsorption experiments. Comparing TOC removal with UV_{254} deduction at the carbon dose of 1 g/L with 15 mins adsorption time, 74% of TOC was removed while 100% UV_{254} deduction was detected. As stated earlier, both TOC and UV were used to quantify the organic matter. The big difference in the TOC removal and UV deduction results implied that some of the organic compounds in the water sample cannot absorb UV light at the wavelength of 254 nm. From another point of view, it also illustrates that this CBPP AC is more effective in the adsorption of light-sensitive organic matters. The same phenomenon was also discovered in the column experiment in the next chapter.

Figure 4-3 displays the TOC adsorption isotherm by CBPP AC with different doses. From the isotherm, the adsorbed TOC by each gram of activated carbon is 3.7 mg/g, 1.1 mg/g and 0.6 mg/g for doses of 0.5 g/L, 1 g/L and 2 g/L, respectively. The use of 0.5 g (AC) /L (water) in the batch test has the highest adsorption effectiveness and the lowest cost of AC. This dose is thus determined to be appropriate in the following experiment.

Table 4-1 Characteristics of CBPP clean fly ash and activated carbon

Parameters	**IN** (mg/g)	**MBV** (mg/g)	**Surface area** (m^2/g)	**Micropore area** (m^2/g)	**Pore volume** (cm^3/g)
CBPP FA-Clean	289.53	61.89	486.44	402.50	0.18
CBPP AC-850°C-2hr	704.53	193.47	847.26	619.49	0.28

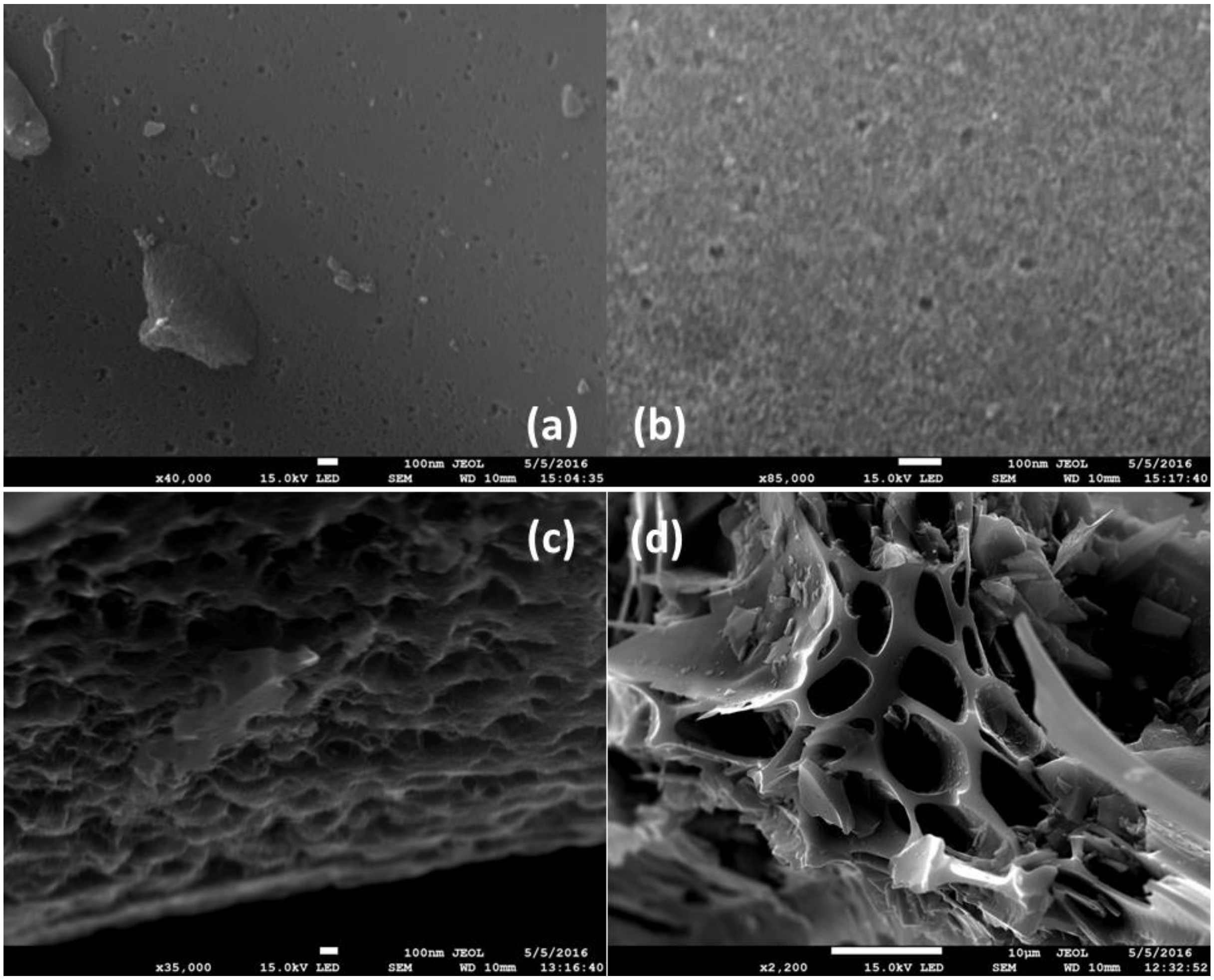

Figure 4-1 Surface microstructure images of carbon particles: (a) & (b) before activation; (c) & (d) after activation

