MONITORING OF EMERGING DRINKING WATER DISINFECTION BYPRODUCTS FOR MICROBIAL INACTIVATION

BY

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2010-NUST-MS PhD-EnvS-10

Institute of Environmental Sciences and Engineering (IESE)

School of Civil and Environmental Engineering (SCEE)

National University of Science and Technology (NUST)

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IN

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CERTIFICATE

This dissertation submitted by **MS Sidra Abbas** is accepted in its present form, by the Institute of Environmental Sciences and Engineering (IESE), School of Civil and Environmental Engineering (SCEE), National University of Science and Technology (NUST), Islamabad as satisfying the requirement for the degree of Masters of Environmental Sciences.

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DEDICATED….!!!

To my family and friends

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LIST OF ABBREVIATIONS

BDCM	Bromodichloromethane
CAR-PDMS	Carboxen-polydimethylsiloxane
CDBPs	Chlorinated disinfection byproducts
DBCM	Dibromochloromethane
DBPs	Disinfection byproducts
DOC	Dissolved organic content
DVB-CAR-PDMS	Divinlybenzene-carboxen-polydimethylsiloxane
ECD	Electron capture detector
HAAs	Haloacetic acids
HANs	Haloacetonitriles
HKs	Haloketones
HS-SPME	Headspace solid phase microextraction
ITHMs	Iodinated trihalomethanes
LLE	Liquid-liquid extraction
MHE	Multiple headspace extraction
NEQS	National environmental quality standards
NOM	Natural organic matter
TDS	Total Dissolved Solids
THMs	Trihalomethanes
TOC	Total organic carbon
TTHMs	Total trihalomethanes

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ABSTRACT

Water quality assurance is at present a significant concern at national as well as at international level. Proper management and treatment of drinking water is tremendously vital for the benefit of society. This study presents the outcomes of an experimental analysis on various parameters from two water supply and distribution networks in twin cities Islamabad and Rawalpindi, Pakistan. Research was carried out in two phases. In first phase factors affecting the formation behaviour of THMs (Trihalomethanes) were studied and in the second phase drinking water samples of the twin cities were analysed. To ascertain factors affecting the THM formation and chlorine decay laboratory experiments were carried out under controlled conditions. Water quality characteristics that effect the formation of DBPs (Disinfection byproducts) e.g. type and concentration of organic precursors, pH, temperature, and disinfectant were monitored. The results showed that concentration of THMs was mostly amplified with rise in pH, contact time and organic content in water. Reaction rates were normally increased with temperature, resulting higher amount of THMs formation. Gas chromatographic method was established to analyse the samples on GC instrument. Stock solutions of standard analytes were prepared using GC grade methanol. Retention times, peak areas and intensities of the standard analytes were calculated. A simple and rapid method solid phase micro-extraction (SPME) was used for the extraction of TTHMs (Total Trihalomethanes). Concentration of four species of THMs was monitored namely chloroform, bromodichloromethane, dibromochloromethane and bromoform. At present no significant data, relating THMs have been reported in Pakistan. None of the DBPs are regulated in the Pakistan and internationally it is obligatory by regulation that the sum of four THMs does not exceed 80 µg/L. The result indicated that key factors reflecting a high impact on THM formation in the supply system were the chlorine dose and presence of the natural organic matter (NOM) in water. The results suggested that the effect of temperature and

chlorine dosage was found to be more significant than that of pH. In the second phase of study samples were collected from 30 selected sampling sites comprising water filtration, underground storage tank and consumer taps. The results indicated presence of THMs in 95% of drinking water samples collected after chlorination. Results from the investigation indicated the occurrence of Trihalomethanes in the water sample collected from 26 sampling stations. Only four sites met the standard value of 80 µg/L.

Keywords: trihalomethanes, distribution network, disinfection byproducts, chlorination, gas chromatography, solid phase micro-extraction (SPME).

Chapter 1

INTRODUCTION

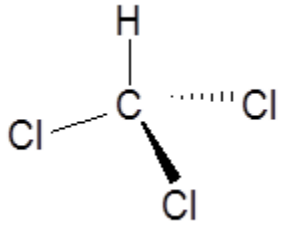
Disinfectants are added into drinking water since the last century. It is the most essential step during treatment of drinking water distribution system, because it eliminates or inactivates pathogenic organisms that contribute in waterborne diseases such as dysentery, cholera and typhoid fever so as to control spread of diseases. Chlorination of drinking water is considered to be an efficient, simple and most inexpensive process of decontamination. Though, in 1970s it was discovered by Rook (1974) and Beller *et al*., (1974) that chlorine reacts with naturally occurring organic matter (NOM) and yields possibly harmful chlorinated disinfection by-products. More than 600 DBPs have been reported in drinking water or simulated laboratory disinfection experiments, as a result of use of chlorine and other disinfectants, particularly chloramines (Krasner *et al*., 2006).

There are two major types of disinfection byproducts produced during chlorination, trihalomethanes (THMs) and haloacetic acids (HAAs). Trihalomethanes are the utmost significant disinfection by products, produced due to reaction of chlorine with naturally occurring organic matter primarily fulvic and humic acid. Trihalomethanes have been further classified into four type chloroform ($CHCl_3$), bromodichloromethanes ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$). Bull *et al.*, (2001) reported that compounds formed are not only mutagenic but also potential carcinogenic.

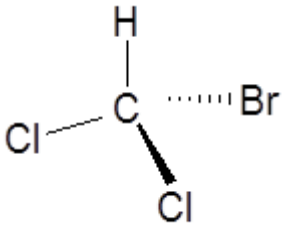
Overall, the brominated DBPs are genotoxic as well as more carcinogenic than are chlorinated compounds, and iodinated DBPs were the most genotoxic of all but they were not investigated for carcinogenicity (Richardson *et al*., 2007).

The nature of chlorinated disinfection byproducts (CDBPs) formed depends on the amount and the chemical composition of organic species originally present. Number of other

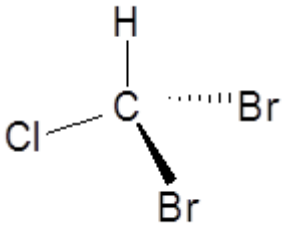
factors such as temperature, pH, chlorine dose, retention time and amount of organic matter present also affect formation of chlorinated disinfection byproducts (CDBPs) in water.



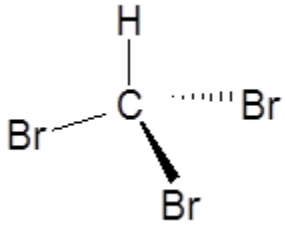
Chloroform ($CHCl_3$)



Bromodichloromethane ($CHBrCl_2$)



Dibromochloromethane ($CHBr_2Cl$)



Bromoform ($CHBr_3$)

Figure 1.1: Structure of trihalomethanes

Most technologically advanced nations have issued regulations so as to regulate DBPs and curtail consumers' contact to these potentially hazardous chemicals in the same time maintaining satisfactory disinfection and control of specific pathogens. During past 30 years ever since the THMs were recognized as DBPs in drinking water, significant researches have been carried in order to increase our understanding of DBP formation, existence, and most important their health effects. Even though more than 600 DBPs have been stated in the literature, merely a minor number has been evaluated either in quantifiable existence or health-effects studies.

The Maximum Contaminant Level (MCL) at present controlled by the US-EPA for TTHM and total HAA are 80µg/L and 60 µg/L respectively (Serrano and Gallego, 2007). In Australia, Spain and Italy; and Germany the maximum allowable contaminant levels in

drinking water for total THMs were 250, 100, 30 and 10 µg/L respectively (Pavelic *et al*., 2005; Sorlini and Collivignarelli, 2005). So it is important to control and observe the formation of THMs with the view to confirm the compliance of the guidelines set.

THMs concentrations found in natural and human consumption water are about the order of ng $L^{-1}$to µg L^{-1}. For this reason a very sensitive analytical procedure is required. These volatile compounds are separated by gas chromatography using capillary columns of medium polarity, followed by electron capture detector (ECD) or mass spectroscopy detection (MSD). There are several analytical methods for the analysis of THMs such as solid phase microextraction (SPME), liquid-liquid extraction, static headspace technique and many others (Kuran and Sojak, 1996; Van Langenhove, 1999). Among all these techniques SPME is the latest, sensitive and most convenient technique for the analysis of THMs.

Water supply and management system should be maintained and operated properly or they could be potential source of disease outbreak. Thus continuous surveillance and monitoring of drinking water source is required to avoid any unfavorable occurrence (Gallard and Gunten, 2002).

1.1 Objectives

Water quality assurance is always a vital issue at national as well as international level. Therefore, it is absolutely essential to correctly regulate and treat drinking water for the benefit of society. This research is mainly focused on the environmental and health impacts of chlorinated water, which is a worldwide issue. The study aimed to investigate the formation behaviour of CDBPs, namely THMs in main water supply systems and distribution networks and analysis of the pollutant concentration in drinking water of the twin cities i.e. Islamabad and Rawalpindi.

Experimental procedure was designed to address the objectives mentioned below.

- Calibration of GC technique for Total Trihalomethanes (TTHMs).
- Identification of the factors that affect the THM formation such as pH, temperature, chlorine dosage, reaction time and analysis of total organic carbon content (TOC).
- Detection of THMs in spiked water and isolation of these compounds from water through microextraction in immersion mode on optical fibres coated with polydimethylsiloxane (PDMS) phase.
- Calculate amount of THMs in Rawalpindi and Islamabad drinking water by gas chromatography.

Currently no significant study is being carried in Pakistan on THMs. This study is aimed to understand behaviour patterns of THMs after spiking of surface water. The methodology is to optimize the whole process and conditions to study the effect of various parameters on CDBPs through experimental investigation using the water samples from two major supply systems in Rawalpindi and Islamabad.

Chapter 2

LITERATURE REVIEW

Water is the most significant compound to sustain life; however it may possibly well also contribute in many diseases. Many organic pollutants may possibly be present in at higher levels in drinking water and they may contribute in negative health impacts. Ingestion of drinking water having these pollutants might cause damage to liver and kidney, sometimes may contribute in nervous system, and reproductive system complaints as well as numerous sorts of cancers (Calderon, 2000; Fawell, 2000). Since water is always treated before human consumption. Still, the practices in drinking water treatment plants such as addition of chemicals disinfectants to the water for specific treatment may possibly result in development of particular chlorinated disinfection byproducts such as trihalomethanes (THMs).

The disinfection of water has been conducted regularly since the early twentieth century to remove and deactivate pathogens in drinking water. In addition to removing pathogens, disinfectants also act as oxidants. They are also used to remove the taste and color, oxidized Fe and Mn, preventing the resurgence of biological elements in the water distribution system (USEPA, 1999a).

Chlorination for drinking water started in New Jersey (USA) in 1908 and has continued to be in force, as it is one of the most commonly used disinfectant because of its low cost and efficiency against microorganisms (Zogorski *et al.*, 2006). One of the disadvantages of using chlorine in treating surface water is linked to the reaction of the disinfectant with organic content in untreated waters, thus bring about the production of disinfection by-products that consist of two main groups, which are produced during chlorination process are haloacetic acids (HAAs) and trihalomethanes (THMs). THMs are produced as by-products during the process of disinfecting the drinking water in water treatment plants by the reaction between the naturally occurring organic content present

already in untreated surface water and the chemicals used for disinfection, particularly chlorine. Of all the natural organic matter (MON), only the fraction of dissolved organic matter, where humic substances are divided as humic and fulvic acids, has been recognized as the precursor of disinfection byproducts during water treatment with chlorine (Weaver *et al.*, 2009). The wide variety of organic macromolecules found in aquatic environments, especially refractory substances such as humic acids, are located largely in the dissolved organic matter (DOM), mainly due to the low biodegradability of these materials in aquatic environments (Gonzalez-Vila, 2001).

A disinfectant predominantly used in water treatment is chlorine and its compounds. Its widespread use is not only because of its low total cost, but also due to its oxidizing capacity, that delivers a least possible level of residual chlorine within the water supply system and thereby protects the pipes in drinking water distribution networks against microbial recontamination (Rodríguez, 2007).

Besides chlorine there are many other disinfectants for example ozone and chloramine. Bougeard and her team (2010) did a comparative study of chlorination and chloramination. DBPs monitored comprised trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), iodinated THMs and nitrosamines. They found that treatment plants that were using chloramine as disinfectant were capable of meeting the European THM guiding limit of 100 µg/L.

Also, maximum THM levels are detected at the end of drinking water supply networks subsequently the reaction amongst free residual chlorine and naturally occurring organic content endures all the way through the water distribution networks and chlorine is added at particular interims as a defence from water related illnesses (Gelover *et al*., 2000; Golfinopoulos, 2000).

In spite of drinking water guidelines and control practices, THM levels may possibly reach as high as 300 μg/L (Fawell, 2000). Numerous scientists have studied THM formation in drinking waters and assessed the health threats through ingestion course (Hsu *et al*., 2001; Sofuoglu *et al*., 2003; Lee *et al*., 2004). Even though the influence of various parameters on THM production including seasonal and spatial variations in THM levels have been investigated in treatment plant discharges and at intervals all through the drinking water supply networks (Çapar and Yetiş, 2002; Toroz and Uyak, 2005).

