Laboratory investigation on bromoform formation in potable water of Kuwait

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Declaration statement

All the ideas and work are original except where referenced in the text. The work contained in the thesis has not previously been submitted for any other qualification. This thesis is submitted for the degree of Doctor of Philosophy in the Department of Civil and Structural Engineering at the University of Sheffield, UK. The thesis is based on independent work performed by the Author between October 2009 and June 2015 under the supervision of Professor Adrian J Saul.

Abstract

Bromoform compound is occasionally found in concentrations above 100 µg/l (WHO guideline limit for bromoform is 100 µg/l) in the potable water of Hawali city, Kuwait. The compound has been classified as a "possible human carcinogen". In this research study, a laboratory investigation was carried out to assess bromoform precursors in the sources (i.e. groundwater and recarbonated water) of potable water at the Doha blending facility, Kuwait; to perform correlation analysis between bromoform and the following parameters: Δ chlorine, ultra violet (UV_{254}) absorbance, and the pH of the water samples; to determine the significant effects of the preparation method (i.e. blending of the sources water during production of potable water), storage period, temperature, and their interactions on the development of bromoform; to determine under which of the tested laboratory conditions the development of bromoform in the simulated residence time tests was the lowest; to formulate bromoform predictive models, and the development of a bromoform management strategy to overcome such problem. The methodology that was used to answer the research objectives included chemical analysis for the source water samples collected from Doha blending facility, a series of laboratory tests to a simulated residence time, a statistical technique to develop a mixed effects model, a correlation analysis, and a multiple regression analysis.

The results indicated that the groundwater consisted of bromide (0.71 mg/l), thus, increasing the groundwater percentage during production of potable water would result in the development of more bromoform. The other source of potable water (recarbonated water) consisted of a considerable amount of bromoform (30 µg/l). This amount may reach the WHO guideline limit either during the potable water production cycle or during the delivery of water to the consumers. The results of the correlation analysis showed that there was a strong positive correlation between bromoform and Δ chlorine, a positive moderate correlation between bromoform and UV_{254} absorbance, and a negative weak relationship between bromoform and the pH of water samples. The results of the mixed effects model analysis indicated that the preparation method, temperature, and storage period (represented the main effects in the model) have a highly significant effect ($p < 0.001$) on the development of bromoform in water samples. Furthermore, the interaction effects of the temperature and preparation method, and also the preparation method and storage period, showed a highly significant effect ($p < 0.001$). Meanwhile, no significant interaction effect was observed between temperature and storage period on the development of bromoform. The lowest average bromoform concentration (29.28 µg/l) was measured in the simulated residence time test conducted on synthetic potable water samples comprising 2.9% groundwater under 20° C temperature conditions which represents the optimum operation conditions to be considered at the Doha blending facility in the production of potable water.

Bromoform predictive model was formulated using water quality data obtained from the simulated residence time tests conducted on synthetic potable water samples. The performance of the model was evaluated by calculating mean absolute errors using separate data sets. Assessment of the bromoform model indicated that the model has a good prediction ability. Finally, a bromoform management strategy was proposed to control the presence of bromoform covering all stages of the potable water production cycle which include introducing guidelines toward water quality and operational conditions, using alternative disinfection methods for the treatment of seawater and the finished potable water, management of the groundwater utilised in the production of potable water, and organising a maintenance plan for the related water distribution system.

Dedication

This work is dedicated to Alkandari's family, whom they took the responsibility to deliver drinking water to the residence of Kuwait in the past before the introduction of the modern means of water treatment and distribution.

Acknowledgment

First of all, I would like to thank my supervisor Professor Adrian J Saul who provided me the help and support I needed during my study period at the University of Sheffield, UK. I thanks Lindsay Hopcroft and Caroline Brookfield from the Civil engineering department for helping through this study.

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A special thank goes to my mother for being always around me even when I'm far away. Finally, a big thank you for my wife and my little boys for their patience, love, and lovely moments we spent during conducting my study.

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Chapter 1

Introduction

1.1 Background

Throughout the history of humankind, civilisations and human societies have been founded near to sources of water as the water represents the elixir of life. Humans have managed and controlled water resources, using it for drinking, farming, food, sanitation, transport, and energy. The prosperity of any human settlement is directly related to the availability of a sufficient amount of drinking water that covers basic water requirements for human consumption and activities. Therefore, in order to maintain prosperity and sustainable development, the production of drinking water should meet the growing demand of societies and at the same time follow specific standards regarding water quality in order to protect human health.

At the present time, the quality of drinking water is one of the main concerns for the regulators, suppliers, and consumers of potable water. Regarding the regulators, new contaminants are discovered in potable water by research studies utilising newly-developed analytical techniques (Shen et al., 2010; Pereira et al., 2011). On the other hand, potable water suppliers are often required by law to comply with drinking water regulations (KEPA, 2001; WHO, 2004) in order to protect consumer health. Furthermore, a significant number of potable water consumers are drifting towards other, questionable sources of drinking water due to their lack of confidence in the quality of potable water (Lalumandier and Ayers, 2000).

The quality of potable water is often altered as a result of the chemical, biological and physical processes which occur in water networks (Sarin et al., 2004; Patel et al., 2011). These processes are either applied during the production of potable water, to purify water at a treatment works, or occur unintentionally during the transition of water from its sources to a consumer’s tap. The disinfection of potable water is one of these processes, in which the microbial pathogens present in water are eliminated.

As a result of the water disinfection processes, some compounds present in potable water are often transformed into harmful ones, such as brominated trihalomethane compounds. These compounds may affect potable water consumers’ health if they occur above a specific concentration level. The occurrence of these compounds in drinking water presents a challenge to drinking water sectors around the world.

The issue of brominated trihalomethane compounds’ occurrence in potable water varies in different countries according to the country’s development and the characteristics of its water sources. The issue has been more optimised in industrialised countries (i.e. utilising of advanced treatment technologies and adaption of effective potable water monitoring program) when compared to the developing and poor countries. Kuwait, one of the developing countries, experiences such problems, with elevated concentrations of such compounds being detected in drinking water samples along water distribution systems.

1.2 Production of potable water in Kuwait

Like many other countries located in arid regions, Kuwait has an ever-growing issue related to water supply due to limited natural fresh water resources. The climate is characterised by being very hot in summer and relatively cold in winter. Rainfall is scarce, occurring only in winter with an average annual equal to 110 mm (Hamoda, 2001). As a result, surface runoff is absent or occurs for only a short period of time on a small scale during the winter season. The only natural fresh water resource is groundwater and this is only available in quantities insufficient to meet the country’s demand. Accordingly, the Maplecroft organisation water stress index has rated Kuwait as one of the world’s most water-stressed countries (Maplecroft, 2011). Therefore, as a result of the scarcity of natural fresh water resources, the Kuwaiti authorities have relied on seawater desalination as a primary option to meet the daily demand for fresh water. The demand and production of fresh water in addition to the population growth of the Kuwait between the years 1985 and 2008 is presented in Figure 1.1 (MEW, 2010).

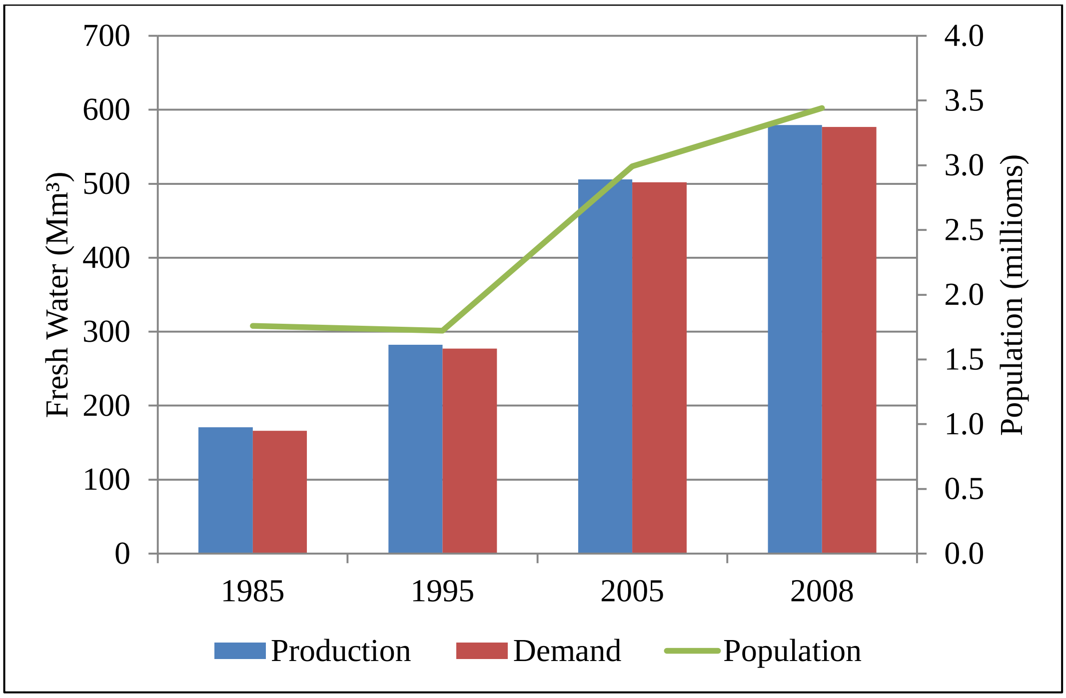


Figure 1.1 The demand and production of potable water in Kuwait

As can be seen in Figure 1.1, the population growth was stable and slightly decreased in the first ten years, then a sharp increase in the population has occurred in the following years. Overall, the population has almost doubled in 23 years, between the years 1985 and 2008. According to that , the demand and production of fresh water has dramatically increased from around 170 Mm^3 in 1985 to around 580 Mm^3 in 2008 which is more than three folds. Surprisingly, during the almost zero increase in the population in the first ten years, the demand and production of fresh water was doubled which is possibly related to factors other than the population growth (e.g. industrial and agricultural growths).

In general, the production of drinking water in Kuwait is achieved through two major processes. The first process involves desalting seawater by using different distillation methods to produce water with very low salinity (≈ 5 mg/l). The second process involves blending the water produced by a distillation plant with groundwater (salinity between 2000 mg/l and 6000 mg/l) at a certain ratio, in order to produce water that is suitable for human consumption (Al-Ruwaih et al., 2010).

Kuwait built the first distillation plant for potable water production at Shuwaikh city in 1950s. The plant's production capacity was equal to 4546 m^3/d of water (Al-Zubaidi, 1987). At present, six distillation plants (Fig. 1.2) are under continuous operation with a total production capacity of around 1.66 million m^3/d (MEW, 2010) to meet the daily fresh water demand of Kuwait.

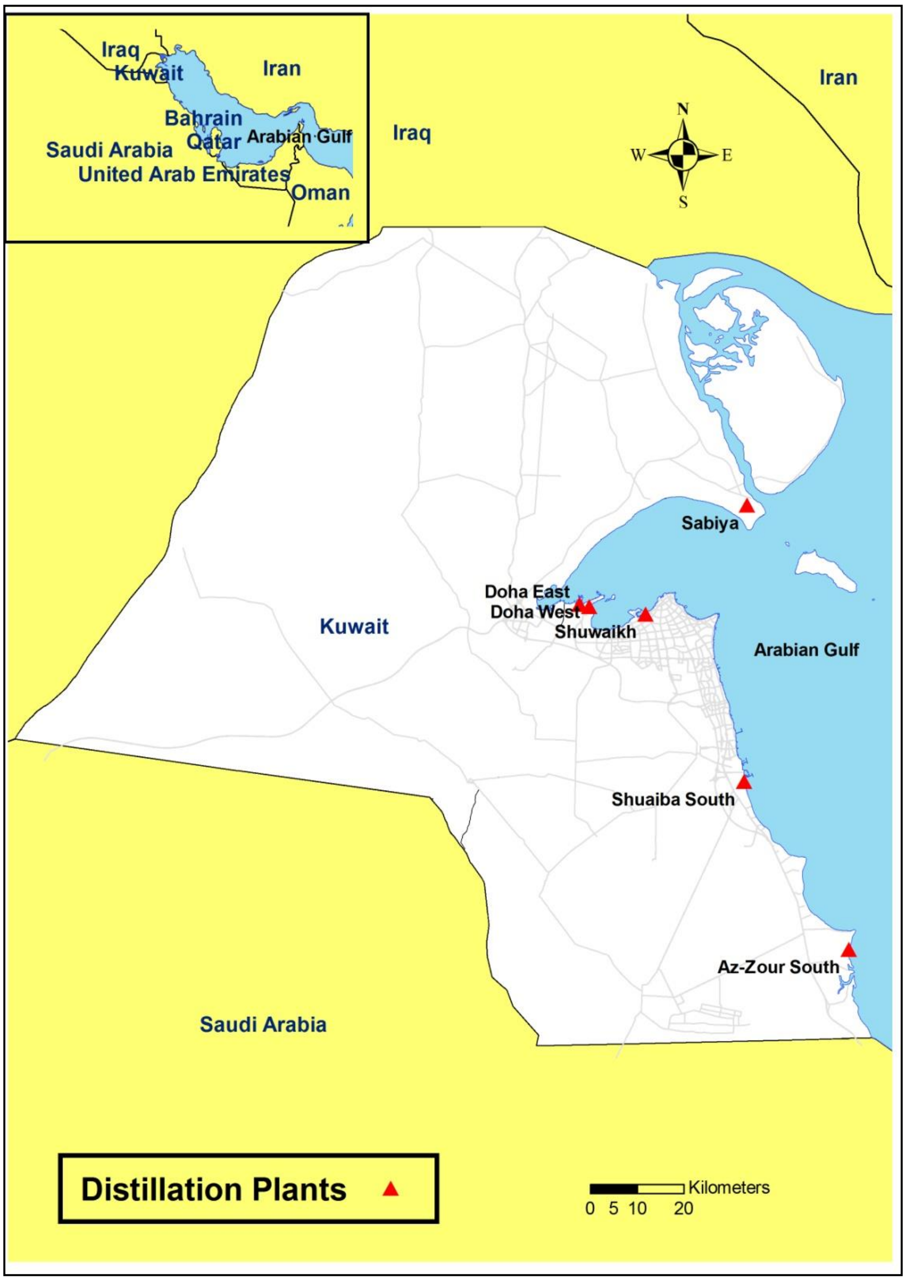


Figure 1.2 Location of seawater distillation plants in Kuwait

Nowadays, the Kuwaiti water authority has adopted the multi-stage flash (MSF) method as the primary option in the distillation of seawater. Basically, the method is based on the flash evaporation phenomenon. This phenomenon occurs when the pressure of a saturated liquid (e.g. seawater) is significantly reduced, for example by using a throttling device. This reduction in the pressure of seawater leads to a partial vaporisation of the water and hence to the development of water vapour. In practice, condensation of the vapour is conducted to obtain a distillate of high purity.

Inside the distillation plant, the MSF method is used in desalting seawater (salinity ≈ 42800 mg/l) by passing a stream of seawater into several successively-placed evaporator units. The movement of seawater in these successive evaporator units is achieved through the use of a vacuum system which is controlled by air ejectors. The pressure of the evaporator units decreases significantly throughout the successive stages to enhance the development of the flashed vapour. Then, the flashed vapour undergoes a condensation processes to form distilled water with a salinity of around 6 mg/l (Latif, 1991).

The distilled water thus produced is characterised by very low salinity with a total alkalinity which is less than 1.0 mg/l $CaCO_3$ (Al-Rqobah and Al-Munayyis, 1989). Such water is classified as very soft, and as an aggressive type of water toward metals. This type of water had a long history in the corrosion of water distribution systems and in occurrences of the "red water" problem in the past in Kuwait. This problem was resolved by increasing the alkalinity and calcium contents of the distilled water through a water recarbonation process.

The recarbonation process has been adopted since 1987 to protect the distribution systems from corrosion in Kuwait. Recarbonation of distilled water is conducted throughout three main stages, namely CO_2 absorption, limestone dissolution, and CO_2 stripping. The aim of these three stages is to increase the total alkalinity of the distilled water to somewhere in the range of 60-80 mg/l $CaCO_3$. In the first stage, acidification of the distilled water is achieved by using CO_2 gas in an absorption tower. After that, the acidified distilled water is passed through several limestone dissolution filters for the production of recarbonated water. Finally, any excess CO_2 gas present in the recarbonated water is degasified by air in a stripping tower (Al-Rqobah and Al-Munayyis, 1989). Additionally, a caustic soda (NaOH) solution (15% wt) is applied to the recarbonated water in order to adjust the water pH to around 8.0 before it leaves the distillation plant for blending facility (Al-Rqobah and Al-Munayyis, 1989; Al-Deffeeri, 2008).

The production of recarbonated water in the distillation plant is conducted in parallel to groundwater abstraction activity from several groundwater fields (Fig. 1.3). These parallel works are carried out in order to maintain sufficient quantities of these waters, which are both necessary for the production of potable water in Kuwait.

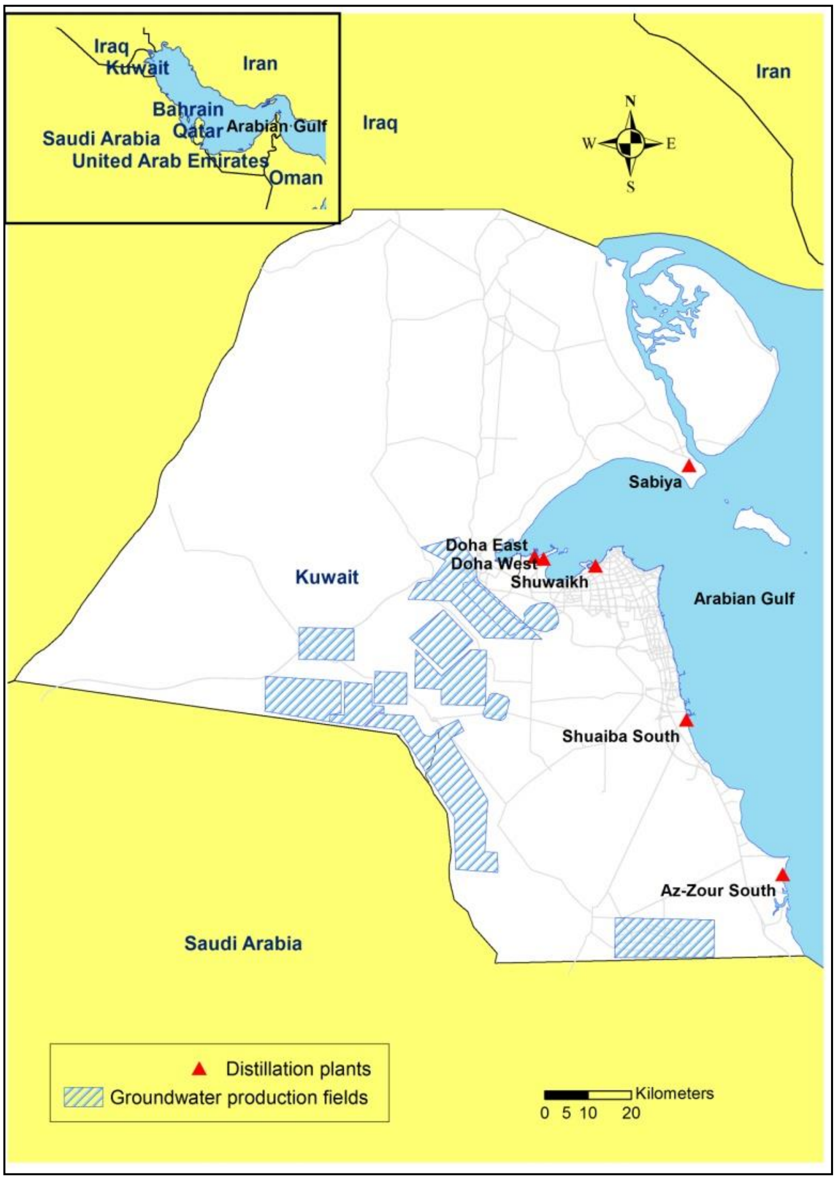


Figure 1.3 Location of groundwater production fields in Kuwait

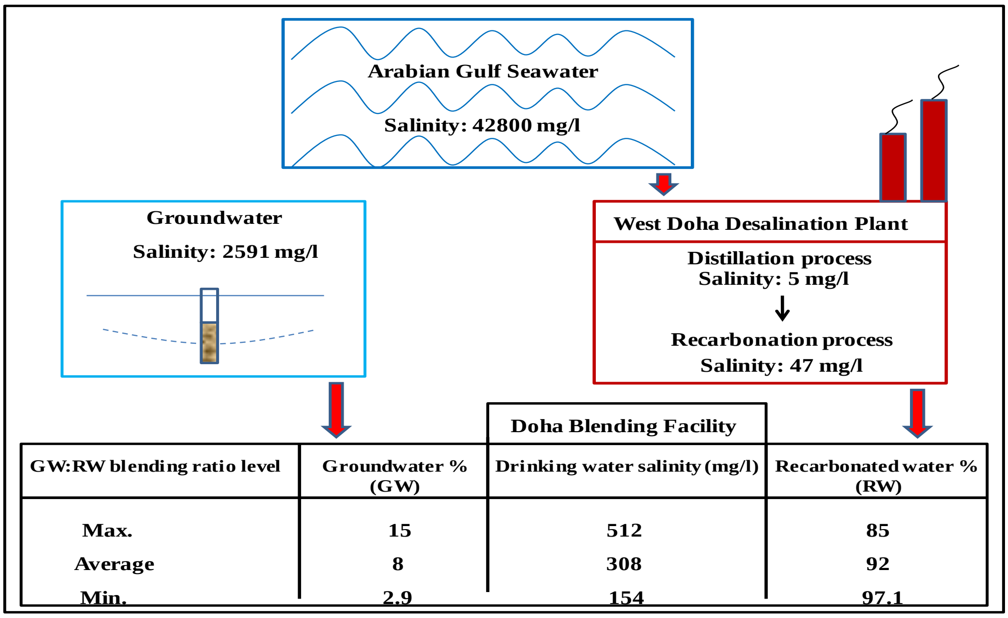
The abstraction of groundwater is carried out by different groundwater fields located in the Sulaibiya, Um-Qudair, Shigaya, Al-Atraf, and Al-Wafra areas. The groundwater is abstracted from two geological Groups, the Kuwait and the Hasa Groups, where these two Groups (i.e. groundwater aquifers) extend along the groundwater production fields (Al-Ruwaih et al., 2010).

The production of groundwater is mainly conducted by using dual-screened wells. These dual production groundwater wells have been opened throughout the Kuwait and Dammam Groups to maximise the groundwater production capacity in order to meet the requirements of the blending water facilities for potable water production, as well as those of other sectors (Al-Ruwaih et al., 2010).

Lithologically, the Kuwait Group overlies the Dammam formation where the thickness of the Kuwait Group is between 150 – 230 m and the thickness of the Dammam formation is between 122 – 300 m. The Kuwait Group consists of siliciclastic sediments and rocks, whereas the Dammam formation is composed of sequences of carbonate rocks (Hadi, 2002).

The hydrochemistry of the groundwater at the production fields varies significantly in terms of the salinity of the groundwater. The highest salinity is found in Al-Atraf groundwater field which has a salinity of between approximately 4500 and 7500 mg/l, while the lowest salinity is located in the groundwater of the Shigaya field which has the range of 3100 to 3800 mg/l (Al-Ruwaih et al., 2010).

The groundwater that has been produced is collected and stored in groundwater reservoirs, then transferred to a blending facility for potable water production. The blending facility is the final phase in the potable water production cycle in Kuwait (Fig. 1.4).



GW:RW blending ratio level	Groundwater % (GW)	Drinking water salinity (mg/l)	Recarbonated water % (RW)
Max.	15	512	85
Average	8	308	92
Min.	2.9	154	97.1

Figure 1.4 Typical potable water production stages at the Doha blending facility in Kuwait

Currently, the Ministry of Electricity and Water in Kuwait is operating five blending facilities located near to the distillation plants. The blending facility is considered to be the final stage in the production of potable water. The facility is supplied routinely with groundwater and recarbonated water in two separates pipelines to maintain sufficient water sources for the production of potable water. The recarbonated water is transferred from the nearest distillation plant, whereas groundwater is pumped from an allocated groundwater reservoir.

At the blending facility, recarbonated water and groundwater are mixed together at a certain ratio in order to produce a palatable drinking water that fulfils drinking water standards. The blending ratios used depend mainly on the quality of the groundwater that is produced from different groundwater fields around the country, and on world health organisation (WHO) guidelines for the quality of drinking water (Latif, 1991). The percentages of groundwater that makes up potable water which were used between the years 2003 and 2008 (Table 1.1) at the five blending facilities were between 1.7 % – 15.0 % (Al-Ruwaih et al., 2010).

Table 1.1 The groundwater percentages used in the production of potable water (source: Al-Ruwaih et al., 2010)

No.	**Blending Facility**	**Minimum groundwater %**	**Maximum groundwater %**
1	Sabiya	2.0	9.0
2	Shuwaikh	6.1	13.7
3	Doha	2.9	15.0
4	Shuaiba	2.3	14.1
5	Az-Zour	1.7	6.4

In summary, the mixing process is conducted in a mixing tank, which is equipped with a fountain in the middle of the tank that introduces a chlorine solution to the blended water. The addition of a chlorine solution is crucial to disinfect the water just before it enters the distribution system. In the tank, the chlorine dose is controlled and managed so that it does not exceed 1.0 mg/l (disinfection practice applied so potable water reach consumer with residual chlorine range between 0.2 – 0.5 mg/l) of residual chlorine in the finished water. This amount of residual chlorine is often sufficient to protect potable water consumers' health along the water distribution system. Additionally, an adjustment of the pH of the blended water is carried out inside the tank which keeps the water pH at around 8.0 via the addition of a sodium hydroxide solution.