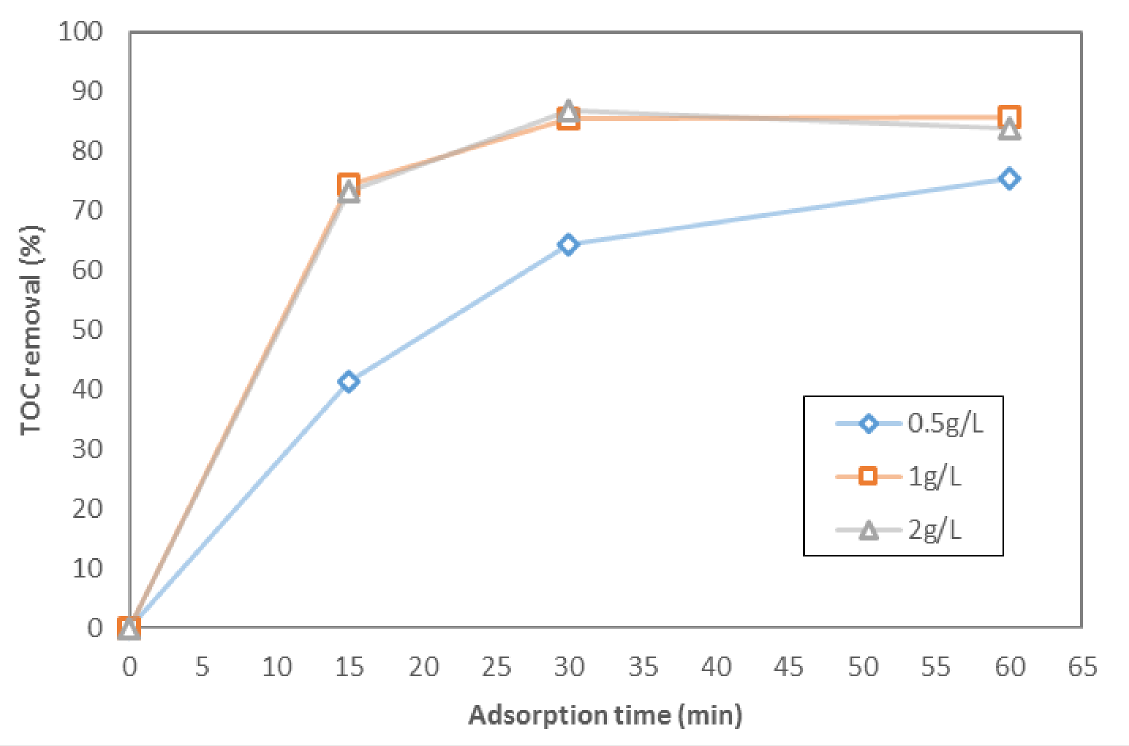

Figure 4-2 TOC adsorption kinetics by CBPP AC with different doses

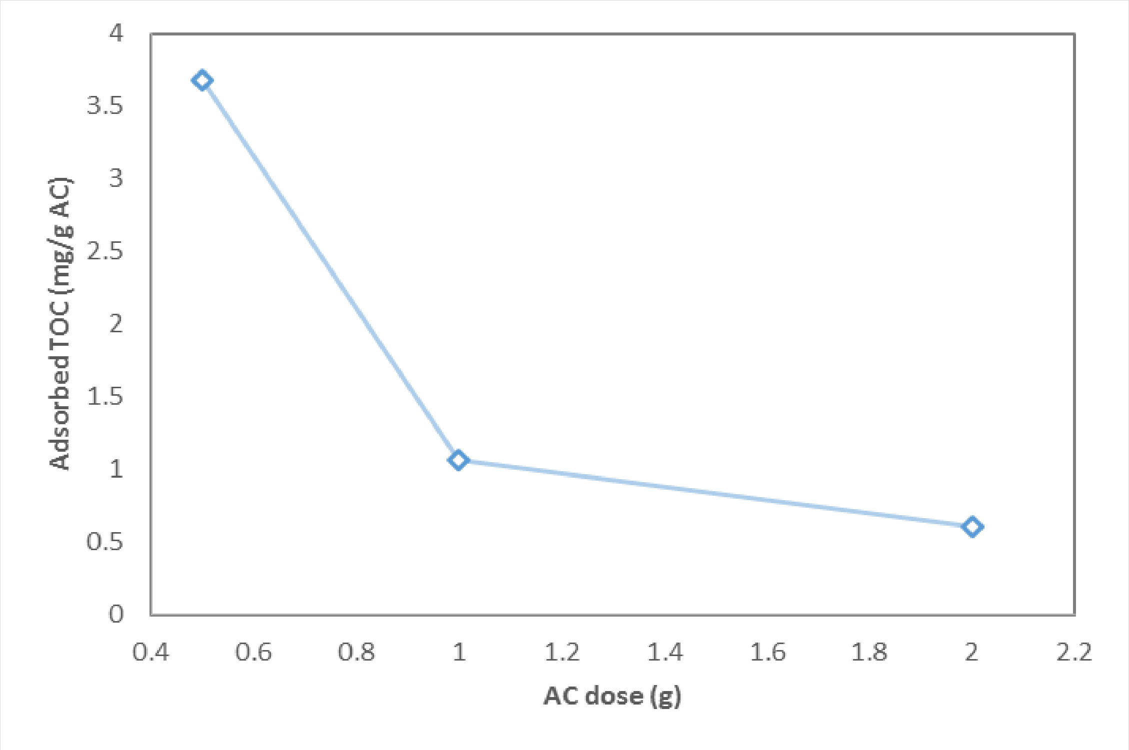

Figure 4-3 TOC adsorption isotherm by CBPP AC with different doses

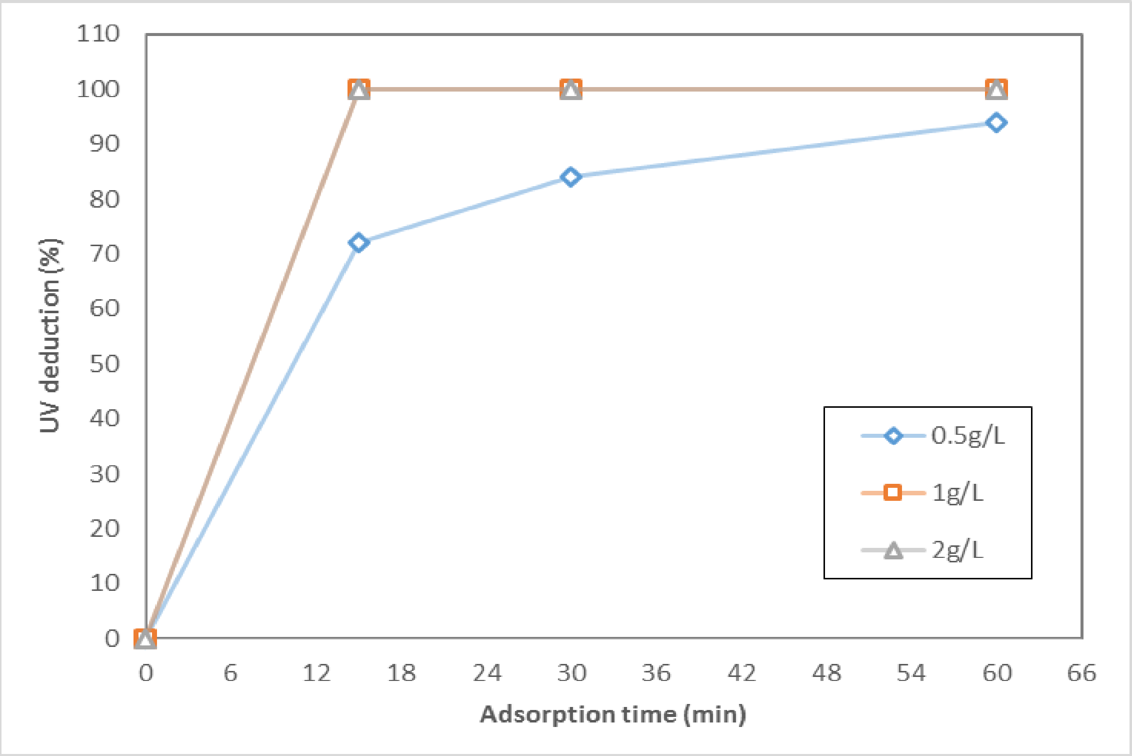

Figure 4-4 UV deduction by CBPP AC with different doses

5 Assessment of NOM Removal through Column Filtration

5.1 Column filtration system

Carbon filtration technology has been widely applied in water and wastewater treatment for many years. Commercialized carbon filtration systems are frequently designed to be in the form of fixed bed adsorption units. In our previous study, a lab scale fixed bed carbon filtration system was developed and applied to evaluate a carbon adsorbent. As shown in Figure 5-1, a column with 30 cm length and 40 mm diameter is made to implement the carbon filtration technology. In general, a 0.45 μm membrane filter paper is placed at the bottom of the column and 5 g CBPP AC-850°C-2hr sample is then packed into the column. The column top part is connected to a water reservoir which contains water samples to be treated, and the water will pass through the column in a down flow mode. A peristaltic pump is connected at the column outflow to control the filtration speed. When the water enters the column, and passes through the carbon barrier, the natural organic matter in water can be adsorbed by the activated carbon so that the formation of DBPs can be avoided or mitigated. Above all, this system was employed to estimate the adsorption efficiency of CBPP AC on natural organic matter in the source water samples from the three communities.

5.2 Evaluation of system performance

5.2.1 Methodology

A 24-hour column filtration test was conducted to evaluate the adsorption performance of the lab-generated CBPP AC. The source water from the three communities, respectively, was passed through the column in a down flow mode. The flow rate of this test was kept in the range of 6 to 8 mL/min and about 10 L in total of the source water has been filtered within the 24-hr period. Due to the difficulties in sample collection, the source water collected from Salvage was not enough for the 24-hours filtration. Hence, the column filtration experiment using Salvage source water was conducted for only 12 hours. For Sunnyside and New-Wes-Valley, the column effluent was sampled at the 1st, 2nd, 3rd, 6th, 12th and 24th hour for the analysis of TOC, and the 6th, 12th and 24th hour for the analysis of UV_{254}. For Salvage, the column effluent was sampled at the 1st, 2nd, 3rd, 6th and 12th hour for the analysis of TOC, and the 6th and 12th hour for the analysis of UV_{254}.

5.2.2 Results and discussion

5.2.2.1 TOC

Figure 5-2 to 5-4 present the TOC of raw and filtered column effluent samples from all the three towns. From

Figure 5-2, the TOC of the Sunnyside column effluent samples decreases from 8.86 mg/L to 3.2 mg/L in the first two hours, and then increases to 7.8 mg/L at the twenty-forth hour. Comparing the original source water with the column effluent sample at the end of the second hour, more than 64% of the organic matter has been adsorbed or removed by the carbon barrier. After 2 hours, the organic matter in the column effluent starts to increase but still below the original level, which implies that the adsorption rate of the carbon barrier is decreasing. After 24 hours, the TOC of the column effluent sample is close to 8 mg/L, which reveals that the carbon barrier has gradually become saturated. Continuous filtration of Sunnyside source water for more than 24 hours is therefore not suggested.

The TOC change in the column effluent for New-Wes-Valley and Salvage has a similar trend to that for Sunnyside. For New-Wes-Valley (

Figure 5-3), the TOC of the column effluent decreases from 13 mg/L to 3 mg/L within two hours filtration. It indicates a maximum AC adsorption rate of 77% has been reached at the end of the second hour. After that, the adsorption rate starts to decrease until the end of 24 hours. The TOC of the 24 hour effluent sample is 10.4 mg/L which also implies the carbon barrier is close to saturation. For Salvage (

Figure 5-4), however, the carbon barrier is nearly saturated after 12 hours filtration. The maximum AC adsorption rate appears to be 74% which occurs at the end of the 1st hour. The TOC of the 1 hour effluent sample is 3.9 mg/L, and it increases to 10.6 mg/L after 12 hours filtration.