Chlorination disinfection greatly reduced bacteria and virus in drinking water. However, there is an unintentional concern of disinfection, the development of chemical disinfection by-products (DBPs). Dissolved organic nitrogen (DON) that is a significant precursor of DBPs is of present concern. Chu and his fellow researchers studied formation pathways for THMs during chlorination. In addition also factors affecting formation of THMs such as chlorine dosage, pH, temperature, Br (-) ion concentration and contact time were investigated. The results indicated that all three factors have important effects on formation of THMs, especially Br (-) ion concentration, chlorine dosage and contact time. The capacity of THMs generation varies very little when Br (-) ion has a constant concentration. Generation amount of THMs confer maximum under the condition where dosage of active chlorine, Br (-) concentration and contact time is 8.77 mg/L, 0.77 mg/L at 6.20 h respectively. Bromine ion plays a catalysis role on THMs formation. Controlling the concentration of bromine ion can reduce total generation amount of THMs (Chu *et al*., 2009).

In (2008) Chowdhury and Champagne carried out a study on effect of various parameters using four different water supply networks in Newfoundland Canada. They found strong associations among total organic carbon (TOC), dissolved organic carbon (DOC) and formation of THMs.

Wong and Mok (2008) did an investigation on the formation behaviour of two CDBPs, namely THMs and HAAs, in a treatment plant and within the water supply network of Macau. At different phases of treatment process as well as at two distinct points in the water supply network concentrations of the targeted THMs and six classes of HAAs were observed throughout February 2006 to January 2007. The outcomes indicated that the overall concentration of HAA was generally lower than that of THMs in chlorinated water with a ratio ranging from around 1:1 to 2:1. The results recommended that in the treatment process main steps that influenced the formation of CDBPs are pre-chlorination and coagulation. The concentration of THMs increasing steadily as the CDBPs formation occurs continuously in the distribution system. The effect of temperature was found to be more significant on the formation of HAA than on that of THMs. In an alkaline condition, both THMs and dihaloacetic acids were more readily formed but the concentration of certain trihaloacetic acid declined.

2.1 DBP formation mechanisms

The addition chlorine gas to water results in formation of hypochlorous acid (HOCl) which as a result of reaction with naturally occurring organic content (also known as precursors) that again result in the development of THMs and other DBPs. While presence of natural bromide in the raw or untreated water, results in the formation of hypobromous acid during disinfection that results in swing in distributing the DBPs to extremely brominated classes (Richardson *et al*., 2007; Sadiq *et al*., 2002).

These reactions can be represented as below:

$$Cl + HO \rightarrow HOCl$$

$$HOCl + HOBr + NOM \rightarrow \text{THMs and other DBPs}$$

There are several factors as descried in many researches that influence THM formation in drinking water (Golfinopoulos *et al*., 1998; Sohn *et al*., 2001; Gallard *et al*., 2002). These are includes features of the raw surface water, chlorine dosage, contact time, temperature, pH, bromide levels, the conditions in which water is being stored and supply conditions. As groundwater seldom comprises elevated concentrations of natural organic content, chlorinated private water supply network and community bores are less prone to the formation of THMs. THMs are more commonly found in surface waters treated with chlorine that is consumed for communal drinking water purpose as stated by Golfinopoulos (2000) and Nissinen *et al*. (2002). In addition to usage of chlorine as a disinfectant in drinking water treatment plants, chlorine is also added at few points all the way through water supply networks to retain some chlorine residual. This helps in the protection of drinking water from re-growth of microorganisms and reduces the frequency of waterborne diseases. Nevertheless, this residual chlorine will promote formation of THM till organic matter is present in the distribution system and the depletion of free chlorine residual (Golfinopoulos, 2000). As a result of these ongoing reactions, drinking water samples from treatment plant discharges or at interval all through the supply network may not be the precise level of THMs in tap water (Cohn *et al*., 1999; Hofer and Shuker, 2000, Sohn *et al.*, 2001).

The effects of dissolved total organic carbon (TOC), TOC/Br^- ratio, bromide ion levels, chlorine to ammonia-N ratio (Cl:N), monochloramine dose and the chlorine dose concentration on the development of trihalomethanes (THMs) (comprising chloroform, bromodichloromethane, dibromochloromethane, and bromoform) from chlorination were investigated using aqueous humic acid (HA) solutions. The profile of the chloramine decay was also studied under various bromide ion concentrations. Monochloramine decayed in the presence of organic material and bromide ions. The percentage of chloroform and brominated THMs varied according to the TOC/Br^- ratio. Total THMs (TTHMs) formation increased

from 112 to 190 μg/L with the upsurge concentrations of bromide ions from 0.67 to 6.72 mg/L, but the chlorine-substituted THMs were replaced by bromine-substituted THMs. A strong linear correlation was obtained between the monochloramine dose and the formation of THMs for Cl:N ratios of 3:1 and 5:1. These ratios had a distinct effect on the formation of chloroform but had little impact on the formation of bromodichloromethane. The presence of bromide ions increased the rate of monochloramine decay.

2.2 Disinfection byproducts regulation

United States Congress ratified the Safe Drinking Water Act (SDWA) in year 1974 to safeguard citizen's wellbeing by regulating communal drinking water supplies. SDWA authorized the United States Environmental Protection Agency (US-EPA) to establish national health-related goals for drinking water to ensure protection from both natural as well as man-made pollutants that possibly will be present in drinking water supplies (US-EPA, 2004).

There are two major types of drinking water standards that have been defined by US-EPA, Primary and Secondary. These are Primary standards or Maximum Contaminant Levels (MCLs) and secondary standards. MCLs are the standards that are enforced for public water supplies. These standards are established by keeping in view public health concerns so as to safeguard them from harmful microorganisms, toxic contaminants, radionuclides, and many additional health impacts. In 1979 the federal guidelines that were regulating THMs in drinking water had set a MCL of 100 μg/L (ppb) for total THMs (TTHMs) for networks serving area of more than 10,000 populations. Ever since then, the growing consciousness of health threats posed by microorganisms in drinking water has headed in greater use of disinfectants than earlier, and as a result causing DBPs to become more of an concern.

THM monitoring limit was lowered to 80 μg/L in 1998. The MCLs for THMs are showed in Table 2.1 along with standard values that were recommended by the World Health

Organization (WHO) and those incorporated in the European Communities (EC) drinking water guidelines. In addition to these guidelines, stringent management prerequisite for surface waters are further levied by the USEPA to decrease DBP precursors.

The MCLs shown in table 2.2 are fixed as near as possible to the Maximum Contaminant Level Goal (MCLG), the level where no acknowledged or predictable adversative health effects come about. Nevertheless, keeping in mind the health effects, USEPA also think through the practicability and joint cost of treating water to eliminate the pollutants. Consequently, the MCLs are typically less strict than the MCLGs which are given in Table 2.2.

Table 2.1: Maximum contaminant levels goals in drinking water

Contaminant	Maximum Contaminant Level Goals (µg/L)
Chloroform	70[a]
Bromodichloromethane	0[b]
Dibromochloromethane	60[b]
Bromoform	0[b]

a. US-EPA (2003b) b. 40CFR141.53(2002) c. 40CFR141.50 (2002)

Table 2.2: MCLs for THMs of concern

Contaminant	Guideline Values / Maximum Contaminant Levels (µg/l)		
	WHO[a]	USEPA	EC[d]
Chloroform	200	-	-
BDCM	60	-	-
DBCM	100	-	-
Bromoform	100	-	-
TTHMs	‡	80[b]	150[†]

- Not included in regulations

‡ The sum of the ratio of the concentration of each THM to its respective guideline value should not exceed 1, WHO (2004)

† 100 µg/L must be met by 25 December, 2008.

a. WHO (2004)

b. 40CFR141.64 (2002)

c. 40CFR141.61 (2002)

d. SI No:439 (2000)

2.3 Human health risk assessment

Possible concerns of drinking water comprising volatile organic compounds, particularly DBPs. Ever since the detection of these compounds in drinking water in 1970s; these compounds have been investigated keeping in view their toxicology and epidemiology. According to many studies carried out on animals have verified that liver, kidney, and intestinal tumours have a strong association with chronic consumption of THMs (King *et al.*, 2000). Several toxicological researches have revealed numerous DBPs (e.g., bromodichloromethane, bromoform, chloroform) to be carcinogenic in research laboratory animals.

As summarized by Calderon (2000) after several epidemiological studies that there is strong association amongst ingestion of DBPs and negative reproductive as well as developmental consequences e.g. intrauterine growth retardation, stillbirths, neonatal deaths, low birth weight, preterm delivery, petite body length, and birth deficiencies such as major cardiac flaws and oral clefts. According to several studies such as short-range, high-dose animal screening on separate by-products (e.g., DBCM) have also stated undesirable developmental and reproductive effects, such as whole litter resorption and decreased foetal body weight, which are analogous to those described in the human epidemiology studies (USEPA 2003).

A weight-of-evidence methodology is practiced by the USEPA to categorize the probability that the chemical of concern is a human carcinogen and as an outcome every chemical is located into one of the five classifications presented in Table 2.1.

Table 2.3: USEPA's Carcinogenicity Classification of Chemicals

Group	Category
A	Human carcinogen
B	Probable human carcinogen B1 indicates limited human evidenced B2 indicated sufficient evidence in animals, inadequate/no evidence in humans
C	Possible human carcinogen
D	Not classifiable as to human carcinogenicity
E	Evidence of noncarcinogenicity for human

*USEPA (1992a)

USEPA has categorized chloroform, BDCM and bromoform as possible human carcinogens, as enumerated in Table 2.3. The Group B2 is established on adequate confirmation of carcinogenicity in lab animals and insufficient data about human. DBCM and toluene are not being categorized as human carcinogen, Group D is then again established on the absence of sufficient data on the subject of the carcinogenicity of these compounds in humans or animals.

Table 2.4: USEPA's Carcinogenicity Classification of THMs

Contaminant	Group
Chloroform	B2
Bromodichloromethane	B2
Dibromochloromethane	D
Bromoform	B2

* IRIS (2005)
† Inadequate evidence of carcinogenicity

Probable cancer threats due to consumption of drinking water treated with chlorine in Taiwan were assessed for THMs (Hsu *et al*., 2001). Concentrations of THMs in drinking water were acquired from the yearly report of the Environmental Protection Administration of Taiwan between years 1994 to 1997 to evaluate cancer possibilities consuming the twenty two approaches delivered by the USEPA. Cancer possibilities were mostly differs with various water sources, water distribution areas, and consumption averages. However, in entire cases, approximately 10^{-6} levels were surpassed by every THM class. The utmost risk was estimated as $1.8x10^{-4}$ for chloroform in tap water from water distribution plants of South Taiwan estimating 3l/day every day intake. Lee *et al*. (2004) assessed the lifespan cancer possibility and vulnerability quotient for THMs by contact from tap water by means of statistics gathered in 1997 and the USEPA guiding principle for human health risk assessment.

In one of the study Richardson along with her co-worker (2007) reviewed studies carried out over last 30 years on existence, genotoxicity, and carcinogenicity of eighty five DBPs, out of which 11 are at present controlled by the US, while rest of seventy four are thought to be emergent DBPs as a result of their restrained incidence levels and/or toxicological properties. These seventy four comprise halonitromethanes, iodo-acids and further unregulated halo-acids, iodo-trihalomethanes (THMs), halomethanes, halofuranones (MX [3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone] and brominated MX DBPs), haloacetonitriles, tribromopyrrole, aldehydes, and N-nitrosodimethylamine (NDMA) and other nitrosamines. Generally, the brominated DBPs are more genotoxic as well as cancer causing than chlorinated compounds, whereas iodinated DBPs were the utmost genotoxic of all however, they have not been verified for their carcinogenicity.

2.4 Factors affecting DBPs formation

A study was carried out in 2010 to evaluate the impacts of ammonia and pH value combinations on the production of bromate and THMs during process of ozonation and chlorination in semi-batch reactor. The outcomes showed that the effects of bromate and THMs formation were intensely affected by concentration of ammonia rather than pH value. The addition of ammonia intensely reduced the development of brominated THMs (Wang *et al*., 2010).

Formation of DBPs is primarily governed by the source water quality characteristics and on the location in the treatment process where disinfectants are added (Liang and Singer, 2003). The water quality characteristics that effect the formation of DBPs include: type and concentration of organic precursors, pH, temperature, and disinfectant. The disinfectant dose, point of addition, contact time, and residual concentration are integral to the formation of DBPs.The environmental and treatment factors that influence DBP formation include: pH, contact time, temperature, season, type of NOM, chlorine dose and residual, and Br^- concentration.

Results of some of the factors previously investigated are as follows:

2.4.1 Contact time increases THM formation

Formation of DBPs continues in the distribution system if chlorine residual is present. HAA formation occurs quickly once the chlorine reacts with NOM and formation slows with increasing contact time. As the chlorine and DBP precursors are exhausted, hydrolysis reactions can reduce the concentration of DBPs. Meanwhile THMs are distinctive hydrolysis products and end products as a result of chlorination, the development of THMs are normally amplified by contact time (Xie, 2004). Halogenated DBP formation escalates with the activated aromatic content of NOM as revealed by Reckhow *et al.,* 1990.

