TRIHALOMETHANES FORMATION POTENTIAL IN GROUNDWATER AND SURFACE WATER

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TRIHALOMETHANES FORMATION POTENTIAL IN GROUNDWATER AND SURFACE WATER

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.

ABSTRAK

Pengklorinan digunakan secara meluas sebagai kaedah pembasmian kuman di Malaysia yang bertujuan memastikan kualiti air minuman yang boleh diterima dan selamat. Walau bagaimanapun, kajian yang dijalankan menunjukkan bahawa semasa proses pengklorinan, tindak balas antara klorin dan bahan organik semula jadi dalam sumber air boleh menyebabkan pembentukan trihalometana berpotensi (THMFP). Dalam kajian ini, faktor yang mempengaruhi pembentukan THMs seperti UV_{254}, pH, dan terlarut karbon organik (DOC) telah dikaji. Eksperimen ini telah dijalankan terhadap dua sumber air yang berbeza iaitu air bawah tanah dan air permukaan. Sampel air bawah tanah diambil dari lubang jara, USM manakala sampel air permukaan diambil dari Loji rawatan air, Jalan Baru, Perak. Sodium hipoklorit digunakan sebagai disinfektan. Sampel air yang diklorinkan diuji pada pH 6, 7 dan 8 dan masa tindak balas 1 jam, 3 jam, 6 jam dan 24 jam. Selepas tempoh tindak balas selesai, julat kepekatan TTHM untuk air bawah tanah dan air permukaan diukur. Hasil kajian ini telah menunjukkan bahawa pembentukan THM meningkat dengan peningkatan masa tindak balas. Selain daripada itu, kadar pembentukan THM adalah antara 7.7 μg / L kepada 49.4 μg / L untuk air bawah tanah manakala 13.8 μg / L kepada 40.3 μg / L untuk air permukaan. Kepekatan tertinggi TTHM ditemui pada pH 7 untuk kedua-dua sumber air.

ABSTRACT

Chlorination is widely used as disinfection method in Malaysia which aim ensuring an acceptable and safe drinking water quality. However, studies conducted demonstrated that during chlorination process, the reaction between chlorine and natural organic matter in source waters may cause the formation of Trihalomethanes potential (THMFP).

In this study, factors influencing THM formation such as UV_{254}, pH, and Dissolved organic carbon (DOC) was investigated. This experiment were conducted with two different water sources which are groundwater and surface water. The samples were taken from Borehole, USM and Jalan Baru WTP, Perak. Sodium hypochlorite were used as disinfectant. The water samples were chlorinated at different pH and contact time of 1 hr, 3 hrs, 6 hrs, and 24 hrs. After completed contact time, the range of TTHM concentration for groundwater and surface water were measured.

The results of this study have shown that THM formation increases with increasing contact time. Besides that, THM formation rates ranged between 7.7 µg/L to 49.4 µg/L for groundwater while 13.8 µg/L to 40.3 µg/L for surface water. The highest concentration of TTHM were found at pH 7.

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LIST OF ABBREVIATIONS

BF	Bromoform
CF	Chloroform
BDCM	Bromodichloromethane
DBCM	Dibromochloromethane
DBPs	Disinfection by-products
DOC	Dissolved Organic Carbon
HAAs	Haloacetic Acids
HOCl	Hypochlorous Acid
NOM	Natural Organic Matter
SUVA	Specific Ultra Violet Absorbance
THMs	Trihalomethanes
THMFP	Trihalomethanes Formation Potential
TTHM	Total Trihalomethanes
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
UV_{254}	UV absorbance at 254nm
VOC	Volatile Organic Compound
WHO	World Health Organization
WTP	Water Treatment Plant

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Disinfection is an important process in water treatment and as the final stage to protect water from pathogenic organisms. Disinfection process is to remove or inactive the microorganism and avoid any waterborne diseases spread in drinking water. There are several method of disinfection that are widely used such as chlorination, chlorine dioxide, chloramines, ozone and ultraviolet (UV) but the primary disinfection used is chlorination. This method most widely adopted because of its effectiveness, relative ease of use, lasting residual, and cost effectiveness (Brown, 2009).

During the chlorination process, the existing of natural organic matter (NOM) are the precursor of formation undesirable disinfection by-product (DBPs) such as Trihalomethanes (THMs) and Haloacetic acids (HAAs). Natural organic matter (NOM), mainly humic substances, in surface water has been considered the predominant THM precursor for the water resources with sufficient protection (Odling-Smee et al., 2003). NOMs are not harmful to human life but when it react with some disinfectants such as chlorine, they will form a compounds which have potential to be carcinogenic (Yee et al., 2006). In general, THMs are form in four species which are chloroform (CF), bromoform (BF), bromodicholoromethane (BDCM) and dicholorobromomethane (DCBM). Mishra & Dixit (2013) had shown chloroform is dominant of human carcinogenic. Furthermore, usage of water containing DBPs such as drinking and

swimming will expose to the risk of cancer such as bladder and anal cancer (Burgess & Michael, 1999).