At this final stage, the produced water is considered ready and is pumped into the water distribution system (Latif, 1991).

1.3 Statement of the problem

The occurrence of disinfection by-product compounds (DBPs) in potable water is one of the major water-quality issues in drinking water sectors around the world (Richardson et al., 2007). The sensitivity of the issue in terms of public health has led many international and local organisations related to the water industry to adopt guidance limits for such disinfection by-product compounds in drinking water in order to protect the health of potable water consumers.

The Kuwait Environment Public Authority (KEPA) has adopted a monthly routine drinking water sample analysis plan to ensure that the drinking water produced in Kuwait meets KEPA drinking water standards. The drinking water samples analysis plan is carried out using water samples gathered from different water-distribution systems. The water sample is collected from the potable water service connection of governmental building (e.g. schools and health clinics) in the residential areas around Kuwait. The analysis of this drinking water includes testing water quality parameters such as water pH, salinity, cations, anions, microbiological tests and trihalomethane compounds.

In recent years, KEPA has reported an elevated concentration of the bromoform compound, which is one of the brominated trihalomethane compounds (KEPA, 2009). It was detected in drinking water samples from different water distribution systems during the monthly routine analyses of water samples. It can be seen in Figure 1.5 that the bromoform concentration levels in some of the drinking water samples analysed during the year were found to be more than double those recommended in KEPA drinking water standards.

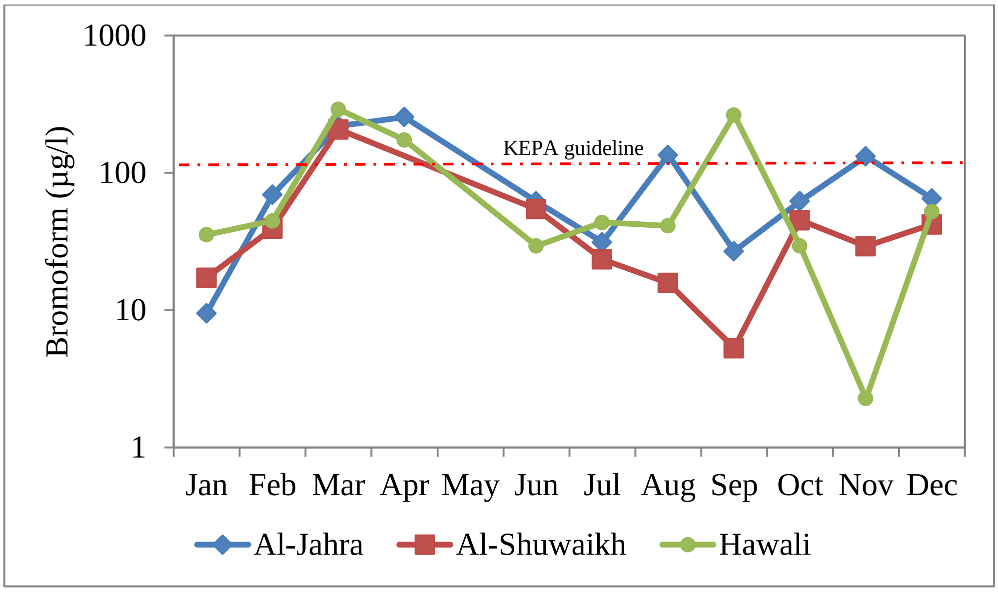


Figure 1.5 Concentrations of bromoform in different networks

Furthermore, Figure 1.5 shows that the trends of bromoform concentrations for the three different distribution systems (e.g. Al-Jahra, Al-Shuwaikh and Hawali) followed the same pattern in the first six months of 2009, after which they significantly changed for the rest of the year. This fluctuation in bromoform concentrations is possibly attributable to the operational difficulties (e.g. distillation unit failure due to operating at the maximum capacity for the high temperature) often encountered by the potable water production sector during recent summer periods as a result of high potable water demand and a shortage of water (Personal interview, Eng. Khajah A.A., 15th of October, 2010). The recorded temperature during the summer period in the year 2009 for a weather station near to the study area is illustrated in Figure 1.6 (Tutiempo Network, 2009).

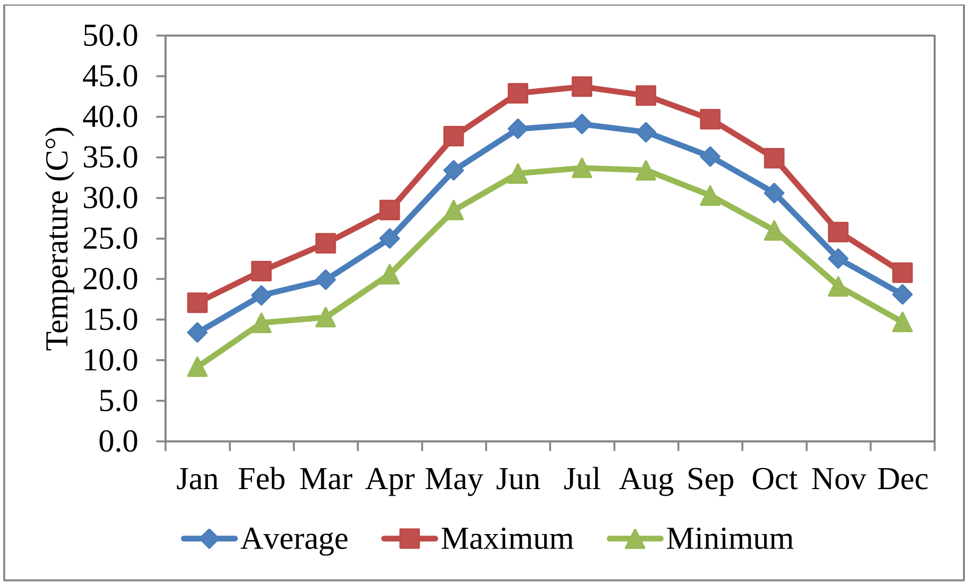


Figure 1.6 Monthly temperature variations in the year 2009

According to Figure 1.6, the maximum temperature was recorded in the month of July at 43.7° C, whereas the minimum temperature was recorded in the month of January at 13.4° C. The summer season extends from May to September where high demand of potable water occurs. This high demand of potable water is frequently exceeded the potable water production capacity of the country during summer seasons. Consequently, the Ministry of Electricity and Water in Kuwait has adopted a scheduled cut-off program of potable water to maintain the strategic reserve of the fresh water at an acceptable level.

However, as for the relative distribution of trihalomethane compounds, an assessment of bromoform concentration levels in relation to those of the other three trihalomethane compounds in potable water samples collected from Hawali city water distribution system during 2009 is presented in Figure 1.7 (KEPA, 2009). It is worth mentioning, however, that during the month of May no trihalomethane compounds analysis was conducted. As shown in Figure 1.7, absolutely no chloroform ($CHCl_3$) compounds (NB: KEPA guideline limit for chloroform < 200 μg/l) were reported in the potable water samples and only traces of dichlorobromomethane ($CHBrCl_2$) compound (NB: KEPA guideline limit for dichlorobromomethane < 60 μg/l) were detected in September and October 2009.

Additionally, bromoform ($CHBr_3$) (KEPA guideline limit for bromoform < 100 μg/l) and chlorodibromomethane ($CHClBr_2$) (NB: KEPA guideline limit for chlorodibromomethane < 100 μg/l) were frequently detected in water samples throughout the year. Noticeably, only the bromoform compound was reported as being above the guideline limit on three different occasions. Moreover, it can be seen that the bromoform compound is the dominant one among the trihalomethane compounds found in the analysed drinking water samples.

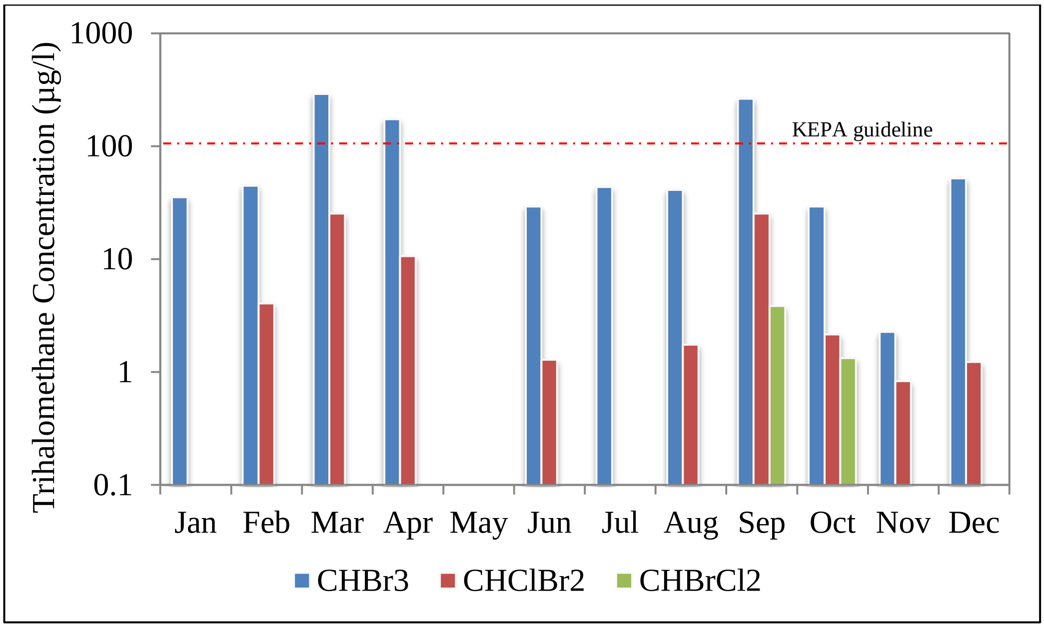


Figure 1.7 Trihalomethane compounds detected in potable water in 2009, city of Hawali, Kuwait

As a result of the elevated concentration of bromoform in potable water samples, as reported by KEPA, this research study is intended to shed light on the problem of bromoform compound development during the production of drinking water in Kuwait, and eventually to propose a strategic management plan to minimise the occurrence of such compound in future.

1.4 Summary and need for research

It is obvious that a further understanding of bromoform compound is required in potable water network system of Kuwait. This research study aimed to provide this understanding of how the blending practices applied in water treatment facilities encourage the development of bromoform compounds in the produced potable water. Additionally, the effects of water residence time, and temperature on the formation of the bromoform compound were investigated in some detail in the study.

The study was conducted in cooperation with the Ministry of Electricity and Water (MEW) in Kuwait, and the Kuwait Institute for Scientific Research (KISR). The Ministry of Water and Electricity provided access to the Doha blending facility, which is the water treatment plant that feeds Hawali city with potable water. Meanwhile, the laboratory experiments and analyses of potable water samples were performed in Kuwait Institute for Scientific Research.

1.5 Objectives of the research study

In this study, an attempt was made to investigate the effects of several factors including the blending of recarbonated water with groundwater, temperature, and water residence time on the development of bromoform in the potable water of Kuwait. Specifically, the following research study objectives were explored:

A. Assessment of bromoform, bromide and natural organic compounds present in the sources (i.e. groundwater and recarbonated water) of potable water, and their ultimate concentration levels in the synthetic potable water samples.

B. Investigation of the effects of the water preparation method, temperature, storage period, and the interactions between these on bromoform formation, using a simulated residence time tests, and a mixed effects model as follows:

    i. To determine the significance of the following main factors affecting bromoform formation in water

        - Preparation method
        - Temperature
        - Storage period

    ii. To determine the significance of the following interacting factors for bromoform formation in water

        - Preparation method and temperature
        - Preparation method and storage Period
        - Storage period and temperature

    iii. To compare the results of average bromoform concentration developed in the nine simulated residence time tests conducted on different synthetic potable water samples comprising 2.9%, 8.0% and 15.0% groundwater.

    iv. To determine which preparation method, and temperature conditions would minimise bromoform formation in potable water produced by Doha blending facility.

v. To assess the correlation between bromoform compounds, Δ chlorine, UV_{254} absorbance, and pH of the water samples.

C. Development of a predictive model to forecast the formation of bromoform in potable water produced by the Doha blending facility.

D. Development of a strategic management plan for controlling bromoform formation in the potable water of Kuwait.

1.6 Significance of the study

This study is designed to provide the Ministry of Electricity and Water in Kuwait with necessary information related to the development of the bromoform compound during production of potable water as a result of the practice of blending recarbonated water with groundwater. This information could be used to optimise the practice of blending recarbonated water and groundwater at the blending facilities, and hence a reduction in the level of bromoform compound in the finished potable water could be achieved. In addition, a strategic management plan is proposed to overcome the presence of elevated concentrations of the bromoform compound in the drinking water of Kuwait.

1.7 Limitations of the study

Although this study is mainly concerned with the blending practice that is used in all the operating blending facilities around the country, most of the study’s findings are only useful for the Doha blending facility. This is due to several reasons. For example, the quality of recarbonated water produced by the seawater desalination plants is relatively different as a result of using different desalting methods such as multi-stage flash and reverse osmosis techniques. In addition, the quality of groundwater is different according to the utilised groundwater field. Also, the five blending facilities apply different groundwater to recarbonated water blending ratios in the production of potable water. Therefore, the outcome of the study is limited and applicable only to the Doha blending facility because the water samples (e.g. recarbonated water, groundwater, and fresh potable water) were directly collected from the Doha blending facility and the blending ratios which are used in the experiments are currently applied in that facility.

1.8 Description of the dissertation chapters

This section provides a brief description of the thesis chapters and the sub-heading subjects included in the study. The introduction chapter starts by addressing the importance of drinking water for human prosperity. The thesis then focuses on the issue of drinking-water quality and how it affects drinking-water stakeholders. Furthermore, the deterioration in the quality of potable water in terms of the development of brominated disinfection by-products as a result of chlorination is addressed. This is then followed by a detailed explanation of the methods used to produce potable water and of the occurrence of bromoform in the potable water of Kuwait. Finally, the research objectives section is included at the end of this chapter.

Chapter two begins with introduction paragraph demonstrates the sections of the chapter which were classified based on the gathered literature information related to bromoform. This is then followed by a discussion of occurrence, epidemiological studies, and the regulation of the bromoform compound in drinking water. Then, information from literature related to bromoform precursors, including chlorine, bromide, natural organic compounds, water temperature, pH, and reaction times are presented. The bromoform precursors section is followed by a bromoform development mechanism model. Subsequently, a brief demonstration on the published research studies of bromoform predictive models. Finally, a section explains motivation of the study was included at the end of the chapter.

In chapter three the materials, methods, experimental procedures, and the utilised statistical analyses are demonstrated. The chapter begins with a detailed description of the instruments employed in the research study. This is followed by the experimental procedure used to determine the concentration of bromide and organic compound i.e. dissolved organic compound and UV_{254} absorbance in different synthetic potable water samples. Subsequently, the simulated residence time tests utilised to assess bromoform development are described. The description of the tests is followed by a detailed description of the statistical method of the mixed effects model used to assess the bromoform results obtained from the tests which are described. The chapter ends with a description of the proposed bromoform predictive model design.

Chapter four includes the results and findings for the laboratory investigation work and a discussion of these. The chapter is divided into sections; each section provides a separate answer for each of the research objectives. The results of the assessment of bromoform precursors in the water samples are demonstrated at the beginning of this chapter. This is followed by a report of the results of bromoform and other water quality parameters obtained from the simulated residence time tests. After that, the results of correlation analyses between bromoform and water quality parameters are reported. The results of the utilised mixed effects model analysis is followed by the correlation analysis section. At the end of the chapter the proposed bromoform predictive model is presented.

Chapter five describes the proposed bromoform management strategy in eight main sections. The management strategy is divided into sections according to the potable water production cycle in Kuwait. The first section demonstrate guidelines toward water quality and operational conditions which provides action plans to control bromoform precursors in sources of potable water i.e. groundwater and recarbonated water. This is followed by action plans suggested to control bromoform during the potable water production stage. Several disinfection alternatives are proposed in the following section. Finally, at the end of this chapter, actions are suggested to control bromoform in water distribution systems.

Chapter six includes two main sections in which the conclusions of the research study and the proposed future works are presented.

Chapter 2

Literature review

2.1 Introduction

This chapter demonstrates the published studies related to the presence of bromoform mainly in potable water. In addition, information related to the factors that affects development of bromoform have been included. The research studies related to the factorial experiments and predictive models related to the development of bromoform are presented. At the end of this chapter, gaps in the literature were identified especially the ones related to the occurrence of bromoform in potable water of Kuwait.

2.2 Bromoform compound

Bromoform is a halogenated organic compound where a bromine molecule is attached to an aliphatic hydrocarbon compound (Torkelson, 1994). The compound is produced naturally by seaweeds and phytoplankton in a marine ecosystem. In industry, the bromoform compound has been used as solvent and flame retardant; nowadays, it is mainly used as a laboratory reagent (ATSDR, 2005). The compound is found in potable water due to water chlorination practices. The following sections discuss occurrence, epidemiological studies, and regulation of the bromoform compound.

2.2.1 Occurrence

In the mid-1970s, Rook identified the first disinfection by-product compounds formed during water chlorination processes. The reported by-product compounds were trihalomethanes, and were found in finished drinking water samples (Rook, 1975). Since that time, many research studies on trihalomethane compounds in drinking water have been conducted around the world. These studies have often reported the four trihalomethane compounds (chloroform, dichlorobromomethane, chlorodibromomethane, and bromoform) in one value as ‘total trihalomethane compounds’ (TTHMs).

The distribution of the four trihalomethane compounds is dependent on the molecular concentration of chlorine and bromine. The higher the concentration of bromide compound in the water during chlorination, the more brominated trihalomethane compounds would form in that water. In such a situation, the distribution of trihalomethane compounds would shift towards the formation of bromoform and the other brominated compounds.

Bromoform is found in drinking water in countries that utilise high-bromide source water, such as seawater. In Israel, the concentration of bromoform compound in potable water sometimes exceeded 100 µg/l as a result of the chlorination of high-bromide source water (≈ 2.0 mg/l) before the introduction of other disinfection methods (Richardson et al., 2003).

2.2.2 Epidemiological studies

Although the practice of water chlorination has dramatically decreased waterborne infectious disease incidents since its adoption in the 1900s, many research studies have suggested that certain compounds that are by-products of chlorination are responsible for numerous adverse health problems (Landi et al., 2003; Porter et al., 2005; Windham and Fenster, 2008; Bull et al., 2011; Colman et al., 2011; Zhang et al., 2012). Several epidemiological studies have associated the presence of disinfection by-product compounds in drinking water, and the consumption of such water, with the occurrence of health problems such as stillbirth (King et al., 2000), developmental effects on infants (Hamidin et al., 2008), and bladder cancer (King and Marrett, 1996). Other studies have pointed out that brominated DBPs may be more carcinogenic than chlorinated DBPs (Nokes et al., 1999; Richardson, 2005; Parinet et al., 2012). However, bromoform, one of the DBP compounds, has not been classified as carcinogenic to humans by the International Agency for Research on Cancer (WHO, 2011). In contrast to that, U.S. EPA has classified bromoform compound as a “probable human carcinogen” (Faust, 1995).

2.2.3 Regulation

Access to safe drinking water is an important issue around the world. The development of both water supply and sanitation sectors improves and benefits any economy. The benefits are achieved by the reduction in adverse health problems and the resulting minimisation of the health care costs associated with such problems (WHO, 2011). As a result, many local and international organisations related to the drinking water sector have published water quality guidelines to protect water consumers’ health. In the guidelines, all natural and anthropogenic chemical compounds found in water are regulated to certain levels, so as not to affect the health of consumers. Bromoform, as one of the anthropogenic compounds, is regulated in many countries (Table 2.1).

Table 2.1 Guidelines for Bromoform in drinking water

Country	Guideline level (µg/l)	Remarks
Kuwait[1]	100	
UK[2]	100	as TTHM
WHO[3]	100	
EU[4]	100	as TTHM
U.S[5]	80	as TTHM
Australia[6]	250	as TTHM

1. Kuwait Environment Public Authority, drinking water guidelines, 2001.
2. Department for Environment, Food and Rural Affairs; drinking water safety, 2009.
3. World Health Organisation, guidelines for drinking-water quality, 2011.
4. European Communities (drinking water) (No. 2) regulations, 2007.
5. United States Environment Protection Agency, drinking water standards and health advisories, 2011.
6. Australian drinking water guidelines (No. 6), 2011.

It can be seen from Table 2.1 that most of the countries mentioned here have not issued a separate guideline value for bromoform concentration levels in drinking water, but rather have considered it a part of trihalomethane group. Nevertheless, the World Health Organisation and Kuwait have regulated the bromoform compound separately, not to exceed 100 µg/l in finished drinking water.

2.3 Factors influencing bromoform formation

The development of bromoform compound in potable water is influenced by many factors. The most important factors include the concentrations of chlorine, bromide ions, natural organic compounds, pH, temperature, and reaction time (Heller-Grossman et al., 1993; Ichihashi et al., 1999; Platikanov et al., 2010). The role of each of these factors in bromoform compound formation is different; some of the factors influence the compound yield while others affect the stability of the compound in water. It is worth mentioning that the formation of bromoform in water is accomplished through a complex process and would only take place if the right configuration of the above-mentioned factors was present. The effects of these main factors are discussed in some detail in the following sections.

2.3.1 Chlorine

Chlorine gas is an element belonging to the halogen group which has a greenish yellow colour. It is characterised by high electron affinity and electronegativity. Therefore, chlorine is considered a strong oxidising agent. Naturally, chlorine is always found combined in soluble chloride forms, such as sodium chloride (NaCl) and sylvite (KCl) salts. Commercial production of chlorine is carried out using for example electrolytic cells (White, 1992).

As a result of being a strong oxidising agent, chlorine is known to be an effective water treatment chemical in the potable water industry. The practice of adding chlorine to potable water (the chlorination process) helps to eliminate microbial pathogen activity that is responsible for outbreaks of waterborne disease. This is the primary objective of using chlorine in the industry; however, there are many other areas of application for chlorination process related to water quality during the production of potable water, such as the control of taste and odour, iron and manganese removal, and algal growth prevention (Choo et al., 2005; Shen et al., 2011).

Furthermore, there are technical issues related to the application of chlorine in drinking water which make it favourable among other disinfectant options; it is easy to apply, measure and control while at the same time it provides persistent residual disinfection along water distribution systems. Additionally, chlorination is popular because it is relatively inexpensive compared to other alternative practices. Therefore, the majority of municipal water supplies around the world are disinfected using chlorine, either as the sole disinfectant agent or combined with other disinfection methods such as ozone, ultraviolet radiation, or filtration (White, 1992).

The disinfection of potable water using chlorine is conducted using different forms of chlorine, such as elemental chlorine, chlorine dioxide, calcium hypochlorite and sodium hypochlorite. Usually, the selection of a specific form of chlorine in a water treatment works is based on economic, technical and safety issues. Specifically, the selection criteria include, but are not limited to, cost, equipment reliability, the size of the plant, hazardous by-products, staff and transportation safety concerns (Spellman, 1999). This research study only covers disinfection using sodium hypochlorite, as this is the method that is being used in the disinfection of potable water in Kuwait.

Historically chlorine, in the form of hypochlorite, was one of the first disinfectant agents used to disinfect drinking water and was known as chloride of lime (White, 1992). In 1850, chloride of lime was used as a disinfectant agent by physician John Snow in an attempt to disinfect the water supply of the Broad Street Pump in London, to protect water consumers from an outbreak of cholera which had been caused by sewage contamination. Since then, growing attention has been paid to the disinfection of drinking water by the drinking water production sector to protect water consumers from waterborne diseases.

A solution of sodium hypochlorite (NaOCl) can be produced through the reaction of chlorine (Cl_2) with sodium hydroxide (NaOH). The products of this reaction include sodium chloride (NaCl), water (H_2O), and heat, in addition to sodium hypochlorite. The stability of the sodium hypochlorite solution is dependent on solution concentration, length of storage, temperature, pH, exposure to light, and the availability of heavy metals (White, 1992). The chemical reaction is expressed as follows:

$$2\,NaOH + \ Cl_2 \rightarrow NaOCl + NaCl + H_2O + Heat \qquad (2\text{-}1)$$

During the chlorination process, the application of sodium hypochlorite to potable water produces hypochlorous acid (HOCl), sodium (Na), and hydroxyl ions (OH^-). In this reaction, the hydroxyl ions increase the pH of the potable water. The following equation explains this reaction:

$$NaOCl + H_2O \rightarrow HOCl + Na^+ + OH^- \qquad (2\text{-}2)$$

Hypochlorous acid is a weak acid which dissociates into hypochlorite ions (OCl^-) and hydrogen (H^+) according to the pH of the potable water. The dissociation of hypochlorous acid will be incomplete in water with a pH of between 6.5 and 8.5 where both hypochlorous acid and hypochlorite ions exist. Furthermore, in water with a pH below 6.5, only hypochlorous acid will be present. On the other hand, water with a pH above 8.5 encourages the dissociation of hypochlorous acid where only hypochlorite ions exist (White, 1992). The following equilibrium reaction describes the situation:

$$HOCl \leftrightarrow H^{+} + OCl^{-} \qquad (2\text{-}3)$$

Typically, the pH of potable water falls within a range of between 6 to 9; within this range, both hypochlorous acid and hypochlorite ions exist (Fig. 2.1). It can be noted from the figure that hypochlorous acid is predominant in water with a pH of around 6, whereas hypochlorite ions prevail in water with a pH of 9 (Deborde and von Gunten, 2008).