2.4.2 Effect of temperature on THM formation

THM has been shown to increase in the water supply system by 1.2-1.8 times that of the finished water (Toroz and Uyak, 2005). The largest variety of THM levels in the water supply network from the finished water occurs when temperatures exceed 24°C. Moreover, Rodriguez and Serodes (2001) indicated that as the temperature rises there will increase in THM development. Additionally, an Ontario drinking water survey determined that water temperature was possibly the solitary one of the most significant issue that influence seasonal difference in THM levels (Stevens *et al.*, 1989). Also, the effect of temperature on THM formation has been investigated for not only the distribution systems, but also in the home of the customer. Finally, the further formation of THMs when water is heated at home was studied by Li and Sun (2001). Samples were heated for 5 minutes and were observed for a 35 minute period. The samples revealed a significant increase in THM concentrations from 104 to 211 μg/L and 115 to 386 μg/L in water samples with an initial free chlorine residual concentration of 0.1 mg/L and 1.2 mg/L respectively. The preliminary heat increase above 80°C showed a rapid THM formation, indicating that temperature close to water boiling point was the favored condition for THM formation. They also studied THM volatilization. A sample with an initial THM concentration of 75 μg/L was heated in a temperature range of 85-90°C. To avoid any THM formation, ascorbic acid, a strong reducing agent, was added to the water samples prior to the heating process. The results revealed a decrease from 75 to 55 μg/L during the heating phase, and an additional decrease to 34 μg/L during the remainder of the 55- minute testing period. Higher THM concentrations were also investigated, which revealed better removal during the heating period from the initial concentration of 120 μg/L to 40 μg/L and further removal during the cooling period to 14 μg/L.

2.4.3 Effect of chlorine residual

Some amount of chlorine residual is maintained in the distribution system to prevent organism re-growth in finished water. However, field data from studies indicating that THM levels will increase over time in the distribution system are inconsistent. In fact, Myerchin *et al.,* (2006) showed that DBPs in finished water samples were similar in magnitude to the chlorine consumed over a period of time.

2.4.4 Effect of residence time

Chen and Weisel (1998) based a study on DBP concentrations in drinking water on the premise that the location with the maximum residence time in the distribution system will have the highest THM concentration. A distribution system in central New Jersey was monitored for a year at zero, one, two, and three-day residence time locations with a 0.5 mg/L of chlorine residual leaving the plant. These scientists explained that seasonal differences in temperature account for the differences in chemical reaction rates. Thus, higher temperatures in the warm season accelerated the rate of THM production in the distribution BVMAs compared with the cold season. During both seasons, the free chlorine at the last sampling point was essentially depleted. The results indicate that the highest concentrations of THMs in the water distribution system were found at the farthest point from the treatment plant during the warm season. The higher temperatures and possibly differences in the organic matter present at the source during the warm season increased the production of THMs; and HAAs are favored over THM formation under certain conditions (Speight and Singer, 2005). Because HAAs tend to form quicker than THMs, they are more likely to be formed in the treatment plant. But, HAA precursors are more likely to be removed by coagulation than THM precursors, thus leaving THM precursors in the finished water to form in the distribution system. Liang and Singer (2003) studied the water quality and treatment characteristics of five water utilities. Each of the five was evaluated under controlled

chlorination conditions to determine their influence on the formation and distribution of HAA and THMs in drinking water. All samples were then chlorinated and pH adjusted to 6.0 or 8.0 for contact times of 1, 2, 4, 8, 24, and 72 hours. HAA and THM formation occurred rapidly during the first few hours, and then slowed as the concentration of NOM and chlorine decreased over time. Rodriguez *et al.* (2004) studied a distribution system with a storage reservoir for DBP occurrence. The main objective was to study the occurrence of DBPs in drinking water with emphasis on seasonal and spatial evolution in a distribution system. Differences in the amount for different seasons were significant for both THMs and HAAs. The highest THMs were in the summer and fall, almost a fivefold increase from 13 the winter

2.5 Selection of technique for analysis

The mounting tendency to monitor the levels of THMs in various environmental matrices involves the use of techniques that provide low detection limits. In view of physical and chemical properties of these compounds, Gas chromatography (GC) technique is used for their identification and quantification. Solid phase micro-extraction (SPME) is an innovative method of sample extraction centered on the setting up of the analyte balance amongst the sample and a polymeric coating on a fused silica fiber. The adsorbed analytes on the coating are then desorbed into a GC injection port by heating. Both qualitative and quantitative analysis of samples can be done different types of detectors. Most common detectors are ECD (Electron Capture Detector), FID (Flame Ionization Detector) and MS (Mass Spectroscopy).

Mauricio Aguirre-González and his co-workers (2011) studied three fibres, (PDMS-100 μm), (CAR/PDMS-75 μm) and (PDMS/DVB-65 μm). Among these three fibres CAR/PDMS of 75 μm fiber was selected for the best efficiency extraction of the THMs compounds, based on its characteristics of polarity, since this fiber gives bipolarity by having

both polar and nonpolar group in its coating and taking into account that the compounds to be analyzed are moderately polar.

In another study Lara-Gonzala and her colleagues (2008) did a comparative study of solid phase microextraction technique and purge and trap method for analysis of eight volatile organic compounds (VOCs), including trihalomethanes (THMs), in drinking water samples. They explored for the 2 sample preparation methods comprised SPME type of fibers, SPME modality, P&T gas flow, extraction and desorption times and desorption temperatures. They concluded that retrievals from 80 to 119% were accomplished with the SPME-GC-MS technique.

Serrano and Gallego did extensive study in 2007 on assessment of trihalomethanes from the drinking water. They were successful in developing a technique for fast analysis of trihalomethanes index in drinking water by using headspace mass spectrometry (HS-MS) method. They established that the practice of using classification chemometric method as soft autonomous modeling of class analogy prior to the PLS regression enhanced the outcomes by HS-MS technique as associated to conventional chromatographic method.

Chapter 3

MATERIALS AND METHODS

3.1. Identification of sampling sites

In order to monitor the influence of specific parameters on THMs development, their correlation and changeability were analyzed with the help of experimental investigation by means of water samples from two main water reservoir supplying water to Islamabad and Rawalpindi. Sampling strategy was planned in consultation with the WASA and CDA staff. Surface water from different water supply systems was collected throughout October 2011 to February 2012. These are Simly Dam and Rawal Dam supply system. Water from Rawal Lake and Khanpur filtration plant is supplied to Rawalpindi area, which is monitored by Water and Sanitation Agency (WASA) with respect to water quality. Islamabad is receiving water from Simly Dam as well as from Khanpur Dam. Raw water samples as well as treated samples were collected for THM analysis.

3.2. Equipment and supplies

Sample containers – 1 litre glass bottles were used for sample collection. Prior to use or following each use, bottles were washed using cleansing agent and tap water then rinse meticulously with distilled water. Then allowed to dry at room temperature and oven dried to 100°C for 30 minutes. After removing from the hot air oven sampling bottles were allowed to cool in a space recognized to make them organic free. Caps were rinsed with distilled water, then rinsed in a flask with GC grade methanol and placed in a hot air oven at 100°C for one hour. Glassware must be meticulously washed. Entire glassware was cleaned as rapidly as possible after usage by cleaning with the solvent previously used. Followed by use cleansing agent and then rinsing with tap and distilled water. After drying, the glassware was sealed and kept in an uncontaminated location to stop any accretion of dirt or further pollutants.

3.2.1. Cleaning of glassware

To inhibit contamination into the sample at any time during the sample processing and analytical analysis, it is crucial that entire glassware and other materials that come in contact with the sample must be meticulously prepared. Appropriate sampling and storage is very precarious for precise results. Cleaning of sampling devices and containers are critical to avoid remnant from earlier samples.

Equipment required for study were vials, micro syringes, pipettes, volumetric flask, disposable Pasteur pipets and gas chromatography system equipped with a linearized electron capture detector (ECD), fused silica capillary column.

3.3. Reagents and standards

3.3.1 Reagents stock standard solutions

Bromodichloromethane, dibromochloromethane, chloroform and bromoform (Standard analyte were purchased from Dr Ehrenstrofer. Methanol was purchased from Merck. Stock standard solutions were prepared by measuring accurately in 10 and 100 mL volumetric flasks with GC grade methanol and stored at 4 °C.

3.4. Sample collection

Much care is needed in sample collection. Air bubbles should not pass through the sample during bottle is being filled, or be trapped in the sample when the bottle is sealed.

Water samples were collected from the main water distribution systems and purification plants. The raw water samples were collected in 1-litre sterilized glass flasks. The glass bottles cleaned and dried in hot air oven 100 °C for 30 minutes prior to use. Composite sampling was done for water collection. Samples were collected from 15-20 feet away from the starting point at irregular interval from 4 different sites of each dam.

For Trihalomethane analysis samples were collected in 40 ml clean glass vessels. For head space SPME 25 ml of vial were filled with water and rest 15 ml is left for head space. For liquid solid phase micro-extraction glass vials were fully filled with water.

3.4.1. Sample handling and transportation

The samples were stored at 4°C during collection and upheld at that temperature till analysis. Field samples that were not analyzed at the research laboratory on same day were stored in refrigerator. Water samples were placed in icebox after collection and were brought back to IESE laboratory for investigation.

3.4.2. Sample storage

Samples were stored at 4°C till examination. The sample storage area must not contain any organic solvent vapors. All samples were investigated within 14 days of collection. Samples that were not analyzed within these time periods were castoff. Treated water samples were studied within few hours of collection. While untreated water samples were collected 1-litre and were stored at 4 °C. The chlorine demand for 1, 3, 6, 24 and 48 hours were determined for each of the source waters.

3.5. On-site analysis

On-site samples were analyzed for turbidity (Hach 2100), pH (Hach pH meter sension 1), TDS and electrical conductivity were measured by Hach meter (sension 5).

3.5.1. Lab analysis

Physiochemical analysis was performed in IESE lab as per methods in Standard Methods (APHA, 2005).

3.6. Physical parameters

Techniques and instruments used for physical parameters

Table 3.1: Methods and instruments used for physical parameters

Parameters	Instruments	Methods
pH	pH meter (HACH Sens ion1 b)	Standard method (APHA, 2005)
Temperature	Thermometer (HACH Sens ion 1 b)	Standard method (APHA, 2005)
TDS	TDS meter (HACH Sens ion 5)	Standard method (APHA, 2005)
Turbidity	UV visible spectrophotometer (SpectronicGensey 5)	Spectrometric method (APHA, 2005)
Conductivity	Conductivity meter (HACH Sens ion 5)	Standard method (APHA, 2005)

3.7. Chemical parameters

Table 3.2: Methods and instruments used for chemical parameters

Parameters	Instruments	Methods
Total organic carbon (TOC)	TOC analyser (Analytic)	High-Temperature combustion method
Total chlorine	--------	DPD Ferrous Titrimetric method
Free chlorine	--------	Titrimetric method (APHA.2005)
Monochloramine	--------	Titrimetric method (APHA.2005)
Dichloramine	--------	Titrimetric method (APHA.2005)

3.8. Gas chromatographic analysis

Gas chromatographic analysis was carried out using a Shimadzu 2010 series gas chromatograph equipped with ECD detector. The column used was fused silica capillary whose length is 30 cm, inner diameter is 0.53 mm, thickness is 0.88 µm and filling material is 5% diphenyl, 95% dimethyl-polysixolane. Figure 3.1 is diagrammatical representation of Gas Chromatogram equipped with ECD.

Figure 3.1: Shimadzu 2010 Gas Chromatogram coupled with ECD

Split injection mode was used with split ratio of 90. Helium was used as carrier gas and the pressure of the gas was 48.2 Kpa with total flow 126.9 mL/min. Column flow was 1.36 mL/min and purge flow was 3.0 mL/min. make-up flow of nitrogen was 5.0 mL/min.

3.8.1. Trihalomethanes standard dilution preparation

Stocks were prepared by means of a 10 µL syringe and instantly adding 10.0 µL of standard material into the bottle by keeping the syringe needle slightly above the surface of the methanol. Care should be taken to make sure that the standard material falls as droplet directly into methanol without contacting the inner wall of the volumetric flask.

To check the signal and retention time of the analytes liquid injection of 1 µL was injected to instrument.

Table 3.3: Standard dilutions

Standard analyte	Concentration (µL/100 mL)
Chloroform	10
Bromoform	10
Bromodichloromethane	10
Dibromochloromethane	10

3.8.2. Dilution of stock solutions

Dilutions of certain stock solution were prepared according to the signals and peak areas to get reproducible peak signals. Bromodichloromethane, dibromochloromethane and chloroform stock solution were diluted 100 times to get reproducible peaks. To prepare the dilution 0.1mL if the stock was added in a 10 mL volumetric flask, then inverting the flask several times.

3.8.3. Mixture of standard analyte

Mixture of standard stock solution was obtained by mixing the individual stocks in a specific ratio. 10 mL of stock solution was prepared in the following table. 10 µL of this stock mixture was injected in instrument to observe the sequence of resulting peaks.