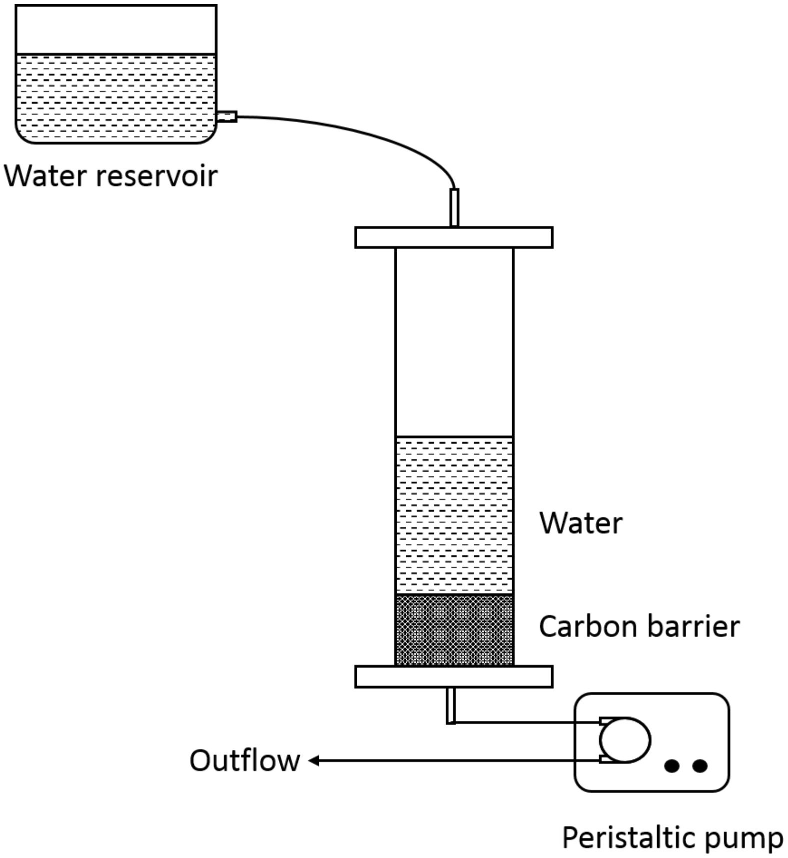

Figure 5-1 A sketch of carbon filtration system

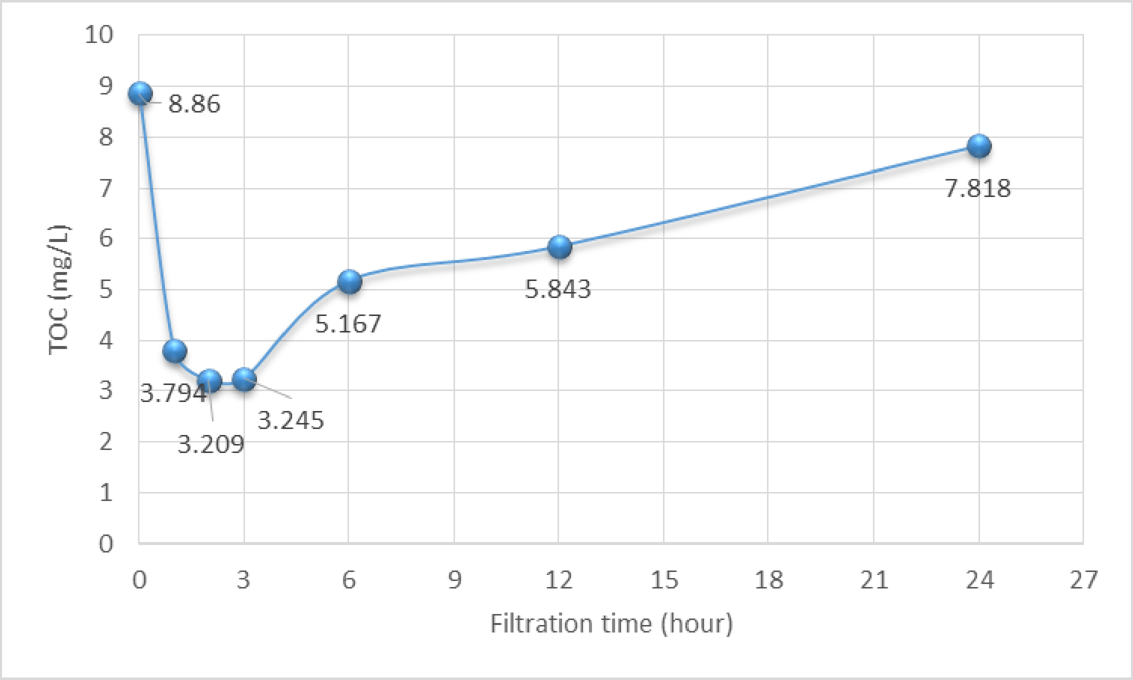

Figure 5-2 TOC of Sunnyside raw and filtered water samples from column test

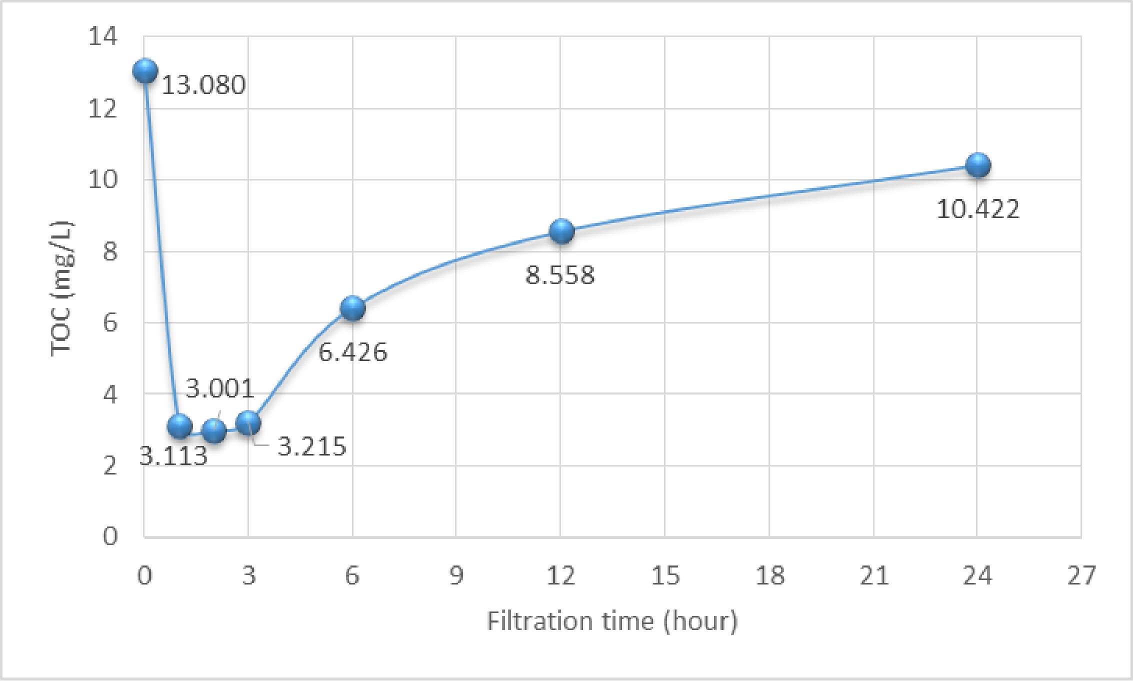

Figure 5-3 TOC of New-Wes-Valley raw and filtered water samples from column test

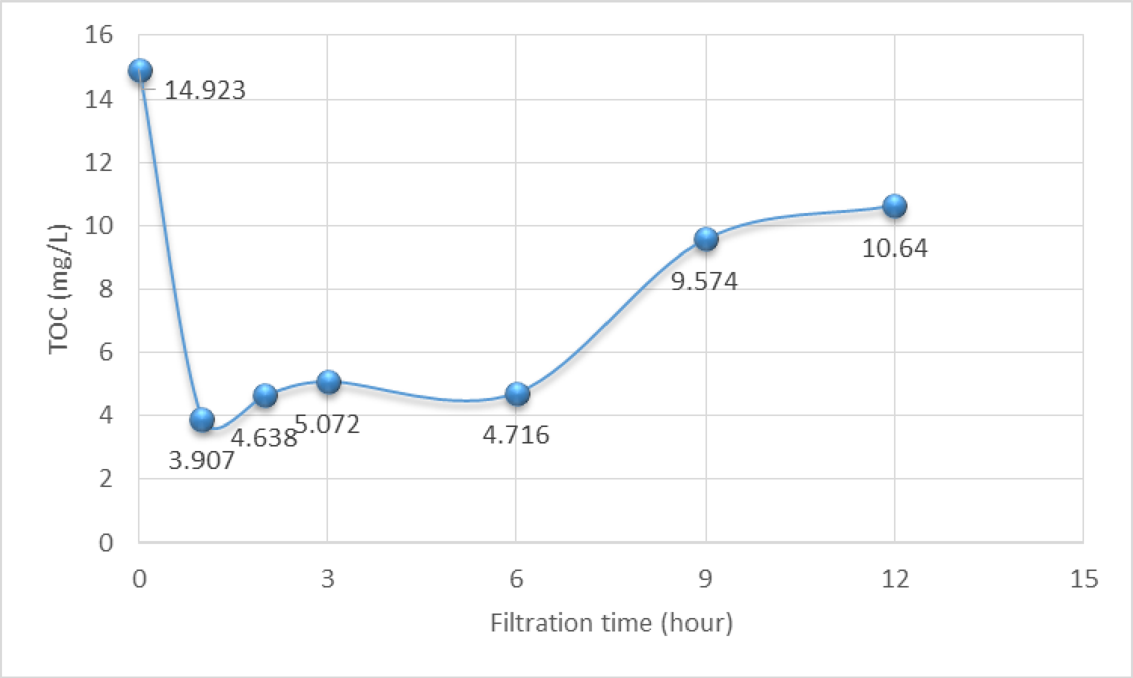

Figure 5-4 TOC of Salvage raw and filtered water samples from column test

The TOC change in the column effluent samples could have such a similar trend for all the three communities is possibly due to the unstable flow rate in the column. Since the CBPP AC used in column test is in powder form, it can easily cause blocking problems sometime in the middle of the experiment. The flow rate is usually high in the beginning of the filtration, and it will gradually become slow. When the flow rate slows down, the contact time between carbon and water sample will be extended. Therefore, the TOC in the column effluent was decreasing in the first few hours. To overcome the blocking problem, a granular type of activated carbon is suggested in future study.

5.2.2.2 UV

From

Figure 5-5 to

Figure 5-7, the results of UV_{254} have similar trends as that of TOC, because of the blocking problem in the column. In

Figure 5-5, the UV_{254} of the Sunnyside column effluent sample decreases from 0.271 A to 0.129 A within 6 hours filtration, and then it increases to 0.19 A at the end of 24 hour. The TOC of the 24th hour sample is about 88% of the original water sample, which indicates the carbon barrier is 88% saturated. However, the UV_{254} of the same sample is only 70% of the original water sample, which implies the carbon barrier is only 70% saturated. Similarly, the UV_{254} of the New-Wes-Valley column effluent sample (

Figure 5-6) decreases from 0.679 A to 0.248 A within 6 hours filtration, and then it increases to 0.467 A at the end of 24 hour. The TOC result indicates the carbon barrier is 88% saturated after 24 hours filtration, while the UV_{254} result leads to a 69% saturation of the carbon barrier. Such difference between TOC and UV can also be found in the filtration of Salvage water samples. Comparing

Figure 5-4 with

Figure 5-7, the result of TOC demonstrate the carbon barrier becomes 71% saturated when the result of UV_{254} shows a 49% of saturation in the carbon barrier. The big difference in the saturation degree from both TOC and UV results could perhaps because some natural organic matters in the source water do not have UV-absorbing chemical structures. It also proves that the CBPP AC is more effective in adsorbing light sensitive organic matters. This phenomenon is also observed in the batch test, which may hint that the TOC results are more reliable than the UV results.