Based on a study conducted by U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) has found chloroform are the most frequently detected volatile organic matter (VOC) when the groundwater are not chlorinated. Chloroform occurs when the haloform reaction of chlorine with organic matter. U.S. Environmental Protection Agency (2000) has noted that improperly designed, maintained, or operated septic systems can result in groundwater contamination in the vicinity of the system, especially if the degradation of the organic matter is incomplete. The chloroform or other THMs formation is invited to health problems because of the presence of pathogenic microorganisms, especially to the untreated groundwater (Ivannenko & Zogorski, 2006)

1.2 Problem Statement

Disinfection process is important in water treatment plant to prevent the growth pathogen microorganism in the plant and distribution system thus protect public human from water borne disease. The most commonly alternative disinfection method used is chlorination. It is being preferred to be used due to higher oxidizing potential, efficiency in killing pathogenic organisms and cost effective (Ibrahim & Aziz, 2014). However, during the chlorination process, chlorine can cause the formation of disinfection by product (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAA) (Liu et al., 2008). DBPs are formed due to the reaction between natural organic matter (NOM) and chlorine disinfectant in the water (Tokmak et al., 2004).

The presence of THMs have been concern since 1970s due to the perceived risk to human health. The formation of THMs cause dangerous side effects to the human body. Not only can these be ingested from drinking water, but also inhaled while bathing and from swimming in water that has been treated with chlorine (Mohamadshafiee & Taghavi, 2012a). Moreover, THMs have a negative health impact which may cause liver and kidney, rectal, bladder and breast cancers. There is a higher risk of asthma when exposed to THMs as well as eczema, and eroding dental enamel. The exposure to THM also can cause a higher rate of miscarriage and birth defects (Mohamadshafiee & Taghavi, 2012). Another research, chlorination by product can generate a potential health risk of cancer on human such as cardiovascular disease, and adverse reproductive outcomes such as spontaneous abortion, birth defects and low birth weights (Brown, 2009). To reduce the factor of cancer risk, the optimum control is necessary to control the formation level of THMs in water supply. Therefore many organisation in the world have been set drinking water guideline for DBPs such as 80 µg/L in the United States (US), 100 µg/L in Canada and the European Union (EU), and 100 µg/L in World Health Organization (WHO) (Zainudin et al., 2016).

In this study, the focus is to determine THM formation potential (THMFP) in two different water source which are surface water and ground water and to correlate THMs formation between water quality parameters.

1.3 Objectives

The objectives of this research are:

i. To determine Trihalomethanes (THMs) formation in chlorinated surface water and groundwater

ii. To correlate THM formation to water quality parameters such as pH, UV_{254}, DOC

1.4 Scope of Study

The scope of this study are as follows:

i. The water sample were taken at two different water sources which are surface water from Jalan Baru, Perak and groundwater from borehole in Universiti Sains Malaysia.

ii. All the water sample were determined concentration of THMs and water quality parameter which are DOC, pH, temperature and $UV_{254.}$

iii. All the water samples were using chlorine disinfectant.

All the water samples were extracted using MTBE and THMs determination using Gas chromatography-Mass Spectrophotometer (GC/MS) as per USEPA 551.1 method.

1.5 Important and Benefits of Study

The importance of the proposed research project is to determine THM levels are in the allowable limit as listed in the Malaysian Drinking Water Quality Standard. This standard has regulated that the total THMs must not exceed 1 mg/L. If the level of THMs in water sample has exceeded the recommended standards, then it must be investigated by personnel of the Department of Health and the water purveyor to ensure the cause and to remove the source of contamination. Besides that, in this proposed research project, we can also understand the relationships between water quality such as pH, UV_{254}, DOC

and THM formation level and also can predict THM formation from water quality results. The understanding of this relationship can minimize the THM formation and indirectly can provide good drinking water quality. In addition, we can reduce the risk of carcinogenic to human health and maintain a healthier life.

1.6 Dissertation Outline

In this study, Chapter 1 describes about the importance of the study and objectives to monitored water quality parameter and identified the concentration of water quality parameter and THMs compounds in two different of natural waters.

Next in Chapter 2 explains about literature review of the study mostly about natural organic matter (NOM), disinfectant method, reaction chlorine in the water, the formation of disinfection by-products (DBPs) and the potential health effects on humans.

For Chapter 3 were shows the location for water sampling and the information about the location selected. Besides that, method used and the procedure to determined water quality parameter and THMs concentration were explained in this chapter. Overall, in this chapter explains the flow of experiment from preliminary work until analysis of sample by GC-MS.

In Chapter 4, the results of water quality parameter and THMs analysis were included in this chapter to discuss and all data collected was presented in Appendix D. Chapter 5 were covers about the conclusion based on the results and recommendation the future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural Organic Matter (NOM)

Natural organic matter (NOM) are predominantly presence in raw waters (EPA, 2012). NOM is defined as a complex mixture derived from natural processes in the environment such as through decay of vegetation, runoff from organic soils and animal material (Hua & Yeats, 2010). As reported by Ibrahim & Aziz (2014), the origin of NOM are from two category which are autochthonous and allocthonous. Autochthonous is NOM that originates from decayed of biota living in water bodies such as macrophites, algae and bacteria's. Meanwhile allocthonous NOM comes from external sources that enter the streams through natural cycle such as human activities and snow melting. Garcia (2011) also noted another type of organic matter which is anthropogenic. This category are comes from agricultural, industrial and domestic waste and from other material in watercourses and NOM composed mainly of fulvic and humic acids. In raw water, normally humic and fulvic acids can cause colour change and bad odour. In addition NOM can be quantified by total organic carbon (TOC) or dissolved organic carbon (DOC) and UV_{254} measurement.