Table 3.4: Mixture of standard analyte

Standard analyte	Concentration (mL)
Bromoform	9.5
Chloroform	0.4
Bromodichloromethane	0.05
Dibromochloromethane	0.03

3.8.4. Selection of extraction technique

A series of analytical methods have been identified for the study of THMs and other volatile organic compound in water. In last few years numerous new microextraction techniques have tested including solid-phase microextraction (SPME) and single-drop microextraction (SDME). SPME is a solvent-free extraction technique based on a thin fused

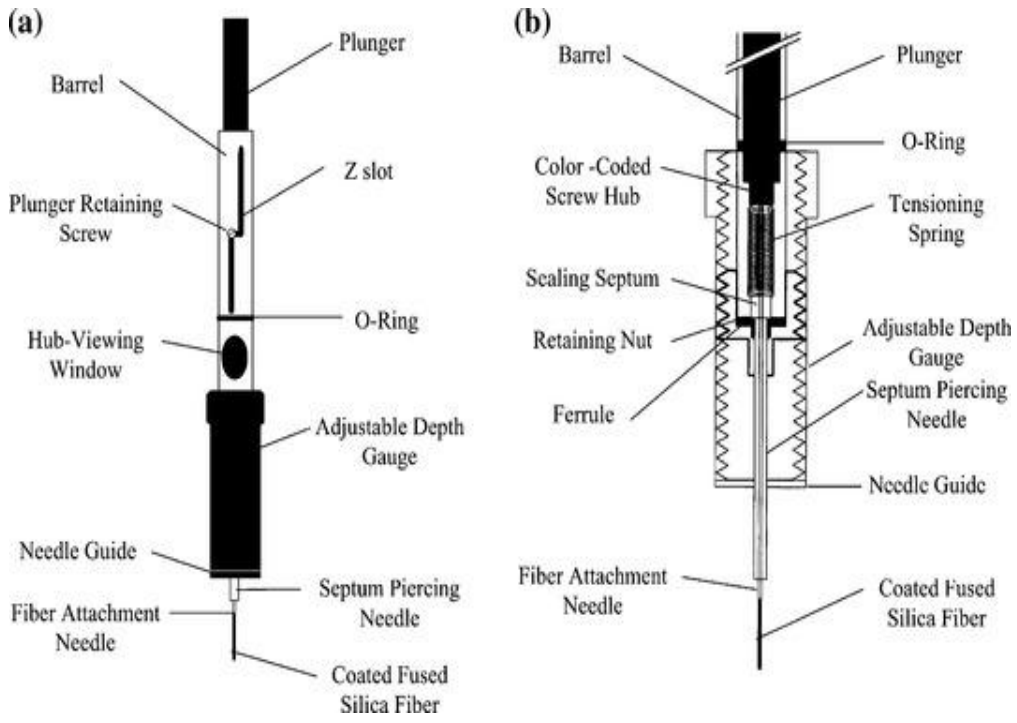
silica fiber coated with a polymeric stationary phase. During the extraction process the fiber is submerged straight into liquid samples or in the headspace just above the liquid. After extraction is completed the SPME fiber is positioned in the injection port of a GC where the analytes are thermally desorbed. Risticevic *et al.*, 2009 also studied the recent developments in SPME technique and concluded that it is most current, including sample preparation and compatibility with many compounds. For this reason SPME has quickly found applications in various fields and it is also effective in analysis of low molecular weight compounds in polymers

3.8.5. Sample extraction and preparation

i. Solid-phase micro-extraction

SPME is an exclusive sample investigation method for complex matrices and for analytes requiring lower levels of detection. SPME removes maximum shortcomings linked with extracting organics. SPME needs no solvents or complex device. SPME has gained common acceptance as the technique preferred in many applications including: flavors, fragrances and contaminants in food; forensic and toxicology applications; environmental and biological matrices; organic volatiles in pharmaceutical compounds.

SPME was performed using a Supleco cat. No.57344-U solid-phase micro extraction fibre assembly fitted with a 75 µm (Car PDMS) fibre. The fibre was conditioned at 250 °C for 30 min to 1 h prior to use.



(a) **(b)**

Figure 3.2: Diagram showing (a) SPME fibre holder (b) SPME fibre

ii. Headspace

Several Headspace methods are now developed while some are commercialized, such as "purge and trap", vial pressurization for static headspace sample transfer, and multiple headspace extraction (MHE) in static headspace. In this method, water sample is transferred to a headspace vial and placed in a thermostat to drive THMs in the HS.

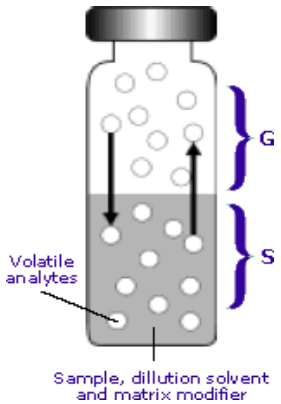


Figure 3.3: Multiple headspace extraction (MHE) in static headspace

iii. Headspace SPME

Samples were moved to SPME vials (40 ml) that contain saturated sodium chloride salt solution and a magnetic stir bar. The vials were held in place on a magnetic stirring plate and the SPME assembly was secured above the vial cap. The fibre was place above the liquid layer of the samples with the stirring rate of 250 rpm. Fibre was retracted back after 15 mins and transferred without delay to the injection port of the gas chromatograph with 200°C desorption temperature.

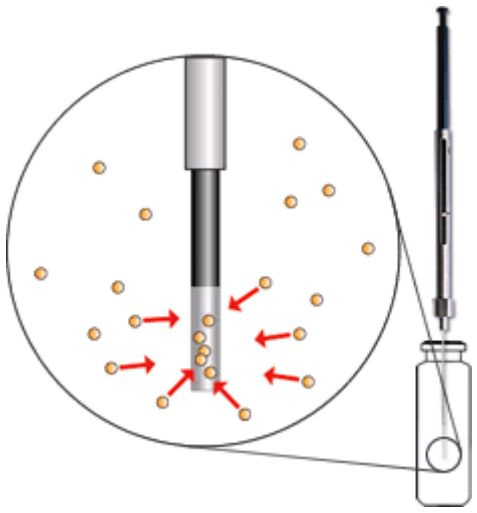


Figure 3.4: Solid phase microextraction (SPME)

3.8.6. Conditioning of SPME fibre

SPME fibre was conditioned at a very high temperature with injector temperature 250 °C, column temperature was 200 °C and detector temperature was 220°C. The fibre was conditioned for 1 h prior to first time use to desorb all the contaminants. Daily conditioning of SPME fibre is very important for accurate results. Conditioning of 15 min is required on daily basis.

3.8.7. Extraction of THMs

For solid-phase micro extraction 1.5 mL amber glass gas chromatographic vials with PTFF septa were used. Different extraction times 1, 5, 10 and 15 minutes were selected to optimize the extraction time. Best extraction time of 15 min was selected after an extensive

study which gave maximum concentration of standard analyte. Gas chromatographic vials were filled with stock solution of standard analyte and after 15 mins the fibre was retracted back and injected into the injector of GC without the delay of few seconds. Signals of trihalomethanes were observed.

3.8.8. Selection of SPME fibres

The sensitivity of this technique largely depends on the type of fiber selected for the analysis. In addition to the type of fiber.Static headspace solid-phase microextraction (SPME) was evaluated for the quantitative measurement of hexanal in various samples. Three fibre materials Carboxen/PDMS, PDMS/DVB and Carbowax/DVB with fibre thickness of 75, 65 and 65 µm, respectively, were compared for linearity, limit of detection. Carboxen/PDMS was the most sensitive.

Table 3.5: SPME fibres and their characteristics

Fiber	Properties
75µm/85 µm Carboxen/polydimethylsiloxane	For analyte group gases and low moleculer weight compounds (MW 30-225) Maximum exposure temperature 340ºC Desorption temperature 220-320ºC
100 µm polydimethylsiloxane	Analysis of PAHs, food safety testing, non-polar, processing and packaging contaminants Maximum exposure time 220 ºC Desorption temperature 200 ºC
7 µm polydimethylsiloxane	Non-polar high molecular weight compounds (MW 125-600) Maximum exposure temperature 250ºC Desorption temperature 200-220 ºC
30 µm polydimethylsiloxane	Non-polar semi-volatiles (MW 80-500) Maximum exposure temperature 280ºC Desorption temperature 200-270 ºC

3.9. Field samples

Study was carried in two phase. In first stage drinking water samples of the twin cities were analysed. Samples were collected from the predetermined sites. The field samples were transported and stored according to standard method. Gas chromatographic analysis was carried out conferring to conditions optimized. Gas chromatographic parameters and their condition have been shown in Table 3.6.

Table 3.6: Gas chromatographic conditions

Parameters	Values
1. Injector	
Pressure	48.2 Kpa
Column flow	1.36 mL/min
Total flow	126.9 mL/min
Temperature	200 ^{o}C
Injection mode	Split
Flow control mode	Pressure
Linear velocity	24.4 cm/sec
Purge flow	3.0 mL/min
2. Column	
Initial temperature	50 ^{o}C
Final temperature	200 ^{o}C
Temperature ramp	15 ^{o}C/min
3. Detector	
Temperature	220 ^{o}C
Current	1 nA
Gas flow	5 mL/min

In the second phase key factors that influence the THM formation, the chlorine decay and THM formation kinetics were analysed in laboratory experiments. Water quality characteristics that influence the formation of DBPs e.g. concentration of organic precursors,

pH, temperature, and disinfectant were monitored. To achieve this objective three test sets were prepared. Results of these tests are discussed in next chapter.

Table 3.7: Setting of potential test

Test set	**Influencing factor**	**TOC (mg/L)**	**Chlorine dose (mg/L)**	**pH**	**Temp.(°C)**
1	Chlorine dose	5, 9	3.38, 6, 8, 10	8.0	8.2
2	pH	5, 9	3.38, 10	6.5, 7.0, 7.5, 8.0, 8.5	8.0
3	Temp	5, 9	3.38, 10	6.5, 8.5	4, 20, 30

Chapter 4

RESULTS AND DISCUSSION

The surface water samples of two different water supply systems from Islamabad and Rawalpindi were collected, namely were Simly dam and Rawal dam supply systems. Water from Simly Dam is supplied to Islamabad and Rawal dam supplies drinking water to Rawalpindi area. The pretreated surface water i.e. before addition of chlorine was collected from the water treatment plant. The pretreated water samples were collected in glass bottles of 2-litre capacity and were stored at 4±1 °C. Whereas drinking water from 30 selected sampling sites within twin cities were also investigated to define varied concentration of marked DBPs. This study was carried with the contribution and collaboration of water authorities such as Capital Development Authority (CDA) and Rawalpindi Development Authority (RDA). All analytes were quantified using the peak area ratios relative to the standard analytes bases on single point calibration from stock solutions**.** Response factor for the stock solution of standard analytes were calculated using single point calibration against their concentration of 11.9, 1.9, 2.41 and 260 µg/L and is shown in Table 4.1.

Table 4.1: Response factor for the stock solution of standard analytes

Analytes	**Retention time (min)**	**Peak areas**	**Concentration (µ/L)**	**Response factor**
Chloroform	4.17	4388.1	11.93	3.68
Bromodichloromethane	5.36	6520.1	1.98	33.9
Dibromochloromethane	6.71	4858.5	2.41	20.2
Bromoform	7.02	34989.6	260	1.34

4.1. Gas Chromatographic study

Drinking water samples were collected from selected sites of Rawalpindi and Islamabad. Standard analytes were acquired from Dr. Ehrenstrofer i.e. chloroform,

bromodichloromethane, dibromochloromethane and bromoform. Prepared stock solutions were run on gas chromatograph so as to spot their retention times and signals. 1µL of standard analytes was injected into the injection port of gas chromatograph. Essential dilutions were prepared to get single and reproducible peak of the individual analyte.

Gas chromatographic conditions were optimized for THMs detection. Carrier gas used was Helium. It flows throughout the analysis in the column at a flow rate of 126.9 mL/min. Makeup gas used was nitrogen gas with the flow rate of 5.0 mL/min. Nitrogen gas flows only at the time of sample analysis. Temperature of column, detector and injector was adjusted according to the signal. Injector temperature was set at 220 °C whereas temperature of detector was set at 200 °C. Similarly a temperature ramp was for the column was prepared by using 50 °C for 1 min as initial temperature followed by temperature ramp of 15 °C for every min was used. Final temperature was 200 °C for the column and which was held for 2 mins. Current of one ampere was applied to the detector 15 min prior to the analysis.

Research was carried out in two phases. In first phase drinking water samples of the twin cities were analysed. In second phase factors affecting the formation behaviour of THMs were studied. To detect factors that stimulate the THM formation, the THM formation kinetics were carried out in laboratory trials. Water quality characteristics that effect the development of DBPs e.g. type and concentration of organic precursors, pH, temperature, and disinfectant were monitored. Table 4.2 shows the concentration, retention times and peak areas of the stock solutions of the standard analytes.

It is well known that interaction time of the fiber with the sample is very important parameter; it effects the extraction retrieval considerably. Four different extraction times were studied (8, 10, 15, 20 min). The results showed that 15 min extraction time accomplished the finest extraction recovery and greatest reproducibility.

Concentration of THMs in drinking water ranges from ng/L to µg/L. Figure 4.1 represents the chromatogram obtained from SPME of standard stock trihalomethanes mixture at 25 °C. Exposure and desorption time is an important parameter to accomplish distribution equilibrium of analytes between fibre and sample. Extraction and desorption time was 15 and 10 minutes respectively, while desorption temperature was 200 °C.