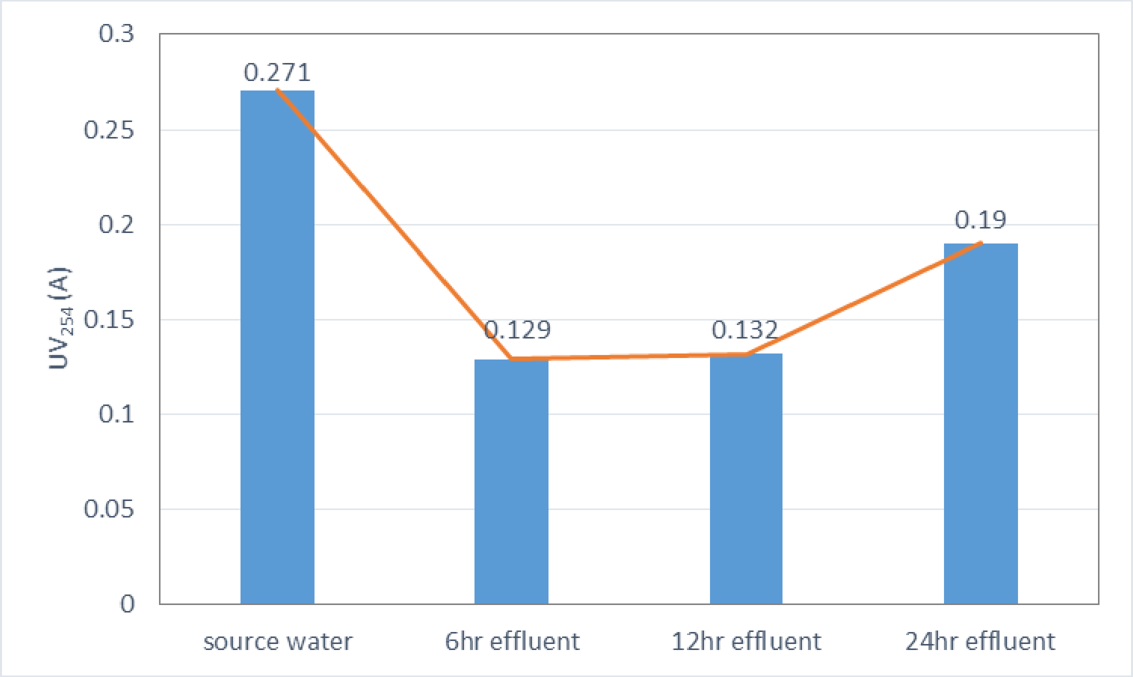

Figure 5-5 UV of Sunnyside raw and filtered water samples from column test

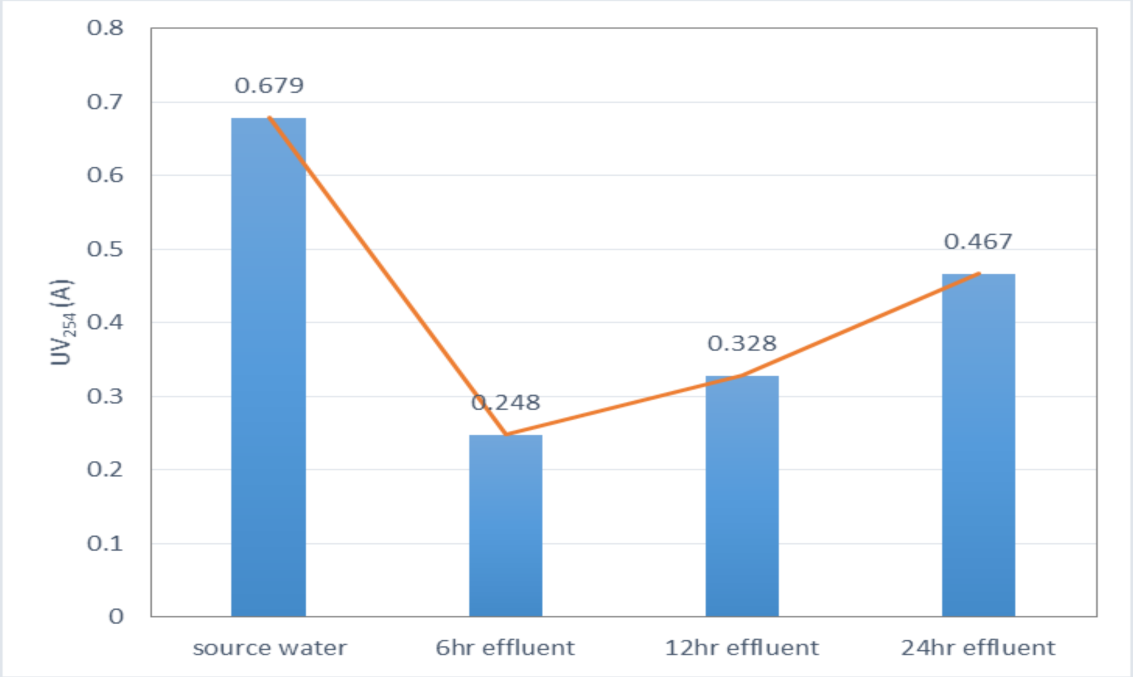

Figure 5-6 UV of New-Wes-Valley raw and filtered water samples from column test

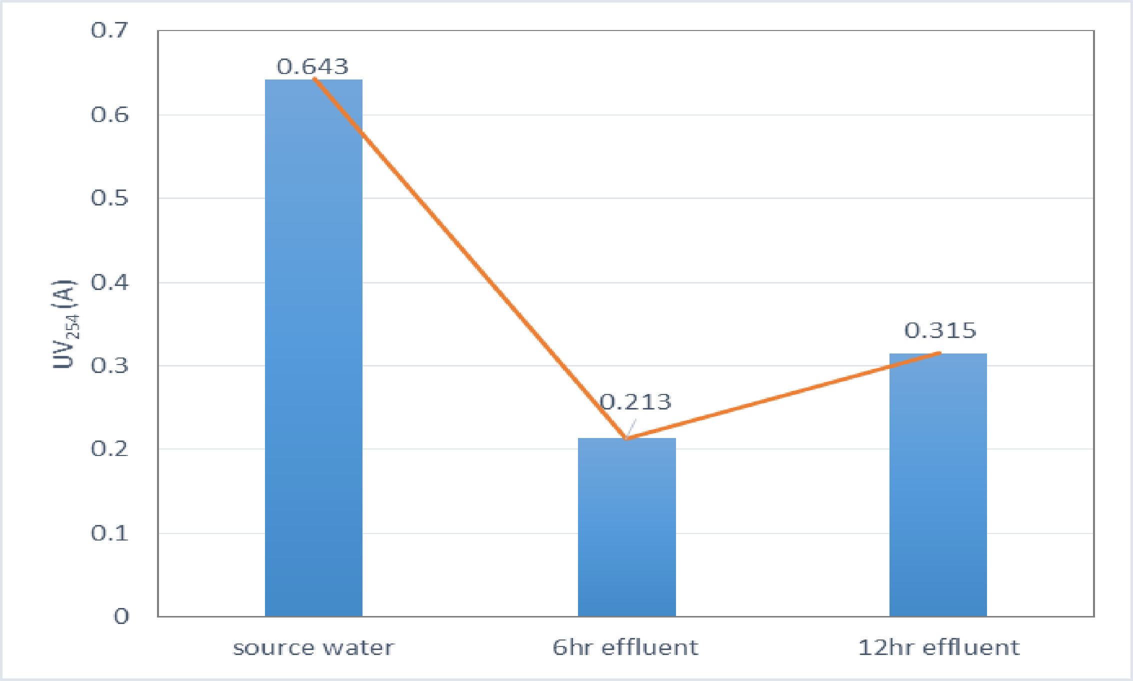

Figure 5-7 UV of Salvage raw and filtered water samples from column test

6 Assessment of DBP Formation

Chlorination, as a common disinfection process, has been widely utilized for pathogen control in drinking water in NL. Since most of the rural communities in the province does not have any intake water pre-treatment system installed, once there is NOM in the source water the DBPs will form in the drinking water after chlorination. The carbon filtration system was proved to be effective in the organic matter removal from all the three local communities in the column filtration experiments. It is also crucial to assess the DBP formation in the unfiltered and filtered water. Hence, in this part of study, the formation potential of two major groups of DBPs (THMs and HAAs) were examined for all the three communities and for both raw and filtered water samples. More details are provided in the following sections.

6.1 Methodology

In this part of experiment, a sodium hypochlorite 5% usp solution (A&C Ltd., NaClO assay: 4.0 – 6.0%) was used as a disinfectant. Both raw and column filtered source water samples from the three communities were chlorinated by sodium hypochlorite and stored at a dark place for 24 hours. According to GCDWQ, free chlorine in the majority of the drinking water distribution systems is in the range of 0.04 mg/L to 2 mg/L. To keep the concentration of free chlorine after 24 hours of our chlorination experiment in the same range, different amount of sodium hypochlorite solution was added into the water samples from different communities. The formation of THMs and HAAs were monitored after 1 hour, 4 hour, 12 hour and 24 hour of chlorination. Meanwhile, the concentrations of four typical THM compounds, including chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), bromoform ($CHBr_3$), and all of nine HAA compounds, which are Monochloroacetic acid (MCAA), Monobromoacetic acid (MBAA), Dichloroacetic acid (DCAA), Trichloroacetic acid (TCAA), Bromochloroacetic acid (BCAA), Bromodichloroacetic acid (BDCAA), Dibromoacetic acid (DBAA), Chlorodibromoacetic acid (CDBAA), Tribromoacetic acid (TBAA), were also analyzed.

6.2 Results and discussion

6.2.1 Town of Sunnyside

Figure 6-1 displays the total THM concentrations of both raw and column filtered water samples during the chlorination process. As shown in Figure 6-1, the total THM concentrations of all the samples are increasing as the chlorination time increases. For Sunnyside raw water, the majority THMs are formed within 12 hours chlorination. For the column filtered water samples, the THM concentrations are gradually increasing at relatively lower rates during the whole chlorination process. The Sunnyside raw water has a THM concentration of 935 µg/L after 24 hours, while the THM concentrations of the column 6hr, 12hr and 24hr effluent samples are about 404 µg/L, 345 µg/L and 521 µg/L, respectively. It indicates that the column filtration is effective in NOM removal, hence can significantly reduce the THM amount formed in the chlorination processes. Among the column 6hr, 12hr and 24hr effluent samples, the 12hr column effluent sample holds the lowest level of THM concentrations throughout the chlorination process, which implies the 12hr column effluent sample contains the least NOM amount. This is possibly because of the blocking problem occurred in the middle of the column filtration, as blocking can lead to longer contact time between water and carbon barrier and more NOM can be adsorbed.

From Table 6-1, it is revealed that the chloroform plays a predominant part in the total THM concentrations. Comparing the raw water results and the column filtered water results, it is interesting to find that the bromine-containing THM compounds are only formed in the raw water other than filtered water samples during chlorination.