Generally, NOM can be divided into two fractions which are hydrophobic and hydrophilic fraction where the most commonly present in the water is hydrophobic acid (HA) and primary consists of humic and fulvic acids (humic substance, HS) (Matilainen et.al, 2010). The hydrophobic (humic fraction) is less soluble in water, high molecular weight, yellow to brown-black in colour and poor in nitrogen while the hydrophilic (non humic-fraction) is considered to be less reactive and rich in nitrogen, which consists of

carbohydrates, lipids, hydrophilic acids, and amino acids. Figure 2.1 describes the fraction of NOM. Humic acids is more reactive than fulvic acid. It can be easily removed by coagulation due to the higher molecular weight, large size and lower solubility in water. Fulvic acid is less reactive and need higher coagulation dosage due to the low molecular weight, smaller size and more soluble in the water (García, 2011). Based on previous study, HS consists of more than 50% of the NOM present whereas for the hydrophilic acid it can be expressed as a non-humic which are contains of carboxylic acids, carbohydrates proteins, amino acids, polysaccharides and lipids (Santschi et al.,1999).

Based on previous study by King & Marrett (1996), NOM is acts as precursor to the formation of potentially harmful disinfection by-products (DBPs) when it reacts with chlorine. Ibrahim & Aziz (2014), stated that hydrophobic fraction is more reactive with chlorine compared to hydrophilic fraction. Generally, two classes of DBPs formation in example Trihalomethanes (THMs) and Haloacetic acids (HAAs) are considered to be dominant DBPs on a weight basis in portable water (Bazrafshan et al., 2012). The formation is establish to be carcinogenic or genotoxic that might be harmful to the human and organism (Albrektiene et al., 2014). NOM (humic substances) must be removed from in any sources of waters due to reactions with disinfectants which will produces disinfection by-products. Other researcher demonstrated that NOMs can cause the microbial regrowth in distribution system and impede the removal of iron and manganese from the water. Thus, minimization of the THMs precursors became serious issues in the production of high quality drinking water from water sources (Qin et al., 2006).

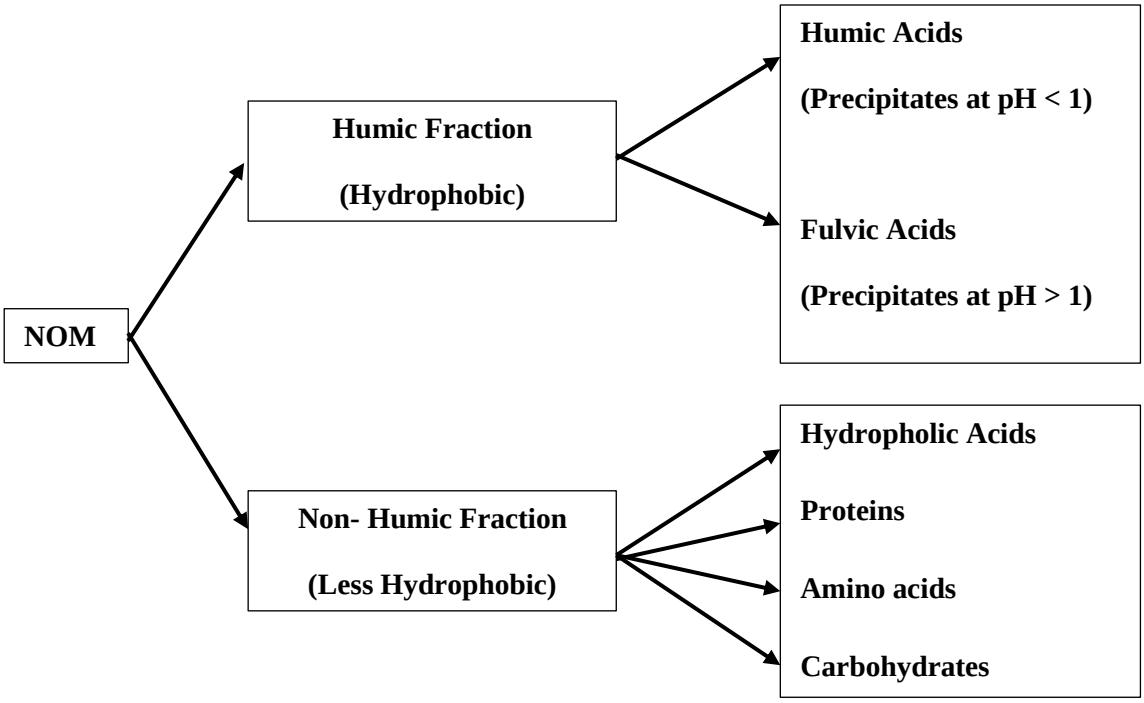


Figure 2.1 The fraction of NOM (García, 2011)