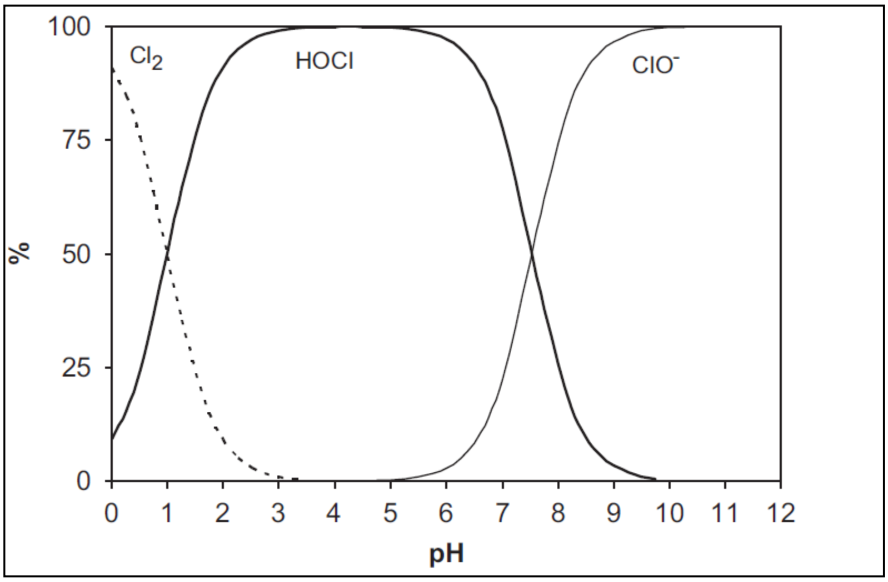


Figure 2.1 Distribution of chlorine species as a function of pH
(Source: Deborde and von Gunten, 2008)

The effect of hypochlorous acid is much stronger than that of hypochlorite ions in terms of the efficiency of water disinfection against microbial pathogens. This effectiveness is due to the similarities in structure between hypochlorous acid and water. Their structures are both characterised by modest size and both have a neutral electrical charge. As a result, the hypochlorous acid compound has the same ability as water to easily penetrate the cell walls of microorganisms. Once such penetration has been accomplished, the compound is capable of attacking the enzyme group of a microorganism, thereby destroying it (White, 1992). Therefore, it is preferred and recommended that the chlorination of potable water be carried out on water with a lower pH value (e.g. < 6.5), as hypochlorous acid compounds predominate in these pH conditions.

2.3.2 Bromide

Bromide is a chemical compound that contains the element bromine bonded with other electropositive or radical elements. The compound is found in natural waters mostly as a trace concentration and in the form of dissolved salts. However, the concentration of bromide in sea water is reported to be around 65 mg/l (Magazinovic et al., 2004; Darwish et al., 2008). Industrially, bromide compounds are produced for and used in different activities including medicine, fertiliser, laboratories, and other sectors (Lundström and Olin, 1986; Ikegaya et al., 2006).

These anthropogenic sources of bromide have led to a significant increase in the levels of bromide compounds in natural water sources. In a study conducted by Batjer et al. (1980), the authors reported an elevated concentration of bromide, in a range between 1.0 and 1.5 mg/l, in Weser river waters, located in Germany, as a result of potash mining activities along the river’s upper course. In another study, as a result of soil fumigation in the Polder district of the Netherlands, high bromide concentration levels of 0.98 mg/l, 41 mg/l, and 17 mg/l were reported in rain, surface water, and groundwater, respectively (Wegman et al., 1983). In the United States, Kharaka el al. (2007) have indicated that a significant amount of brine water (with up to a 53 mg/l concentration of bromide) produced by oil production activities has contaminated the Skiatook surface water reservoir and groundwater through percolation from the brine bits.

In Kuwait, less attention has been given to the presence of bromide compounds in natural waters. This is mainly for two reasons: bromide compounds are naturally present in groundwater in relatively low concentrations which makes them difficult to be determined (Mishra et al., 2001), and no health adverse effects are associated with the intake of the compound bromide in such low concentrations (Magazinovic et al., 2004).

However, several research studies have reported concentrations of the bromide compound in the potable water, groundwater, and seawater of Kuwait. Ali and Riley (1990) carried out one of the first published studies on halomethane distribution in Kuwaiti potable water. The authors reported bromide concentration levels in groundwater, distillate water, and potable water samples as 2.0 mg/l, 0.25 mg/l, and 0.5 mg/l, respectively. Also, Latif (1991) measured the concentration of the bromide compound in groundwater and seawater of Kuwait as 1.96 mg/l and 85 mg/l, respectively, during a study of trihalomethane occurrence in drinking water samples. Furthermore, Darwish et al. (2008) addressed the problem of disinfecting seawater with a high bromide content (e.g. 65 mg/l) in order to control marine biofouling inside a desalination plant, and the effects of this on aquatic marine life.

As previously mentioned, bromide intake by humans within the concentration levels present in natural fresh water has no adverse health effects. In some situations, the bromide compound is transformed into other types of harmful compound, as occurs during drinking water disinfection. Although the practice of water disinfection has saved millions of people’s lives from waterborne diseases since it was adopted, many toxic and carcinogenic compounds are produced during the disinfection of bromide source water as by-products.

These by-product compounds, including brominated trihalomethanes (Nokes et al., 1999), brominated haloacetic acids (Heller-Grossman et al., 1993), and bromate (Legube et al., 2004) are often found in finished disinfected water. The disinfection by-product compounds which develop in water are associated with the type of disinfection method used to disinfect that water. Disinfection methods that are responsible for such disinfection by-product compounds include chlorine, chloramines, ozone, and others.

When the chlorination method is used, the addition of chlorine to the water produces hypochlorous acid (HOCl), as previously described in equation (1-2). Hypochlorous acid oxidises the bromide ions which result in the formation of bromine (Br_2), as follows (White, 1992):

$$HOCl + 2Br^{-} + H^{+} \rightarrow Br_2 + H_2O + Cl^{-} \qquad (2\text{-}4)$$

The bromine formed in the previous reaction undergoes rapid hydrolysis which results in the formation of hypobromous acid (HOBr). Sohn et al. (2006) indicated that hypobromous acid has a much higher level of activation energy than hypochlorous acid. Also, Uyak and Toroz (2007) have shown that, in terms of oxidation, hypobromous acid is twenty times stronger than hypochlorous acid. The following reaction describes formation of hypobromous acid (White, 1992):

$$Br_2 + H_2O \leftrightarrow HOBr + H^{+} + Br^{-} \qquad (2\text{-}5)$$

In the above equilibrium reaction, hypobromous acid dissociates, which results in the formation of the hypobromite compound ion (BrO^-), as follows

$$HOBr \leftrightarrow H^{+} + BrO^{-} \qquad (2\text{-}6)$$

The bromine species HOBr and BrO^- react with natural organic compounds faster than chlorinated species do. This reaction favours the production of brominated disinfection by-product compounds such as bromoform and other brominated trihalomethane compounds.

2.3.3 Natural organic compounds

A natural organic compound is a compound which originates from the decomposition of animal or plant tissues. Such compounds are found in all natural waters in different concentration levels, ranging from less than 1.0 mg/l in seawater and groundwater, to over 10.0 mg/l in river and lake waters (Visco et al., 2005). The predominant compound groups which represent natural organic compounds are humic and fulvic acids, hydrophilic acids, carboxylic acids, carbohydrates, amino acids, and hydrocarbon (Peters, 1991). These groups of compounds exist in particulate, dissolved, and colloidal states in natural waters, where the dissolved organic compounds represent a major percentage of such organic compound groups (Thurman, 1985; Weishaar et al., 2003; Hudson et al., 2007).

Although natural organic compounds play an important role in geochemical and biochemical reactions within aquatic ecosystems (Huo et al., 2008), the presence of these compounds in water during the production of drinking water is undesirable. This is mainly because of the many water treatment problems associated with such compounds, including colour, odour, taste, and the development of disinfection by-product compounds in the water (Chang et al., 2001; Li et al., 2012). Natural organic compounds are known to be one of the main precursors to the development of by-product compounds during the disinfection of potable water (Lu et al., 2009; Zhang et al., 2009).

As a result of water disinfection practices, natural organic compounds in the presence of other precursors are sometimes transformed into harmful organic compounds, such as: trihalomethanes, haloacetic acids, haloacetonitriles, haloketones, aldehydes and others (Woo et al., 2002; Richardson, 2005; Bull et al., 2011; Colman et al., 2011).

The reactivity of natural organic compounds with disinfectant agents such as chlorine are significantly different among the various groups of organic compounds. Groups of certain organic compounds react faster and more rapidly than other groups. For instance, compounds of carbohydrates, hydrocarbons, and carboxylic acids react slowly with chlorine and may not produce any organochlorine compounds (Peters, 1991). Meanwhile, the aromatic carbon content of a dissolved organic carbon is an important indicator for the potential reactivity of the carbon with aqueous chlorine (Weishaar et al., 2003; Guo and Chen, 2009).

Reckhow et al., (1990) suggested that the aromatic fraction of a dissolved organic carbon is the primary precursor for trihalomethanes. In the potable water industry, measurements of dissolved organic carbon levels and UV_{254} absorbance are important parameters to enable assessment of DOC aromaticity. Both of these measurements are used to calculate specific UV_{254} absorbance. The specific UV_{254} measurement is an average measure of absorpitivity for all the aromatic reactive constituents of dissolved organic carbons in a water sample (Traina et al., 1990). The US EPA's final rule for disinfectants and disinfection by-products requires the use of enhanced softening or coagulation techniques to reduce the total organic carbon levels only if the specific UV_{254} absorbance value is found to be above 2.0 L mg^{-1} m^{-1}. The EPA requires that this rule be followed by water treatment facilities in order to control the formation of disinfection by-product compounds in potable water (Weishaar et al., 2003).

In Kuwait, the concentration of dissolved organic compounds in different types of waters were investigated by Ali (1984) as a part of his study on occurrence of trihalomethane compounds in potable water. The author has reported the concentration of dissolved organic compound in seawater, distillate water (e.g. product of a distillation plant), groundwater, and potable water, as 2.36 mg/l, 0.3 mg/l, 0.2 mg/l, and 1.85 mg/l, respectively.

2.3.4 Water temperature

Generally, the rate of halogentation reactions, and hence the development of bromoform compounds, increases with temperature. Richardson et al. (2003), pointed out the effect of temperature on bromoform occurrence in potable water in Israel. The authors observed that the levels of bromoform in water samples were higher during the summer season. These observations were attributed to the increase in the reaction rate of disinfection species with natural organic matter which was caused by elevated temperature conditions in that season.

The effect of temperature on bromide ion incorporation into brominated trihalomethanes was investigated by Sohn et al., (2006). The authors found that an increase in water temperature from 15º C to 25º C resulted in an increase in the percentage of bromide ion incorporation into THMs from 17 % to 22 % respectively.

However, in a study conducted by Platikanov et al. (2010) to assess the effect of different temperature conditions (specifically 10º C, 17.5º C and 25º C) and other factors on bromoform formation, the authors found that a temperature of around 25º C led to a reduction in bromoform formation in conditions of high organic compound concentration (e.g. 5 mg/l) and high chlorine residual (e.g. 2.4 mg/l).

2.3.5 Water pH

Water pH plays an important role in influencing the process of bromoform development in potable water. It affects the stability of bromoform precursors (e.g. chlorine derivates) to aid the formation of bromoform compounds in water. Nokes (2003) suggested that water pH has two main effects on concentration levels of brominated trihalomethane compounds in water, namely, promoting compound yields and influencing the stability of the compounds.

These effects were observed in a study. The authors reported that the occurrence of brominated trihalomethane compound formation increased with pH condition around 6 and such compound developed much slower at pH around 9.0 (Ichihashi et al., 1999). It was speculated that the reason for this is the predominance of hypochlorite and hypobromite ions at pH 9. These ions are unlike hypochlorous and hypobromous acids (predominate around water pH equal 6): they oxidise natural organic matter more slowly, and hence less brominated trihalomethane would form in water with such a high pH.

In a different study, the effect of water pH on the contribution of organic carbon to the formation of trihalomethane was investigated by Adin et al., (1991). It was found that, in water with a low pH, a low concentration of organic compounds is less effective in encouraging the development of trihalomethane. This was attributed to the neutralisation of organic carbon as a functional group. As a result of the low pH, the solubility and stability of the organic carbon was decreased. This in turn led to the formation of aggregation molecules - this phenomenon is known as the ‘folding of molecules’. Therefore, few sites of the organic carbon were readily available for chlorine attack.

2.3.6 Reaction time

The development of bromoform in water usually occurs in two phases during the reaction period. At the beginning of a reaction, the formation of bromoform proceeds rapidly and lasts for the first few hours. During this stage, the chlorine reacts with the highly reactive and readily oxidised part of the organic compounds in the water. The next phase of bromoform development is often slow and may continue for several days or weeks (Luong et al., 1982; Shams El Din et al., 1998; Nokes, 2003).

The effect of reaction time on the development of bromoform throughout this indirect chemical reaction was thoroughly researched in one study. Heller-Grossman et al., (1993) demonstrated the process by which tribromoacetic acid (which belongs to the second predominance DBP group after the THM group) is, over time, transformed into bromoform compounds. In their study, it was found that tribromoacetic acid (CBr_3COOH), which is a product of the chlorination of high-bromide source water, decomposed into bromoform as a result of the decarboxylation process, according to the following reaction:

$$CBr_3COOH \rightarrow CHBr_3 + CO_2 \qquad (2\text{-}7)$$

The instability of the tribromoacetic acid compound at ambient temperature is due to the relatively low activation energy of such compounds. It was concluded in the study that the decomposition of tribromoacetic acid is one of the main factors which led to the occurrence of elevated concentrations of bromoform compounds.

Further development of bromoform compounds in drinking water over time is mainly dependent on the availability of chlorine residual, bromide ions and activated sites in natural organic matter (Nokes, 2003). Furthermore, the half-life of the developed bromoform compounds in water with a pH of 7 and 25^{o} C ambient conditions is estimated to be around 20 days (Moore, 1984).

2.4 Bromoform development mechanism

In order to understand the mechanism behind bromoform reactions, the character of the kinetics of the reaction between chlorine, bromide, and natural organic compounds is an important step to be considered. Also, information related to the concentrations of reactants, intermediates, and products would provide necessary knowledge of the chemical pathway of the bromoform compound. However, an understanding of the bromoform pathway is often hampered because of the complexity of organohalogen chemistry (Nokes, 2003). Therefore, for simplicity, the following conceptual reaction pathway of the bromoform compound has been proposed (Nokes et al., 1999):

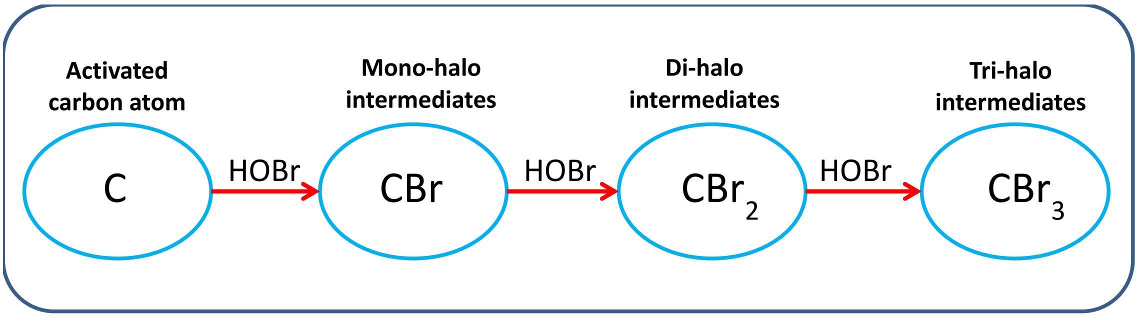


Figure 2.2 Conceptual framework of bromoform reaction pathway (Adapted from Nokes et al., 1999)

During chlorination, the development of bromoform takes place in the presence of bromide and natural organic compounds. Chlorine derivatives (e.g. hypochlorous acid and hypochlorite ions) oxidise the bromide compound which results in the formation of the element bromine. This is followed by the rapid formation of bromine derivatives such as hypobromous acid and hypobromite ions which are analogous to chlorine derivatives. The bromine derivatives react with the activated carbon atoms of natural organic molecules to form, successively, mono-halo intermediates, di-halo intermediates, and finally tri-halo intermediates, which represent the bromoform compound.

2.5 Factorial experiment

A factorial experiment is an experimental design in which two or more factors are used to investigate their effects on the output response as part of a controlled experiment. This type of experiment is widely used in modern scientific studies to obtain valuable information with regard to a specific process (Montgomery and Runger, 2011). There has been a considerable amount of literature on the application of factorial experiments to real world problems associated with the drinking water industry.

In the research into drinking water quality, factorial experimental designs have been used in the research fields related to the removal of biodegradable organic compounds (Gagnon and Huck, 2001), the inactivation of microbial pathogens (Dow et al., 2006), the determination of cadmium in water (dos Santos et al., 2006), odorous aldehyde formation in drinking water as a result of application of different disinfection methods (Froese et al., 1999), the detection of bromate in drinking water using a chemiluminescent flow system (Esteves da Silva et al., 2001), the application of coagulation and ultrafiltration processes for the removal of natural organic matter during drinking water treatment (Zularisam et al., 2009), and others.

Furthermore, in addition to the above-mentioned research fields, factorial experiment has also been used in disinfection by-product studies. Korn et al. (2002), have utilised factorial experiments to develop a statistically-based model which is capable of predicting the formation of two common disinfectant by-product compounds related to the application of chlorine dioxide, namely, chlorate and chlorite. In this study, the authors have used explanatory factors including temperature, chlorine dioxide concentration, reaction time and water organic content (e.g. non-purgeable organic compound and ultra violet absorbance at 254 nm) in building the model.

Also, in one study, Chowdhury et al. (2010) used five factors in the form of chlorine dose, dissolved organic carbon, pH, temperature, and reaction time to formulate a predictive model of trihalomethane for the water supply systems of Ontario, Canada. These factors were obtained from a statistically designed experimental program. The authors showed that the trihalomethane model so developed has good predictive abilities in terms of the examined water supply systems.

Platikanov et al. (2010) have used the factorial analysis technique to investigate the effects of different dissolved organic matter fractions - colloidal, hydrophobic, and transphilic fractions, on trihalomethane compounds formation. The study revealed that bromoform formation was not significantly dependent on colloidal and hydrophobic fractions.

2.6 Bromoform predictive model

The emergence of the disinfection by-product problem in the mid-1970s (Rook, 1975) subsequently led many research organisations to carry out many research studies related to disinfection by-product compounds (Richardson et al., 2007). These research studies have identified and characterised some of the significant parameters that encourage the formation of disinfection by-product compounds in drinking water. Based on these significant parameters, numerous predictive models have been formulated to predict disinfection by-product compounds in drinking water (Serodes et al., 2003; Al-Omari et al., 2004; Nikolaou et al., 2004).

Many of the models published in the literature focus on the formation of group compounds collectively, for example by developing a prediction model for the total of the four trihalomethane compounds (Serodes et al., 2003; Al-Omari et al., 2004; Nikolaou et al., 2004; Sohn et al., 2004; Toroz and Uyak, 2005). Meanwhile, other studies have developed prediction models for a single disinfection by-product compound such as chloroform (Rathbun, 1996; Garcia-Villanova et al., 1997), bromodichloromethane (Golfinopoulos and Arhonditsis, 2002; Hong et al., 2007), dibromochloromethane (Rathbun, 1996), and bromoform compounds (Rathbun, 1996; Rodrigues et al., 2007). However, since the discovery of the disinfection by-product compounds problem, only a few research studies related to the modelling of bromoform compound have been conducted, mainly because the compound is often found in trace concentrations in most potable waters.

Obolensky and Singer (2008) have developed a DBP predictive model using generalised multiple linear regression method, in which, they utilised turbidity, bromide, temperature, TOC, UV_{254} absorbance, alkalinity, chlorine consumed, chlorine contact time, and chlorine residual as model independent variables. The authors demonstrated the validity of regression model in handling complex relationships between the independent variables selected in their study.

Ged et al., (2015) have examined 87 models from different publications using a common data set. The study addresses that there is a lack of published models investigating the individual THM and HAA species.

In one of these few studies, Siddiqui et al. (1994) developed an empirical model for predicting bromoform compound during water ozonation practices. The factors that were included in the model comprised ozone doze, DOC, pH, bromide ion, ozonation temperature, incubation temperature and reaction time.

In another study, Rathbun (1996) has utilised the results of the trihalomethane formation potential experiment for three different water samples (e.g. Mississippi, Ohio, and Missouri Rivers) in building a mathematical model. The author used regression analysis to formulate statistical models for bromoform and the other trihalomethane compounds, by employing residual chlorine, pH, DOC, and bromide factors in the models.

Moreover, an attempt was made by Rodrigues et al. (2007) to assess the effect of chlorine on the formation of trihalomethane compounds using fulvic acid concentration, chlorine dose, temperature, pH, and bromide concentration as explanatory factors in a fractional factorial design experiment. The results of the study indicate that the most significant factors that affect the formation of bromoform compound are chlorine dose and bromide concentration. The authors have utilised the explanatory factors assessed in their study and formulated a bromoform predictive model.

The following table (Table 2.2) lists the bromoform predictive models published in the literature in the past two decades:

Table 2.2 Bromoform predictive models published in the literatures

Author	**Year**	**Bromoform predictive model**	**Remark**
Malcolm Pirnie Inc.	(1993)	$= 1.28(TOC)^{-0.167}(UV_{254})^{-0.167}(D - 7.6 \times NH_3 - N)^{-2.22}(t)^{0.294}(Br^-)^{1.48}(T)^{0.553}(pH - 2.6)^{0.198}$	As cited in (Chowdhury et al., 2009)
Montgomery Watson	(1993)	$= 6.533(TOC)^{-2.031}(Br^-)^{1.388}(pH)^{1.603}\ (D)^{1.057}(t)^{0.136}$	As cited in (Chowdhury et al., 2009)
Siddiqui et al.	(1994)	$= 2.68(DOC)^{1.28}(pH)^{-1.31}(O_3)^{0.742}(Br^-)^{1.55}(T)^{0.956}(t_m)^{0.353}$	
Rathbun, R.E.	(1996)	$= 0.29(pH)^{3.51}(D)^{-0.347}(DOC)^{-0.33}(Br^-)^{1.84}$	
Rodrigues et al.	(2007)	$= 4.0 - 0.2FA + 0.03D + 0.09T - 0.6FA \times T - 0.5FA^2 - 0.8D^2$	

TOC: total organic carbon, UV_{254}: ultra violet absorbance at 254 wave length, D: chlorine dose, t: reaction time, Br: bromide, T: temperature, DOC: dissolved organic carbon, FA: fulvic acid, O_3: ozone dose, NH_3-N: ammonia nitrogen.

The bromoform predictive models in Table 2.2 were designed to predict bromoform compound using several key explanatory factors. However, three bromoform models formulated by Malcolm Pirnie Inc. (1993), Montgomery Watson (1993), Siddiqui et al. (1994) have included the factor of storage time in their models. Furthermore, the bromoform models created by Montgomery Watson (1993) and Rodrigues et al. (2007) have not included the water pH as an explanatory factor during the model formulation. A comparison table (Table 2.3) is prepared to demonstrate the difference between bromoform predictive models in table 2.2.

Table 2.3 Comparison between the utilised parameters in bromoform predictive models

Author of bromoform model	**Factors utilised in bromoform model**										
	DOC	**TOC**	**Fulvic acid**	**UV_{254}**	**NH_3**	**time**	**temperature**	**pH**	**bromide**	**Chlorine dose**	**Ozone**
Malcolm Pirnie Inc.	No	Yes	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No
Montgomery Watson	No	Yes	No	No	No	Yes	No	No	Yes	Yes	No
Siddiqui et al.	Yes	No	No	No	No	Yes	Yes	Yes	Yes	No	Yes
Rathbun, R.E.	Yes	No	No	No	No	No	No	Yes	Yes	Yes	No
Rodrigues et al.	No	No	Yes	No	No	No	Yes	No	No	Yes	No

Therefore, in this study, an attempt was carried out to include the explanatory factors of storage time and water pH in the design of bromoform predictive model, as it was shown in the literatures, these two factors are considered important in affecting development of disinfection by-products. In addition to the previous explanatory factors, the residual chlorine and UV_{254} absorbance were considered in the attempt of formulation of the predictive model. At the end of the study, the formulated bromoform predictive model would be the first to predict bromoform compound in the potable water of Kuwait.

The type of predictive model approach utilised to formulate bromoform model in this study is multivariate regression technique. The reason is that regression models both linear and nonlinear provides good accuracy in terms of output forecasting and the development time of regression models is fast. There are other predictive model techniques used in forecasting for example neural network, fuzzy logic systems and rule-based systems. These predictive techniques require large dataset and long time for model development. Table 2.4 shows a comparison between predictive model techniques.

Table 2.4 Comparison between different predictive model techniques (source: Bardan R., 2004)

No.	**Model technique**	**advantage**	**disadvantage**
1	Multivariate regression (linear and nonlinear)	Good accuracy. Fast development time. Moderate decision insight.	Must assume intervariable relations and in some applications the distribution of data within variables.
2	Neural network	Makes no assumptions about the variables. Highest accuracy.	Lengthy development time. Lowest decision insight. Prone to overfitting.
3	Fuzzy logic systems	Non-rigid decision boundaries.	Difficult to derive for complex problem.
4	Rule-based systems	Highest decision insights.	Less accurate because of rigid decision boundaries.