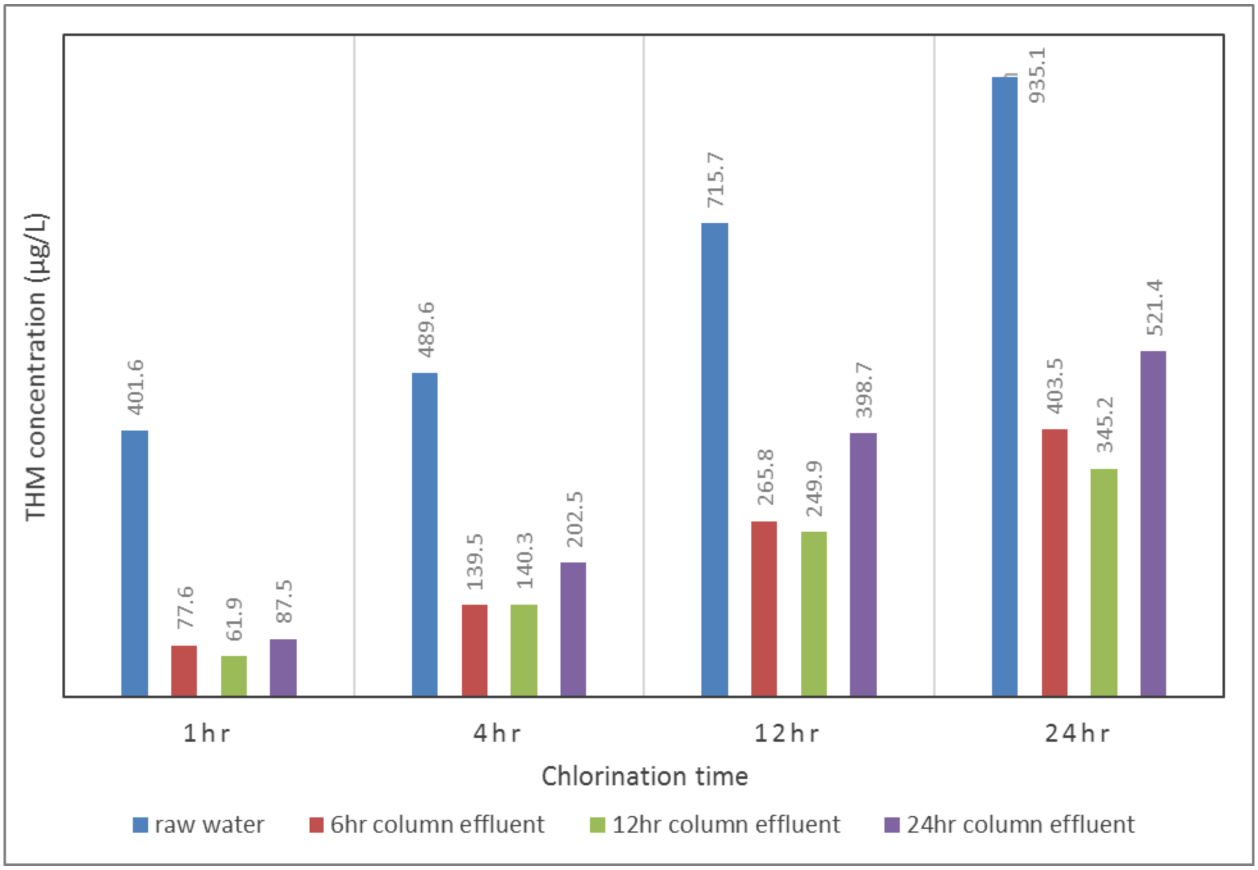

Figure 6-1 Total THMs of Sunnyside raw and column samples during chlorination

Table 6-1 Typical THM compounds in Sunnyside water samples

Samples	**raw water**				**6hr column effluent**			
Chlorination time	1hr	4hr	12hr	24hr	1hr	4hr	12hr	24hr
Concentration	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
$CHCl_3$	327.6	440.2	700.7	918.9	77.6	139.5	265.8	403.5
$CHCl_2Br$	35.2	20.9	15.0	16.2	0	0	0	0
$CHClBr_2$	18.4	9.1	0	0	0	0	0	0
$CHBr_3$	20.4	19.3	0	0	0	0	0	0
Total THMs	401.6	489.6	715.7	935.1	77.6	139.5	265.8	403.5
Samples	**12hr column effluent**				**24hr column effluent**			
Chlorination time	1hr	4hr	12hr	24hr	1hr	4hr	12hr	24hr
Concentration	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
$CHCl_3$	61.9	140.3	249.9	345.2	87.5	202.5	398.7	521.4
$CHCl_2Br$	0	0	0	0	0	0	0	0
$CHClBr_2$	0	0	0	0	0	0	0	0
$CHBr_3$	0	0	0	0	0	0	0	0
Total THMs	61.9	140.3	249.9	345.2	87.5	202.5	398.7	521.4

Figure 6-2 presents the total HAA concentrations of Sunnyside raw and column filtered water samples during different period of chlorination. Same as the THM results, the total HAA concentrations of all the samples are continuously increasing within 24 hours. The raw water sample shows higher total HAA concentrations than that of column filtered effluent samples at all times during chlorination, which proves that the carbon filtration has the ability to prohibit the HAA formation. Comparing all the column filtered effluent samples, the HAA concentrations of the 6hr column effluent is close to that of the 12hr column effluent, and they are slightly lower than that of the 24hr column effluent. This reveals the adsorption rate of the carbon barrier was slowly decreasing in the column filtration process. Even though the carbon filtration can result in lower concentrations of DBPs, when looking at both THM and HAA concentrations of the raw and column effluent water samples at the 24th hour of chlorination, the THM formation was prohibited at a higher degree than the HAA formation. It is therefore investigated the column filtration is more efficient in the reduction of THM formation potential than that of HAA.

The concentration of each of the nine HAA compounds for all the chlorinated water samples are listed in Table 6-2. For all the chlorinated water samples, DCAA exhibits the highest concentration among all the nine HAA compounds. TCAA is also an important component in the total amount of HAAs. The formation of BCAA, BDCAA, DBAA, CDBAA and TBAA are very limited during the chlorination process for all the water samples. In some of the samples, such as raw water for instance, the concentration of MCAA is decreasing in the first 12 hours of chlorination but the concentrations of DCAA and TCAA are increasing. This phenomenon may hint that the MCAA is transformed into DCAA and/or TCAA during chlorination process indicating more C-H bonds in acetic acid was substituted by Cl atoms and formed C-Cl bonds with the presence of free chlorine. Similar phenomenon was also found in other water samples, which demonstrates that the longer contact time can lead to a higher degree of chlorination.

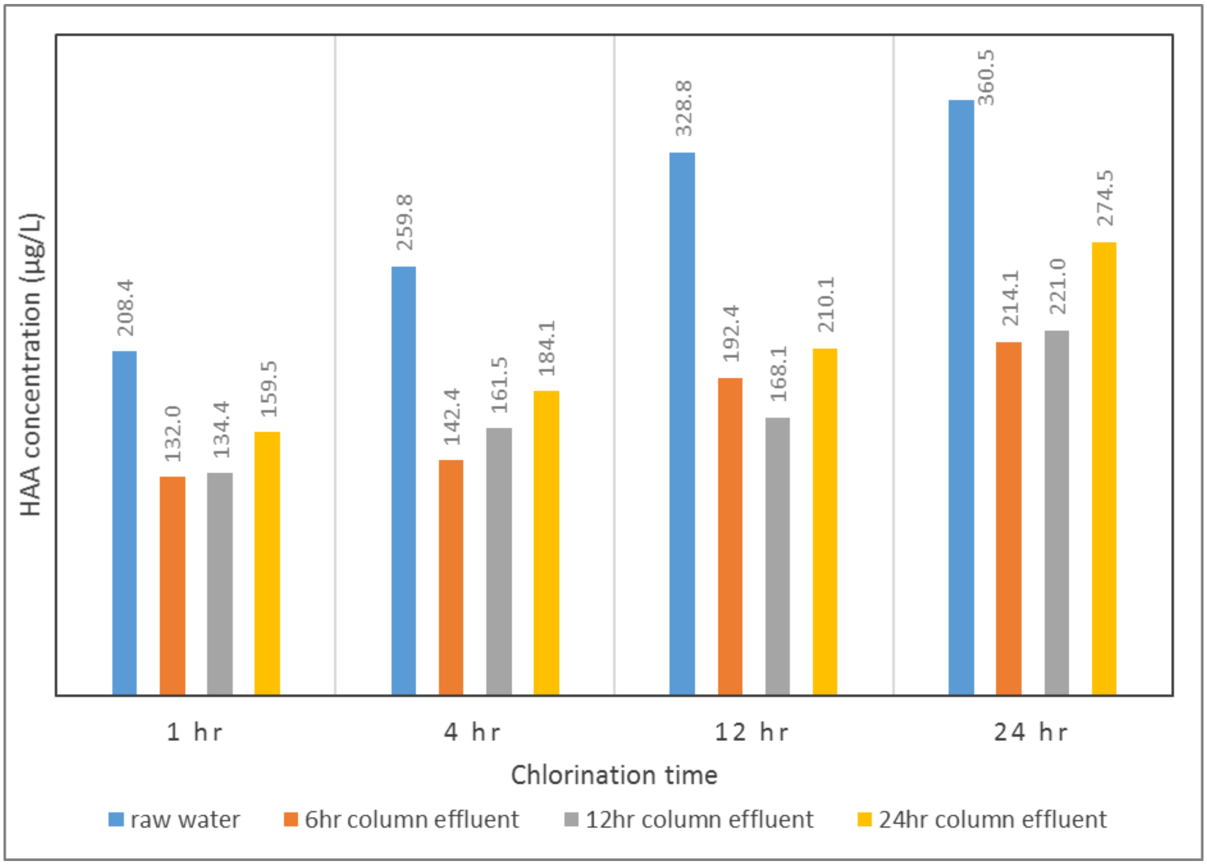

Figure 6-2 Total HAAs of Sunnyside raw and column samples during chlorination

Table 6-2 HAA compounds in Sunnyside water samples

Samples	**raw water**				**6hr column effluent**			
Chlorination time	1 hr	4 hr	12 hr	24 hr	1 hr	4 hr	12 hr	24 hr
Concentration	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
MCAA	36.8	9.9	7	10	10.3	0.0	0.0	0.0
MBAA	0	0	0	0	11.1	22.2	24.7	17.5
DCAA	127.3	200.9	274.8	281.5	76.3	88.7	126.1	154.3
TCAA	37.6	38.1	38.3	55.8	26.2	24.5	34.3	36.3
BCAA	0	0.3	1.1	1.5	1.1	1.3	1.9	2.3
BDCAA	0.5	0.7	0.8	1.1	0.7	0.7	0.8	1.0
DBAA	0	0	0	0	0.1	0.1	0.1	0.1
CDBAA	5.4	8.4	5.3	9.4	4.5	4.4	4.2	3.5
TBAA	0.6	1.5	1.4	1.1	1.6	1.0	1.5	1.6
Total HAAs	208.4	259.8	328.8	360.5	132.0	142.4	192.4	214.1
Samples	**12hr column effluent**				**24hr column effluent**			
Chlorination time	1 hr	4 hr	12 hr	24 hr	1 hr	4 hr	12 hr	24 hr
Concentration	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
MCAA	0.0	0.0	4.4	7.1	0.1	0.0	0.0	0.0
MBAA	14.8	23.6	1.4	17.8	6.4	14.9	0.2	4.9
DCAA	84.3	102.3	121.5	152.5	107.2	128.6	165.0	218.2
TCAA	28.7	27.5	32.4	35.2	35.1	32.2	38.1	42.6
BCAA	1.1	1.4	1.6	2.2	1.5	1.8	2.3	2.9
BDCAA	0.7	0.8	0.8	1.0	0.9	0.9	0.9	1.1
DBAA	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1
CDBAA	5.0	4.6	4.2	3.5	6.4	5.9	5.7	4.6
TBAA	2.2	1.6	1.7	1.7	1.8	0.1	0.4	0.4
Total HAAs	134.4	161.5	168.1	221.0	159.5	184.1	210.1	274.5