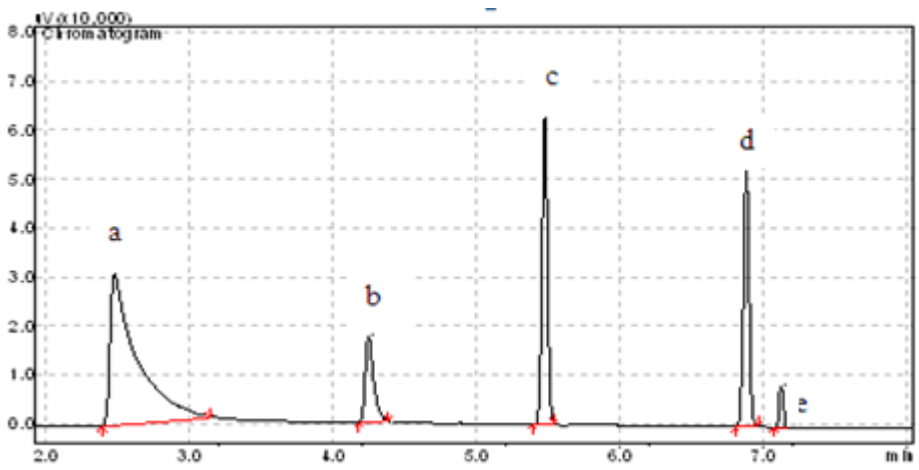


Figure 4.1: Chromatogram signifying the retention time and sequence of standard analytes (a) Methanol (b) Chloroform (c) Bromodichloromethane (d) Dibromochloromethane (e) Bromoform

Figure 4.2 signify relationship between retention times and peak areas of stock solutions of standard analytes. It is obvious from figure that with increase in retention time peak areas also increases. Chloroform has retention time of 4.17 min with peak area of 3989. Whereas bromoform elutes at 7.02 min which is later than all the analytes. Bromoform has the peak area of 41763.

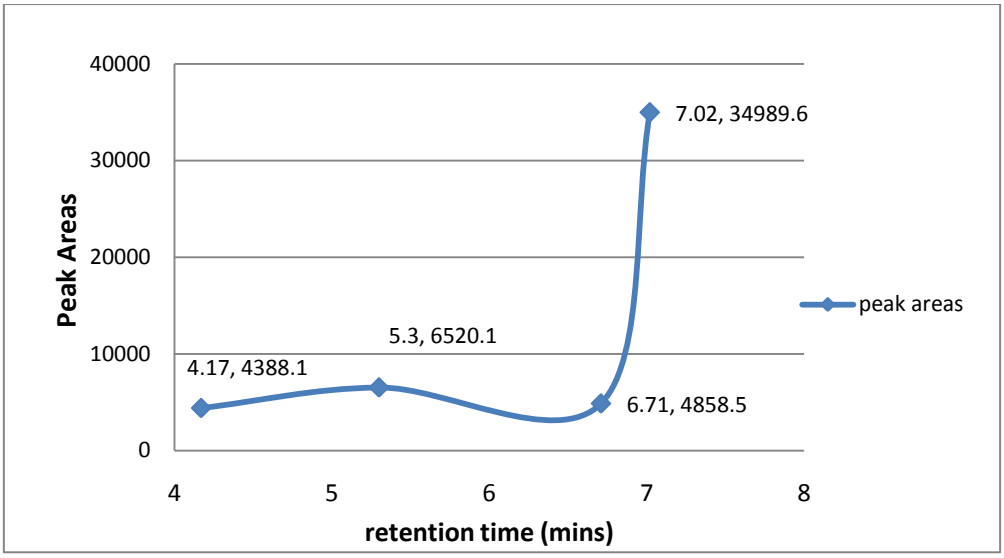


Figure 4.2: Graph signifying correlation between peak area and retention time

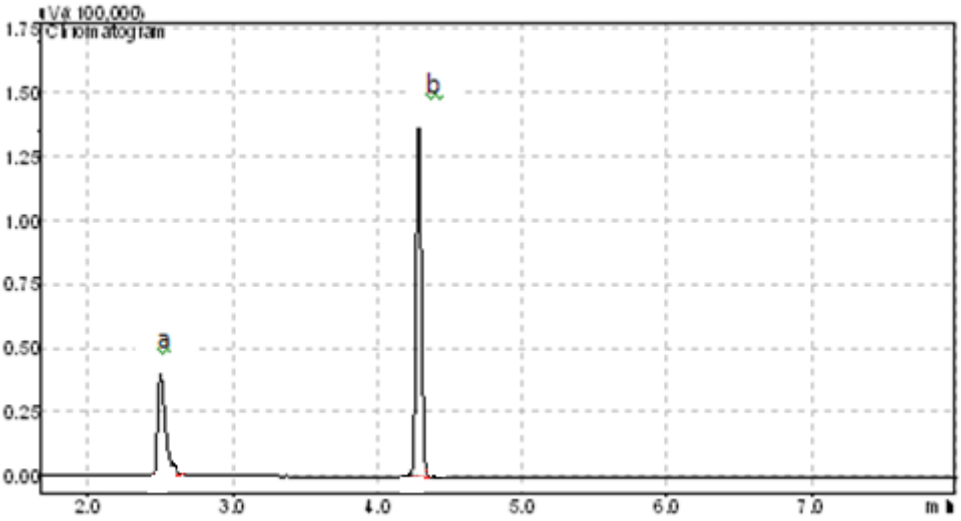


Figure 4.3: Chromatogram signifying the retention time and peak area (a) Methanol (b) Chloroform

Figure 4.3 represents chromatogram of chloroform and methanol. First peak is of methanol with the retention time of 2.5 min. GC grade methanol was used in this study due to polar nature of the analyte as methanol is also polar. Second peak is of chloroform with retention time of 4.15 min. Chloroform has lowest boiling point of 61.7 °C among all four analytes therefore it elutes earlier.

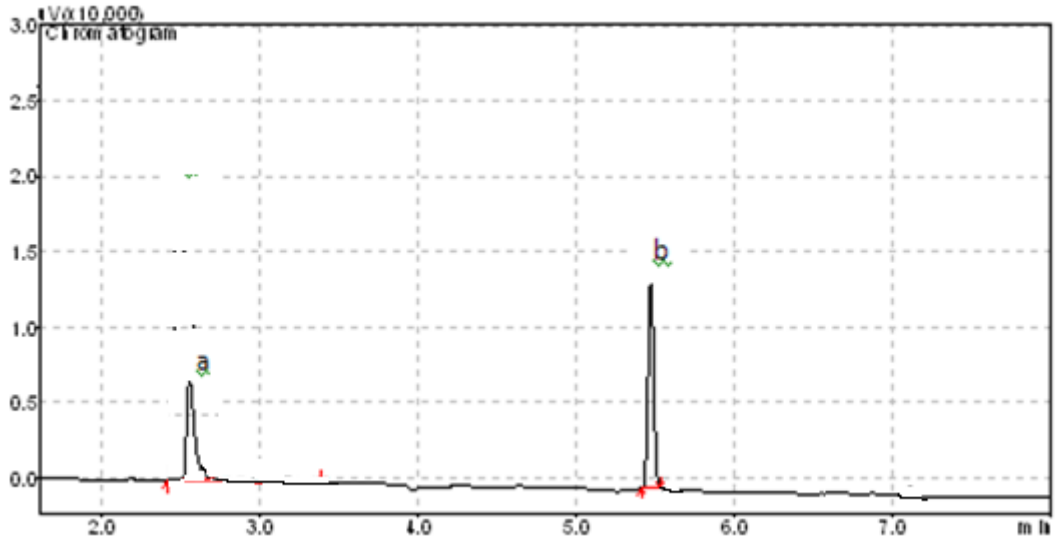


Figure 4.4: Chromatogram signifying the retention time and peak area of (a) Methanol (b) Bromodichloromethane

The above displayed figure is representing two very well defined peaks. First peak is of the solvent methanol. The second peak which is relatively large and narrow with the retention time of 5.3 min is of bromodichloromethane. Boiling point of bromodichloromethane is 90°C. Stock solution of bromodichloromethane was diluted 100 times to get reproducible and well define peak. Peak width extended to 1 min is not reproducible. Peak width should be between 20 to 30 seconds.

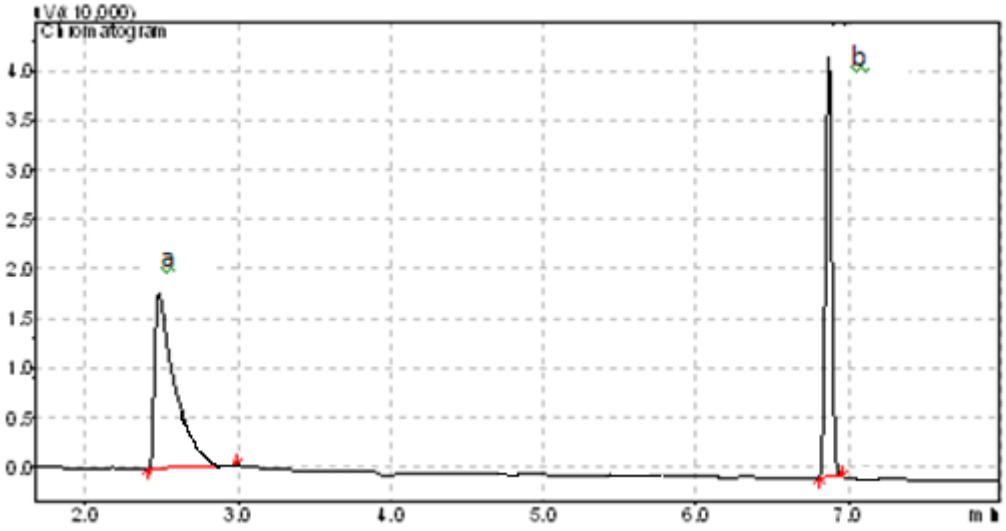


Figure 4.5: Chromatogram signifying the retention time and peak area of (a) Methanol (b) Dibromochloromethane

Figure 4.3 is presenting two very distinct and well clear peaks. First peak is of solvent and second peak is of dibromochloromethane with retention time of 6.71 minutes, boiling point of Dibromochloromethane is 120 °C which is higher than both chloroform and dibromochloromethane. Stock solution of dibromochloromethane was also 100 times diluted to get reproducible peaks.

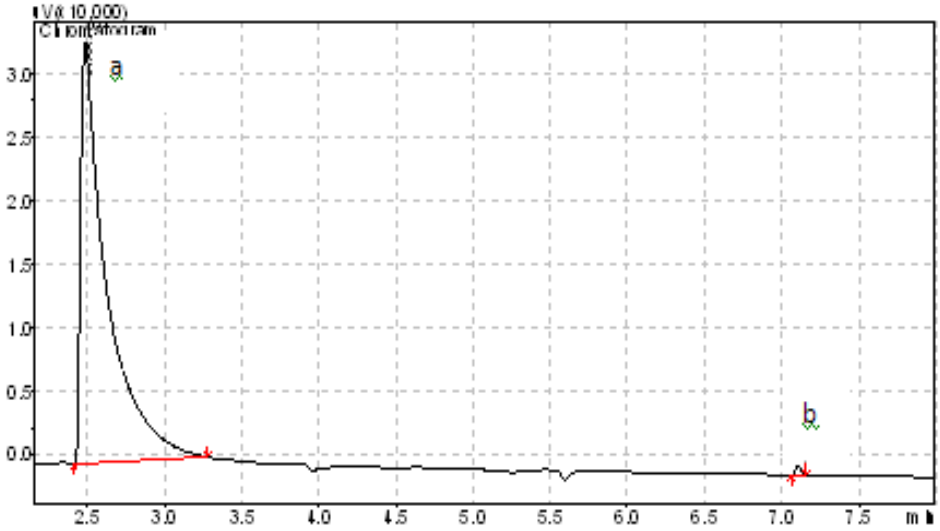


Figure 4.6: Chromatogram signifying the retention time and peak area of (a) Methanol (b) Bromoform

Above chromatogram represents the chromatogram of bromoform. Peak area of bromoform is very small as compared to other analytes. Even though stock solution of all the four analytes were prepared in same concentration. Peak area actually is dependent on the fragmentation of the analyte rather than the concentration of the stock solution. So the compound that produces more fragments will illustrate high peak as it will transmit more current to the detector thus generating more signal.

4.2. THMs analytes mixture

A series of THMs mixtures were prepared by number of trials as illustrated in table 4.3, 4.4 and 4.5. The chromatogram attained from the mixture of trihalomethanes was matched with the real water chromatogram. So stock solution mixture of analytes was prepared in such a percentage that they give reproducible and well resolved chromatogram.

Chromatogram that gave a clear and well resolved chromatogram of the sequence and retention times of the four analytes was used in the rest of the study.