NOM is usually quantified by several conventional analytical techniques such as total and dissolved organic carbon (TOC and DOC), ultraviolet absorbance at 254 wavelength (UV_{254}) or chemical and biochemical oxygen demand (COD and BOD) (Penru et al., 2013). Another research stated that, the specific ultraviolet absorbance (SUVA) expressed as UV_{254}/DOC (Matilainen & Sillanpää, 2010) can be used to forecast DBPs formation because there have no currently acceptance parameter to identify DBP precursor (Harris, 2001). Thus, SUVA is an important parameter to evaluating NOM reactivity and treatability (Bazrafshan et al., 2012). In addition, SUVA is often used as an indicator of the aromatic carbon content of HS. Higher value of SUVA shows that the organic matter is largely composed of hydrophobic while low SUVA value indicates that water includes mainly organic compounds which are hydrophilic (Bazrafshan et al., 2012 ; Matilainen et al., 2010).

A study conducted by Albrektiene et al. (2014) , found that human substances in the groundwater from Nida and Preila-Pervalka (Lithuania) wellfields on the coast of Baltic sea is rich in organic compounds with approximately 70% fractional of hydrophobic acids fraction forms. The minimum and maximum result of TOC for water of Nida and Preila-Pervalka are 9.6 mg/L - 9.7 mg/L and 5.6 mg/L -7.1 mg/L NOM also found in water samples from Limmat river (tributary of Lake Zurich, Switzerland) where the minimum DOC content is 1.8 mg/L - 2.1 mg/L (Gallard & Von Gunten, 2002). A study conducted by Bessiere et al., (2009) of the raw water investigation in Albert Water Treatment Works (AWTW) in north of England. The minimum and maximum result showed that TOC content for raw water before and after 0.45µm filter were 9.8 mg/L & 8.3 mg/L, respectively, while SUVA were 4.3 L mg^{-1} m^{-1} and 5.1 L mg^{-1} m^{-1} respectively. It shows that NOMs is present in many sources of water (Bazrafshan et al., 2012). In central Banat, Republic of Serbia, it was also found there were NOM in the groundwater where the source used as a water supply for the city of Zrenjanin. They found that NOM in the groundwater is high based on the minimum and maximum amount of DOC 6.41 - 9.85 mg/CL. They also found UV_{254} value were 0.442 cm^{-1} and 0.520 cm^{-1}, SUVA value were 4.97 - 6.96 L mg^{-1} m^{-1} (Tubić et al., 2011).

One previous study was conducted by Bazrafshan et al., (2012) showed that the concentration of NOM in the raw water entering drinking water treatment in Zahedan Drinking Water Treatment is high. The result of maximum TOC was 12.962 mg/L. The DOC content was between 4.72 mg/L -10.37 mg/L, UV_{254} was 5.87 - 0.73 cm^{-1} and they obtained minimum and maximum SUVA were 5.87 L/mg.m & 8.21 L/mg.m, respectively (Bazrafshan et al., 2012). The suggested relationship between SUVA and TOC is illustrated in Table 2.1 (Matilainen et al., 2010). If SUVA value of 2 L/mg.m or

less is considered difficult to treat by coagulation and TOC will not control the coagulant dosage while with higher SUVA value is considered to be easy to treat because the amount of NOM available in the water typically has a greater coagulant demand than the particles (García, 2011). Relationship between SUVA value and DOC during coagulation presented in Table 2.1.

Table 2.1 Relationship between SUVA and DOC during coagulation and expected DOC removal (Matilainen et al., 2010)

SUVA	Composition	Coagulation	DOC removals
>4	Mostly aquatic humics, high hydrophobicity, high MM compounds.	NOM controls, good DOC removals.	>50% for alum,little greater for ferric.
2-4	Mixture of aquatic humics and other NOMs, mixture of hydrophobic and hydrophilic NOM, mixture of MMs.	NOM influences, DOC removals should be fair to good.	25-50% for alum, little greater for ferric.
<2	Mostly non-humics, low hydrophobicity, low MM compounds.	NOM has little influence, poor DOC removals.	<25% for alum, little greater for ferric.

2.1.1 Purpose Removing Natural Organic Matter

The presence of NOM in source water is the primary precursor for the formation of DBPs. DBPs are formed when chlorine is applied to the water. Removing NOM in water is important to reduce the formation in preventing harmful human health. Common DBPs formed from this reaction are THMs and HAAs (Au et

al., 2011). Besides that, the purpose to remove NOM is also to avoid affecting aesthetic water quality because of colour, taste and odour also make the water less palatable to human. Presences of NOM is the key to DBPs formation in waters. To mitigate the formation of DBPs, NOM must be removed properly using with a conventional treatment step such as coagulation, flocculation, sedimentation and filtration. The process are interdependent each other to produce water with high quality (Matilainen et al., 2010).