2.7 Studies related to DBPs in potable water of Kuwait

In general, research studies related to the quality of potable water and particularly to disinfection by-products are limited in Kuwait. These few studies have mainly focused on concentration levels of trihalomethanes and some other disinfection by-products for spot-water samples along drinking water networks. Only in one research study, conducted by Ali (1984), did the author try to develop an understanding of the processes of trihalomethane formation over time in sources of drinking water.

Ali (1984) carried out a research study which aimed to evaluate the development and concentration of trihalomethanes in potable water samples. The study comprised two main activities, the formation of trihalomethane compounds in the laboratory, and an analysis of trihalomethane compounds from potable water samples obtained from different water-distribution systems. Additionally, the author has evaluated several factors which influence the formation of trihalomethanes, such as chlorine dose, reaction time, and other factors not mentioned here because they are not relevant to the scope of the current study.

In the laboratory part of the study, the results showed that the majority of the trihalomethanes produced were bromine-containing compounds. Also, the author pointed out that there was a shift toward the formation of brominated trihalomethane compounds due to the presence of bromide in the water sources at significant concentration levels. It was shown in the laboratory investigation that the predominant trihalomethane compound was bromoform (e.g. ≈ 68 %), whereas chloroform was almost absent from the water samples. Moreover, the study results indicated that there were positive effects of chlorine doses (e.g. 1.65 gm/l and 2.9 mg/l), and a reaction time (e.g. last for 48 hours) for bromoform formation in potable water. However, no significant bromoform concentration levels were reported by the end of the conducted experiments. As for an analysis of bromoform levels in potable water samples in different distribution systems, concentrations of bromoform in the water samples were below the guideline limit. Additionally, it was found in the field investigation that the bromoform compound represented around 50% of trihalomethane compounds in the potable water samples analysed by this study.

In the Ali study, the author thoroughly addressed the effects of reaction time and residual chlorine on the development of bromoform and other trihalomethane compounds in potable water; however, there was one main drawback with the methodology used. The drawback of this study was that the author used tap water rather than fresh water sources of potable water in the experiments. The tap water was purged of volatile organic compounds prior to the commencement the experiments, as described in the study. This practice resulted in the loss of bromoform and other trihalomethane compounds formed during the production of the water, and of a portion of the pre-existing natural organic compounds. Therefore, there is an uncertainty associated with the results of this research study.

Latif (1991) investigated the occurrence of trihalomethanes in water at Doha distillation plant, Doha blending facility, and along the associated water distribution system, all of which represents the drinking water production cycle in Kuwait. At the blending facility, the study focused on trihalomethane concentrations in water at different locations during the production of drinking water. The locations of water samples included groundwater and recarbonated water inlets, water mixing tanks and water reservoirs. The author found that the recarbonated water produced by Doha distillation plant contains a low concentration of trihalomethanes (2.33 ± 1.88 µg/l) before it enters the blending facility. The concentration of trihalomethanes at the mixing tank was reported as 7.60 ± 5.55 µg/l, which is a bit higher than the concentration found in the recarbonated water. Finally, the concentration of trihalomethanes just after the water left the Doha blending facility was found to be 20.42 ± 6.84 µg/l. In Hawali area, which is located at the extremes of Doha blending facility (25 km), the trihalomethanes was found between 17.86 µg/l and 44.82 µg/l. However, an elevated concentration of trihalomethanes of 92.35 µg/l, was found at one of the sampling points at Al-Sharq area which is not supplied by Doha blending facility.

A nationwide survey of trihalomethane concentration levels in 624 drinking water samples was conducted by Al-Mudhaf and Abu-Shady (2008). The water samples were collected from residential and governmental buildings at 99 different locations in Kuwait during 2003-2005. Additionally, drinking water samples were collected inside and outside properties where storage tanks were used inside buildings to store drinking water, which is a common practice in Kuwait. The authors found that bromoform was the dominant compound among the other trihalomethane species where the percentage of bromoform was 93.5% of the total THMs. Moreover, the maximum trihalomethane concentration was reported as being 91.01 µg/l, which is above the US EPA maximum contaminant level (MCL). Interestingly, the study showed that there was a seasonal variation in trihalomethane concentration levels; high trihalomethane concentration levels in potable water were reported in the winter season. The concentration of trihalomethane compounds in drinking water was higher outside the surveyed buildings than inside the buildings' storage tanks. Finally, the study has indicated that the reported maximum trihalomethane concentration in drinking water samples had significantly increased, from 50.5 µg/l in 1988 to 90.1 µg/l during the period of the study (2008).

Although bottled drinking water is not relevant to the scope of this study, it is discussed briefly here because the production of bottled water in Kuwait depends mainly on tap water. Al-Mudhaf et al. (2009) evaluated the concentration of trihalomethane compounds in drinking water and different bottled water brands in Kuwait. The study showed that several brands of bottled water contained trihalomethane compounds, with the maximum reported concentration level being 37.5 µg/l. This study revealed that the presence of trihalomethane compounds in bottled water is mainly due to the origin of the water; mains water, which contains such compounds.

The spatial variation in trihalomethane compounds was modelled using a self-organising map approach (Al-Mudhaf et al., 2010). This study aimed to evaluate the trihalomethane in drinking water produced by the Az-Zour, Shuaiba and Shuwaikh blending facilities as it travels away from treatment plants. In the study, several water quality variables were used, including trihalomethane compounds, total dissolved solids, residual chlorine, pH, temperature, and conductivity. The study indicated that trihalomethane compounds were below the guidance level in all drinking water samples. Also, the lowest trihalomethane concentration in drinking water was found in Umm Al-Haiman city. This reflects the good drinking water production practices used by the Az-Zour and Shuaiba blending facilities which supply the city with drinking water. However, cities relying on the Shuwaikh blending facility were found to have received potable water with significantly higher concentrations of trihalomethane compounds than Umm Al-Haiman city.

2.8 Motivation of the study

The primary motivation of the study was the detection of elevated bromoform concentrations (> 100 µg/l) in the potable water samples in Hawali city, Kuwait. Nevertheless, several gaps in the literature were identified and considered in the study concerning the presence of bromoform in the potable water of Kuwait. First of all, there were only a few studies conducted on the occurrence of such compound. In addition, no research studies have addressed the possible effect of blending the groundwater with recarbonated water on development of bromoform in the finished potable water. Moreover, the country is characterised by very hot weather in summer season (> 40ºC), yet, the effect of such factor (temperature) on development of bromoform in potable water was not considered in the previous studies. Therefore, based on the identified research gaps, this research study was designed in order to better understand the development of bromoform in potable water of Kuwait. The design includes preparation of synthetic potable water with different groundwater to recarbonated water blending ratios (typical blending ratios utilised at Doha blending facility including 2.9%, 8.0%, and 15.0% groundwater), and running twelve simulated residence time tests to assess bromoform development under different temperature conditions (20ºC, 25ºC, and 30ºC). The following chapter describes in detail the methodology followed to assess the development of bromoform.

Chapter 3

Materials and Methods

3.1 Introduction

Although there is a reasonable number of research studies published concerning the development of the compound bromoform in potable water, few of these studies have investigated the effects of utilising seawater and groundwater on the development of bromoform in potable water in arid countries. As an example of these countries, the Ministry of Electricity and Water in Kuwait has been relying on seawater distillation and groundwater abstraction in the production of potable water for more than sixty years. Yet, little knowledge is available on the development of bromoform in the potable water produced or on the source of the precursors that encourage the formation of such a compound.

In this research study, the characteristics of the water quality of the source water utilised was considered, including both groundwater and recarbonated water. In addition, the investigation into the development of bromoform in potable water was carried out on synthetic potable water samples prepared in the laboratory and also for fresh potable water samples collected from the Doha blending facility, Kuwait. The Doha blending facility was selected for this study for two main reasons; first, because elevated concentrations of bromoform have been reported in water samples taken from the associated water distribution system and, secondly, because of the advantageous location of the Doha blending facility which is near to the laboratory of the Kuwait Institute for Scientific Research. The laboratory experiments were carried out using the facilities of the Central Analytical Lab (CAL) and the Hydrology Department at the Kuwait Institute for Scientific Research.

The following sections explain in detail the research activities conducted. The research activities were divided into three main laboratory works: the assessment of bromoform precursors in the source waters and the fresh potable water samples collected from the Doha blending facility; the investigation into the development of bromoform over time in the synthetic potable water samples and the investigation into the development of bromoform over time in the fresh potable water samples collected directly from the Doha blending facility. In addition to the laboratory works, a predictive model of bromoform was formulated using the water quality data set obtained from the experiments.

3.2 Assessment of bromoform precursors in the water samples

3.2.1 Introduction

The preliminary assessment of bromoform precursors in both the source water samples and the fresh potable water samples was conducted in order to obtain essential information on the source and concentrations of such precursors in the source water utilised. This assessment was initiated to identify the key precursors present in the source water that are responsible for the development of bromoform. Furthermore, this part of the research activity was carried out in order to provide an answer to objective A of the research study (section 1.5). The following sections describe the activities that were conducted in order to achieve the required objective.

3.2.2 Chemical analysis of the water samples

Several visits were made to the Doha blending facility with the aim of gathering information on the procedures used in the production of potable water and for the collection of enough water samples as required for the laboratory experiments. The investigation into the characteristics of the recarbonated water, groundwater and fresh potable water, collected from the Doha blending facility, were conducted to identify the bromoform precursors and water quality parameters. The key precursors investigated included organic constituents (represented by dissolved organic compounds and UV_{254} absorbance), residual chlorine, and bromide compound in the water samples. As these precursors if exists together are directly responsible in the development of bromoform compound in potable water (Chowdhury et al., 2009). In addition to the determination of bromoform precursors, other water quality parameters that were measured included the pH of the water and water salinity for the collected water samples. Furthermore, a determination for the presence of bromoform was conducted for both the recarbonated water and fresh potable water samples as they experienced a chlorination process. As quality control measures, blank samples, standard solutions, quality control samples sent to BIOFOCUS LADR laboratory in Germany, and duplicate set of water samples were analysed in this study. The analytical methods (Table 3.1) that were used to measure the required parameters, in addition to the preparation of the chemical reagents are discussed in the following sections.

Table 3.1 Analytical instruments and their detection range

No.	Parameter	Analytical method	Method detection range
1	Dissolved organic carbon	ANATOC TOC analyser	0.05 – 5000 mg/l
2	UV_{254} absorbance	HACH DR/4000	1000 – 0.0001 cm^{-1}
2	Residual chlorine	HACH DR/2000	0.02 – 2.00 mg/l
3	Bromide	Dionex Ion Chromatography	0.025 – 100 mg/l
4	pH	Jenway pH meter	2.00 – 16.00
5	Electrical conductivity	Orion EC meter	0 - 3000 mS/cm
6	Bromoform	Aglient purge & trap gas chromatography – mass spectrometry	0.5 – 200 µg/l

3.2.2.1 The chemical reagents and glassware

The chemical reagents used in the experiments were prepared with organic-free water (TOC < 1.0 ppb; resistivity 18.2 mΩ-cm) using a water purification system (Ultra Clear TWF series 2001-D-60). As one of the chemical reagents, a sodium sulphite solution was prepared by dissolving 10 gram of sodium sulphite (Na_2SO_3) in 100 ml organic-free water (APHA, 2005). This solution was used to dechlorinate water samples prior to the analysis of bromoform in order to stop any further development of bromoform. A fresh sodium sulphite solution was prepared every two weeks for dechlorination of the water samples (APHA, 2005). Furthermore, a dilute hydrochloric acid (1:1) was prepared by adding 25 ml of concentrated HCL (37%) to 25 ml of organic-free water while stirring the solution gently. The prepared hydrochloric acid (1:1) was used to preserve the water samples for the bromoform analysis (APHA, 2005). A perchloric acid solution (0.1 M) was prepared by the dilution of 9 ml of concentrated perchloric acid (70%) in one litre of organic-free water. This solution was used to adjust the pH of potassium hydrogen phthalate standard solution during the calibration of total organic carbon analyser.

The glassware used in the experiments was cleaned using an automatic glassware washer-dryer instrument (LANCER series 815LX, USA). In addition, the glassware used was rinsed several times with organic-free water before the collection of the water samples and before commencing the experiments.

3.2.2.2 Dissolved organic carbon

The dissolved organic carbon concentration of the groundwater, the recarbonated water and the fresh potable water were determined using a total organic carbon analyser equipped with auto-sampler (ANATOC series II by SGE International Pty Ltd, Australia). The instrument detection technique is based on photo-catalytic oxidation of organic compounds present in the water sample using titanium dioxide (TiO_2). The calibration of the analyser was carried out using the compound potassium hydrogen phthalate (Analytical reagent 399-500G by Ajax Finechem) and by following the procedure as described explicitly in the instrument's user manual. Firstly, a stock solution of 200 mg/l carbon was prepared by the dissolving of 0.2125 g of pure potassium hydrogen phthalate (47.05% carbon) into 500 ml of organic-free water, the solution pH was adjusted to a pH value equal to 3 using perchloric acid. After that, the required working solution (1.0 mg/l) was prepared from the 200 mg/l stock solution by using the relationship between the concentration (C) and the volume (V) of the stock and working solution as the follows

$$(CV)_{stock} = (CV)_{working}$$

$$V_{stock} = \frac{(CV)_{working}}{C_{stock}}$$

$$V_{stock} = \frac{1.0 \times 500}{200} = 2.5\ ml$$

The 2.5 ml of the stock solution was diluted into organic-free water to make up to 500 ml volume of a working solution of 1.0 mg/l, the working solution pH was adjusted to around 3 pH using perchloric acid solution (0.1 M). Finally, the 1.0 mg/l solution was used to calibrate the total organic carbon analyser. It is worth mentioning that the detection range of the instrument was from 0.05 mg/l to 5000 mg/l which covers the range of organic constituents of most natural water. Furthermore, all the water samples analysed were filtered using 0.45 µm filter paper, giving dissolved organic carbon.

3.2.2.3 UV_{254} Absorbance

The analysis of the UV_{254} absorbance for the different water samples was carried out using a spectrophotometer instrument (Method 10054, DR/4000U by HACH). The analysis of the water samples was conducted at 254 nm against organic-free water (the sample blank). However, as a result of the low absorbance result obtained in the analysis of the water samples, the 1.0 cm sample cell was replaced by a 10.0 cm sample cell which is designed for low range results. In addition, all the water samples were filtered using 0.45 μm filter paper before commencing the analysis. The method detection limit cannot be estimated because it is a non-specific measurement (APHA, 2005).

3.2.2.4 Residual chlorine

The determination of the residual chlorine was carried out on site for the fresh potable water and also for the recarbonated water samples to measure any chlorine existing from the pre-chlorination practice applied during the distillation of seawater. The residual chlorine measurement was conducted using a spectrophotometer instrument (Method 8021, DR/2000 by HACH) with a 25 ml sample cell. The detection limit of the instrument is in the range of 0.02 to 2.00 mg/l (APHA, 2005).

3.2.2.5 Bromide compound

The measurement of bromide compounds was carried out for the different types of water samples by using an ion chromatography instrument (Dionex series 300 by Dionex Corporation, USA). The instrument consisted of an analytical column (Dionex, IonPac AS9-HC, 2 x 250 mm), a guard column (Dionex, IonPac AG9-HC, 2 x 50 mm), a suppressor device (Dionex, ASRS-Ultra II 2 mm) and a conductivity detector (Dionex, suppressed conductivity CD25). The instrument was calibrated using potassium bromide salt (ACS reagent grade by Panreac). The potassium bromide was used to prepare a number of bromide standard solutions (i.e. 5.0 mg/l, 1.0 mg/l, 0.5 mg/l, 0.25 mg/l, 0.1 mg/l, 0.05 mg/l and 0.025 mg/l), in order to cover the range of concentrations of bromide compounds in the water samples collected. A bromide calibration curve was developed using the prepared standard solutions (Fig. 3.1). During the bromide analysis, the volume of the injected water sample was equal to 25 µl. The bromide separation was conducted using a sodium carbonate eluent (9 mM Na_2CO_3) at a flow rate equal to 0.25 ml/min. The operation pressure of the instrument was around 1300 psi (APHA, 2005).

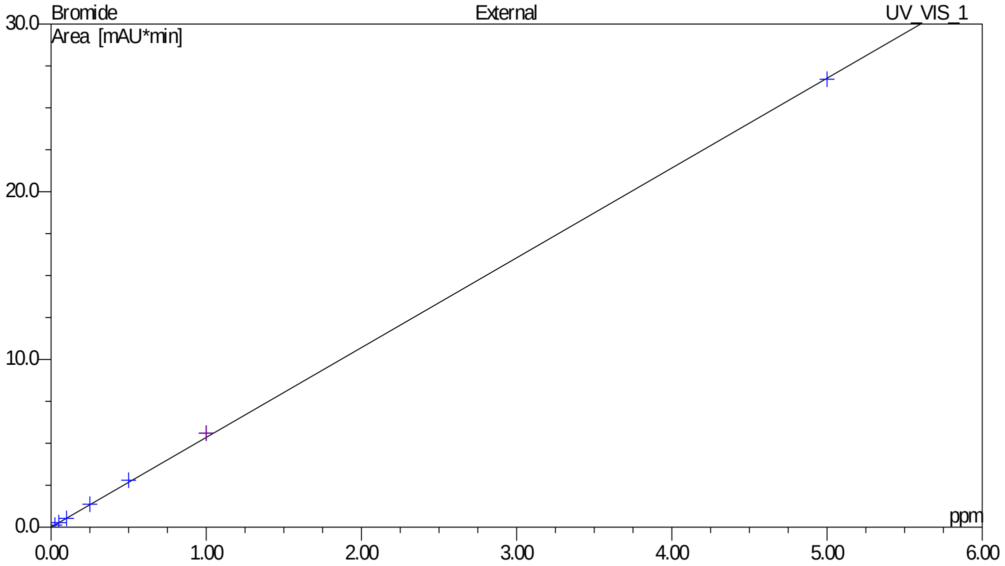


Figure 3.1 Calibration curve of bromide compound

3.2.2.6 Water pH

The determination of the pH for the water samples was conducted using a portable pH meter (JENWAY series 370). The calibration of the meter was performed using two different pH buffer solutions (i.e. 7.00 and 10.01 pH buffer solutions by HACH) which covered the pH range of the water samples collected. The detection limit of the meter is between 2.00 to 16.00 with accuracy equal to ± 0.02 (APHA, 2005).

3.2.2.7 Salinity of water

The salinity (total dissolved solids in mg/l) of the water samples was estimated indirectly through measuring the electrical conductivity (EC) of the water samples in unit (µS/cm). The estimation was obtained by multiplying the electrical conductivity measurement of the water samples by a suitable correction factor which was equal to

0.55 (Walton, 1989). The electrical conductivity of the water samples was measured using a portable conductivity meter (Orion 5-Star meter by Thermo Scientific, USA). The meter has a range between 0 to 3000 mS/cm, a resolution down to 0.001 µS/cm, and an accuracy equal to ± 0.01 µS/cm (APHA, 2005). The calibration of the meter was performed using conductivity calibration solutions (100 µS, 1413 µS, 12900 µS, and 111000 µS).

3.2.2.8 Bromoform compound

The analytical determination of bromoform was performed by using a gas chromatograph mass spectrometer (gas chromatograph series 6890 and mass spectrometer series 5973 by Agilent Company) fitted with a purge and trap sample concentrator system (purge and trap series 3100 by Tekmar Dahrmann). The calibration of the system was conducted by using 1.0 ml of 200 µg/l trihalomethane calibration mix in methanol (Catalogue No. 48746 by SUPELCO Analytical, USA). During the calibration, five standard solutions were prepared from the trihalomethane calibration mix including 10 µg/l, 25 µg/l, 50 µg/l, 100 µg/l, 200 µg/l in which they were used to prepare a calibration curve for measuring bromoform in the water samples. The operating conditions of the instrument, under which the analysis of bromoform in the water samples was carried out following USEPA 1624C method for determination of volatile organic compounds, and were as shown in Table 3.2.

Table 3.2 Operating conditions for bromoform determination

Parameter	**Operation setting**
Purge and trap system	
Purge ready temperature	35°C
Transfer line temperature	150°C
Valve temperature	150°C
Purge time	11 min
Trap pressure control	4 psi
Baking time	8 min
Baking temperature	250°C
Desorbing temperature	180°C
Desorbing preheating temp.	175°C
Dry purge time	4 min
Gas chromatograph - Mass spectrometer (GC-MS)	
Injector	220°C
Column (DB-624)	30 m x 0.25 mm x 0.25 µm
Temperature programmed	38° C accelerate to 240°C
Carrier gas	helium
MS source temperature	230°C
MS quadropole temperature	150°C
Electron multiplier	1600 eV
MS scanning range	40-250 amu
Detector temperature	280° C

3.2.3 Concentration of bromide compounds in a mixture of waters

The development of bromoform in potable water is mainly due to the presence of bromide compounds in the source water. The presence of even a small concentration of bromide can lead to the formation of bromoform as is pointed out in the literature review. Therefore, as a result of not detecting bromide compounds in the fresh potable water samples in the previous section, this laboratory activity was designed to investigate the effect of mixing different ratios of groundwater with re-carbonated water on the presence and eventual concentration of bromide compounds in the water produced.

The mixed water was prepared using the groundwater and the recarbonated water collected from the Doha blending facility. The groundwater and recarbonated water were blended together in different ratios (i.e. comprising 50%, 45%, 40%, 35%, 30%, 25%, 20% and 15% groundwater) using a measuring cylinders and mixed with a magnetic stirrer. The procedure was repeated seven times in order to produce 100 ml each of seven different mixtures of water according to the assigned blending ratio. Then, after the preparation of the water mixtures, these water samples were analysed for bromide compound concentration using the ion chromatography instrument (refer to section 3.2.2.5).

3.2.4 Organic constituents of the synthetic potable water

The type and concentration of organic constituents present in source water plays an important role in the development of bromoform in potable water. As a result of using different groundwater to re-carbonated water blending ratios throughout the year at the Doha blending facility, different concentrations of organic constituents can be expected to be present in the potable water produced. In this section, the concentration of the organic constituents present in the prepared synthetic potable water samples was investigated in the laboratory. The dissolved organic carbon and UV_{254} absorbance tests were utilised to assess the organic constituents. Furthermore, these tests were conducted for three different synthetic potable water samples.

At the laboratory, three mixtures of groundwater and recarbonated water (i.e. synthetic potable water samples) comprising 2.9 %, 8.0 % and 15.0 % (i.e. blending ratios) groundwater were prepared using a pipette and measuring cylinders to produce synthetic potable water samples. These blending ratio figures represent the actual blending ratios used by the Doha blending facility in the production of potable water. The three blending ratios represent the maximum, average and minimum values applied in the Doha blending facility throughout the year (Al-Ruwaih et al., 2010). After the preparation of 100 ml of each of the three synthetic potable water samples, the determination of the dissolved organic carbon and UV_{254} absorbance were carried out immediately.

3.3 Investigation of bromoform development in the synthetic water

3.3.1 Introduction

The practice of blending recarbonated water with groundwater is one of the main processes used in the production of potable water in Kuwait. However, as a result of the production variation of recarbonated water and groundwater in terms of their quantities, different groundwater to recarbonated water blending ratios are used in the production of potable water throughout the year. The effect of such a practice on the development of bromoform over time in the finished potable water has not been studied previously. Accordingly, this research activity was carried out to assess the effect of using different blending ratios of the source waters on the development of bromoform in the finished potable water over time, with a view to providing an answer for objective B of the research study (refer to section 1.5).

In this part of the study, an attempt was carried out to investigate the effect of using three different blending ratios (i.e. comprising 2.9 %, 8.0 % and 15 % groundwater) on the development of bromoform over time in the laboratory. In the following sections, the experimental design, laboratory experimental procedure and the statistical analysis of the data obtained are discussed.

3.3.2 The experimental design

The investigation into the presence of bromoform in synthetic potable water was carried out using a factorial experimental design. The factorial design is often considered in many research fields such as engineering, science and sociology (Wallander, 2009; Chowdhury et al., 2010; Platikanov et al., 2010). This type of design is employed by the researcher in order to obtain knowledge about the processes responsible for many phenomena presented in practical life. Moreover, the design is often used to investigate the effect of a single and/or a combination of two or more explanatory factors on a response variable.

In the experimental design of the study, the preparation method (i.e. the blending ratio percentage), temperature and storage period, were used as explanatory factors in the prediction of bromoform formation in the water samples. The factor of preparation method includes three different synthetic mixtures of waters (i.e. groundwater and re-carbonated water) comprising 2.9 %, 8.0 % and 15.0 % groundwater. On the other hand, the temperature factor consisted of a number of different temperatures, namely 20ºC, 25ºC and 30ºC. Finally, the storage period factor included six successive analyses of bromoform during the time-period of the experiments.

In order to assess the factorial experimental design, the experimental runs were performed using all possible combinations of the different factors. As a result, there were nine experiments included in the study, namely three preparation methods multiplied by three temperature conditions. Furthermore, each of the nine experiments comprised six random measurements of bromoform over the duration of the experiment.