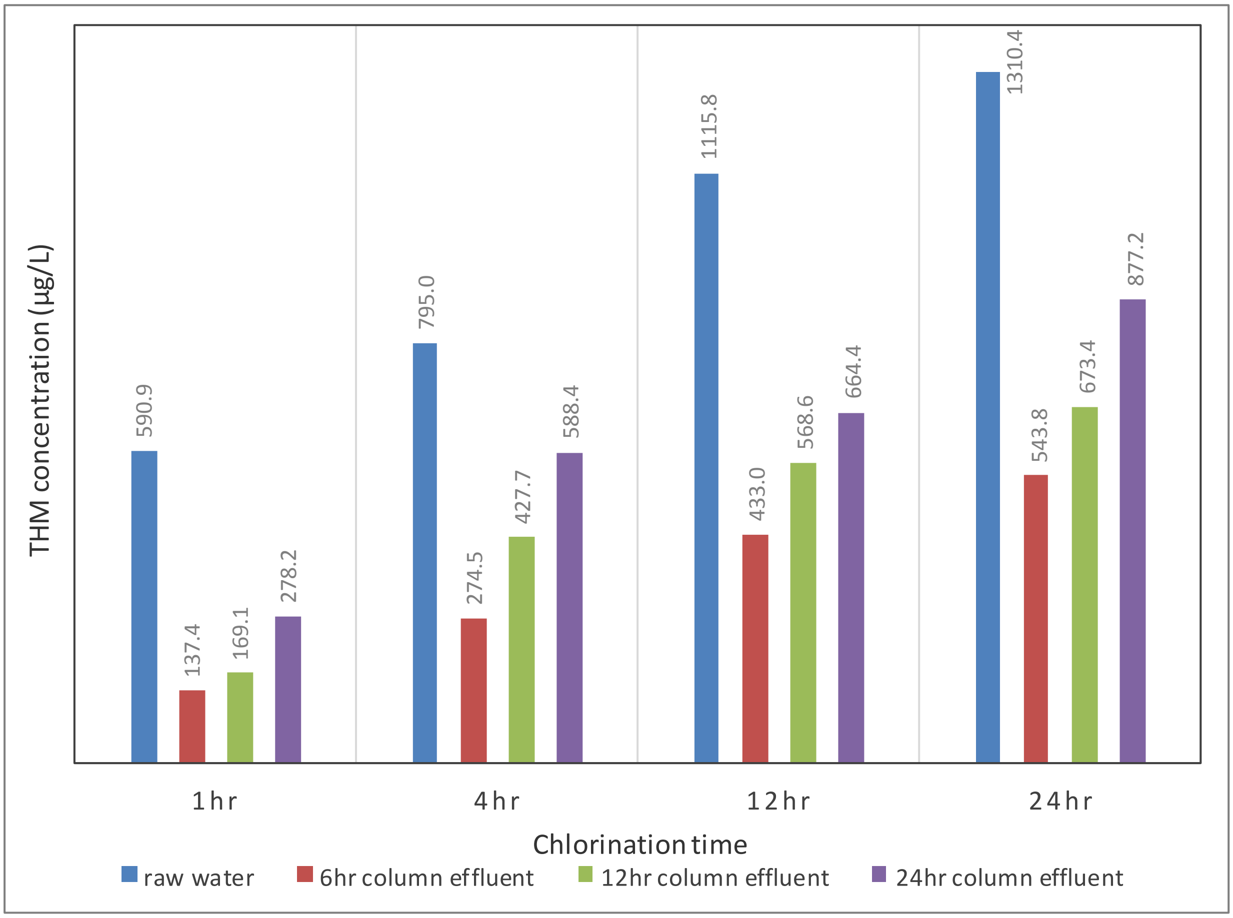

Figure 6-3 Total THMs of New-Wes-Valley raw and column samples during chlorination

Table 6-3 Typical THM compounds in New-Wes-Valley water samples

Samples	**raw water**				**6hr column effluent**			
Chlorination time	1hr	4hr	12hr	24hr	1hr	4hr	12hr	24hr
Concentration	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
$CHCl_3$	589.4	795.0	1115.8	1310.4	137.4	274.5	433.0	543.8
$CHCl_2Br$	1.5	0	0	0	0	0	0	0
$CHClBr_2$	0	0	0	0	0	0	0	0
$CHBr_3$	0	0	0	0	0	0	0	0
Total THMs	590.9	795.0	1115.8	1310.4	137.4	274.5	433.0	543.8
Samples	**12hr column effluent**				**24hr column effluent**			
Chlorination time	1hr	4hr	12hr	24hr	1hr	4hr	12hr	24hr
Concentration	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
$CHCl_3$	169.1	427.7	568.6	673.4	278.2	588.4	664.4	877.2
$CHCl_2Br$	0	0	0	0	0	0	0	0
$CHClBr_2$	0	0	0	0	0	0	0	0
$CHBr_3$	0	0	0	0	0	0	0	0
Total THMs	169.1	427.7	568.6	673.4	278.2	588.4	664.4	877.2

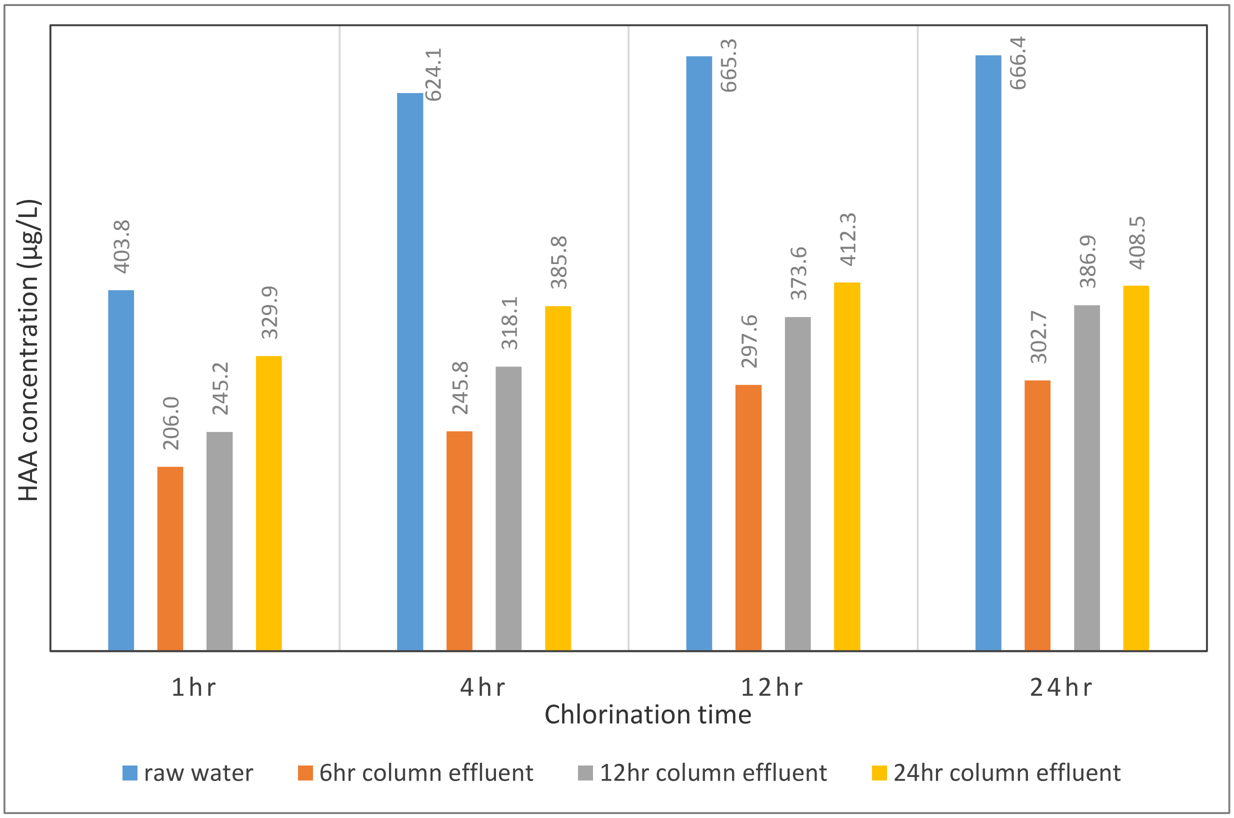

Figure 6-4 Total HAAs of New-Wes-Valley raw and column samples during chlorination

6.2.2 Town of New-Wes-Valley

Figure 6-3 and

Table 6-3 show the total THM concentration and the concentrations of each compound of the raw and filtered water samples of New-Wes-Valley. The raw water sample displays the highest total THM concentrations at all times during chlorination. The total THM concentration of the column filtered water samples follows the order of 24*hr column effluent* > *12hr column effluent* > *6hr column effluent*, which is in compliance with carbon barrier's adsorption capability to organic matter of source water in the column filtration experiment. Similar to that of the water samples from Sunnyside, the total THM concentrations of raw and column filtered New-Wes-Valley water samples were steadily increasing in the 24 hours chlorination period. About the four THM compounds (

Table 6-3), only bromodichloromethane ($CHCl_2Br$) was found in the raw water sample in the first hour of chlorination. Chloroform ($CHCl_3$) is the only THM compound formed in all of the other samples during the whole chlorination process.

Figure 6-3 and Table 6-4 present the total HAA concentration and the concentrations of each HAA compound of the raw and filtered water samples. The HAA formation of New-Wes-Valley water samples have similar trends to the THM formation. Comparing both THM and HAA formation between Sunnyside and New-Wes-Valley water samples, it is identified that since the amount of organic matter in New-Wes-Valley raw water is higher than that in Sunnyside raw water, the total THM and HAA concentrations of raw water is higher in New-Wes-Valley than in Sunnyside. The same circumstances were also recognized in the column filtered samples. Moreover, there was very limited amount of bromine-substituted THM compounds formed during the whole chlorination process. On the contrary, higher levels of various bromine-substituted HAA compounds were formed at different time period of chlorination. It seems the bromine substitution in HAA formation can take place faster than that in THM formation.

Table 6-4 HAA compounds in New-Wes-Valley water samples

Samples	**raw water**				**6hr column effluent**			
Chlorination time	1 hr	4 hr	12 hr	24 hr	1 hr	4 hr	12 hr	24 hr
Concentration	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
MCAA	15.1	27.3	19.3	17.7	7.9	11.5	16.7	15.5
MBAA	0	0	0	0	20.9	18.1	0.3	8.3
DCAA	265.3	447.2	529.7	552.6	111.2	145.3	202.2	214
TCAA	104.6	107.5	90.0	79.3	49.1	53.5	60.2	47.9
BCAA	1.5	2.6	3.2	3.4	2.5	2.8	3.3	3.5
BDCAA	0.2	0.2	0.2	0.2	3.1	3.2	3.2	3.3
DBAA	0	0	0	0	1	1	1	1

CDBAA	16.5	37.9	21.7	11.5	8.7	8.7	8.6	7.3
TBAA	0.8	1.5	1.3	1.7	1.7	1.7	2.1	1.7
Total HAAs	403.8	624.1	665.3	666.4	206	245.8	297.6	302.7
Samples	**12hr column effluent**				**24hr column effluent**			
Chlorination time	1 hr	4 hr	12 hr	24 hr	1 hr	4 hr	12 hr	24 hr
Concentration	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
MCAA	9.9	17.7	21.2	11.3	13.9	7.1	15	14.7
MBAA	11.2	7.1	0	0	0	0	0	0
DCAA	143.3	203.3	267.6	301.7	208.6	276.2	317.2	334.6
TCAA	59.7	67.8	61.2	53.4	72.3	67	48.2	45
BCAA	2.9	3.3	3.7	4	3.4	3.8	4	4.2
BDCAA	3.3	3.4	3.3	3.6	3.5	3.6	3.6	3.7
DBAA	1	1	0.9	0.9	0.9	0.9	0.9	0.9
CDBAA	12	12.6	13.9	9.6	25.6	25.2	21.4	3.4
TBAA	1.9	1.8	1.8	2.5	1.7	2	2.1	2.2
Total HAAs	245.2	318.1	373.6	386.9	329.9	385.8	412.3	408.5