Table 4.2: THMs mixture #1

Standard analyte	Concentration (mL)
Bromoform	9
Chloroform	0.8
Bromodichloromethane	0.1
Dibromochloromethane	0.1

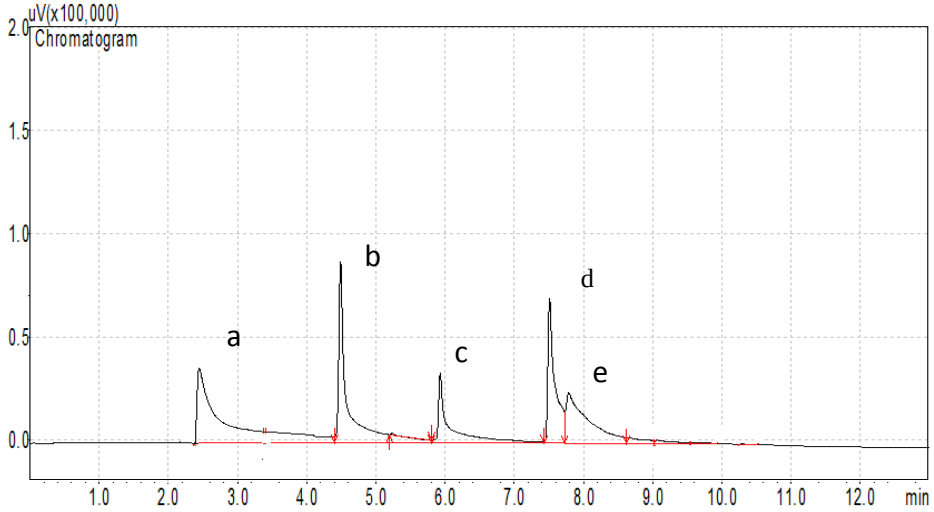


Figure 4.7: Chromatogram of THMs mixture #2 by SPME (a) Methanol (b) Chloroform (c) Bromodichloromethane (d) Dibromochloromethane (e) Bromoform

Chromatogram displayed in figure 4.5 clearly shows that it is not reproducible. In this chromatogram peak area of chloroform and dibromochloromethane is very high. And secondly peaks of dibromochloromethane and bromoform are not resolved. Baseline of the chromatogram is also not set. So this chromatogram cannot be used for comparison with the original water samples. To overcome this problem another mixture of THMs was prepared modifying the volumes of the stock solution.

Table 4.3: THMs mixture #2

Standard analyte	Concentration
Bromoform (mL)	8.0
Chloroform (mL)	0.8
Bromodichloromethane (µL)	50
Dibromochloromethane (µL)	50

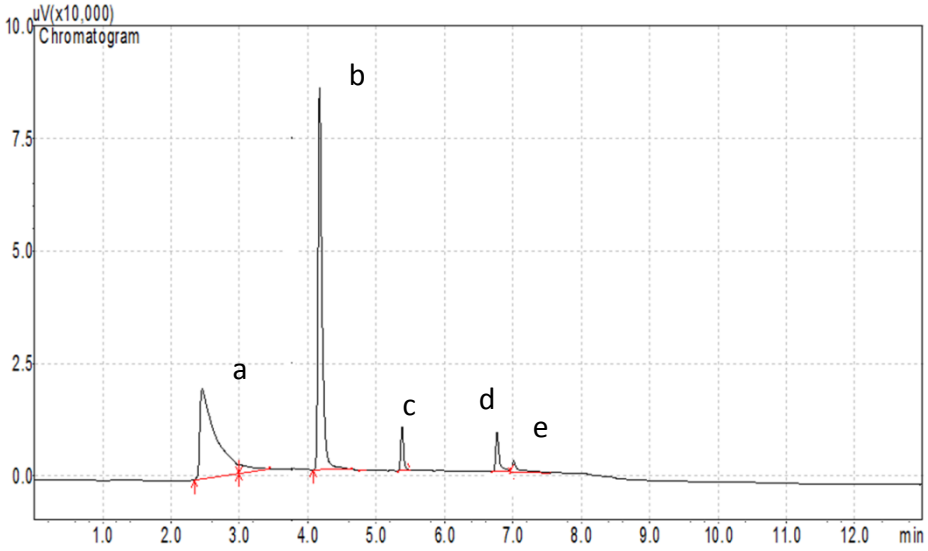


Figure 4.8: SPME stock mixture of trihalomethanes (a) Methanol (b) Chloroform (c) Bromodichloromethane (d) Dibromochloromethane (e) Bromoform

Figure 4.6 represent chromatogram which is yet again not reproducible as peak of chloroform is very high. And peaks of both bromodichloromethane and bromoform are not resolved. Bromoform is giving very low peak signals. So this chromatogram cannot be used as reference for the analysis of original drinking water samples. Due to this reason third mixture was prepared again modifying the composition of the analytes.

Table 4.4: THMs mixture #3

Standard analyte	Concentration
Bromoform (mL)	9.5
Chloroform (µL)	400
Bromodichloromethane (µL)	50
Dibromochloromethane (µL)	30

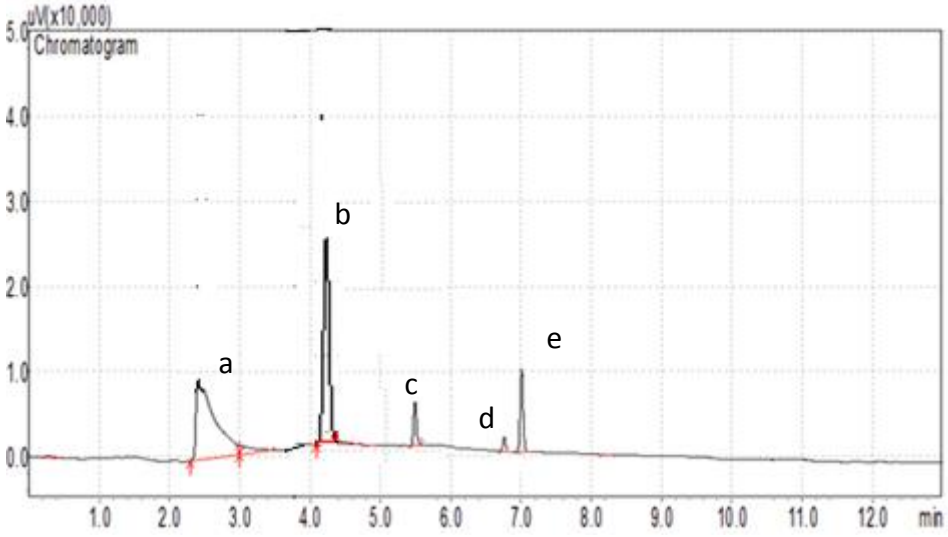


Figure 4.9: SPME stock mixture of trihalomethanes (a) Methanol (b) Chloroform (c) Bromodichloromethane (d) Dibromochloromethane (e) Bromoform

Finally a composition of stock mixture of THMs was established which gave the maximum reproducible results. All the peaks were very clear and reproducible. The subsequent chromatogram now is compared with original drinking water samples.

Samples were analyzed using optimized SPME and GC conditions. The proficiency of this extraction and concentration technique is influenced by numerous factors, including flow rate and kind of sorbent. Original samples were collected from the selected sampling sites according to the Standard Method (APHA, 2005). The original samples were kept at 4°C before analysis. Samples were then moved into 1.5 ml amber glass vials by using sterilized 3 cc syringes for SPME. Extraction was done for 15 mins; fibre was then injected into injector. Gas chromatographic parameters as well as their respective conditions have been shown in table 3.6.

Almost 95% samples were found to be contaminated with THMs. Chloroform concentration was found to be maximum in all samples from entire drinking water supply network i.e., underground tank, overhead reservoir and filtration plants. Chloroform was

comparatively lower in concentration in underground tank and sampling station no 14 and this may be due to the fact that underground tanks have low concentration of organic matter for chlorine to react. Concentration of TTHMs ranged from 44.51 to 595.86 at different sampling station (Annexure A). These results show a strong link between concentration of TOC and trihalomethanes. The potential reason for contamination at different point is presence of natural organic matter. Trihalomethanes formation occurs when chlorine is added to such water sources. Speciation of THMs can vary conditional on the nature of the source water.

Figure 4.8 signify the chromatogram acquired from drinking water sample of consumers house in E-9 sector. Peaks of all four compounds of interest are clearly identifiable and were confirmed by comparing the retention times of standard analytes. Out of 30 sampling sites only 3 sites met the USEPA drinking water quality standard values, whereas remaining 27 sites were exceeding the standard value of 80 µg/L. Results indicated that water samples from the filtration plants have high concentration of chloroform ranging from 106- 417.7 µg/ L. Contamination in filtration plants are alarming, it may be due to any organic source of contamination or human activity.

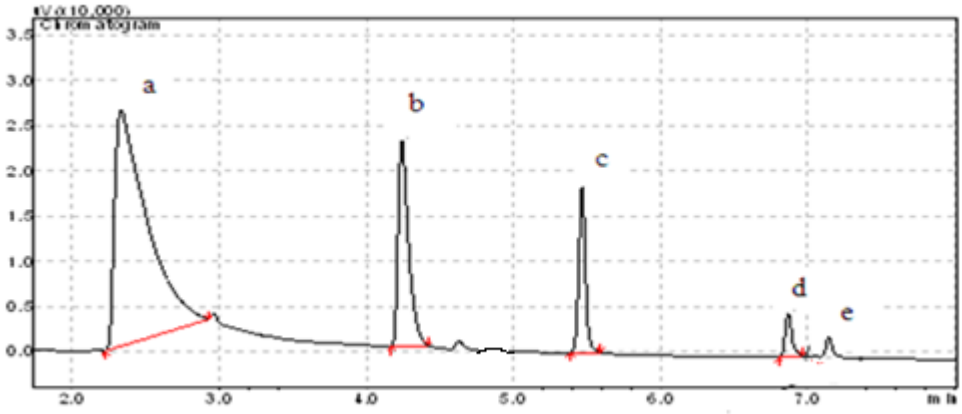


Figure 4.10: Chromatogram of filtration plant at E-9 sector

4.3. Physiochemical analysis

Surface water from Simly dam and Rawal dam were selected for the analysis. Physical and chemical parameters of water samples from both treatment plants along with surface water samples is given in Annexure B.

It is always important to know the organic load of the waterway because considerably high content of organic pollutant will results in trihalomethanes formation. *Disinfectants and Disinfection byproducts Rules* by the US environmental protection agency specifies maximum total organic content levels of 2 mg/L in treated water and 4 mg/L in source water to ensure acceptable levels of disinfection byproducts. TOC value for drinking water supply with chlorination is 4 mg/L (USEPA 2004).

The World Health Organization recommends maintenance of a disinfectant residual of 0.2 to 0.5 mg/L in the distribution systems under normal operating conditions (WHO, 2004). In general developing countries maintain higher concentrations of residual chlorine than the estimated 0.2 mg/L maintained by developed countries water supplies (Chen and Weisel, 1998). Maintenance of residual chorine in distribution network is important for microbial quality of water being supplied to consumer.

4.4. Lab investigation

Although there are many parameters that play role in THMs formation. However this study concentrates on the utmost recurrently used parameters such as chlorine dose, TOC, pH and temperature.

4.4.1. Natural organic matter

Naturally occurring organic matter in raw surface water includes humic substances, fulvic acids and organic composites. The NOM is one of the most significant precursor of THMs development and it does have any direct measurements. The NOM can be stated in terms of substitute measures, such as TOC or DOC (White *et al*., 2003). Trihalomethanes

(THMs) will form as a result of chlorine reaction with organic carbon leading to a serious water quality issue. The US environmental protection agency have newly developed *Disinfectants and disinfection byproducts rule* according to which maximum total organic levels of 2 mg/L is allowed in treated water and 4 mg/L in source water to guarantee the satisfactory level of disinfection byproducts (USEPA, 2004).

4.4.2. Total and dissolved organic carbon

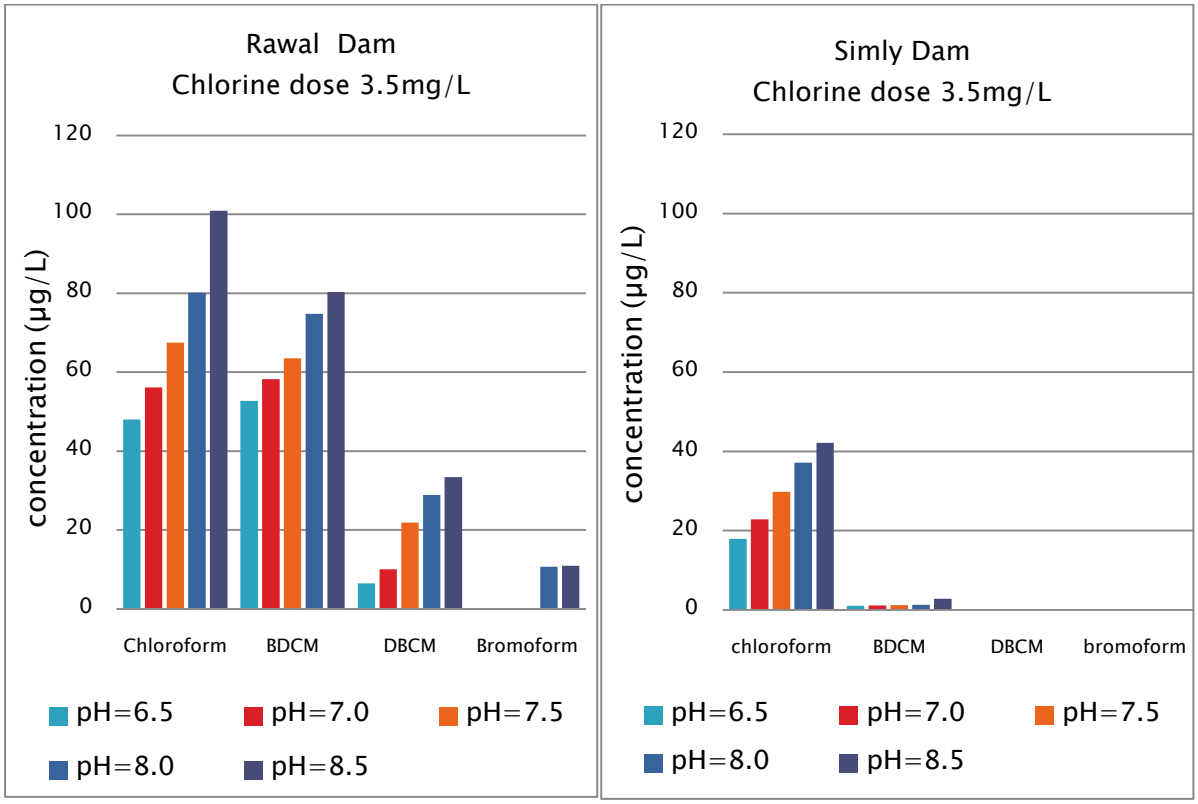
The direct measurements of organic content are total organic carbon (TOC) and dissolved organic carbon (DOC). Higher level of TOC will result in increased level of THMs formation (Chang *et al.*, 2001). The concentration of organic matter might be calculated as DOC or UV254 as suggested by Muller (1998). Similarly, Korshin and his co-workers in 1997 stated that particular UV absorbance (SUVA) is a good indicator of NOM in water, which is a ratio amongst DOC and UV absorbance capacity,