The measurements of bromoform from the nine experiments in response to the explanatory factors can be described using a mixed effects model. The general form of the mixed model is as follows (Brown and Prescott, 2006):

$$\begin{aligned} y_i = \mu + \alpha_1 x_{i1} + \alpha_2 x_{i2} + \dots + \alpha_p x_{ip} \\ + \beta_1 z_{i1} + \beta_2 z_{i2} + \dots + \beta_q z_{iq} + e_i \end{aligned} \qquad (3.1)$$

$$var\ (e_i) = \sigma^2$$

Where y_i represents observed values, μ represents intercept of the model, α represents fixed effects parameters, x represents design matrix for fixed model, β represents random effects parameters, z represents design matrix for random model and e represents residual error. The notation $var\ (e_i) = \sigma^2$, means that the residual error is assumed to have a zero mean and to be independent with normal distribution.

In this study, the bromoform concentration measurement was considered as the dependent parameter, the preparation method and temperature were assigned as fixed parameters, and the storage period of the water samples was considered as a random parameter. The model, which involves these parameters, can be described as

$$y_i = \mu + \alpha_1 x_{i1} + \alpha_2 x_{i2} + \beta_1 z_{i1} + e_i \qquad (3.2)$$

Where y_i represents bromoform concentration, $\alpha_1 x_{i1}$ represents the effect of the first fixed parameter which is preparation method, $\alpha_2 x_{i2}$ represents the effect of the second fixed parameter which is temperature, $\beta_1 z_{i1}$ represents the effect of the random parameter which is storage period. Also, the model can be described by the linear statistical model in a simple form as follows:

$$Bromoform_{ijkl} =$$
$$\mu + \ Preparation\,Method\ _i + \ Temperature_j + \ Storage\ Period_k$$
$$+ e_l \begin{cases} i = 1,2,3,4,5,6. \\ j = 1,2,3,4,5,6. \\ k = 1,2,3,4,5,6. \\ l = 1,2,3,4,5,6. \end{cases} \tag{3.3}$$

The arrangement of the three explanatory factors (i.e. A: temperature, B: preparation method and C: storage period) and the dependent parameter (i.e. Y: bromoform compound measurement) are presented in Table 3.3. As can be seen from the table, the A and B factors have three values each, whereas, the C factor is composed of six consecutive random measurements obtained over the duration of the experiments. The C factor represents the time at which the bromoform analysis was performed, namely 1C: 24 hours, 2C: 48 hours, 3C: 72 hours, 4C: 96 hours, 5C: 120 hours and 6C: 144 hours. Moreover, each of the random measurements (i.e. Y: bromoform compound) was impacted by the combined effects of AB factors (i.e. temperature and preparation method factors).

Table 3.3 The explanatory factors and response arrangement for the experimental design

		Factor B				
		1	**2**	**3**	**Totals**	**Averages**
Factor A	**1**	$Y_{(1,1,1C)}$ $Y_{(1,1,2C)}$ $Y_{(1,1,3C)}$ $Y_{(1,1,4C)}$ $Y_{(1,1,5C)}$ $Y_{(1,1,6C)}$	$Y_{(1,2,1C)}$ $Y_{(1,2,2C)}$ $Y_{(1,2,3C)}$ $Y_{(1,2,4C)}$ $Y_{(1,2,5C)}$ $Y_{(1,2,6C)}$	$Y_{(1,3,1C)}$ $Y_{(1,3,2C)}$ $Y_{(1,3,3C)}$ $Y_{(1,3,4C)}$ $Y_{(1,3,5C)}$ $Y_{(1,3,6C)}$	$\sum \boldsymbol{A1}$	$\overline{\boldsymbol{A1}}$
	2	$Y_{(2,1,1C)}$ $Y_{(2,1,2C)}$ $Y_{(2,1,3C)}$ $Y_{(2,1,4C)}$ $Y_{(2,1,5C)}$ $Y_{(2,1,6C)}$	$Y_{(2,2,1C)}$ $Y_{(2,2,2C)}$ $Y_{(2,2,3C)}$ $Y_{(2,2,4C)}$ $Y_{(2,2,5C)}$ $Y_{(2,2,6C)}$	$Y_{(2,3,1C)}$ $Y_{(2,3,2C)}$ $Y_{(2,3,3C)}$ $Y_{(2,3,4C)}$ $Y_{(2,3,5C)}$ $Y_{(2,3,6C)}$	$\sum \boldsymbol{A2}$	$\overline{\boldsymbol{A2}}$
	3	$Y_{(3,1,1C)}$ $Y_{(3,1,2C)}$ $Y_{(3,1,3C)}$ $Y_{(3,1,4C)}$ $Y_{(3,1,5C)}$ $Y_{(3,1,6C)}$	$Y_{(3,2,1C)}$ $Y_{(3,2,2C)}$ $Y_{(3,2,3C)}$ $Y_{(3,2,4C)}$ $Y_{(3,2,5C)}$ $Y_{(3,2,6C)}$	$Y_{(3,3,1C)}$ $Y_{(3,3,2C)}$ $Y_{(3,3,3C)}$ $Y_{(3,3,4C)}$ $Y_{(3,3,5C)}$ $Y_{(3,3,6C)}$	$\sum \boldsymbol{A3}$	$\overline{\boldsymbol{A3}}$
Totals **Averages**		$\sum \boldsymbol{B1}$ $\overline{\boldsymbol{B1}}$	$\sum \boldsymbol{B2}$ $\overline{\boldsymbol{B2}}$	$\sum \boldsymbol{B3}$ $\overline{\boldsymbol{B3}}$	$\sum \boldsymbol{Grand}$	$\overline{\boldsymbol{Grand}}$

The effect of the interaction between the three factors, specifically the preparation method, temperature and storage period, on bromoform formation is crucial and is of equal importance to the effect of a single factor. In this study, the interactions between the three explanatory factors, including the preparation method with temperature, the preparation method with storage period and the storage period with temperature, were assessed in order to determine the significance of their impact on the development on bromoform in the synthetic water samples. These interaction effects have been included in the model as follows:

$$\begin{aligned} &Bromoform_{ijkl} = \\ &\mu + \ Preparation\ Method\ _i + \ Temperature_j + \ Storage\ Period_k \\ &\quad + (Preparation\ Method * Temperature)_{ij} \\ &\quad + (Preparation\ Method * Storage\ Period)_{ik} \\ &\quad + (Storage\ Period * Temperature)_{kj} \\ &\quad + e_l \begin{cases} i = 1, 2, 3, 4, 5, 6. \\ j = 1, 2, 3, 4, 5, 6. \\ k = 1, 2, 3, 4, 5, 6. \\ l = 1, 2, 3, 4, 5, 6. \end{cases} \end{aligned} \tag{3.4}$$

3.3.3 Mixed effects method

In many research studies, experimental design and statistical analysis methods are two subsequent and interrelated phases often incorporated to answer research questions. The experimental design is a planned manipulation in experimental conditions to elucidate valuable information regarding the specific subject. Therefore, in this part of the study, the experimental design was followed by a statistical analysis technique to interpret the raw data.

In this part of the research study, the factorial experimental design was assessed by using the statistical method of mixed effects analysis of a variance model (ANOVA). ANOVA is a robust tool and widely-used by researchers in controlled experiments (Rutherford, 2001). The statistical procedure – ANOVA is considered to be a robust tool because it is insensitive to moderate violation of the ANOVA postulated assumptions, i.e., the normality and homogeneity assumptions (Sawyer, 2009).

The assessment procedure of ANOVA includes estimation of total sum of squares (SS_T), model sum of squares (SS_M), residual sum of squares (SS_R), mean squares (MS) and F-ratio for all factors and the interaction between these factors. The estimated F-ratio indicates whether the explanatory factor/s has a significant effect on a dependent parameter. Therefore, this statistical method was used to investigate whether the preparation method, temperature and storage period and their interactions have any significant effect on the development of bromoform (Fig. 3.2).

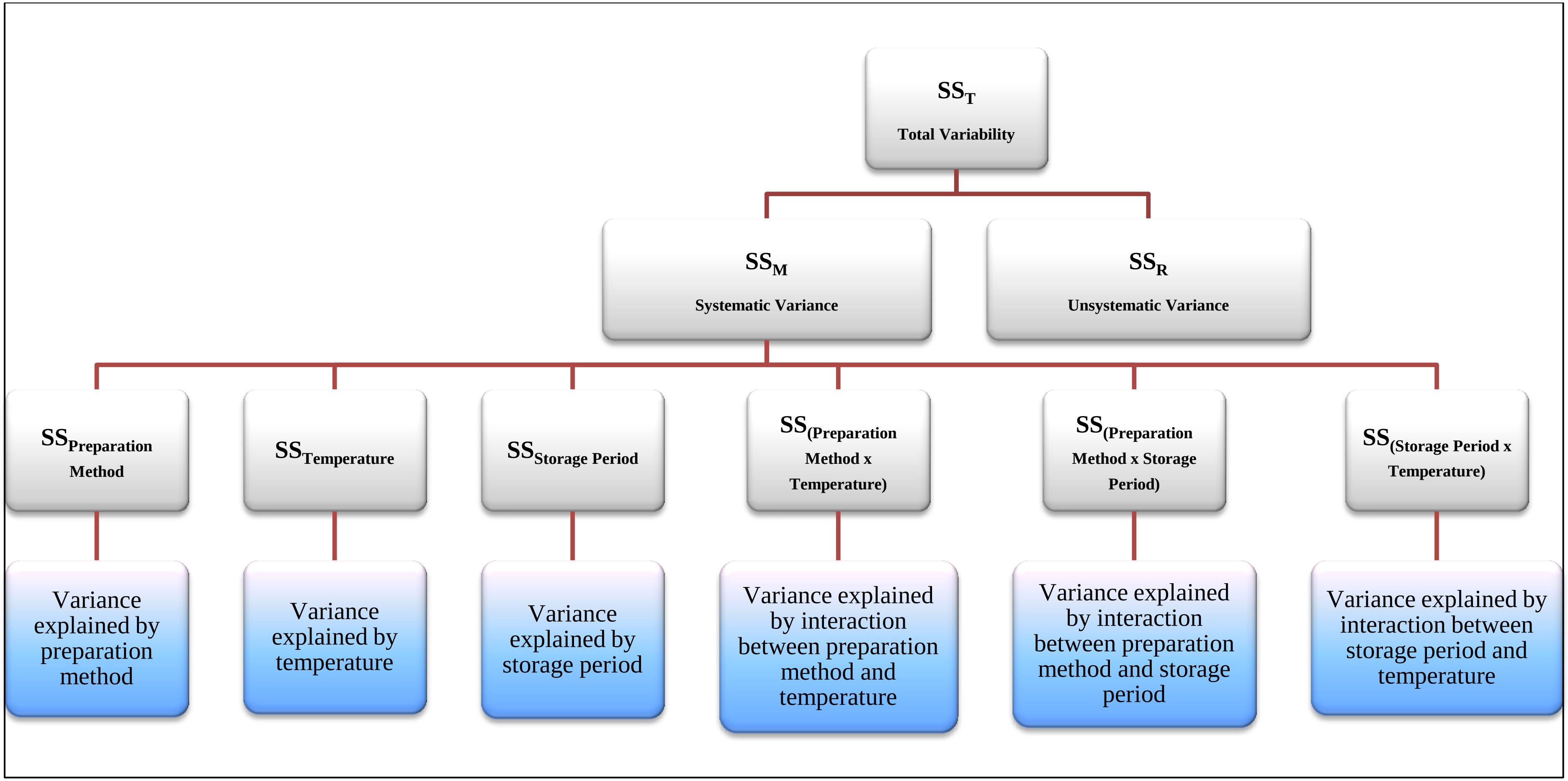


Figure 3.2 Diagram of the main components of the mixed effects model utilised in the analysis

The ANOVA technique is based on assessing the differences between different group means within an experiment. The fundamental idea of the ANOVA technique is based on comparing the ratio of systematic to unsystematic variances within different groups of an experimental study. The ratio variance of both systematic and unsystematic variances is known as the *F*-ratio. This ratio is used to assess the outcome of a regression model compared to the model error (Field, 2005). The advantages of using such a design are in estimating the main average effect of a single factor over all related experiments and in assessing the interaction among the factors considered in a study (Cox and Reid, 2000).

The *F* value obtained, with its corresponding degree of freedom, is compared with the value found in an *F* distribution table in order to conclude whether or not there is a significant effect of the explanatory factors on the response variable. Usually, a significant *F*-ratio means that a difference exists at least between two groups considered within the study but without any further details of which groups are different (Lomax, 2001).

Therefore, it is necessary for many research studies to use further statistical analysis tests, such as multiple comparison procedures, to identify which means are significantly different. The multiple comparison procedure tests (MCPs) are very important and informative tests often used to compare in detail several groups in a study. The test examines all possible two combination groups and determines which one is significantly different.

The following sections explain in detail the assessment of the mixed-effect model, in addition to the multiple comparison procedure tests utilised in this part of the study.

3.3.3.1 Total sum of squares (SS_T)

This is the first step in the analysis which is conducted to estimate the total amount of variation within the whole data set. The estimation of total sum of squares is carried out by subtracting the grand mean of the bromoform measurements from every single result of the compound in the data set, and then the square root of the result is calculated. The same calculation is done for all observed data and summation of the results is carried out to obtain SS_T. The following equation describes calculation of SS_T:

$$SS_T = \sum\left(y_i - \bar{y}_{grand}\right)^2 \qquad (3.5)$$

Where SS_T represents the total sum of squares, y_i represents each bromoform measurement in the experimental design and $\bar{y}$ represents the grand mean of the bromoform measurements. Alternatively, the total sum of squares can be calculated using the following equation:

$$SS_T = s^2_{grand}(N - 1) \qquad (3.6)$$

Where SS_T represents the total sum of squares, s represents grand variance and N is the total number of bromoform measurements in the experimental design. After estimation of the total sum of squares, this total variability is broken down into variance explained by the experiment (i.e. the model sum of squares) and variance that cannot be explained (i.e. the residual sum of squares).

3.3.3.2 Model sum of squares (SS_M)

The estimation of the model sum of squares is conducted to calculate the variation amount in SS_T that the model could explain. In another words, the model sum of squares can provide an estimation of the explained part of the total sum of squares. The group mean is the value predicted by the model in an ANOVA calculation procedure.

The model sum of squares calculation is conducted by subtracting the value predicted by the model from the grand mean and then taking the square root of the result. The value obtained is multiplied by the number of measurements in each group. The procedure is applied to all the values observed, followed by a summation of the results. The following equation describes $SS_{M:}$

$$SS_M = \sum n_k \left(\bar{y}_k - \bar{y}_{grand}\right)^2 \qquad (3.7)$$

Where SS_M represents the model sum of squares, n_k represents the number of bromoform measurements, $\bar{y}_k$ represents the average of a group and $\bar{y}_{grand}$ represents the grand mean across all groups. The result obtained from Equation 3.7 shows the overall variance which can be explained by the model. This overall variance can be broken down into smaller components (e.g. independent variable main effect) to identify the role of each of the independent variables and their interactions separately.

The variances which can be explained by the main effect of preparation method were obtained from the following equation:

$$SS_{Prep.\ Method} = \sum n_{Prep.\ Method} \left(\bar{y}_{Prep.\ Method} - \bar{y}_{grand}\right)^2 \qquad (3.8)$$

Where $SS_{Prep.\ Method}$ represents the main effect of the preparation method, $n_{Prep.\ Method}$ represents the number of bromoform measurements in each level under the preparation method factor and $\bar{y}_{grand}$ represents the grand mean across all preparation method levels.

Furthermore, the variance explained by the main effect of temperature is obtained through the following equation:

$$SS_{Temperature} = \sum n_{Temp.} \left(\bar{y}_{Temp.} - \bar{y}_{grand}\right)^2 \qquad (3.9)$$

Where $SS_{Temperature}$ represents the main effect of the temperature, $n_{Temp.}$ represents the number of measurements in each level of the factor temperature and $\bar{y}_{grand}$ represents the grand mean across all temperature levels. Similarly, the variance explained by the main effect of storage period is estimated through the following equation:

$$SS_{Storage\ Period} = \sum n_{Storage\ Period} \left(\bar{y}_{Storage\ Period} - \bar{y}_{grand}\right)^2 \qquad (3.10)$$

Where $SS_{Storage\ Period}$ represents the main effect of storage period, $n_{Storage\ Period}$ represents the number of measurements in each level of the factor storage period and $\bar{y}_{grand}$ represents the grand mean across all storage period levels.

The variance explained by the interaction between preparation method and temperature is obtained through the following subtraction:

$$SS_{Prep.\ Method \times Temp.} = SS_M - SS_{Prep.\ Method} - SS_{Temp.} \quad (3.11)$$

The variance explained by the interaction between preparation method and storage period is obtained through the following subtraction:

$$SS_{Prep.\ Method \times Storage\ Period} = SS_M - SS_{Prep.\ Method} - SS_{Storage\ Period} \quad (3.12)$$

Finally, the variance explained by the interaction between storage period and temperature is obtained through the following subtraction:

$$SS_{Storage\ Period \times Temperature} = SS_M - SS_{Storage\ Period} - SS_{Temperature} \quad (3.13)$$

At this stage, the model sum of squares and the variance explained by the three independent variables and the three interactions are estimated. The following step was conducted to determine the variance unexplained by the model.

3.3.3.3 Residual sum of squares (SS_R)

At this point, the total variation of the data set is computed (i.e. SS_T) and the part explained by the model is also calculated (SS_M). The SS_R is the amount of data variation which is not explained by the model. This variation is caused by extraneous factors. The residual sum of squares is the difference between the value predicted by the model and the actual observation. The estimation of SS_R is simply carried out by subtracting the model sum of squares from the total sum of squares as follows:

$$SS_R = SS_T - SS_M \quad (3.14)$$

Alternatively, the SS_R can be computed using the following equation

$$\begin{aligned} SS_R = {} & s^2_{experiment\ 1}(n_1 - 1) + s^2_{experiment\ 2}(n_2 - 1) + s^2_{experiment\ 3}(n_3 - 1) \\ & + s^2_{experiment\ 4}(n_4 - 1) + s^2_{experiment\ 5}(n_5 - 1) + s^2_{experiment\ 6}(n_6 - 1) \\ & + s^2_{experiment\ 7}(n_7 - 1) + s^2_{experiment\ 8}(n_8 - 1) + s^2_{experiment\ 9}(n_9 - 1) \end{aligned} \quad (3.15)$$

Where, s represents the variance of each experiment and n represents the number of bromoform measurements in that experiment. The next step in the ANOVA calculation procedure is to estimate the population variance, which is the mean square.

3.3.3.4 Mean square (MS)

The mean square is computed to eliminate the bias presented from adding up different number values during the estimation of SS_M and SS_R. The mean square is obtained separately for each of the three main effects and the three interaction effects in addition to that of the residual term. The estimation of mean squares is conducted through dividing the sum of squares by their degrees of freedom as follows:

$$MS_{Prep.\ Method} = \frac{SS_{Prep.\ Method}}{df_{Prep.\ Method}} \quad (3.16)$$

$$MS_{Temperature} = \frac{SS_{Temperature}}{df_{Temperature}} \quad (3.17)$$

$$MS_{Storage\ Period} = \frac{SS_{Storage\ Period}}{df_{Storage\ Period}} \quad (3.18)$$

$$MS_{Prep.\ Method \times Temperature} = \frac{SS_{Prep.\ Method \times Temperature}}{df_{Prep.\ Method \times Temperature}} \quad (3.19)$$

$$MS_{Prep.\ Method \times Storage\ Period} = \frac{SS_{Prep.\ Method \times Storage\ Period}}{df_{Prep.\ Method \times Storage\ Period}} \quad (3.20)$$

$$MS_{Storage\ Period \times Temperature} = \frac{SS_{Storage\ Period \times Temperature}}{df_{Storage\ Period \times Temperature}} \quad (3.21)$$

$$MS_R = \frac{SS_R}{df_R} \quad (3.22)$$

The estimation of the mean squares is followed by *F*-ratio calculation which is considered as the final stage in conducting an ANOVA. At this stage, the effect of each of the explanatory factors and all of their interactions on the development of bromoform can be determined.

3.3.3.5 F-ratio

The *F*-ratio is a measure of the ratio of the experimental effect (i.e. systematic variation) to the individual differences in performance (i.e. unsystematic variation). If the value of the *F*-ratio is more than one, then it represents a significant effect. This is because the systematic variation is greater than the unsystematic one, and the reverse can also be true. The *F*-ratio is calculated for each effect separately through dividing the model mean square by the residual mean square, as in the following expressions:

$$F_{Prep.\ Method} = \frac{MS_{Prep.\ Method}}{MS_R} \quad (3.23)$$

$$F_{Temperature} = \frac{MS_{Temperature}}{MS_R} \quad (3.24)$$

$$F_{Storage\ Period} = \frac{MS_{Storage\ Period}}{MS_R} \quad (3.25)$$

$$F_{Prep.\ Method \times Temperature} = \frac{MS_{Prep.\ Method \times\ Temperature}}{MS_R} \quad (3.26)$$

$$F_{Prep.\ Method \times\ Storage\ Period} = \frac{MS_{Prep.\ Method \times Storage\ Period}}{MS_R} \quad (3.27)$$

$$F_{Storage\ Period \times Temperature} = \frac{MS_{Storage\ Period \times Temperature}}{MS_R} \quad (3.28)$$

When the *F* value obtained is greater than one (i.e. significant), usually the value is compared with the *F* distribution table to ensure that the value is large enough and did not occur by chance. If the *F* value obtained exceeds the critical value, then the effect of that independent parameter is significant. The value of the *F*-ratio provides a general assessment as to whether the independent parameter is significant or not.

Usually, the significant effect result indicates that there are differences between two or more of the groups' means. However, the *F*-ratio does not specify where or between which groups the differences are presented. Therefore, further analysis is often considered after conducting ANOVA to assess the differences between groups. Usually, there are two types of analysis considered to assess the differences between groups, namely, planned comparisons and post hoc tests. The planned comparison is conducted through dividing the model variance into different levels, which requires prior hypotheses. On the other hand, the post hoc test is conducted by comparing every group included in an experiment and does not require specific hypotheses. As a result, the post hoc test was considered in this study as no hypotheses were included in the study.

3.3.3.6 Post hoc tests

The tests were carried out to compare all different combinations of the treatment groups included in the experiment by utilising pairwise comparisons. There are several types of post hoc test available, such as the least-significant difference (LSD), Bonferroni or Tukey. Application of these tests is mainly dependent on the characteristics of the data (e.g. whether the population variances are equal or not) and experimental design (e.g. whether the group sample sizes are equal or not) (Field, 2005).

In this study, the least-significant difference procedure was used to compare all combinations of the treatment groups. This is because the condition required for using the least-significant difference pairwise comparison is that the overall ANOVA has to be significant (Field, 2005), and this condition was obtained for the experiment data set in the ANOVA analysis. The least-square difference test is conducted through using the following equation:

$$LSD = t\sqrt{\frac{2MS_R}{n}} \qquad (3.29)$$

Where t represents the value obtained from two-tailed test distribution table for the corresponding critical value, MS_R represents the mean squares error and n represents the number of observations per mean. The value obtained from the LSD equation is the minimum difference that is required between any combination of means to satisfy statistical significance conditions.

$$|\,\bar{y}_i - \bar{y}_j\,| > LSD \qquad (3.30)$$

3.3.3.7 Computation of the mixed effects model

The computation of the study model, including all the previous equations, was carried out using an SPSS statistical package. The analysis was run by using a Univariate tool under the general linear model (GLM) option in SPSS software. The SPSS syntax code that includes the commands that were used to run the model is available in Appendix A. Also, for all analyses, a level of 5 % (p=0.05) was used to determine whether a test showed a significant difference.

3.3.4 Laboratory experimental procedure

The evaluation of bromoform development in the synthetic potable water samples was carried out using a simulated residence time test as described in the book of standard methods for the examination of water and wastewater (APHA, 2005). The method is often used to estimate the development of chlorination by-products over time. The time is usually representative of the residence time of potable water within a distribution system. In this study, the residence time was assumed to be six days in the first twelve tests conducted under different conditions. A further three tests were conducted for 35 days to assess the development of bromoform over extended residence time. Therefore, the assumed residence time was assigned as the duration of each experiment to estimate the concentration of bromoform developing in the synthetic potable water sample.

The synthetic potable water was prepared by utilising the fresh water sources (i.e. groundwater and recarbonated water) of potable water. The groundwater and re-carbonated water samples were collected from the Doha blending facility (Figure 3.3) and kept inside cleaned amber bottles, sealed with Teflon-lined screw caps (zero headspace) in sufficient quantities and transported directly to the KISR laboratory. At the laboratory, measurement of the initial water quality parameters, including UV_{254} absorbance, pH, electrical conductivity and bromoform concentration, were carried out for the collected groundwater and re-carbonated water before preparing the synthetic potable water. The synthetic water was prepared by mixing the groundwater and recarbonated water together using three different blending ratios (i.e. comprising 2.9 %, 8.0 % and 15.0 % groundwater) of the two types of water. Furthermore, the effect of three different temperature conditions, namely 20°C, 25°C and 30°C, were investigated for each of the three synthetic potable water samples (Table 3.3). The three selected temperature conditions represent the range of potable water sample temperatures reported by KEPA for the Hawali water distribution system (KEPA, 2009).