2.2 Disinfection/Disinfectants

Disinfection are describes any physical, chemical or non-chemical process which is very important step in water treatment process. It used to treating source water in drinking water treatment by kill or inactivate harmful microorganisms. Disinfection is helping to protect ecosystems and prevent the spread of waterborne disease such as cholera, typhoid, fever and dysentery (Pentamwa et al., 2013). As described by Yee et al.(2008), disinfection is the process by oxidizing organic and inorganic substances and remove the bacteria and viruses.

There are several different techniques of disinfection to deactivate or kill the pathogenic microorganisms such as chlorination, chlorine dioxide, chloramines, ozone and ultraviolet light (Ibrahim & Aziz, 2014 ; Agus et al., 2009 ; Koivunen, 2007). The mechanism of disinfection is mostly through cell wall disruption of microorganisms, changes in cell membrane permeability, damage to protoplasm or inhibition of enzyme activity (Rajamohan et al., 2012).

The most common disinfection techniques for drinking water treatment is chlorination. This techniques used chlorine as disinfectant due to its efficient mechanism and the cheapest of all chemical disinfections. However, it leads to the occurrence of disinfection by product (DBPs) due to the chemical reaction between chlorine and natural organic matter (NOM) in the raw water (Ho et al., 2014).

2.3 Chlorine Disinfectant

Chlorine is the primary disinfectant used in water treatment process with the reduction of infectious disease by removal of pathogen in the raw water. Chlorine is the one which is being extensively used around the worlds (Rajamohan et al., 2012). For example, in Turkey, 90 percent of water supply system used chlorine as their disinfection method (Uyak & Demirbas, 2014). In previous research stated that chlorine is a proven disinfectant against a broad range of pathogens and provides an effective residual against these pathogens throughout the distribution system and prevents microbial re-growth such as bacteria/virus protozoa (Summerhayes, 2014 ; Pentamwa et al., 2013).

The privilege of using chlorine as a disinfectant because due to its low cost, easily applied and more efficient compared to other alternative disinfectants. Besides that, chlorine disinfectant are widely used because of the popularity due to higher oxidizing potential, provides a minimum level of chlorine residual throughout the distribution system or storage tanks to reduce chance of pathogen regrowth (Gopal et al., 2007).

2.3.1 Forms of Chlorine

Chlorine disinfectant can be applied in many forms such as gaseous chlorine (Cl_2), sodium hypochlorite solution (NaOCl) or calcium hypochlorite ($Ca(OCl)_2$) (Retina, 2009 ; USEPA 1999). The destruction of microbial pathogens almost invariably involves the use of reactive chemical agents such as free chlorine (hypochlorous acid and hypochlorite) (Gorchev, 1996).

In chlorination disinfection, gaseous chlorine (Cl_2) or sodium hypoclorite NaOCl (aq), when added to and react with water it will produces hypochlorous acid (HOCl) and hyphochlorite ion (OCl^-). The equation is described as below:

$$Cl_2 + H_2O \longleftrightarrow HOCl + H^+ + Cl^- \qquad (2.1)$$

$$NaOCl\ (aq) + H_2O \longleftrightarrow Na^+ + OCl^- + H_2O \qquad (2.2)$$

Hypochlorous acid and hypochlorite ion reaction depends on pH

$$HOCl \longleftrightarrow OCl + H^+ \qquad (2.3)$$

Gibbons & Laha (1999) stated that hypochlorous acid, HOCl kills microorganism pathogen by attacking the respiratory, transport systems and nucleic acid activity. The decomposition of HOCl and OCl^- are depended on pH (Durmishi et al., 2015). Both of HOCl and OCl^- are good disinfecting agents but HOCl is more effective than OCl^-. The ratio of HOCl to OCl^- is determined by the pH balance and water temperature (Summerhayes, 2014). HOCl is a weak acid which it is dominant at pH between 5.5 and 7.5 while OCl^- in pH is greater than 7.5. Therefore, the pH levels influences the effectiveness of chlorine disinfectants

thus water utilities with chlorinated systems will maintain the pH for the effectiveness of disinfection with chlorine (WHO, 2000 ; Durmishi et al., 2015).

2.4 The Formation of Disinfection by-products (DBPs)

Chlorination is the most commonly used in water disinfection process in worldwide. It has been introduced as disinfectant since 1900 until now to supply safe drinking water by remove or inactive pathogen microbes and protect public human from waterborne diseases. Chlorine as effective agent to remove microorganism and also to ensure concentration for protected microorganism the residual regrowth such as bacterial, virus, protozoa (Hasan et al., 2010). Moreover, it also contributing to reduce incidence of disease such as cholera, typhoid fever and hepatitis (Abdullah, 2014). However, in research by Rook et al. (1974), the effect of use chlorine as disinfectant will form disinfection by product (DBPs) which are potentially harmful to human health (Bellar et al., 1974 ; Kim et al., (2003). DBPs are formed by the reaction of free chlorine with natural organic material in the water (Lantagne et al., 2001).