4.4.3. pH

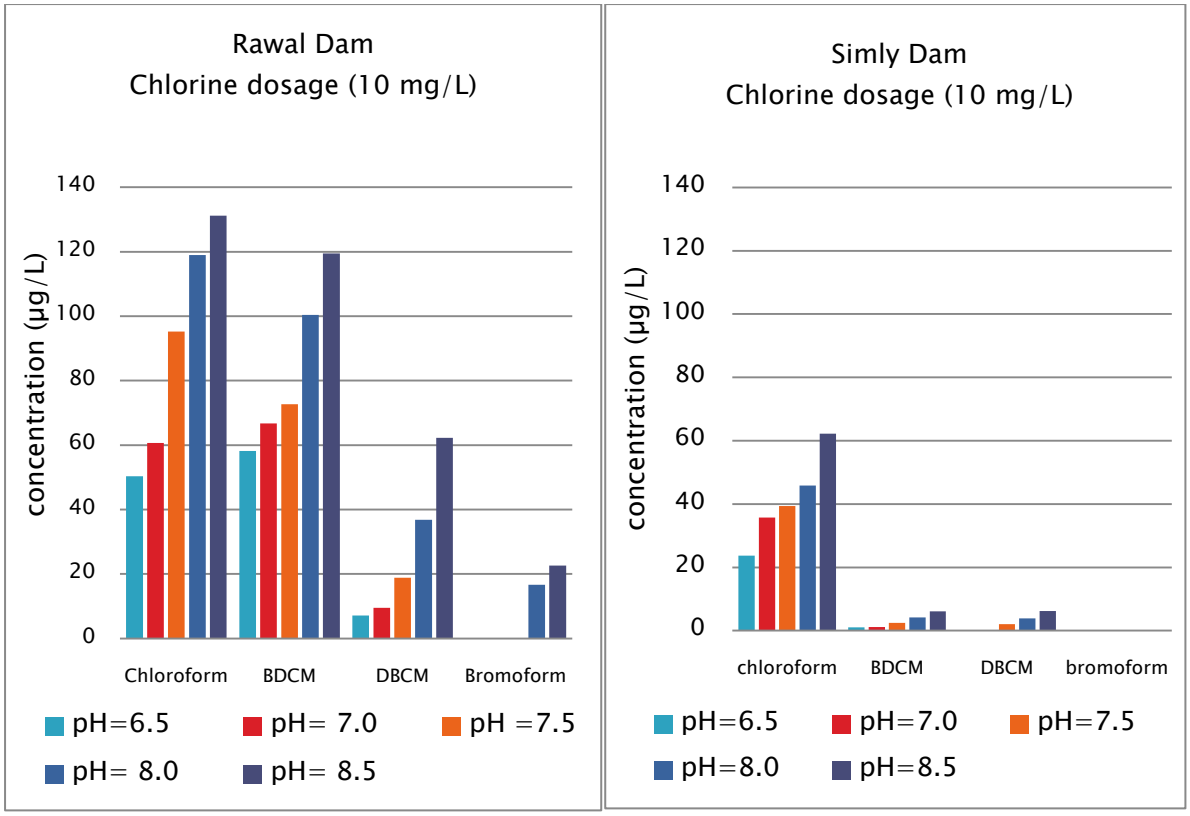
THMs formation is found to be directly correlated with pH. Stevens *et al*. (1989) performed three studies using Ohio River water at the Cincinnati treatment plant with various pH values. The results demonstrated increased THMs production at higher pH. When the pH was increased from 7 to 11 there was 30 to 50% increase in THMs formation. However rate was dependent on the source of organics as well as chlorination conditions (Oliver and Lawrence, 1979). The influence of pH on THMs formation for Simly dam and Rawal dam water samples is presented in Figure 4.8 (i-ii-iii-iv). Trihalomethanes production rise considerably with higher pH, which is incompliance with the earlier studies (Stevens *et al*., 1989; Oliver and Lawrence, 1979; Kim *et al*., 2002).

Water samples from Rawal Dam, THMs formation was found to be almost 50% higher as pH was altered from 6.5 to 8.5; and nearly 30% higher as the pH was switched from 6.5 to 7.5 in Simly Dam water samples. Where as in Simly Dam water samples although chloroform found to 50 % increased when pH was raised from 6.5 to 8.5 but the overall

concentration was fairly low due to lower level of TOC in the original water sample. Though, at high pH such as more than 9, there would be hydrolysis of haloacetic acids and haloacetonitriles takes place thus resulting to lesser total organic halide (Singer, 1994; Krasner *et al.*, 1989).



(i) **(ii)**



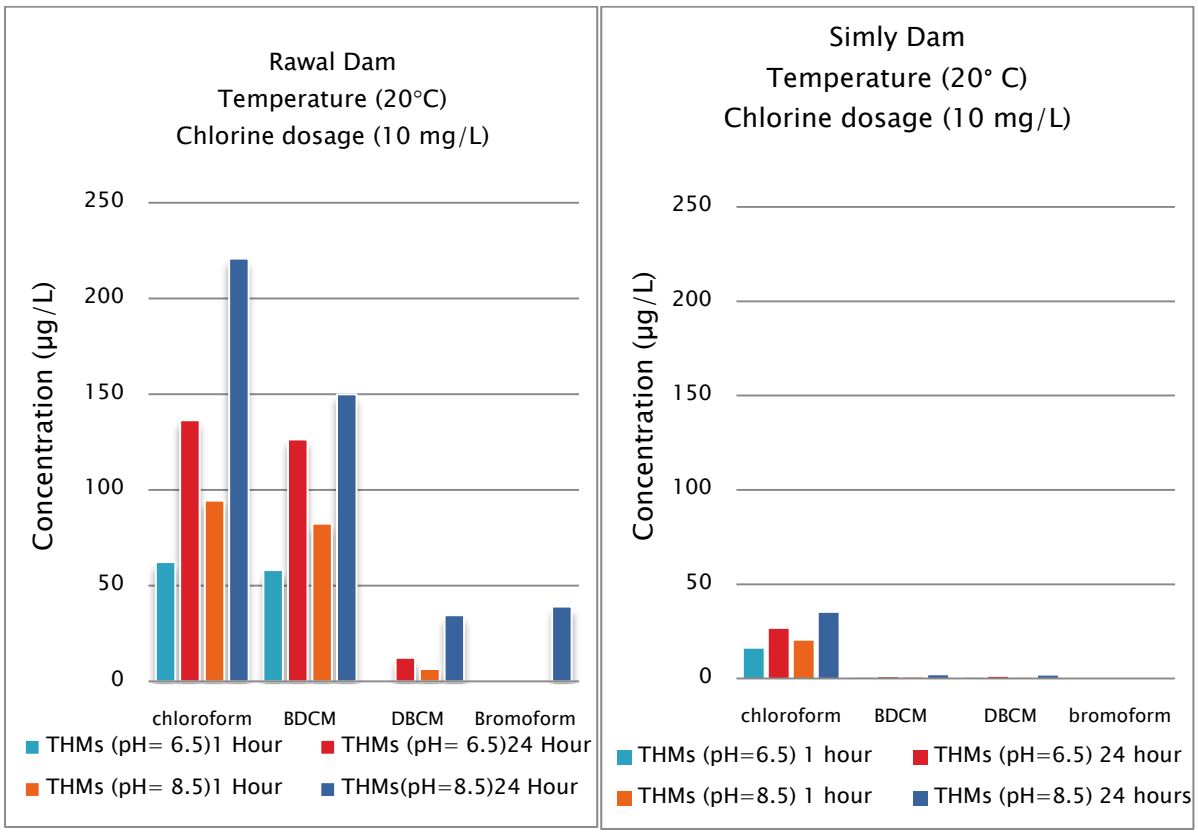
(iii) **(iv)**

Figure 4.11: Effect of pH on THMs formation

4.4.4. Reaction time

Even though substantial amounts of THMs is produced immediately after chlorination (Chang *et al.*, 1996), a prolonged reaction time may likewise add to higher levels of THMs in drinking water (Kim *et al*., 2002), whereas just after a rapid reaction phase there may be decrease in the formation rate of THMs (Gang *et al*., 2002). It was reported in 1996 by Chang and his co-workers that maximum THMs are formed with the first 8 hours of reaction time. Whereas Kolla (2004) and Chang *et al.* (2001) both agreed that there is an insignificant increase in THMs after 48 hours of chlorine addition. To keep drinking water free of microbial contamination all the time it is crucial to maintain sufficient residual chlorine in water supply networks (USEPA, 2006) thus the methodology of sustaining free chlorine residuals may further contribute towards higher THMs levels in drinking water.

The impact of reaction time on THMs formation is demonstrated in Figure 4.10 (i-ii) in which temperature and chlorine of Simly Dam and Rawal Dam water samples were varied, respectively. It was observed that the rates of THMs formation substantially augmented at pH 8.5 with temperature 20 °C after 24 hours. There is approximately 50 % increase in chloroform after the initial reaction phase (Figure 4.9 (i-ii)). It should be noted, however, that lower level of TOC could lead to overall decreased amount of THMs formation, which is obvious from Figure 4.10 (i-ii).



(i) **(ii)**

Figure 4.12: Effect of reaction time on THMs formation

4.4.5. Temperature

Temperature also showed a positive impact on THMs formation in drinking water. Stevens and his fellow workers in 1989 conducted different experimentations using three

altered temperatures (3, 25 and 40°C), with pH constant at 7 and chlorine dosage of 10 mg L^{-1} using water from the Cincinnati water treatment plant where water was supplied from Ohio River. It was noted that the production of THMs increased 1.5 –2 times higher at every stage when the temperature was being altered. The increase in 25-50% of THMs formation per 10 °C temperature increase was observed (Engerholm and Amy, 1983). El-Shahat *et al*. (2001) and Hellur-Grossman *et al*. (2001) stated lesser THMs formation during the winter months than during the summer months, whereas in summer months as result of higher summer temperatures, reaction rates results in amplified rate of THMs formation. Nevertheless, the seasonal changeability of NOM may possibly contribute a substantial role in the upsurge of THMs formation during summer months.

It is evident from the current study that the temperature also has direct effect on the THMs formation. Experimentation was performed using three different temperatures (4, 20 and 30°C). Constant pH of 6.5 and 8.5 with chlorine dosage of 3.5 mg/L and 10 mg/L were used. It was noted that there is 50 % increase in THM formation at 8.5 pH with chlorine dose of 10 mg/L which complies with the previous studies mentioned above. Results showed that when the temperature was adjusted as low as 4^{o}C, THMs formation was very slow even immediately after 1 hour of incubation; there wasn't much change in concentration subsequently even after 24 hours of contact time. Now as the temperature was increased upto 20^{o}C and 30^{o}C THMs were produced constantly starting from 1 hour to 24 hours of contact time.