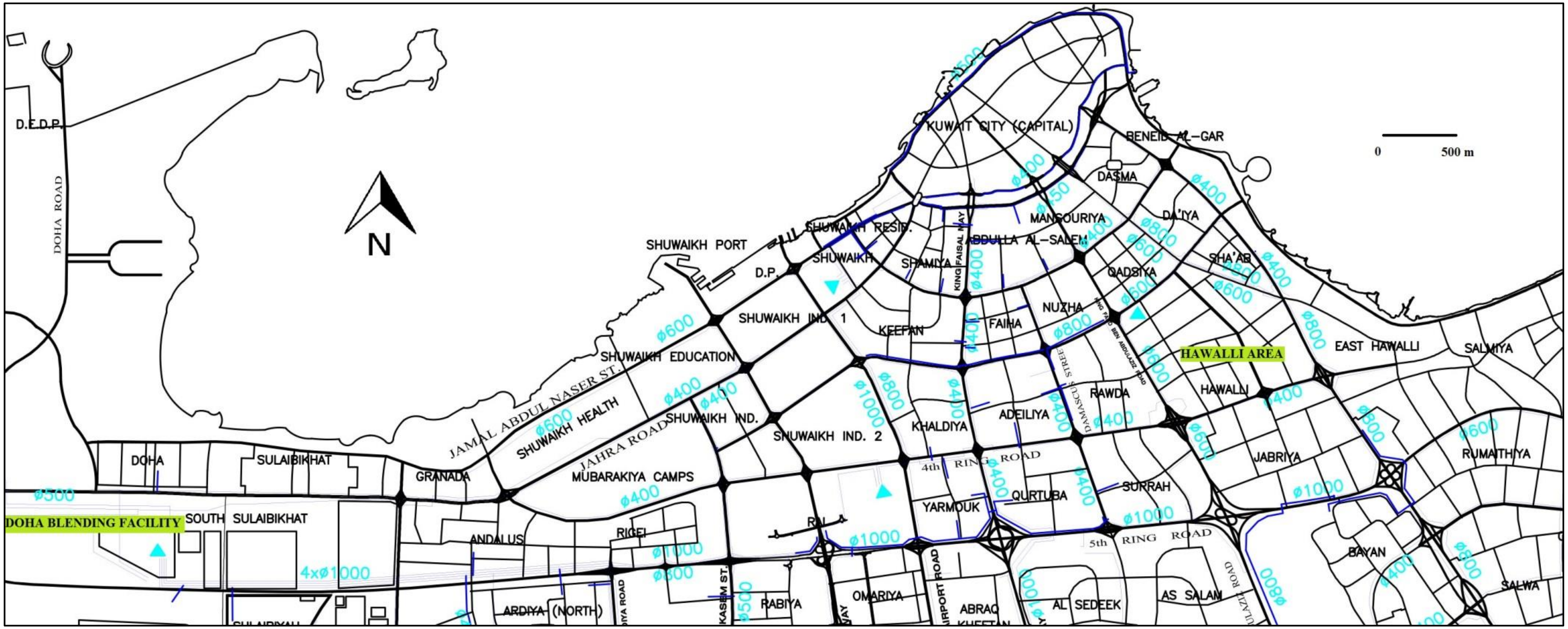


Figure 3.3 Location of Doha blending facility and Hawali area

Table 3.4 Operational conditions of the simulated residence time tests

No. of Experiment	**Groundwater (%)**	**Recarbonated water (%)**	**Temperature conditions (° C)**	**Water samples (litre)**	**Incubation duration (day)**
3	2.9	97.1	20 25 30	6 6 6	6 6 6
3	8.0	92.0	20 25 30	6 6 6	6 6 6
3	15.0	85.0	20 25 30	6 6 6	6 6 6

During the experiments, the preparation of the synthetic potable water was conducted by using a simple 1.0 litre glass reaction vessel placed over a magnetic stirrer (CIMAREC series SP131325Q by Thermo Scientific). The design of the vessel was adapted from a previous study carried out by Morrow and Minear (1987). The vessel has a cylindrical shape, comprising a moveable Teflon plunger (the plunger disk is surrounded by two O-rings with an air relief point drilled through the disk) to maintain a zero-headspace condition during the mixing process, and a Teflon stopcock valve to drain the vessel.

For each of the three experiments, precise quantities of the groundwater and recarbonated water (Table 3.4) were poured into the reaction vessel and mixed for two minutes at a relatively slow speed (i.e. 200 rpm) and then 33 µl of sodium hypochlorite solution (Laboratory reagent grade by RANKEM) was added to the water mixture using a micropipette, to maintain a residual chlorine < 1.0 mg/l, followed by a further two minutes mixing period. After that, the chlorinated synthetic potable water produced was poured into 1.0 litre amber bottles (with zero-headspace). The previous procedure was repeated eighteen times in order to produce, in total, nineteen litres of chlorinated synthetic potable water in separate amber bottles. At this stage, one litre of the water produced was analysed for water quality parameters, including residual chlorine, bromoform concentration, pH, electrical conductivity and UV_{254} absorbance. Meanwhile, the rest of the eighteen amber bottles were divided into three batches and each batch was kept inside different incubators (i.e. at 20°C, 25°C and 30°C). After that, the measurements of the parameters under study were conducted daily for the duration of the simulated residence time test (i.e. six days).

3.4 Predictive model for bromoform

3.4.1 Introduction

A predictive model for bromoform is a useful tool for the management of potable water quality. The model could be used to predict the concentration of bromoform within water networks that experience significant concentrations of this compound. According to the literature, no studies were conducted on the development of bromoform prediction model either in Kuwait or the surrounding countries which utilise seawater for the production of potable water. Therefore, in this part of the study, an attempt was carried out to formulate a bromoform predictive model for the Doha blending facility based on several water quality parameters. In addition, this part was conducted to accomplish objective D of the research study (refer to section 1.5). The following sections explain the design, laboratory procedure and analysis of the bromoform model.

3.4.2 Design of the bromoform predictive model

3.4.2.1 Linear predictive model

The bromoform model was formulated by using water quality parameters obtained from the laboratory experiments conducted on the prepared synthetic potable water samples. These were then compared with a separate data set obtained from the analysis of fresh potable water samples collected from the Doha blending facility. The water quality parameters utilised in the development of the predictive model were residual chlorine, storage period, UV_{254} absorbance, pH of the water, bromide, temperature, temperature*blending ratio, storage period*blending ratio and storage period*temperature. The selection of the water quality parameters for the bromoform model development was based on previously published works cited in the literature.

The predictive model was developed by assigning the water quality parameters and their interactions as the predictor parameters and the bromoform concentration as the response outcome. The relationship between all the previous parameters can be described as follows:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_5 + \beta_6 X_6 + \beta_7 X_7 + \beta_8 X_8 + \beta_9 X_9 + \epsilon$$

Where Y represents the bromoform, X_1 represents the residual chlorine, X_2 represents the storage period, X_3 represents the UV_{254} absorbance, X_4 represents the water pH, X_5 represents the bromide, X_6 represents temperature, X_7 represents the interaction between temperature and blending ratio, X_8 represents the interaction between storage period and blending ratio, X_9 represents the interaction between storage period and temperature, and ϵ represents the random error term. The parameter β_0 is the intercept, whereas $\beta_1, \beta_2, \beta_3, \beta_4, \beta_5, \beta_6, \beta_7, \beta_8, and\ \beta_9$ are the regression coefficients. The error ϵ is assumed to be statistically independent with a mean of zero and variance of σ^2. Furthermore, this model can be expressed in matrix notation as

$$Y = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \\ y_5 \\ y_6 \end{bmatrix} \quad X = \begin{bmatrix} X_{11} & X_{12} & X_{13} & X_{14} & X_{15} & X_{16} & X_{17} & X_{18} & X_{19} \\ X_{21} & X_{22} & X_{23} & X_{24} & X_{25} & X_{26} & X_{27} & X_{28} & X_{29} \\ X_{31} & X_{32} & X_{33} & X_{34} & X_{35} & X_{36} & X_{37} & X_{38} & X_{39} \\ X_{41} & X_{42} & X_{43} & X_{44} & X_{45} & X_{46} & X_{47} & X_{48} & X_{49} \\ X_{51} & X_{52} & X_{53} & X_{54} & X_{55} & X_{56} & X_{57} & X_{58} & X_{59} \\ X_{61} & X_{62} & X_{63} & X_{64} & X_{65} & X_{66} & X_{67} & X_{68} & X_{69} \end{bmatrix} \quad \beta = \begin{bmatrix} \beta_0 \\ \beta_1 \\ \beta_2 \\ \beta_3 \\ \beta_4 \\ \beta_5 \\ \beta_6 \\ \beta_7 \\ \beta_8 \\ \beta_9 \end{bmatrix} \quad and \quad \epsilon = \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix}$$

Where Y is the vector of the observation which is represented by the six bromoform measurements, X is the matrix of the level of the predictor parameters and the columns represent the nine water quality parameters selected for the model. The last two expression (β_{0-9} and ϵ_{1-6}) are the regression coefficients and the error term

3.4.2.2 Nonlinear predictive model

The nonlinear regression (NLR) model is a valuable tool often used to describe physical, chemical and biological systems (Hamby, 1994; Qian et al., 2005). The NLR module of many sophisticated statistical package (e.g. SPSS software) is utilized by researchers from different fields to estimate the unknown parameters of predictive models. In the research studies related to disinfection by-product, the NLRs have been employed to assess disinfection by-product formation (Sadiq and Rodriguez, 2004; Chen and Westerhoff, 2010). The NLRs published in the literature have employed variety of modelling parameters which covers disinfection by-product precursors and disinfection operation conditions (e.g. organic constituent, bromide, reaction time, pH, temperature and disinfection dose).

One of the preliminarily steps before running the NLR for the development of a predictive model is to identify nature of trends between each potential independent variables and dependent variable. Once trends between independent and dependent variables are constructed, functions could be assigned to describe such trends. After that, a statistical software could be used by employing iterative estimation algorithms (e.g.

sequential quadratic programming or Leven-Berg-Marquardt method) to find the least square estimates of model parameters, hence to estimate model coefficients. A nonlinear bromoform predictive model was developed using four independent variables (i.e. residual chlorine, UV_{254} absorbance, storage period and pH measured during conducting the simulated residence time tests) and three interaction terms (i.e. storage period x temperature, storage period x blending ratio and initial bromoform x bromide x storage period).

3.4.2.3 Sensitivity analysis

The sensitivity analysis (SA) is often used to investigate how the change in the model parameter values would impact on model output (Eschenbach and Gimpel, 1990; Lomas and Eppel, 1992; Hamby, 1994; Clemson et al., 1995). The outcomes of SA usually provide information on which of the model input has the greatest effect on a model output. The outcome of the sensitivity analysis would help to develop management strategy to control the development of disinfection byproduct. In this study the SA was carried out to assess the effect of each of the bromoform predictive model parameters (i.e. residual chlorine, bromide, temperature, UV_{254} absorbance, storage period and pH) on bromoform development. The SA of the bromoform predictive model was performed using office excel spreadsheet. The excel was used to generate 1000 random values for each of the model parameters. The random values generated were fed into the predictive model. The predictive model outcome was reported in terms of the highest, average and lowest bromoform concentration. The function that was used to generate the random values for the model parameters is as follows:

Random value = minimum value + (maximum value – minimum value) * RAND()

where RAND() is a random variable in Excel.

The range of values (i.e. the maximum, minimum and average values) utilized in the sensitivity analysis represents the actual operational conditions applied during production of potable water in Doha blending facility. Furthermore, the range of these values reflected the results of the parameters analysis obtained from the tests conducted in the laboratory. During the SA analysis, one parameter of the model was given a random value and the rest of model parameters were kept constant (assigned an average value) for 1000 iterations to identify the degree of sensitivity of each model parameter on bromoform development. The process was repeated six times to assess all the model parameters (Table 3.5). As for the model interaction terms, it was changed spontaneously when the relevant model parameter was altered (e.g. a random value assigned for temperature led to a new value for the temperature*blending ratio interaction term).

Table 3.5 The values of parameters of nonlinear model used in the sensitivity analysis

Model Parameter	**Unit**	**Minimum**	**Maximum**	**Average**
Residual chlorine	mg/l	0.40	0.80	0.60
Bromide	mg/l	0.004	0.020	0.012
Temperature	° C	20	30	25
Initial bromoform	µg/l	6.00	27.00	16.50
UV_{254} absorbance	cm^{-1}	0.0018	0.0066	0.0042
Storage period	hrs	0	840	420
pH	-	7.00	8.00	7.50
Blending ratio	%	2.9	15	8.95

3.4.3 Laboratory experimental procedure

The laboratory activities of this part of the study were carried out as part of the simulated residence time tests. The measurements of the necessary water quality parameters for the development of the bromoform model were obtained during the execution of both of the simulated distributed tests of the synthetic potable water (i.e. synthetic water comprising 2.9 % groundwater) and the fresh potable water produced by the Doha blending facility under different temperature conditions (i.e. 20º C, 25º C, and 30º C). During the simulated residence time tests, the three water quality parameters (i.e. residual chlorine, UV_{254} absorbance, water pH, and bromide) were determined at the beginning of the experiments and every 24 hours for six and thirty five successive days which both were the duration of the experiments (i.e. the storage period of the water samples). The determination of the water quality parameters was conducted in parallel to the analysis of bromoform in the water samples.

3.4.4 The statistical analysis

A multiple regression model was used to assess the relationship between the response parameter (bromoform) and the predictor parameters (i.e. residual chlorine, storage period, UV_{254} absorbance, the pH of the water, bromide, temperature, temperature*blending ratio, storage period*blending ratio and storage period*temperature). The least squares technique was utilised to estimate the regression coefficients in the multiple regression model. The technique is a procedure carried out to determine the line of best fit to the data. The estimation of the regression coefficients of the bromoform model was performed by using an SPSS statistical analysis package.

3.5 Correlation between bromoform, chlorine demand, pH, and UV_{254} absorbance

It has been summarised that the occurrence of bromoform in potable water is due to the effect of several factors (e.g. chlorination, pH, bromide, and the organic constituents of the water). In addition, the extent to which each of these factors encourages bromoform development is different. In this section, the relationships and the correlation between bromoform, Δ chlorine, and UV_{254} absorbance of the water samples were investigated. This part of the study is designed to provide an answer for objective E of the study (refer to section 1.5).

The activity of this part of the study was carried out by utilising the measurements obtained for bromoform, residual chlorine and UV_{254} absorbance from the analysis of all simulated residence time tests conducted. The relationship between bromoform on the one side and the Δ chlorine (i.e. chlorine dosage – residual chlorine), water pH, and UV_{254} absorbance on the other side were assessed by using Spearman correlation analysis.

A Spearman correlation coefficients were estimated for bromoform with chlorine demand, water pH, and UV_{254} absorbance. Usually, the result of the correlation falls between -1 and +1. A negative value represents a negative relationship, whereas a positive value represents a positive relationship. A zero value for the coefficient indicates no relationship. Furthermore, a value of ± 0.1 means that there is a weak relationship, ± 0.3 indicates a moderate relationship and ± 0.5 indicates a strong relationship (Field, 2005).

Chapter 4

Results and Discussions

4.1 Introduction

In section 4.2 the results of an assessment of the presence of bromoform precursors within the sources of potable water i.e. groundwater and recarbonated water, the prepared synthetic potable water samples, and the fresh potable water samples collected from the Doha blending facility, Kuwait are presented. This section is divided into three main subsections which aim to provide an answer to the objective A (refer to section 1.5). This is followed by section 4.3 in which the results of bromoform and the selected water quality parameters obtained from the simulated residence time tests are provided. The assessment of bromoform results using a mixed effects model is also included in this section. Section 4.3 is divided into five main subsections which are designed to answer objective B (refer to section 1.5). Finally, section 4.4 consists of two main subsections and presents the results of the multiple regression analysis carried out for the development of bromoform predictive model which provide an answer to objective C (refer to section 1.5).

4.2 Assessment of bromoform precursors in the water samples

The investigation of the characteristics of source waters (recarbonated water and groundwater) utilised in the production of potable water at the Doha blending facility, in terms of the presence of bromoform, bromide and organic compounds, is important in order to understand the development of bromoform in the potable water of Kuwait. Therefore, in this section, the laboratory’s activities were designed to investigate the bromoform precursors (bromide and organic compounds) and also several water quality parameters including the residual chlorine, pH and salinity of the water samples. The following subsections begin with the demonstration of the results of chemical analysis conducted on the collected water samples (subsection 4.2.1). This is followed by the assessment of bromide concentration in different synthetic potable water samples (subsection 4.2.2). Finally, the results of the determination of organic compounds (dissolved organic compound and UV_{254} absorbance) in the synthetic potable water samples are provided at the end of this section (subsection 4.2.3).

4.2.1 Chemical analysis of the water samples

The result of the preliminary chemical analysis of the water samples is presented and discussed in this subsection. The results (duplicate measurements) of electrical conductivity, salinity, pH, bromide, dissolved organic compound, UV_{254} absorbance, residual chlorine and bromoform analyses for the groundwater, recarbonated water, and fresh potable water samples collected from the Doha blending facility are presented in Table 4.1.

Table 4.1 The chemical analysis for different water samples collected from the Doha blending facility, Kuwait

Parameter	Groundwater	Recarbonated water	Fresh potable water
Electrical conductivity (µs/cm)	4710.0	85.9	275.5
Salinity (TDS in mg/l)	2590.5	47.2	151.5
pH	7.72	8.21	7.91
Residual chlorine (mg/l)	0	0	0.71
DOC (mg/l)	0.29	0.08	0.09
UV_{254} absorbance (cm^{-1})	0.0122	0.0020	0.0031
Bromide (mg/l)	0.71	ND	ND
Bromoform (µg/l)	ND	30.25	32.33

N.B: (-) not measured, (ND) not detected

4.2.1.1 Electrical conductivity and water salinity

The electrical conductivity (EC) measurement reflects the salinity of water. As the electrical conductivity increases, the salinity of water increases. Therefore, the EC parameter was used to estimate the water salinity by using a factor (0.55 × EC). Initially, the result of the electrical conductivity shows that the electrical conductivity values vary between the three types of water. This variation is due to the difference in the salt content level among these water types. The groundwater had a value of 4710 µS/cm which represented a brackish type of groundwater. Meanwhile, the recarbonated water sample had a very small value of around 85.9 µS/cm which resulted from the desalination process of seawater. On the other hand, the fresh potable water had a value equal to 275.5 µS/cm. Based on these electrical conductivity measurements for the different water samples the estimated salinity values for the groundwater, recarbonated water and fresh potable water samples were, respectively, 2590.5 mg/l, 47.2 mg/l, and 151.5 mg/l.

4.2.1.2 Water pH

This parameter was used to indicate the pH environment of the water samples (i.e. acidic or alkaline). The measured pH values were between 7.72 and 8.21. The pH values for the groundwater, recarbonated water, and fresh potable water were 7.72, 8.21, and 7.91, respectively. The three water types represents slightly alkaline water environment. The relatively high pH value of the recarbonated water sample is due to the application of the recarbonation process for the produced water of the Doha desalination plant mainly to protect the network piping from corrosion.

4.2.1.3 Residual chlorine

The residual chlorine measurement was carried out for the groundwater sample and was not detected. This is because that the groundwater is not usually pre-treated with chlorine during production of potable water. Furthermore, the residual chlorine was not detected in the recarbonated water samples. On the other hand, the residual chlorine measured value for the fresh potable water was 0.71 mg/l.

4.2.1.4 Dissolved organic carbon

The dissolved organic compound values for the groundwater, recarbonated water and fresh potable water samples were found to be 0.29 mg/l, 0.08 mg/l, and 0.09 mg/l, respectively. The measured DOC of the groundwater sample is within the DOC range for natural groundwater and was similar to the one reported by Latif (1991) for a groundwater sample collected at the same location – the Doha blending facility. On the other hand, the concentration of DOC for the fresh potable water sample is considered small by comparison to those found in the drinking water samples of other countries; 3.6 mg/l in Scotland (Goslan et al., 2009) and 2.7 mg/l in Finland (Matilainen et al., 2006). The relatively high DOC concentration in potable water found in such countries is often related to the presence of the DOC sources including upland peat, vegetation, and sewage works (Eatherall et al., 2000). These sources of DOC are mostly absent in Kuwait.

4.2.1.5 UV_{254} absorbance

The measurements of UV_{254} absorbance for the groundwater, recarbonated water, and fresh potable water were found to be 0.0122 cm^{-1}, 0.0020 cm^{-1}, and 0.0031 cm^{-1}, respectively. Although these measured values of UV_{254} absorbance in potable water were found to be very low by comparison to those reported in other studies conducted around the world (Matilainen et al., 2006; Swietlik et al., 2009), similar UV_{254}

absorbance values were reported in a study conducted by Chang et. al (2010). The measurement of UV_{254} absorbance is considered a surrogate for the concentration of dissolved organic carbon in water. Therefore, the low UV_{254} values obtained for the water samples reflect the low dissolved organic carbon detected in the same water samples.

4.2.1.6 Bromide

The bromide was only detected in the groundwater sample with a concentration of 0.710 mg/l, whereas, in the recarbonated water and fresh potable water samples the bromide was not detected. These bromide concentration findings are in contrast to what have been reported by Ali and Riley (1990) in a similar type of water. The authors have reported a relatively higher concentration of bromide in the groundwater, and potable water as 2.0 mg/l, and 0.5 mg/l, respectively. In addition, Al-Haddad (1990) reported that the concentrations of bromide in the groundwater samples analysed were between 4.47 mg/l and 6.55 mg/l. Although the bromide results of this study were different from the previous studies, they share the fact that the groundwater contains significant amount of bromide.

4.2.1.7 Bromoform

The measurement of bromoform was carried out for the groundwater sample and was not detected as the water was not pre-treated with chlorine. However, the result of analysis of bromoform for the recarbonated water and the fresh potable water samples were 30.25 µg/l and 32.33 µg/l, respectively. Interestingly, bromoform was detected in the recarbonated water although its source water (seawater) has gone through several stages of evaporation in the multi-stage flash distillation unit at the Doha distillation plant. The measured bromoform concentration for the recarbonated water sample in this study is much higher than what is reported by Latif (1991) for a similar water sample

(1.35 µg/l). The rise in bromoform concentration in the product of the distillation plant (recarbonated water) is possibly due to seawater pollution caused by sewers, oil spills, and city drains. These pollution problems have been addressed by a research study conducted by Abdul Aziz et al., (2000). These sources of pollution increase the organic content of seawater which, with the presence of bromide at significant levels, would eventually develop more bromoform in the product water during pre-treatment of seawater.

4.2.2 Concentration of bromide compounds in a mixture of waters

As bromide was not detected in either of the recarbonated water and fresh potable water samples, and only was found in the groundwater sample (section 4.2.1), the laboratory activity was designed to investigate and assess the concentration of bromide in different mixtures of groundwater and recarbonated water. Mixing both of the groundwater and recarbonated water i.e. blending practice is considered one of the main processes applied during the production of potable water at the Doha blending facility. The result of bromide analysis, in addition to the electrical conductivity measurement and estimated salinity, for the prepared eight different mixtures of the groundwater and recarbonated water are presented in Table 4.2.

Table 4.2 Bromide concentration for different mixtures of groundwater and recarbonated water samples

Water mixture	**Blending ratio (%) groundwater : recarbonated water**	**Electrical conductivity (µS/cm)**	**Salinity (mg/l)**	**Bromide (mg/l)**
1	**100 : 0**	4700	2591	0.700
2	**50 : 50**	2590	1425	0.348
3	**45 : 55**	2356	1296	0.300
4	**40 : 60**	2134	1174	0.241
5	**35 : 65**	1893	1041	0.176
6	**30 : 70**	1658	912	0.134
7	**25 : 75**	1418	780	0.050
8	**20 : 80**	1174	646	0.026

It should be noted that the results of bromide analysis for the synthetic potable water samples comprising 2.9%, 8.0%, and 15.0% groundwater were not included in Table 4.2 because the results were below the instrument detection limit ($Br^- \geq 0.025$ mg/l). However, the relationships noted could be extrapolated to the synthetic potable water samples comprising 2.9%, 8.0%, and 15% groundwater. The estimated bromide concentrations for water samples comprising 2.9%, 8.0%, and 15.0% groundwater are as follows

Table 4.3 Bromide concentration for 15.0%, 8.0%, and 2.9% blending ratios

Blending ratio (%) groundwater : recarbonated water	**Electrical conductivity (μS/cm)**	**Salinity (mg/l)**	**Bromide (mg/l)**
15.0 : 85.0	274	151	0.020
8.0 : 92	561	309	0.010
2.9 : 97.1	923	508	0.004

As can be seen from Table 4.2 and 4.3, there is a clear relationship between the blending ratio (%), electrical conductivity, salinity, and bromide concentration of the prepared eight mixtures. The results show that as the percentage of groundwater was lowered in the water mixture, the electrical conductivity, salinity, and bromide concentrations were decreased. In order to examine the relationship between the bromide and salinity concentrations of the water mixtures a scatter plot was created (Fig. 4.1). The Figure indicates a strong positive linear relationship ($r^2 = 0.986$) between the bromide and salinity of the different water mixtures.