6.2.3 Town of Salvage

Since the source water collected from Salvage is not enough to coduct 24 hours filtration experiment, it is subsequently adjusted to 12 hours. After filtration, the raw water, 6hr column effluent and 12hr column effluent samples were employed in the 24 hours chlorination test. The total THM and HAA formation of each sample at different time of chlorination were shown in Figure 6-5 and Figure 6-6, respectively. The amount of typical THM compounds and each HAA compound are summaried in Table 6-5 and Table 6-6, respectively. The formation of THM and HAA in Salvage water samples are similar to that in Sunnyside and New-Wes-Valley. The raw water contains higher THM and HAA concentrations than filtered water samples, and between two filtered samples, the 6hr column effluent sample presents less THM and HAA amount than the 12hr column effluet sample. This is in agreement with the amount of organic matter in each sample. The TOC of the raw water sample is higher than the 12hr column effluent sample, which is higher than the 6hr column effluent sample. Since the salvage raw water has the highest TOC level among all the three towns, it displays the highest THM and HAA formation potential in its raw water. The column filtration is effective in the adsorption of organic matter from source water, therefore the formation of THMs and HAAs in the column filtered samples are well prohibited during chlorination. The compound analysis results (Table 6-5 & Table 6-6) indicate that the $CHCl_3$ and DCAA are the principal components of the formed THMs and HAAs, respectively, in all the raw and filtered water samples at all times of chlorination. Although the $CHCl_2Br$ is formed in all the raw and filtered water samples, there are various bromine-substituted HAA compounds with total concentration higher than $CHCl_2Br$ formed in the same water samples, which also illustrates that the bromine substitution in HAA formation can take place faster than that in THM formation.

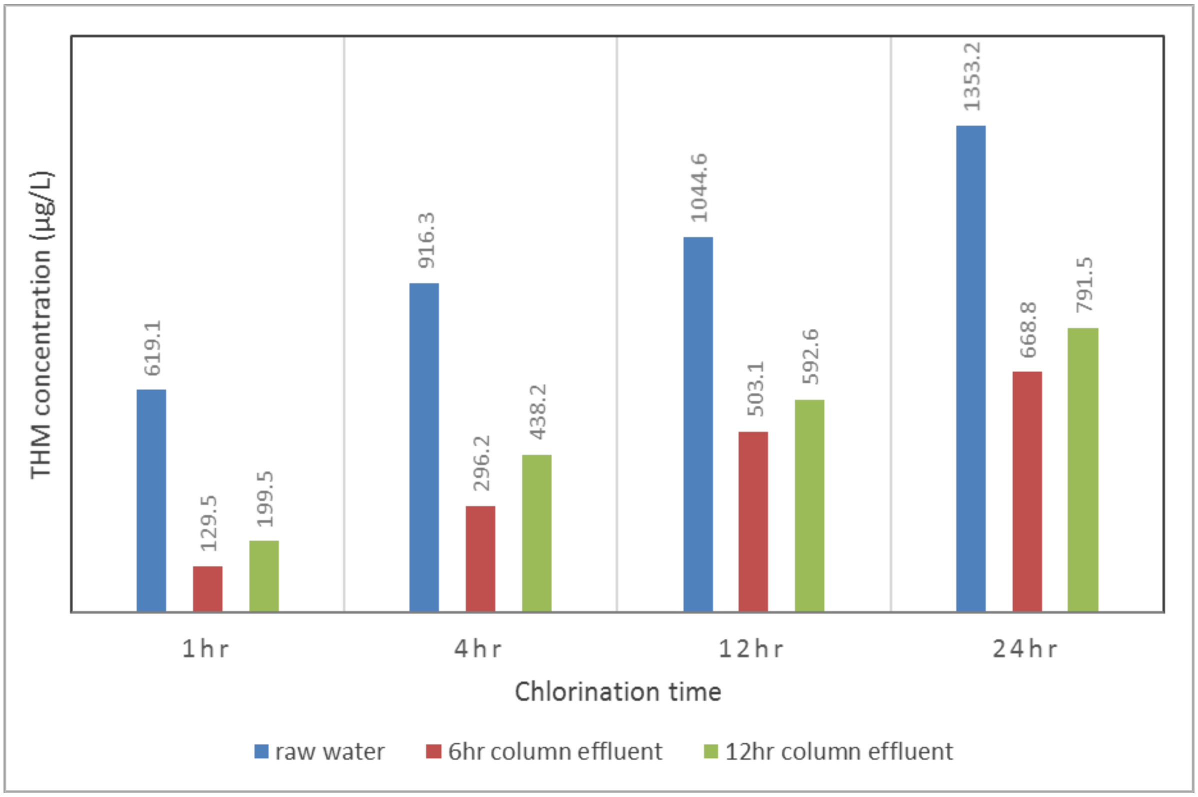

Figure 6-5 Total THMs of Salvage raw and column samples during chlorination

Table 6-5 Typical THM compounds in Salvage water samples

Samples	**raw water**				**6hr column effluent**				**12hr column effluent**			
Chlorination time	1hr	4hr	12hr	24hr	1hr	4hr	12hr	24hr	1hr	4hr	12hr	24hr
Concentration	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
$CHCl_3$	591.5	901.5	1033.8	1344.1	129.5	296.2	503.1	666.0	199.5	434.4	591.7	786.8
$CHCl_2Br$	27.6	14.8	10.8	9.1	0	0	0	2.8	0	3.8	0.9	4.7
$CHClBr_2$	0	0	0	0	0	0	0	0	0	0	0	0
$CHBr_3$	0	0	0	0	0	0	0	0	0	0	0	0
Total THMs	619.1	916.3	1044.6	1353.2	129.5	296.2	503.1	668.8	199.5	438.2	592.6	791.5

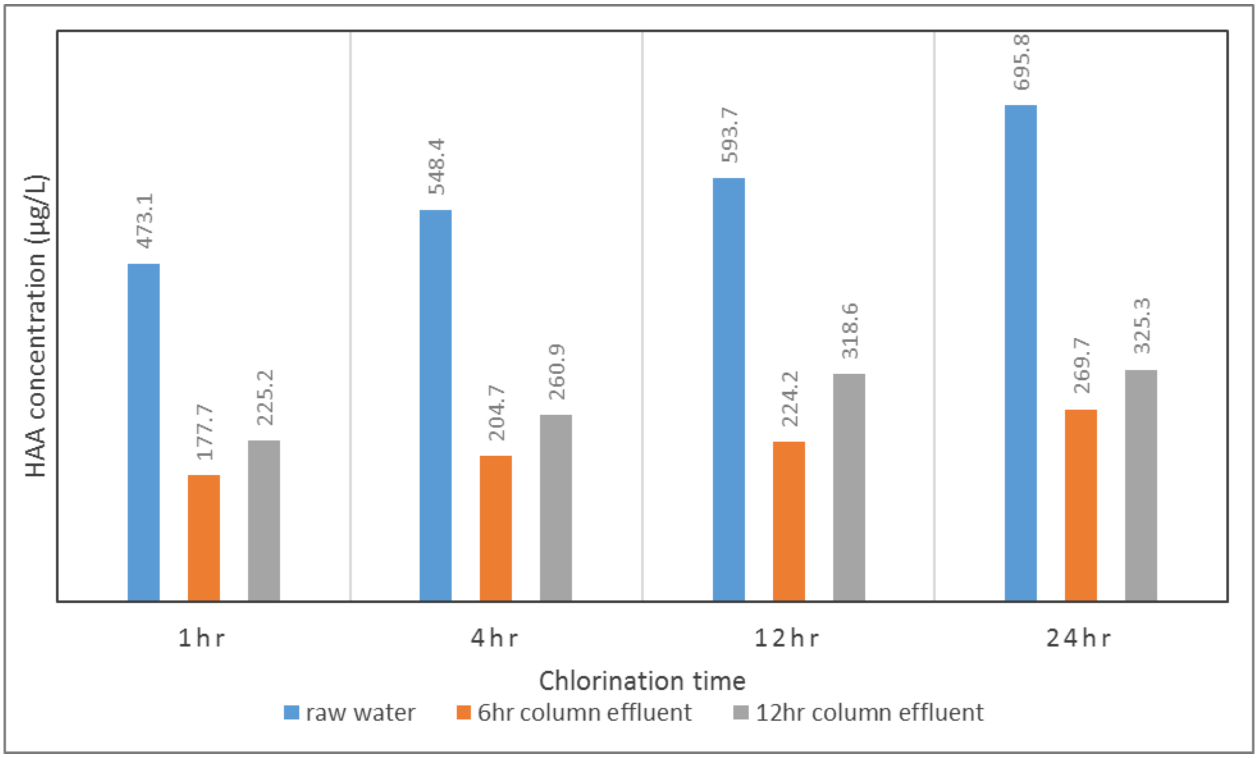

Figure 6-6 Total HAAs of Sunnyside raw and column samples during chlorination

Table 6-6 HAA compounds in Salvage water samples

Samples	**raw water**				**6hr column effluent**				**12hr column effluent**			
Chlorination time	1hr	4hr	12hr	24hr	1hr	4hr	12hr	24hr	1hr	4hr	12hr	24hr
Concentration	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L	μg/L
MCAA	0.4	17.4	16.5	19.8	2.4	6.2	12.2	15.5	11.7	13.0	9.9	10.3
MBAA	8.4	1.7	0	0	29.8	15.8	7.0	3.7	18.3	2.4	0	0
DCAA	309.3	399.0	473.9	564.6	89.3	125.3	149.0	186.3	128.1	182.1	239.0	250.6
TCAA	137.8	111.9	85.2	94.8	38.9	39.6	37.7	45.2	46.8	42.3	47.4	44.7
BCAA	4.8	6.3	7.0	8.6	3.7	4.8	5.3	6.3	4.2	5.0	6.5	6.7
BDCAA	0.2	0.2	0.2	0.2	3.1	3.1	3.2	3.4	3.2	3.2	3.4	3.5
DBAA	0	0	0	0	0.9	0.9	0.9	1.0	0.9	0.9	0.9	0.9
CDBAA	11.5	10.7	9.6	6.3	7.8	7.5	6.6	6.3	10.4	10.4	9.5	6.9
TBAA	0.8	1.3	1.3	1.5	1.8	1.5	2.2	2.0	1.6	1.5	1.9	1.6
Total HAAs	473.1	548.4	593.7	695.8	177.7	204.7	224.2	269.7	225.2	260.9	318.6	325.3

7 Conclusions and Recommendations

7.1 Conclusions

A column filtration technology was developed by utilizing activated carbon as a barrier and applied in the treatment of intake source waters collected from three rural communities in the province. In this study, the TOC as a NOM indicator is identified more reliable than UV, since the UV reading can only reflect the amount of light-sensitive organic matters. Batch test results demonstrate the use of 0.5 g (AC) /L (water) has the highest adsorption effectiveness and the lowest cost of AC. Meanwhile, column filtration results indicate the activated carbon barrier is effective to remove 64, 77 and 74 percent of organic matter from the source water of Sunnyside, New-Wes-Valley and Salvage, respectively. The follow-up chlorination experiment on the raw and column filtered water samples illustrate that the formation of THMs and HAAs can be considerably reduced after the water passed through the column. NOM fractionation of Sunnyside and New-Wes-Valley source water were also discovered in this study, it is found the New-Wes-Valley source water contains higher amount of hydrophobic fraction which can result in the higher concentrations of THMs and HAAs in the disinfection process. This is proved in the chlorination experiments by assessing the formation potential of THMs and HAAs. The fractionations result can also help to predict that the concentration of low molecular size NOM in New-Wes-Valley is higher than that in Sunnyside. In conclusion, the cost-effective carbon filtration technology developed in this study can be potentially applied as a pre-treatment technology for intake source waters for the local communities.