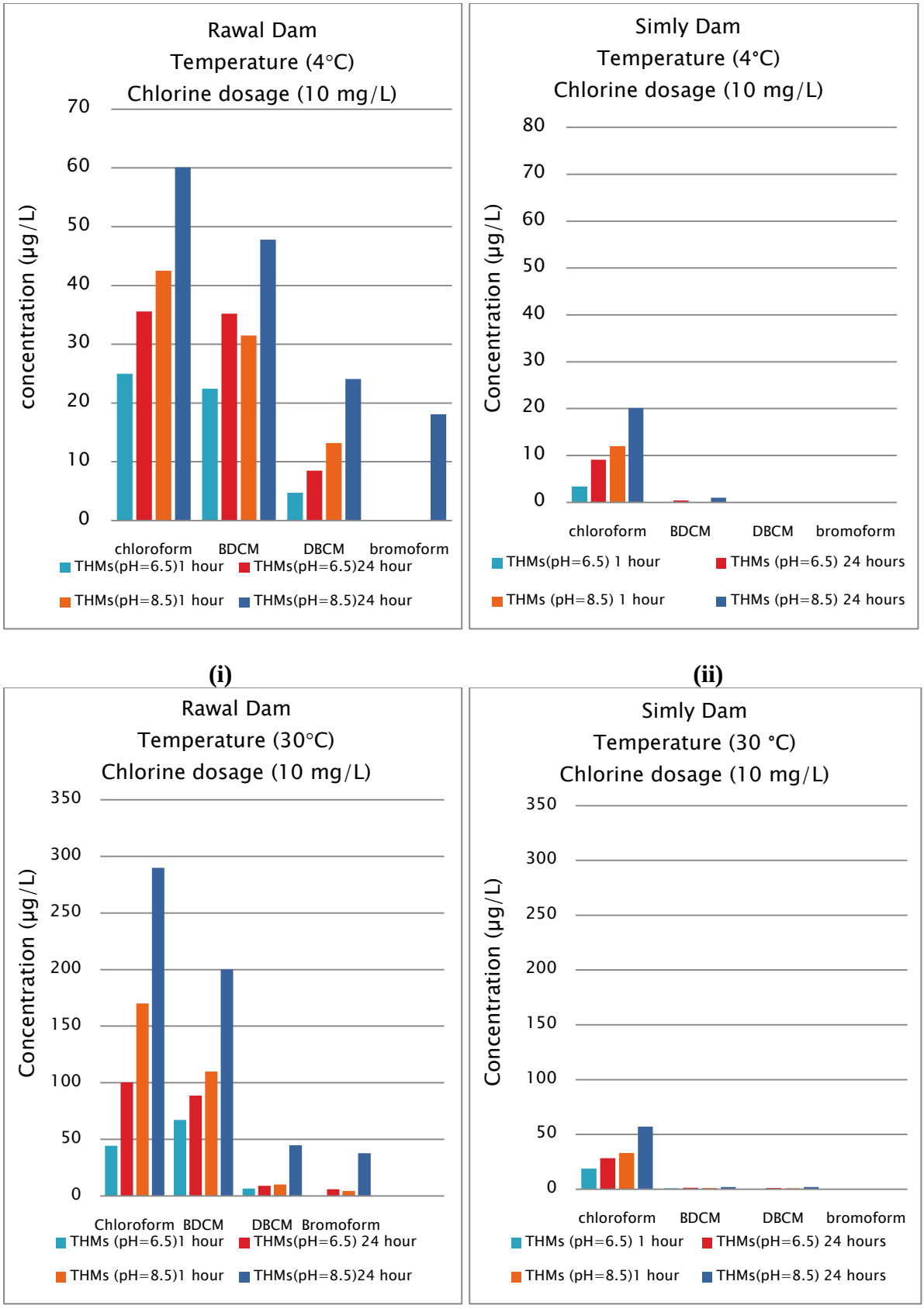


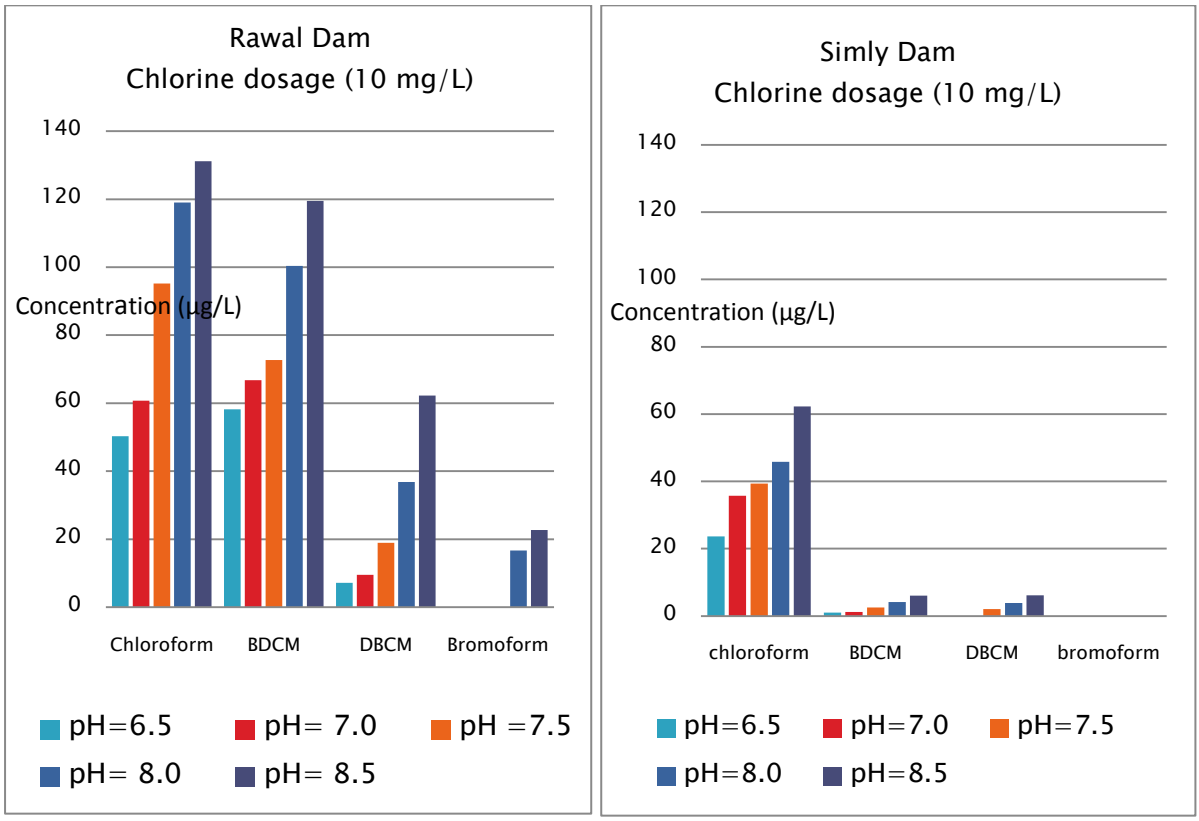
Figure 4.13: Effect of Temperature on THMs formation

4.4.6. Chlorine dosage

The quantity of chlorine that is used for disinfecting the water is known as the chlorine dosage. Figure 4.11 (i-ii) illustrates the impact of chlorine dosage on formation of THMs for the Simly Dam and Rawal Dam water samples. It can be seen in these figures that four chlorine doses were used for both the water samples. From Figures 4.11 (i-ii), it can be observed that, when lower chlorine doses were used, the resulting THMs concentrations were much lower than those at midway chlorine doses. Though, there wasn't much change in THMs formation once the chlorine dosage was augmented further. This may be attributed to the fact that the chlorines beyond breakpoints had inconsequential quantity of organics matter for reaction. This fact partially backs the concept that there is an insignificant increase in THMs formation when chlorine dosage is beyond the breakpoint. Though, slow reaction rates amongst organic content and chlorine in the water supply system may employ partial chlorine demand.

In order to satisfy the real requirement of the water disinfection, chlorine demand is in generally defined in the treatment plants and water supply systems (Sung *et al*., 2000). As such, chlorine demand has been integrated by several researchers into their specific mathematical modeling methodologies (Westerhoff *et al.*, 2000; Clark *et al*., 2001). Nevertheless, the several bodies may oxidizes quickly but cannot be linked with THMs formation and may likewise demonstrates a chlorine demand such as Fe^{2+}, Mn^{2+} and S^{2-} in water (Gang *et al*., 2002; MOE, 2004). Keeping in view these findings usage of chlorine demand may affect the outcomes. The total quantity of chlorine requisite for oxidation reaction is characteristically unimportant in contrast to the chlorine needed by the organic matter (Rodriguez *et al*., 2002). The chlorine dosages used in this controlled study were in ranges of 3.38-10 mg/L for both water samples. It is important to mention here that, the use

of higher chlorine dosage in the treating drinking water is not unusual for drinking water distribution systems (MOE, 2004).



(i) **(ii)**

Figure 4.14: Effect of chlorine dose on THMs formation

Chapter 5

CONCLUSIONS

The experimental results presented in the study indicate strong associations amongst the particular water quality parameters for entire water samples. Whereas natural inconsistency and environmental circumstances at the particular spots of the water sources differences may attribute to differences in correlations. The overall behaviours of the allied parameters may be generally stated as follows:

- Increase in pH, reaction time and NOM results in higher level of THMs formation.
- Temperature generally contributes in higher reaction rates, thus yielding greater rates of THMs formation.
- As NOM content increases, the chlorine demand also increases. Organic content in water generally measured as TOC or DOC. Both TOC and DOC indicated to have strong connection with THMs formation.
- It can be concluded that chlorine beyond the real demand by the organic content in water has inconsequential impact on THMs production.

The outcomes of the study discussed here was carried out using water samples from Simly Dam and Rawal Dam Pakistan and recommends that NOM is an important precursor of THMs formation. Nonetheless, it is difficult to determine the actual chlorine demand by the organic content in water, and may be due to the unpredictability in the water supply systems as well as residence/contact time in the circulation system. For drinking water, chlorine required for oxidation of the reduced substances is normally unimportant; consequently making the use of chlorine dosage as a safe practice. The TOC and DOC are mostly intensely associated with one another and are considered as precursors of THMs in water. Contact time, temperature and pH have indicated to considerably affect the formation of THMs. In future, additional investigation including the characterization and associations of

both these imperative water quality parameters is essential to have well understanding of THMs formation kinetics and the possible risks connected to human health as a consequence of contact to THMs. Importance should be given to the fact that reaction time, pH and temperature are not both directly or indirectly overlooked throughout water treatment practices.

The current study also compared DBPs formation in different parts of the twin cities. The data showed that most of the samples were contaminated. Further investigation is suggested to better understand the formation of DBPs as the levels found were significant. SPME technique was successfully applied to determine the trihalomethanes in drinking water. Unfortunately almost 95% samples were contaminated with THMs. In circumstances where DBP standards are either narrowly approached or surpassed, water experts requires to examine water treatment processes with vision to improve the amputation of organic contents from the water sources proceeding towards the disinfection, by means of substitute decontaminators and decreasing water age in supply system. The possible risks connected with DBPs are relatively not known, although certain toxicological and epidemiological researches deliver selected information. More investigation is required to understand the issues linked with DBPs.

As the DBPs issue rises in momentum in Pakistan, the more emphasis will be to decrease formation of DBP at the same time upholding a microbiologically safe product. Unquestionably, this will pose a number of functioning and operating tasks for local water specialists as well as authorities.

Chapter 6

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ANNEXURES

Annexure A

Table A: Concentration of THMs (µg/L) at different sampling stations

Sr no	Sampling stations	Chloroform $CHCl_3$	DBCM $CHClBr_2$	BDCM $CHCl_2Br$	Bromoform $CHBr_3$
1	UGT # E-9 sector	105	6.5	9.2	BDL
2	H # D 22/6 E-9 sector	150.00	7.5	12.5	BDL
3	H # D 22/ 3 E-9 sector	321	9.7	16.9	7.78
4	H # D 21/6 E-9 sector	360.6	2.2	10	BDL
5	AHQ E-9 sector	337	1.6	3.8	BDL
6	Filtration plant, E-9	106.7	4.9	8.7	BDL
7	Filtration plant, E-8	193.8	1.5	8.5	BDL
8	H# 22, E-8	295	2.8	15.5	BDL
9	H# 25, E-8	575.9	1.6	15.2	3.11
10	H# 316, St # 39 G-9/1	280.0	15.9	22.5	BDL
11	H# 298, St # 39 G-9/1	355	1.7	8.0	BDL
12	H # 35, St # 8,F-7	96	3.8	7.9	BDL
13	Wasa office	314	1.00	22.0	BDL
14	H # 17-C,F-8	23.9	BDL	0.5	BDL
15	H # 6, street 66,F-7	55.7	1.9	3	BDL
16	H # 283, Gomal road, E-7	55.7	2.0	3	BDL
17	H # 309 Aurangzeb road, E-7	171.0	6.0	7.9	BDL
18	H # 205 hill side road, E-7	130.5	BDL	2.0	BDL
19	Filtration plant F-10	40.7	2.0	2.0	BDL
20	H # 202B street 10, E-7	232.4	13.6	33.20	4.11
21	Filtration plant F-7	417.7	1.1	10.0	BDL
22	Treatment plant Simly Dam	89.7	5.0	7.1	BDL
23	Treatment plant Rawal Dam	104.5	0.7	5.7	BDL
24	Filtration plant Chaklala Base	303.6	3.1	8.0	BDL
25	Filtration plant Scheme III	247.0	13.3	14.0	BDL
26	Filtration plant Askari 4	258	17.5	18.7	BDL
27	H# 21 –C Askari 4	172	7.3	10.7	BDL
28	Filtration plant Askari 3	271	18.2	23.7	5.72
29	H# 31-D Askari 3	415.0	2.0	14.0	BDL
30	Filtration plant Askari 2	182	9.00	16.2	BDL

BDL: Below detectable limit. ECD detectable limit 0.02µg/L

Annexure B

Table B: Physiochemical analysis of Rawal Dam and Simly Dam water samples

Parameters	**Treated water**		**Surface water samples**	
	Rawal Dam	**Simly Dam**	**Rawal Dam**	**Simly Dam**
TOC (mg/L)	4.89	2.25	9.0	5.0
pH	8.2	8.0	8.2	8.15
Temperature (°C)	8.5	8.8	14.5	15.6
TDS (mg/L)	160.5	151.0	160	158.5
EC (µS/cm)	334	327	329	321
Turbidity	3.5	2.21	8.5	7.8
Free chlorine (mL)	0.3	0.35	0.0	0.0
Monochloramines (mL)	0.0	0.0	0.0	0.0
Dichloramines (mL)	0.0	0.0	0.0	0.0