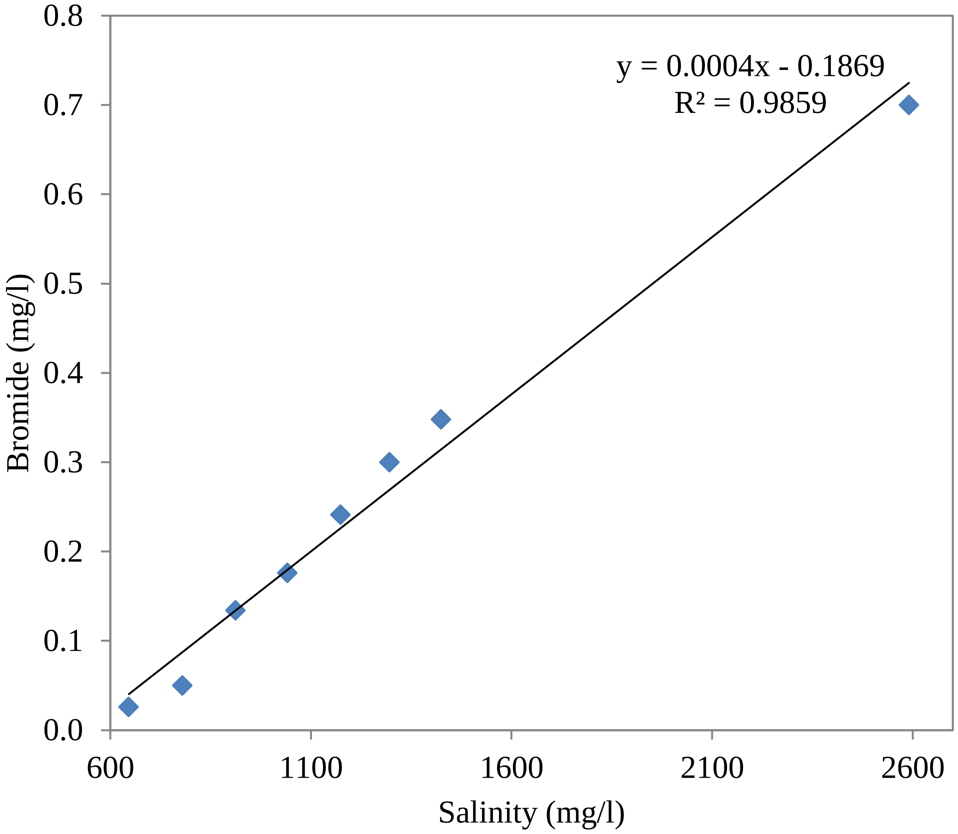


Figure 4.1 Linear relationship between the bromide and water salinity concentrations

Furthermore, a line chart (Fig. 4.2) was constructed for the bromide concentrations against the blending ratios of the water mixtures (i.e. different groundwater to recarbonated blending ratios). It can clearly be seen from the chart that lowering the percentage of the groundwater in the mixture of water led to the decrease in the bromide concentration. This finding could be extrapolated for the synthetic potable water samples comprising 15.0%, 8.0%, and 2.9% groundwater (extrapolation was used because bromide concentration was found to be below method detection level for water mixtures comprising 15.0%, 8.0%, and 2.9% groundwater). The concentration level of bromide is possibly higher in the water sample comprising 15.0% groundwater from those comprising 8.0% and 2.9% groundwater. The lowest bromide level could be found in the water sample comprising 2.9% groundwater.

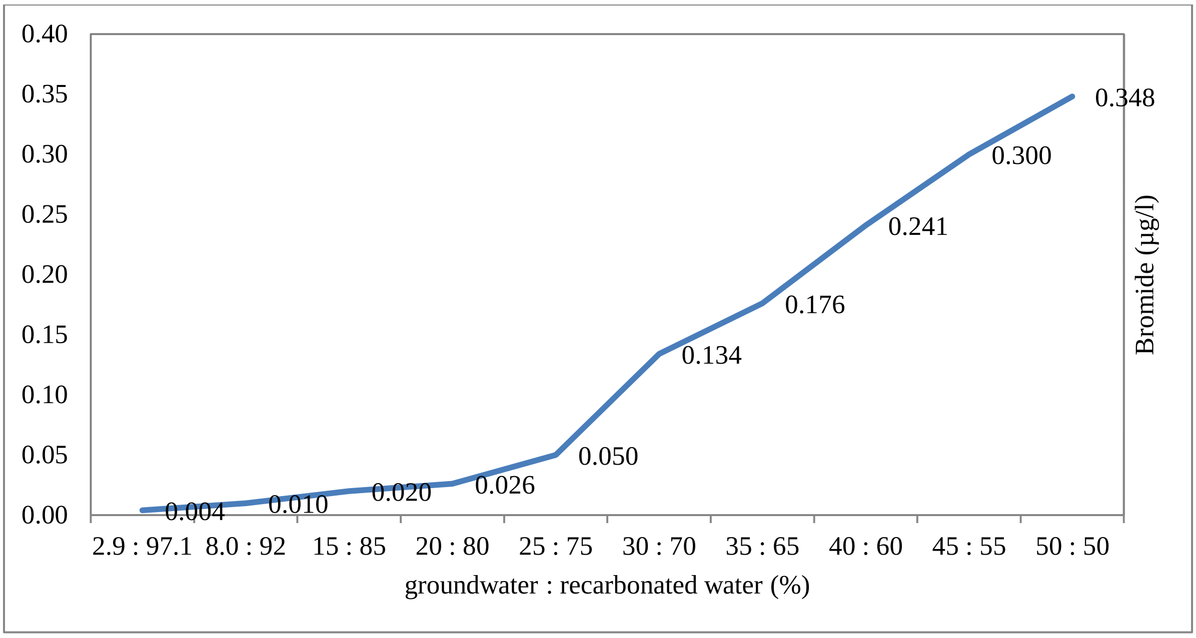


Figure 4.2 The relation between bromide concentration and different mixtures of the water samples

4.2.3 Concentration of organic compounds in synthetic potable water samples

The organic compounds that exist in source water play an important role in the development of bromoform during the chlorination process. In this section, the concentrations of organic compounds within three synthetic potable water samples (comprising of 2.9%, 8.0%, and 15.0% groundwater) were investigated in the laboratory. Assessment of organic compounds was carried out by determining the dissolved organic compound and UV_{254} absorbance of the prepared synthetic potable water samples.

4.2.3.1 Dissolved organic carbon

The result of concentrations of the dissolved organic carbon in the water samples are presented in Table 4.4. It can be seen from the table that the concentration of dissolved organic compound for the groundwater sample is much higher than in the recarbonated water sample. The relatively high dissolved organic carbon concentration in the groundwater is due to the presence of peat and lignite coal seams in the aquifer (Al-Haddad, 2000). Furthermore, the dissolved organic compound concentrations of the three water mixtures was slightly increased by increasing the percentage of groundwater in such water samples. This result indicated that any increase in the groundwater would result in the increase of dissolved organic compound in the water mixture.

Table 4.4 Dissolved organic compound of the water samples

	DOC (mg/l)		
Water Type	1st Measurement	2nd Measurement	Average
Groundwater	0.28	0.29	0.285
Recarbonated Water	0.08	0.07	0.075
Water mixture (groundwater : recarbonated water) 15.0 : 85.0	0.13	0.13	0.13
8.0 : 92.0	0.10	0.09	0.095
2.9 : 97.1	0.08	0.08	0.080

4.2.3.2 UV$_{254}$ absorbance

The organic compounds in the water samples were also assessed by measuring the UV$_{254}$ absorbance of the water samples. The results of UV$_{254}$ absorbance measurements undertaken for the water samples are summarised in Table 4.5. The results show that the groundwater sample has a higher UV$_{254}$ absorbance value than the recarbonated water sample. As a result of the existence of the lignite coal seams in the aquifer (Al-Haddad, 2000). The result of the assessment of the organic content for the groundwater and recarbonated water samples using UV$_{254}$ absorbance method was found to be similar to the result of the dissolved organic compound analysis in terms of the organic content levels. The similarity in the organic content levels for both of the methods is the fact that these two methods are considered a surrogate measure to assess organic content of water (Li & Zhao, 2006). Therefore, similar to the result of the dissolved organic carbon obtained in the previous section (section 4.2.3.1), increasing the percentage of groundwater in the prepared synthetic potable water samples (in the order of 2.9%, 8.0%, 15.0%) had resulted in a slight increase in the UV$_{254}$ absorbance values. This is an indication that relatively more organic compound input was gained for the synthetic potable water sample with higher percentage of groundwater.

Table 4.5 UV_{254} absorbance of the synthetic potable samples

	UV_{254} Absorbance (cm^{-1})		
Water Type	1st Measurement	2nd Measurement	Average
Groundwater	0.0122	0.0116	0.0119
Recarbonated Water	0.0018	0.0014	0.0016
Groundwater : Recarbonated water 15.0 : 85.0	0.0042	0.0036	0.0039
8.0 : 92.0	0.0023	0.0026	0.0025
2.9 : 97.1	0.0020	0.0020	0.0020

4.3 Investigations of bromoform development in synthetic potable water samples

The concentration of bromoform in potable water is often increased over time during transition of water from a water treatment works to a consumer’s tap, as was discussed previously in the literature chapter. Furthermore, there are many factors such as the preparation method and water temperature that promote the development of bromoform in potable water. Therefore, in this section, the laboratory activities were designed to investigate the effect of several factors including preparation method, residence time, and temperature on the development of bromoform in synthetic potable water samples. In the following subsections (4.3.1, 4.3.2, 4.3.3) the results of bromoform and the selected water quality parameters (residual chlorine, UV_{254} absorbance, pH and salinity) taken during the execution of the nine simulated residence time tests are presented. In subsection 4.3.4, the results of the three simulated residence time tests conducted under extended storage period (35 days) and 30ºC temperature conditions for water samples comprising 2.9%, 8.0%, and 15.0% groundwater are demonstrated. The bromoform and water quality parameters results obtained were then assessed by the analysis of correlation in the following section (section 4.3.5). This was followed by fitting the obtained bromoform concentration results from the nine experiments into a mixed effects model (subsection 4.3.6) to assess the significance of the main effects (preparation method, water storage period and temperatures factors) and their interactions on the development of bromoform in the synthetic potable water samples; and to determine in which laboratory conditions the development of bromoform would be found at the lowest concentration in the different synthetic potable water samples.

4.3.1 Simulated residence time tests for synthetic potable water samples comprising 2.9% groundwater

Three separate simulated residence time tests, each under different ambient temperature conditions (20ºC, 25ºC, and 30ºC), were conducted on synthetic potable water samples comprising 2.9% groundwater (the lowest groundwater percentage utilised by the Doha blending facility in the production of potable water) and 98.1% recarbonated water. The results of bromoform, residual chlorine, UV_{254} absorbance, estimated salinity, and pH analyses taken during the experiments are presented subsequently in the following subsections.

4.3.1.1 Bromoform compound

The results of bromoform analysis, in which the compound was analysed on seven consecutive occasions, for the three simulated residence time tests are presented in Table B1 of Appendix B. The table includes the analysis time, duplicate measurement, average and the standard deviation of bromoform. Generally, the results showed that the bromoform concentrations of the three experiments had increased during time progression of the tests. The measurements of bromoform against the time of analysis for the three simulated residence time tests conducted under 20°C, 25°C, and 30°C are plotted in Figure 4.3. According to the graphs, two phases of reaction were observed for the development of bromoform. The first reaction phase was rapid and started at time equal zero and lasted 24 hours, followed by a slow reaction phase and continued to the end of the experiments. This two phase reaction of bromoform development was reported in the literature by several studies (Luong et al., 1982; Shams El Din et al., 1998; Nokes, 2003).

In Figure 4.3, bromoform measurements for the three experiments are plotted together for comparison purposes. The comparison shows that the concentration of bromoform in the synthetic potable water sample in the simulated residence time test conducted under 30°C ambient temperature conditions at the end of the test (31.1 μg/) was relatively higher than those obtained in the tests with 20°C and 25°C. This is because at that elevated water temperature a higher chemical reaction rate is usually took place (Chowdhury et al., 2009); hence, more bromoform would be expected to develop in water.

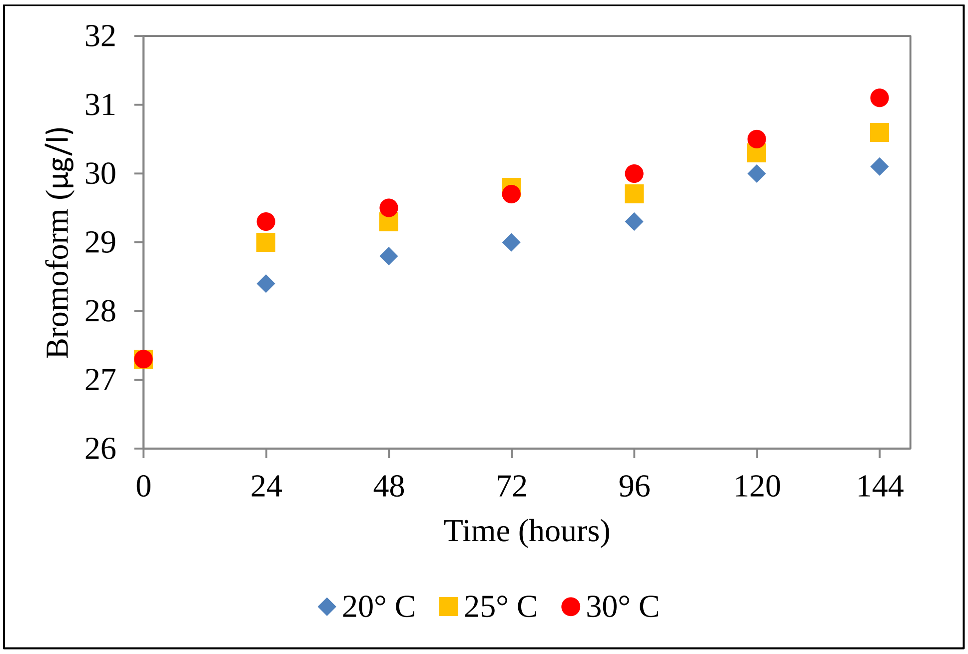


Figure 4.3 Concentrations of bromoform in the water samples comprising 2.9% groundwater for the tests conducted at 20°C, 25°C, and 30°C temp. conditions

4.3.1.2 Residual chlorine

The results of residual chlorine analysis of the synthetic potable water samples comprising 2.9 % groundwater for the simulated residence time tests conducted in 20°C, 25°C, and 30°C ambient temperature conditions are presented in Table B2 of Appendix B. The table shows the time of analysis, duplicate measurements, average, and standard deviation of the residual chlorine results. The results showed that the residual chlorine concentration of the synthetic potable water samples had decreased in the three tests over the length of the tests. The measurements of residual chlorine for the three tests are plotted against the time of the analysis in Figure 4.4. The decay behaviour of residual chlorine in the tested water samples is similar to what has been reported in many published studies in which a gradual decrease of residual chlorine were observed with time (Fisher et al., 2012; Kohpaei & Sathasivan, 2011; Boccelli et al., 2003; Acero et al., 2013; Huang & McBean, 2007).

The results of residual chlorine for the experiments are plotted together against the time of analysis in Figure 4.4. This figure demonstrates the results variation between the three tests. The residual chlorine concentrations for the three tests in which those experiments carried out in 20°C, 25°C, and 30°C temperature conditions ranged between 0.720 – 0.785 mg/l, 0.690 – 0.785 mg/l, and 0.660 – 0.785 mg/l, respectively. Furthermore, it is obviously clear from the results that the lowest concentration of the residual chlorine (0.660 mg/l) was measured at the end of the test conducted in 30°C temperature conditions. This is due to the fact that at a high water temperature the reaction rate would be expected to be high, this in turn leads to a faster chlorine decay (Fisher et al., 2012).

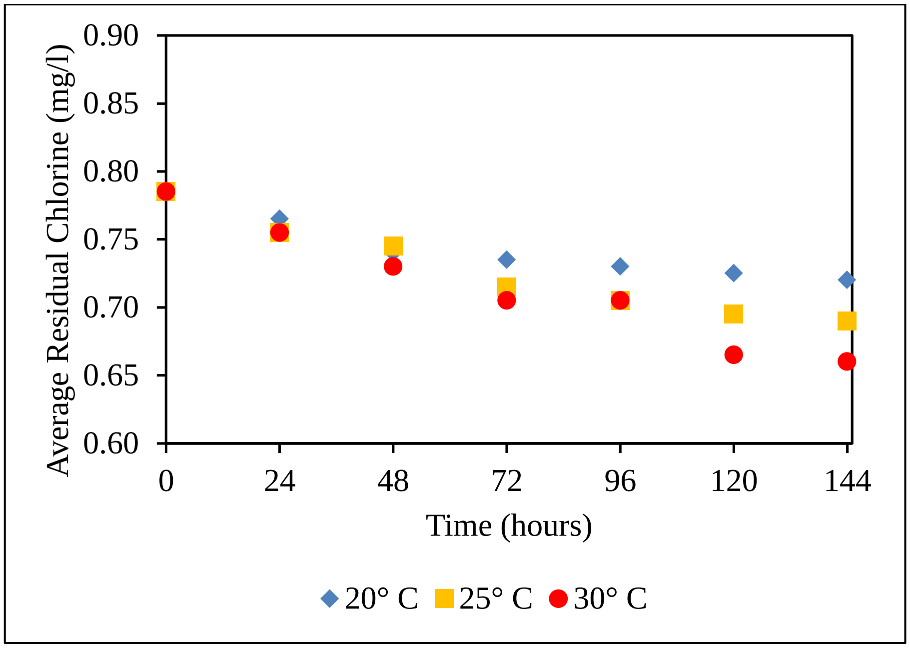


Figure 4.4 The concentrations of residual chlorine in the water samples comprising 2.9% groundwater for the tests conducted at 20°C, 25°C, 30°C temp. conditions

4.3.1.3 UV_{254} Absorbance

The measurements of UV_{254} absorbance of the synthetic potable water samples comprising 2.9% groundwater for the simulated residence time tests conducted under the three temperature conditions (20°C, 25°C, and 30°C) are presented in Table B3 of Appendix B. The design of the table is similar to the previous two tables (Table B1 and B2 of Appendix B) in which the time of analysis, duplicate measurement, average, and standard deviation of the measurements are included. The results of UV_{254} absorbance for the three tests showed that there was a general trend toward reduction in the absorbance values with the time progression of the tests (Fig. 4.5). This reduction in UV_{254} absorbance values is attributed to the chemical reactions which occur during water chlorination (Gang et al., 2003). Therefore, as a result of water chlorination, the unsaturated bonds of the dissolved organic compound (the portion of DOC measured at UV_{254}) become saturated, which result in the alteration of chromophores (the part of a molecule that is responsible for reflecting or absorbing light) in organic compound; hence, reduction in UV_{254} absorbance values is usually observed with time (Li et al., 1998).

The average measured values of the UV_{254} absorbance for the tests conducted under 20°C, 25°C, and 30°C were between 0.0032 – 0.0026 cm^{-1}, 0.0032 – 0.0025 cm^{-1}, and 0.0032 – 0.0024 cm^{-1}, respectively. The lowest UV_{254} absorbance value (0.0023 cm^{-1}) was measured in the test carried out under 30° C temperature (Fig. 4.5). This is due to the fact that at higher water temperature, chemical reaction rate increases, consequently, higher reduction in UV_{254} absorbance value is usually achieved.

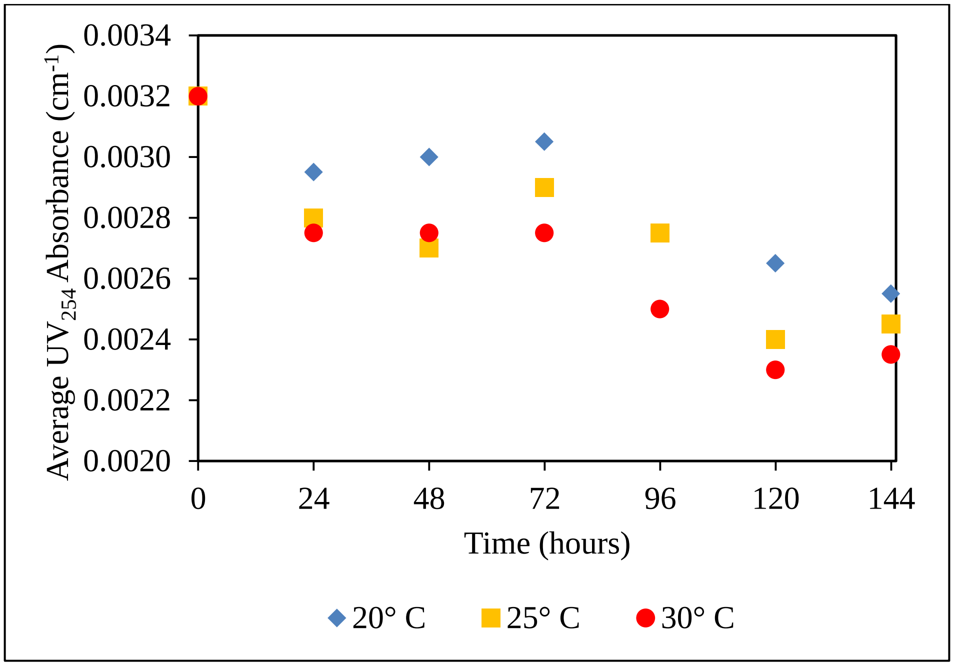


Figure 4.5 UV_{254} absorbance of the water samples comprising 2.9% groundwater for the tests conducted at 20°C, 25°C, 30°C temp. conditions

4.3.1.4 Salinity of water sample

The salinity measurements of the synthetic potable water samples for the three simulated residence time tests conducted under 20ºC, 25ºC, and 30ºC temperature conditions are presented in Table B4 of Appendix B. The result showed that there was a slight change in the value of the salinity in the three tests. The salinity results were plotted against the time of analysis in Figure 4.6 for the tests conducted at temperatures 20°C, 25°C and 30°C, respectively. Generally, the salinity trends in the three figures remained stable along the length of the experiments. This is due to the fact that all of the synthetic water samples undergoing the experiment were prepared from the same source waters (the groundwater and recarbonated water) with similar proportions of the two types of source water. This in turn has led the salinity of the water samples to be almost the same during the experiments.

Moreover, for the purpose of visual comparison, all the salinity results of the water samples obtained from the three tests are plotted together against the time of analysis in Figure 4.6. The Figure shows no clear difference between the salinity trends for the three tests over the time.

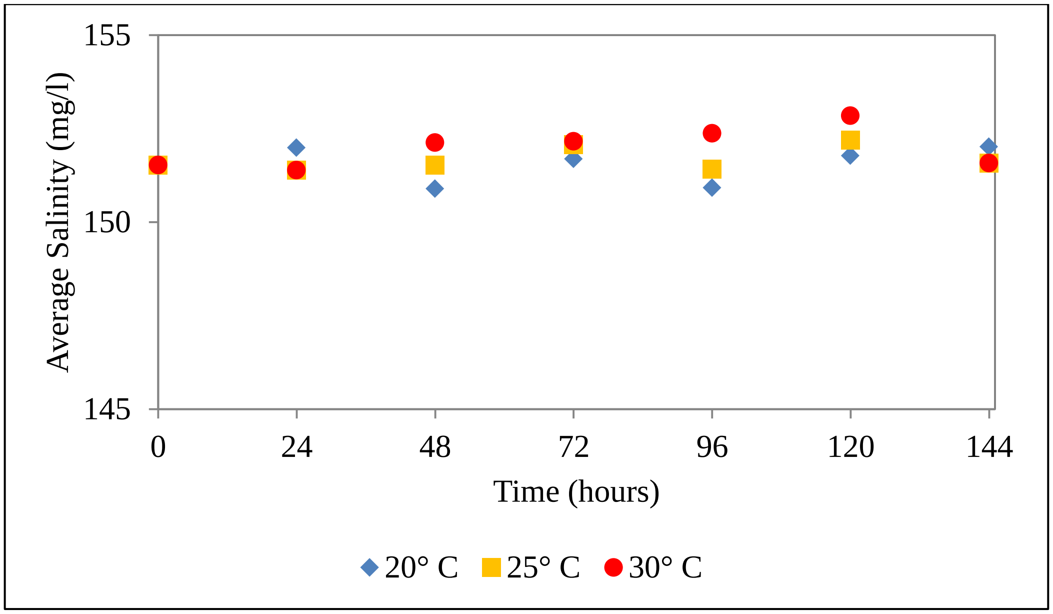


Figure 4.6 Salinity of the water samples comprising 2.9% groundwater for the tests conducted at 20°C, 25°C, 30°C temp. conditions

4.3.1.5 pH of water samples

The measurement of the pH of the synthetic potable water samples taken during the three simulated residence time tests conducted under 20ºC, 25ºC, and 30ºC are presented in Table B5 of Appendix B. The table includes the time of analysis, duplicate measurement, average, and standard deviation of the pH result. The average result of the water pH including the standard deviation was plotted against the time of analysis for the three experiments in Figure 4.7. The pH plots in the three figures have shown a slight increase in the pH trends. The slight upward increase in water pH is possibly due to the formation of hydroxyl ions (OH^-) as a result of chlorination of the water samples with sodium hypochlorite (White, 1992).

The average results of water pH for the three tests are plotted together in Figure 4.7 for comparison purposes. The figure shows no clear difference between the pH trends for the three tests.