Generally, in chlorination process halogenated trihalomethanes (THMs) and haloacetic acids (HAAs) are commonly found and of particular concern since they are good indicators of the overall DBPs (Chang et al., 2010 ; Gopal et al., 2007 ; Hua & Yeats, 2010). It have been established that many DBPs are mutagens, carcinogens, or toxicants (Bazrafshan et.al, 2012). Therefore due to the potential human health effect by DBPs, many countries or international organization have regulated the contaminants of THMs. In the United States, US Environmental Protection Agency (USEPA) has published stage 1 disinfection by-products (DBPs) that specified the maximum contaminant levels allowable in drinking water and for the protection of public health, World Health

Organization (WHO) also set the guidelines for THMs while in Malaysia Drinking Water Quality Standard Guideline by Ministry of Health Malaysia. The summary of the DBPs concentration level for USEPA, and WHO are shown in Table 2.2 and Malaysia Guideline are shown in Table 2.3.

Table 2.2 Drinking water regulation for THMS for USEPA and WHO

(Source from Mishra et.al, 2012 ; Gora et al., 2011)

Disinfection by-product	**USEPA (2002)**	**WHO (2008)**
Total Trihalomethanes	80 µg/L	*total sum of the ratio of the concentration of each to its respective guideline value should not exceed 1
Chloroform		300 µg/L
Bromoform		100 µg/L
Dibromochloromethane		60 µg/L
Dichlorobromomethane		100 µg/L

WHO Index, I_{WHO} for THMs is an overall guideline value to estimate the toxicity with chlorinated drinking water where C is the concentration of each THMs The I_{WHO} value should be less than 1 for compliance with WHO guidelines and was equation as shown below (Salih & Al-azzawi, 2016) :

$$I_{WHO} = \frac{C_{CF}}{GV_{CF}} + \frac{C_{BDCM}}{GV_{BDCM}} + \frac{C_{DBCM}}{GV_{DBCM}} + \frac{C_{BF}}{GV_{BF}} \leq 1 \quad (2.4)$$

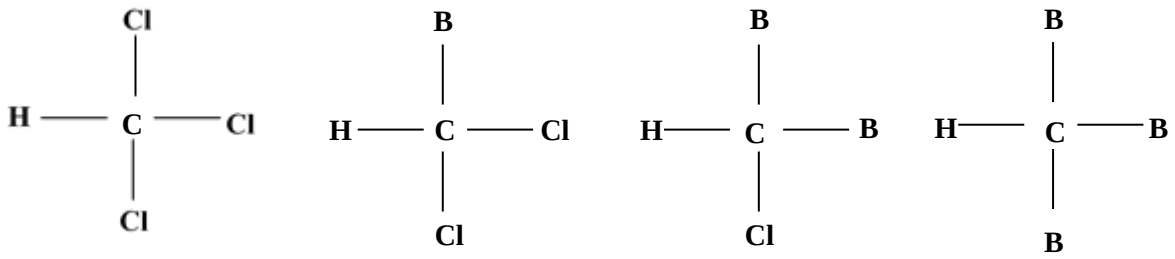
Table 2.3: Drinking Water Quality Guideline from Ministry of Health Malaysia (Source from MOH, 2010)

Parameter	**Drinking water quality standards**
Chloroform	0.2 mg/L
Bromoform	0.1 mg/L
Dibromochloromethane	0.1 mg/L
Bromodichloromethane	0.06 mg/L
Total THMs	1.0 mg/L

DBPs formation constitute a major class of DBPs which are chloroform, CF ($CHCI_3$), bromodichloromethane, BDCM ($CHBrC1_2$), dibromochloromethane, DBCM ($CHBr_2CI$) and bromoform, BF (CHBr3) which are formed through the reactions of hyphochlorous acid (HOCI) with natural organic matter (NOM) (Gallard & Von Gunten, 2002). The compounds of THMs are as shown in Figure 2.2. These four compounds are collectively termed as trihalomethanes (THMs). The presence of bromide in the water can formed hypobromous acid when using chlorine as disinfectant. When hypobromous acid react with NOM, brominated and mixed chlorobromo by-product forms such as BF, BDCM, and DBCM (Hasan et al., 2010).

Mishra et al., (2012) have found that THMs are the most commonly occurring during chlorinated water. Chloroform is the most produced in water after disinfection by chlorine (Mohammadi et al., 2016) and always with the highest concentration compared than other and often represented by more than 90% of the total concentration of THMs (Durmishi et al., 2015). The most common by-product produced in water after

disinfection by chlorine is chloroform. It have been the most received attention because of carcinogenic for mice and rats animal (Lantagne et al., 2001). In addition, in water with high bromide concentrations, chlorination could be caused to brominated THMs formation (Nokes et al., 1999).



Chloroform BDCM DBCM Bromoform

Figure 2.2: Four compounds of THMs (Artug, 2004)

Based on research by Abdullah et al. (2009), the THMs formation depends on the last step of THM reaction pathway, which is base-catalysed as with the haloform reaction. In many researcher reported that THM formation is depends on several factors such as such as chlorine dosage, pH, temperature, disinfection contact time, bromide concentration, content and type of the natural organic matter are the factor of THMs formation (Gallard & Von Gunten, 2002 ; Fooladvand et.al, 2011). Several laboratory and research studies have indicated that the higher values for these parameters, the higher concentrations of THMs caused (Lee & Nikraz, 2015).