7.2 Recommendations

It is recommended that the NOM fractionation for the filtered water samples can be conducted as the extension of the research. As knowing the different fractions of NOM in the source water before and after the filtration can help to better understand the adsorption capacity of the activated carbon to each of the hydrophbic, hydrophilic and transphilic fractions, which will provide further guidance in the design of the carbon filtration technology.

It is also recommended that the adsorption capacity of the activated carbon be further improved in future. The activated carbon in this study is enabled to remove around 60% to 80% of the organic matter from the source water samples, however, the formation potential of THMs and HAAs in the filtered water are still higher than the maximum acceptable concentrations in the Guidelines for Canadian Drinking Water Quality. Hence, it is suggested that the activation process should be optimized so that the porosity and surface area of the activated carbon can be further developed. Once the adsorption capacity is further enhanced, the carbon filtration technology becomes more feasible in the water treatment.

Moreover, kinetic and equilibrium studies of adsorption in source water from New-Wes-Valley and Salvage should be covered in the future study. Since different drinking water sources have different characteristics (pH, TOC, UV, etc.), it could result in different breakthrough time in the adsorption process. To study the adsorption kinetics and equilibriums of the activated carbon to every source water sample will help to determine the optimal carbon dose to source water from each community, which will further enhance the adsorption efficiency of the column filtration.

In addition, the regeneration of activated carbon and its performance in the column filtration process should also be considered in the feasibility study as the regeneration of activated carbon is more convenient and cost-effective to the small communities. The carbon barrier after filtration experiment can be reactivated following the same activation conditions so that the regeneration effect can be evaluated.

Above all, a leaching test should be conducted on the generated activated carbon to make sure no impurities will be leached into the water after treatment.

References

Aslam, Z., Shawabkeh, R. A., Hussein, I. A., Al-Baghli, N., & Eic, M., (2015). Synthesis of activated carbon from oil fly ash for removal of H_2S from gas stream. Applied Surface Science, 327, 107-115.

Babi, K.G., Koumenides, K.M., Nikolaou, A.D., Makri, C.A., Tzoumerkas, F.K., and Lekkas, T.D., (2007). Desalination, 210: 215-224.

CBCL, (2011). Study on Characteristics and Removal of Natural Organic Matter in Drinking Water Systems in Newfoundland and Labrador. Prepared by CBCL limited for the Department of Environmental and Conservation, Water Management Division.

Cheng, W., Dastgheib, S. A., & Karanfi, T., (2005). Adsorption of dissolved natural organic matter by modified activated carbons. Water Research, 2281-2290.

Chow, A. T., Gao, S., & Dahlgren, R. A., (December, 2005). Physical and chemical fractionation of dissolved organic matter and trihalomethane precursors: A review. Journal of water supply: Research and Technology-AQUA, 457-507.

Chow, C. W., Fabris, R., & Drikas, M., (2004). A rapid fractionation technique to characterise natural organic matter for the optimisation of water treatment processes. *Journal of Water Supply: Research and Technology-AQUA*, *53*(2), 85-92.

Davini, P., (2002). Flue gas treatment by activated carbon obtained from oil-fired fly ash. Carbon, 40(11), 1973-1979.

DOE., (2001). Source to Tap: Water Supplies in Newfoundland and Labrador. Government of Newfoundland and Labrador, Department of Environment.

ENVC., (2009). Department of Environment and Conservation. Government of Newfoundland and Labrador, Technical Report, 294 p.

ENVC., (2017a). Department of Environment and Conservation, Government of Newfoundland and Labrador. Disinfection By-Products (DBPs). Available from http://www.ecc.gov.nl.ca/waterres/quality/drinkingwater/DBPs.html

ENVC., (2011). Study on characteristics and removal of natural organic matter in drinking water systems in Newfoundland and Labrador. Government of Newfoundland and Labrador, Department of Environment and Conservation, Water Resources Management Division. St. John's, NL.

ENVC., (2017b). THMs Summary for Public Water Supplies in Newfoundland and Labrador. Government of Newfoundland and Labrador, Department of Environment, Water Resources Management Division. St. John's, NL. http://www.ecc.gov.nl.ca/waterres/quality/drinkingwater/pdf/2016_Summer/THMs_Summer2016_color.pdf

ENVC., (2017c). HAAs Summary for Public Water Supplies in Newfoundland and Labrador. Government of Newfoundland and Labrador, Department of Environment, Water Resources Management Division. St. John's, NL. http://www.ecc.gov.nl.ca/waterres/quality/drinkingwater/pdf/2016_Summer/HAAs_Summer2016.pdf

Health Canada, (2017). Guidelines for Canadian Drinking Water Quality—Summary Table. Water and Air Quality Bureau, Healthy Environments and Consumer Safety Branch, Health Canada, Ottawa, Ontario.

Imai, A., Fukushima, T., Matshushige, K., and Kim, Y.H., (2001). Water Res., 35(17): 4019-4028.

Jegadeesan, G. B., Mondal, K., & Lalvani, S. B., (2015). Adsorption of Se (IV) and Se (VI) Using Copper-Impregnated Activated Carbon and Fly Ash-Extracted Char Carbon. Water, Air, & Soil Pollution, 226(8), 234.

Kent, F., Montreuil,, K., Stoddart, A., Reed, V., & Gagnon, G., (2014). Combined use of resin fractionation and high performance size exclusion chromatography for characterization of natural organic matter. Journal of Environmental Science and Health: Part A, 49(14), 1615-1622.

Krasner, S. W., & Amy, G., (1995). Jar-test evaluations of enhanced coagulation. *Journal-American Water Works Association*, *87*(10), 93-107.

Leenheer, J. A., & Croue, J. P., (2003). Charaterizing dissolved aquatic organic matter. Environmental Science and Technology , 18A-26A.

Liua, P., Kellera, J., & Gernjak, W., (2016). Enhancing zero valent iron based natural organic matter removal by mixing with dispersed carbon cathodes. Science of The Total Environment, 550, 95-102.

Matilainen, A., Gjessing, E., Lahtinen, T., Hed, L., Bhatnagar, A., & Sillanpää, M., (2011). An overview of the methods used in the characterisation of natural organic matter (NOM) in relation to drinking water treatment. Chemosphere, 83, 1431-1442.

Minnes S, Vodden K. and Team, (2014). Exploring Solutions for Sustainable Rural Drinking Water Systems, Technical Report, Harris Centre, Memorial University, 94 p.

Mofarrah A., (2014), Environmental Management and Potential Use of Heavy Oil Flyash, PhD Thesis, Memorial University of Newfoundland, St. John's, NL, Canada.

Nissinen, T., Miettinen, I. T., Martikainen, P. J., & Vartianen, T., (2001). Molecular size distribution of natural organic matter in raw and drinking waters. Chemosphere, 45, 865-873.

Owen, D. M., Amy, G. L., Chowdhury, Z. K., Paode, R., McCoy, G., & Viscosil, K., (1995). NOM: characterization and treatability: Natural organic matter. *Journal-American Water Works Association*, *87*(1), 46-63.

Richardson, S. D., J. E. Simmons, and G. Rice, (2002). Disinfection Byproducts: The Next Generation. Environmental Science & Technology 36(9):198-205.

Salehin, S., Aburizaiza, A. S., & Barakat, M. A., (2016). Activated carbon from residual oil fly ash for heavy metals removal from aqueous solution. Desalination and Water Treatment, 57(1), 278-287.

Schreiber, B., Brinkmann, T., & Schmalz, V., (2005). Adsorption of dissolved organic matter onto activated carbon—the influence of temperature, absorption wavelength and molecular size. Water Research, 39, 3449–3456.

Statistics Canada Census Profile., (2016). http://www12.statcan.gc.ca/census-recensement/2016/dp-pd/prof/search-recherche/lst/results-resultats.cfm?Lang=E&TABID=1&G=1&Geo1=&Code1=&Geo2=&Code2=&GEOCODE=10

Streat, M., Patrick, J.W., and Pe´rez, M.J., (1995). Water Res., 29: 467-472.

USEPA, (1998). National primary drinking water regulations: Disinfectant and disinfection byproducts, Federal register, 63(241): 69390-69476.

USEPA, (2003). National primary drinking water regulations: Stage 2 Disinfectant and disinfection byproducts rule: Proposed rule, Federal register, 49547-49681.

Uyak, V., Yavuz, S., Toroz, I., Ozaydin, S., and Genceli, E.A., (2007). Disinfection by-products precursor removal by enhanced coagulation and PAC adsorption, Desalination, 216: 334-344.

Vieira, R. F., Berenguel, A. T., Silva, M. A., Vilaca, J. S., Domingues, V. F., & Figueiredo, S. A., (2012). Natural Organic Matter Fractionation Along the Treatment of Water for Human Consumption. Global NEST Journal, 14(4), 399-406.

World Health Organization (WHO), (2004). Environmental Health Criteria 216: Disinfectants and Disinfectant By-products. International Programme on Chemical Safety. Available from http://www.who.int/ipcs/publications/ehc/ehc_216/en/

Xia, S., & Ni, M., (January, 2015). Preparation of poly (vinylidene fluoride) membranes with graphene oxide addition for natural organic matter removal. Journal of Membrane Science, 473, 54–62.

Zularisama, A., Ismaila, A., & Salim, R., (2006). Behaviours of natural organic matter in membrane filtration for surface water treatment - a review. Desalination, 194, 211-231.

Appendix

Figure 0-1 Sunnyside - source water river

Figure 0-2 Sunnyside - water dam


Figure 0-3 Sunnyside - water treatment station


Figure 0-4 New-Wes-Valley - Little Northwest Pond

Figure 0-5 New-Wes-Valley - Carter’s Pond

Figure 0-6 New-Wes-Valley - water treatment station

Figure 0-7 Salvage - source water pond