In previous studies, they have found that during chlorination process, a complex mixture of DBPs are formed and more than 300 different types of DBPs have been identified (Gopal et al., 2007). Approximately 600-700 types of DBPs are formed not only for chlorine but also ozone, chlorine dioxide and chloramines (Mech, 2014). Generally,

THMs and HAAs are the major formation found in chlorination by product (Matilainen & Sillanpää, 2010).

Results from past studies by Golea et al., (2017), they found that raw water that used in water treatment plant in Scotland have higher THM level between 142.5 µg/L - 3723.6 µg/L. In 2016, THMs were found in Zayandehroud River at Isfahan city at 1.7- 98 µg/L. The concentrations of TTHMs found in Alur Ilmu River in area Universiti Kebangsaan Malaysia (UKM) were relatively high with 2923 µg/L to 3724 µg/L. The results show that THMs concentration found were higher than regulation limits. This research has conclude that the activities of cleaning, washing and discharge of food waste by cafeteria nearby might contribute to higher concentration of THMs. Moreover, food waste discharge into the river can contribute more organic content (Zainudin, Hasan, & Abdullah, 2016). In Turkey, THMs were found in three water sources where the concentration recorded were 386 to 416, 275 to 338 and 201 to 237 µg/L. The investigation for raw water and water in Gweru, Africa Raw found the maximum for raw water was 18.13 µg/L while for treated water they found a THM concentration between 83 µg/L until 145.50 µg/L THMs (Guyo & Moyo, 2013).

In three treatment water plants in Thailand, THMs level were found at 48.46, 20.55, and 17.24 µg/L (Pentamwa et al., 2013) . As reported by Ahmadi et al., (2012) THMs in Khuzestan water treatment plants, Iran were between 1.7 and 98 mg/L. In India, a research study for Kalpak am township (Palar water), MAPS Open Reservoir (Palar water), and Anupuram (Open well) recorded THM concentrations of 2.28, 10.091, and 23.474 µg/L (Ahmadi et al., 2012). A study conducted on groundwater from Central Banat, Serbia found that the level of THMs is between 301 µg/L - 657 µg/L. They

investigated that groundwater in Central Banat has a high amount of NOM. As a higher amount of NOM (hydrophobic) present in the raw groundwater, high values for THMFP is expected (Tubić et al., 2011).

From a previous study which on determination of THMFP for groundwater in Jajmau, Kanpur have found that the only levels of chloroform are found below the regulated WHO guideline value of 300 µg/L (Mishra et al., 2012). A research by Hasan et al. (2010) stated that chloroform is predominant THM species in the water samples. In addition, another research study Hassani (2010) found TTHM value at Sangar Water Treatment Plant (SWTP) is between 10.56 to 13.56 µg/L. In Korea, Kim et al., (2003) have found TTHM value at Han River, Seoul which is 21.07 µg/L, Daechung Lake, Taejeon 13.32 µg/L, Youngsan River, Kwangju 5.07 µg/L and Nackdong River, Pusan 59.33 µg/L. Golfinopoulos (2002) found TTHM value at Athens (Water Treatment Plant) is between 5 µg/L to 106 µg/L , Mytilene (distribution system) is between 4 µg/L to 27 µg/L and Chalkida (distribution systems) is between 5 µg/L to 96 µg/L . All the THMs and others water parameter were summarized into a Table 2.4 based on the previous research.

Table 2.4: Summarization of formation of THMs and water quality parameters from studies in a few countries

Study Citation	Country	Sources	Water quality parameter					THMs (µg/L)
			pH	TOC (mg/L)	DOC (mg/L)	UV_{254} (cm^{-1})	SUVA (L/mg.m)	
Golea et al., (2017)	Scotland	Water treatment work (raw water)	4.63-9.20	-	1.60-21.40	0.03-0.96	0.53-9.17	142.5-3723.6
Mohammadi et al., (2016)	Iran	Isfahan city (surface water of Zayandehroud River)	8 - 8.5	2.65- 3.4	-	-	-	1.7-98
Zainudin et al., (2016)	Malaysia	River in area Universiti Kebangsaan Malaysia (UKM).	-	-	-	-	-	2923 -3724
Uyak & Demirbas, (2014)	Turkey	Terkos Lake Buyukcekmece Lake Omerli Lake	7.61-7.77 7.82-8.54 7.35-7.52		5.21-5.78 4.41-5.61 3.85-3.90	0.144-0.160 0.105-0.135 0.081-0.105	2.65-3.07 2.27-2.41 2.08-2.71	386-416 275-338 201-237
Guyo & Moyo, (2013)	Gweru, Africa	Raw water Treated water	-	-	-	-	-	ND- 18.13 6.83 – 145.50

Pentamwa et al., (2013)	Thailand	Surface water treatment plant Chaiyaphum province Nakorn Ratchasima province Buriram province	-	-	-	-	-	48.46 20.55 17.24
Ahmadi et al., (2012)	Khuzestan Iran	Khuzestan water treatment plants	7.7-8.12	2.95-4.49	-	-	-	1.7 to 98 mg/L
Rajamohan et al., (2012)	India	Kalpakkam township (Palar water) MAPS Open Reservoir (Palar water) Anupuram (Open well)	-	-	3.70 3.01 5.90	0.154 0.125 0.226	-	10.091 2.828 23.474
Tubić et al., (2011)	Serbia	Groundwater from central Banat	7.18-7.68	-	6.41-9.85	0.442-0.520	4.97-6.96	301-657
Chang et al., (2010)	Taiwan	Northern WTPs Central WTPs Southern WTPs Eastern WTPs Offshore island	-	-	0.4-2.5 0.5-1.8 0.6-7.0 0.7-3.4 1.0-28.5	0.007-0.044 0.002-0.038 0.005-0.043 0.001-0.065 0.003-0.200	0.9-2.5 0.3-2.7 0.2-2.8 0.1-2.3 0.3-3.6	ND-62.9 2.3-30.3 4.8-55.3 2.1-38.0 4.3-133.2

Hassani (2010)	Iran	Sangar Water Treatment Plant (SWTP) –Raw water from Sefedroud and SherBedjar Rivers	6.94-7.23	13.5-17.7	6.1	-	-	10.56-13.56
Hasan et al., (2010)	India	(Treated water) Bhagirathi, Haiderpur, Nangloi, Okhla, Wazirabad, Sonia Vihar	-	-	-	-	-	283.5 459.9 274.2 335.5 268.2 26.86
Kim et al., (2003)	Korea	Han River, Seoul Daechung Lake, Taejeon Youngsan River, Kwangju Nackdong River, Pusan	7.9 7.7 8.0 8.2	-	2.35 2.40 2.35 5.12	0.073 0.080 0.072 0.116	3.11 3.33 3.06 2.27	21.07 13.32 5.07 59.33
Golfinopoulos (2000)	Greece	Athens (Water Treatment Plant) Mytilene (distribution systems) Chalkida (distribution systems)	-	-	-	-	-	5-106 4-27 5-96

2.5 Potential health effects of DBPs

Chlorination is the most important step and has been in practices more than a century in water treatment to protect public health from pathogenic microbes. The formation of DBPs awareness started in early 1970s. In 1974, chloroform-THMs were the first identifies by Rook (Mohamadshafiee & Taghavi, 2012a). Unfortunately, chlorination leads to the formation of DBPs carcinogenic and the disinfection process generate a serious health problem due to THMs resulting in cancer risk and several acute effect to human (Durmishi et al., 2015).

THMs formation have been detected in different aqueous matrixes such as tap water, swimming pool water, distilled water, ultrapure water and even in water that has not been subjected to chlorination processes, such as ground water, mineral water, snow, rain water, river and sea water (Heydari, 2013 ; Mohamadshafiee & Taghavi, 2012). The way human exposed to the cancer risk are not only enter the body by ingestion such as drinking and eating but also through inhalation and through the skin such as in showering or swimming (Villanueva et al., 2007). In another study by (Mohamadshafiee et al., 2012), they found that THMs can cause three types of cancers which are rectal, bladder and breast cancers. Moreover, exposure of THMs will give a higher risk of asthma when as well as eczema, and eroding dental enamel, higher rate of miscarriage and birth defects.

Based on the some epidemiological studies, the ingestion of chlorinated water to have caused various cancers of the esophagus, the pancreas, urinary tract and the stomach (Durmishi et al., 2015). Similar study conducted by Lin & Hoang, (2000) in southern Taiwan, the

exposure to THMs have been identified through ingestion was 47.9 μg/day, while inhalation exposure as a result of showering was 30.7 μg/day. It was determined based on measurements that chloroform constitutes most of the THMs. In Ontario, Canada, about 14–16% of the bladder cancers are attributable to the drinking waters containing relatively high levels of chlorinated by-products (CBPs) (Chowdhury & Husain, 2005). The risk bladder cancer is associated with the exposure to THMs concentrations levels of about 50 μg/L. Around 14–16% suffer bladder cancers which is equivalent to 232–265 bladder cancer incidents per year, might be attributed to exposure the drinking water containing higher concentrations of DBPs (King & Marrett, 1996). The bladder is one of the cancer sites most consistently associated with exposure to chlorination by-products. This cancer was exposure to THMs through ingestion of water and through inhalation and dermal absorption during showering, bathing, and swimming in pool.

Several previous research show the human bladder and anal cancer are positively correlated when exposure to disinfection by-products in drinking water. Furthermore, the studies shows 9% of all cases of bladder cancer and 15% of anal cancer are because of disinfection by-product of drinking water. Some researcher has found that the chlorinated drinking water can increase the risk of bladder and anal cancer. An investigation has found the risk are not decrease when other factor such as smoking, residence and work (Morris et al., 1992).

Another cancer has been found due to the length of exposure of mutagenic and carcinogenic substances in drinking water is renal cancer. The studies shows for men have a relation between exposure and the risk on renal cancer. For women, the relation was not significant. The studies end up with men and women have connection between exposure and bladder cancer is significant (Koivusalo, 1997). Besides bladder and renal cancer, several research