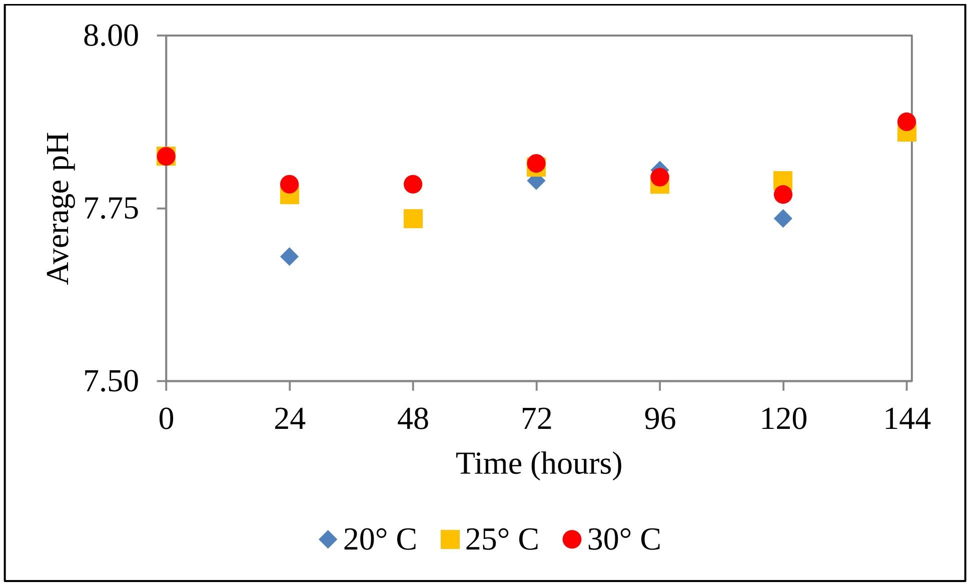


Figure 4.7 pH of the water samples comprising 2.9% groundwater for the tests conducted at 20°C, 25°C, 30°C temp. conditions

4.3.2 Simulated residence time test for synthetic potable water samples comprising 8.0% groundwater

As it was shown in sections 4.2.2 and 4.2.3, increasing the percentage of groundwater had led to the increase of the concentration of bromide and organic constituents within the synthetic potable water samples. Such increase in the bromide and organic compounds in water samples would increase the chance for the development of higher levels of bromoform in the case of water chlorination. Therefore, in this section, an attempt was made to assess the development of bromoform whilst conducting three simulated residence time tests for synthetic potable water samples comprising 8.0% groundwater (a higher percentage of groundwater than the one utilised in section 4.3.1 which was 2.9%). This percentage of groundwater represented the average value employed by the Doha blending facility in the production of potable water. The following subsections demonstrate the results of bromoform, residual chlorine, UV_{254} absorbance, salinity, and pH analyses measured during the execution of the three simulated residence time tests.

4.3.2.1 Bromoform

The results of bromoform analysis for the three simulated residence time tests conducted on synthetic potable water samples comprising 8.0% groundwater under different temperature conditions (20°C, 25°C, and 30°C) are presented in Table B6 of Appendix B. The table shows descriptive analysis for bromoform results. The result shows a gradual increase in the development of bromoform with the time progression for the three tests (Figure 4.8). In comparison to the bromoform results obtained in the previous section (section 4.3.1) for the tests conducted on the synthetic potable water samples comprising 2.9% groundwater, higher bromoform levels were obtained for the tests carried out on the synthetic potable water samples comprising 8.0% groundwater. A detail assessment of the difference between the bromoform concentration levels for all the tests are demonstrated in section 4.3.5.

A visual comparison between the three bromoform trends over the time based on their temperature conditions are presented in Figure 4.8. The concentration of bromoform at the end of the experiments were 33.9 μg/l, 34.2 μg/l, and 35.0 μg/l, for the temperature conditions of 20°C, 25°C, and 30°C, respectively. This result indicated that the increase in temperature conditions (in the order of 20°C, 25°C, 30°C) had resulted in a relative increase in bromoform concentration in the synthetic potable water samples by the end of the tests. The development of more bromoform is attributed to the presence of a relatively faster chemical reaction rate in the test conducted under 30ºC.

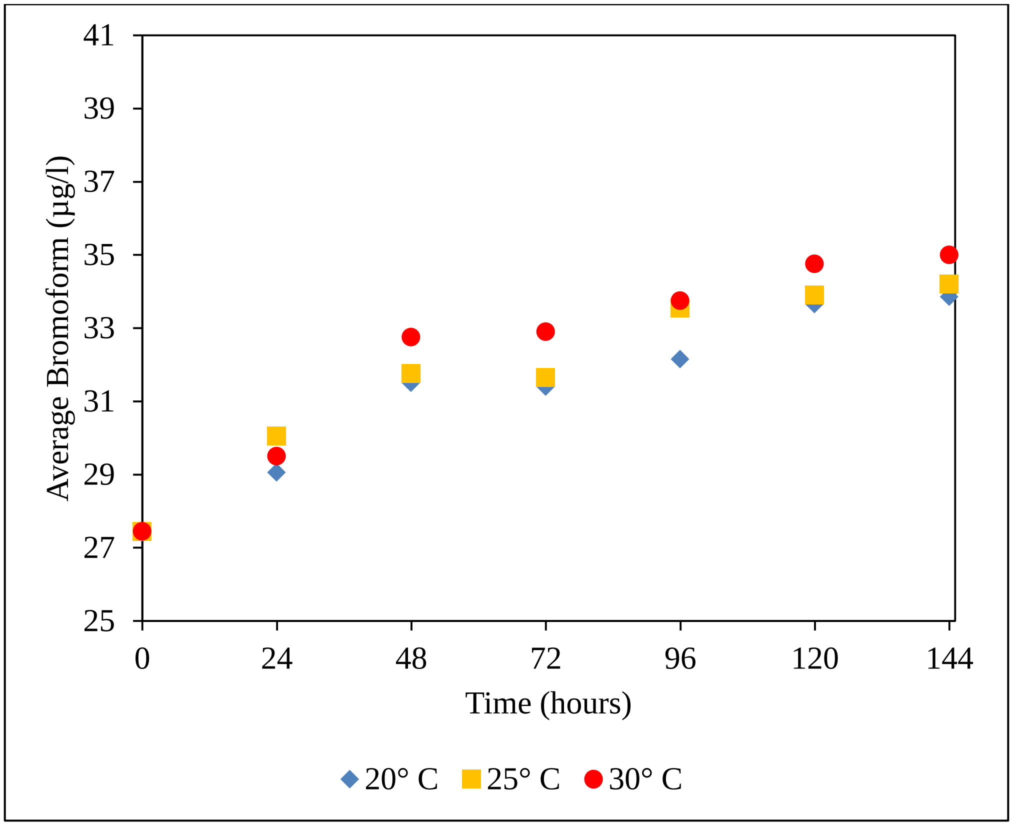


Figure 4.8 Bromoform concentration in the water samples comprising 8.0% groundwater for the tests conducted at 20°C, 25°C, 30°C temp. conditions

4.3.2.2 Residual chlorine

The results of residual chlorine analysis for the three simulated residence time tests conducted under 20°C, 25°C, and 30°C temperature conditions on synthetic potable water samples comprising 8.0% groundwater are presented in Table B7 of Appendix B. The table demonstrates descriptive statistical analysis of the residual chlorine results obtained. The residual chlorine measurements were plotted against the time of analysis for the experiments conducted under 20ºC, 25ºC, and 30ºC temperature conditions in Figure 4.9. The result shows that the residual chlorine in the tests had decreased along the progression of the tests. Furthermore, the lowest concentration of the residual chlorine was measured at the end of the three experiments as 0.680 mg/l, 0.665 mg/l, and 0.650 mg/l, for the temperature conditions of 20°C, 25°C, and 30°C, respectively. Among these concentrations, the residual chlorine of 0.650 mg/l was the lowest concentration measured due to the relatively high temperature conditions of the test (30º C). In comparison to the residual chlorine result obtained in the test conducted on the synthetic potable water samples comprising 2.9% groundwater (section 4.3.1.2), a relatively higher chlorine decay was observed for the synthetic water samples comprising 8.0% groundwater during the test. This is mainly because the synthetic potable water samples comprising 8.0% groundwater consist of more inorganic and organic compounds. As a result more compounds were available in the water samples for the reaction with residual chlorine, hence a faster decay of residual chlorine was observed.

The results of residual chlorine analysis obtained in the three tests (20ºC, 25ºC, 30ºC) were plotted against the time of analysis in Figure 4.9. In comparison to the decay behaviour of residual chlorine for the three tests, the results showed that the decay of residual chlorine for the test carried out with temperature condition equal to 30º C was relatively faster from the 20º C and 25º C temperature conditions. This is mainly because at higher temperature level, the reaction rate would be expected to be high, consequently, this leads to a faster chlorine decay.

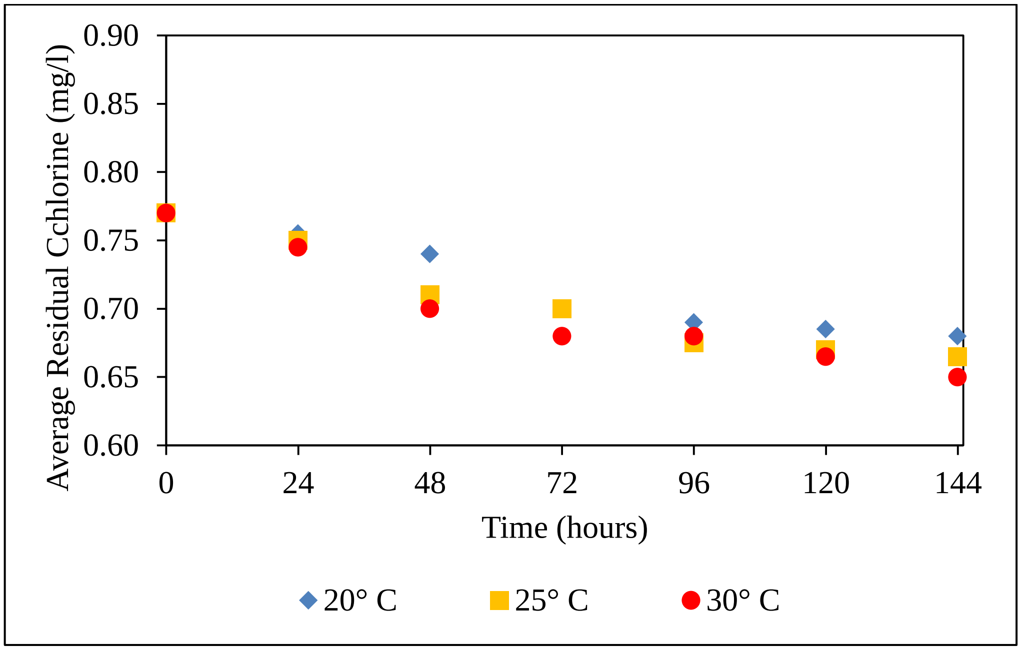


Figure 4.9 Residual chlorine concentration of the water samples comprising 8.0% groundwater for the tests conducted at 20°C, 25°C, 30°C temp. conditions

4.3.2.3 UV$_{254}$ Absorbance

The result of UV$_{254}$ absorbance measurements for the three simulated residence time tests conducted on synthetic potable water samples comprising 8.0% groundwater are presented in Table B8 of Appendix B. This table shows the descriptive statistics of the UV$_{254}$ measurements for the three experiments. The measurements of the UV$_{254}$ absorbance for the three experiments were plotted against the time of measurement in Figure 4.10. The graph shows a general decreasing pattern of the UV$_{254}$ absorbance values over time. The result of UV$_{254}$ absorbance for the test conducted on the synthetic water samples comprising 8.0% groundwater was higher than from those obtained in the experiments conducted on the water samples comprising 2.9% groundwater (section 4.3.1.3). This high UV$_{254}$ absorbance value is because more organic compound was gained in the synthetic potable water samples as a result of increasing the percentage of groundwater from 2.9% to 8.0% in the water samples.

In Figure 4.10 the measurements of the UV_{254} absorbance for the tests conducted under 20ºC, 25ºC, and 30ºC ambient temperature conditions were plotted against the time of measurement. The decrease in the UV_{254} absorbance over time for the water samples in the test conducted under 30ºC was higher than from those observed in the experiments conducted under 20ºC and 25ºC. This is because the high temperature conditions of the test (30ºC) resulted in a faster chemical reaction rate; hence, more chromophores were possibly destroyed in the organic compound over time (Gang et al., 2003).

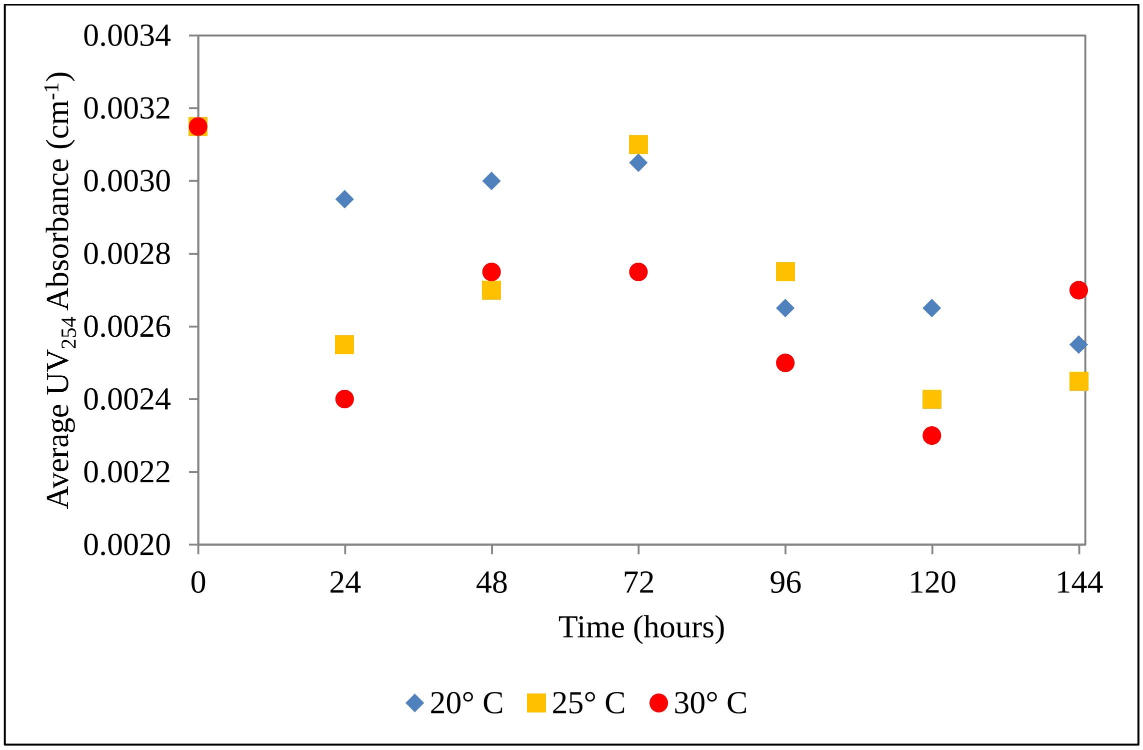


Figure 4.10 UV_{254} absorbance of the water samples comprising 8.0% groundwater for the tests conducted at 20°C, 25°C, 30°C temp. conditions

4.3.2.4 Salinity of water samples

The results of the estimated salinity for the synthetic potable water samples comprising 8.0% groundwater for the three simulated residence time tests are presented in Table B9 of Appendix B. The table demonstrates the descriptive statistics of the salinity results. Moreover, in Figure 4.11, the estimated salinity for the tests was plotted against the time of analysis. The salinity graph (Figure 4.11) shows no considerable change in the direction of the salinity trends. However, in comparison to the estimated water salinity for the synthetic potable water samples comprising 2.9% groundwater which was around 150 mg/l, the estimated salinity for the synthetic potable water comprising 8.0% groundwater was higher (slightly above 300 mg/l). This is due to increasing the groundwater proportion in the synthetic potable water samples which led to the introduction of more salt content to the water samples, hence, increasing the salinity of that water.

In comparison between the three salinity trends of the tests (20ºC, 25ºC, 30ºC), no clear visual difference was observed between those trends (Fig. 4.11). This is because that the salinity of water samples was not altered during the tests.

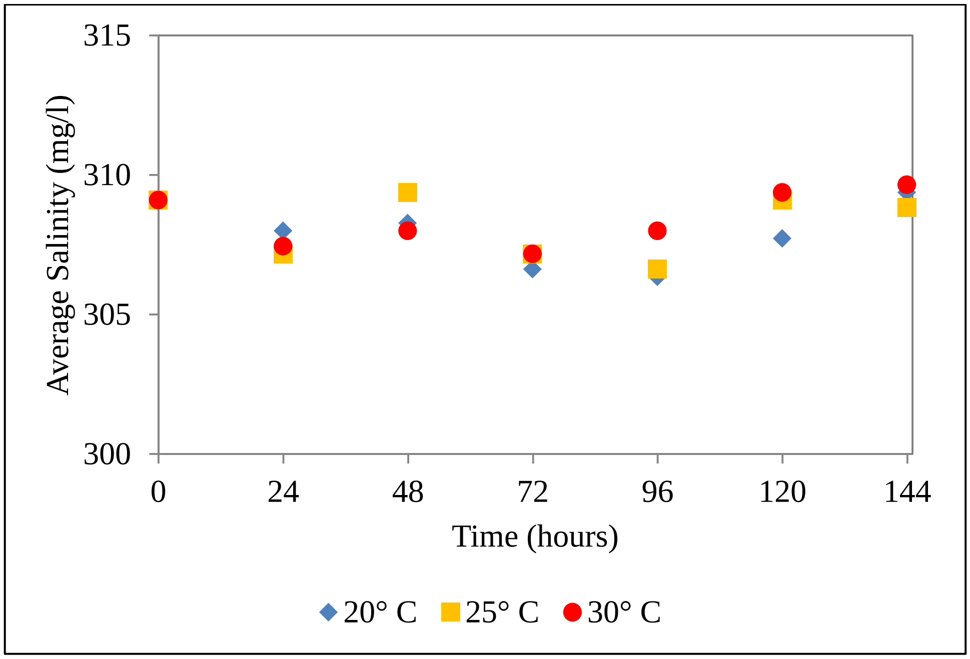


Figure 4.11 Salinity of the water samples comprising 8.0% groundwater for the tests conducted at 20°C, 25°C, and 30°C temp. conditions

4.3.2.5 pH of water samples

The results of the pH measurement of the synthetic potable water samples comprising 8.0% groundwater for the three simulated residence time tests are presented in Table B10 of Appendix B. The table shows a descriptive statistics for the pH measurements. The average pH measurements for the three tests were plotted against the time of measurement in Figure 4.12. The pH trends of the three experiments show a slight upward increase in the pH value over time. This increase in the water pH is due to the formation of hydroxyl ions as a result of chlorination of the water samples with sodium hypochlorite solution during the tests (White, 1992).

Moreover, the pH measurements for the three tests conducted under 20ºC and 25ºC, and 30ºC, temperature conditions were plotted together against the time of measurement for visual comparison of the measurements (Fig. 4.12). The Figure shows no distinct difference between the three pH trends over time. However, a general slight increase in the three trends is presented as previously reported.

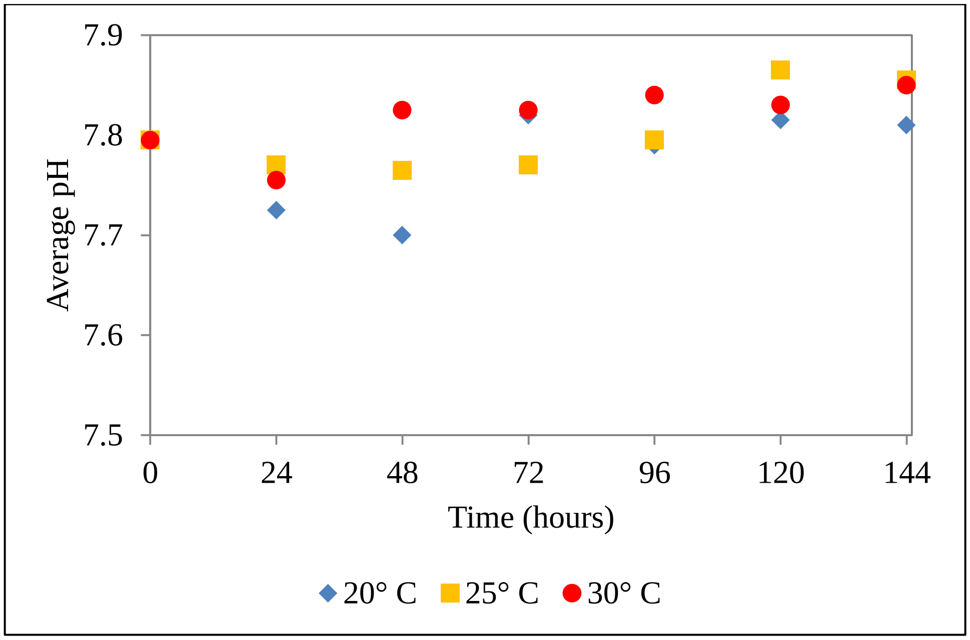


Figure 4.12 pH of the water samples comprising 8.0% groundwater for the tests conducted at 20°C, 25°C, 30°C temp. conditions

4.3.3 Simulated residence time test for synthetic potable water samples comprising 15.0% groundwater

In this section the investigation of the development of bromoform within synthetic potable water samples comprising 15.0% groundwater was carried out. This percentage of groundwater is considered the maximum amount utilised by the Doha blending facility in the production of potable water. Therefore, three simulated residence time tests on synthetic potable water samples comprising 15.0% groundwater under 20ºC, 25ºC, and 30ºC temperature conditions were conducted to reveal the effects of both the groundwater percentage and temperature conditions on the development of bromoform. The result of bromoform, in addition to the residual chlorine, UV_{254} absorbance, salinity, and pH of the water samples analysed are demonstrated in the following subsections.

4.3.3.1 Bromoform

The results of the bromoform analysis of the synthetic potable water samples for the three simulated residence time tests conducted under 20ºC, 25ºC, and 30ºC are presented in Table B11 of Appendix B. This table shows the descriptive analysis for the bromoform result obtained. The table shows that the result of bromoform increased with time for the three tests. Furthermore, the results of bromoform are plotted against the time of analysis for the three tests in Figure 4.13. According to the Figure, a gradual increase in the concentration of bromoform was observed with the progression of time. In comparison to the bromoform result obtained in the test conducted on the synthetic water samples comprising 2.9% and 8.0% groundwater, higher bromoform results were detected during the tests conducted on the water samples comprising 15% groundwater.

Moreover, the development of bromoform in the test conducted in 30ºC temperature conditions was higher than from those obtained from the tests conducted under 20ºC and 25ºC temperature conditions (Fig. 4.13).

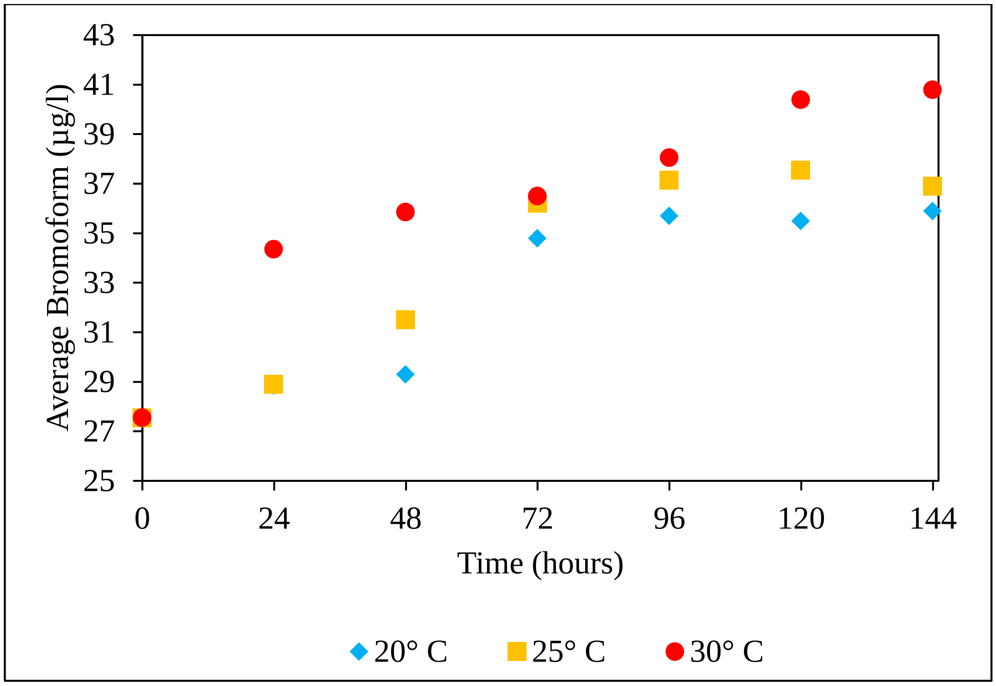


Figure 4.13 Bromoform concentration of the water samples comprising 15.0% groundwater for the tests conducted at 20°C, 25°C, and 30°C temp. conditions

4.3.3.2 Residual chlorine

The results of residual chlorine analysis of the synthetic potable water samples comprising 15% groundwater for the three simulated residence time tests are presented in Table B12 of Appendix B. The table demonstrates descriptive statistics for the residual chlorine results obtained from the experiments. The measurements of the residual chlorine for the three tests conducted are plotted against the time of analysis in Figure 4.14. The result shows that the concentration of residual chlorine for the three simulated residence time tests decreased along the duration of the tests. However, the decay level of residual chlorine in the synthetic potable water samples comprising 15.0% groundwater during the tests was higher than from those conducted on the synthetic potable water samples comprising 2.9% and 8.0% groundwater. The concentrations of the residual chlorine at the end of the nine tests conducted are presented in Table 4.6. In this table the effect of temperature and the percentage of groundwater utilised in the preparation of the synthetic potable water samples on the decay of residual chlorine are presented. The result indicated that both the temperature and the percentage of groundwater had a negative effect on the residual chlorine; the concentration of residual chlorine was relatively decreased by increasing the groundwater percentage and the temperature.

Table 4.6 The concentration of residual chlorine at the end of the tests

groundwater (%)	Temperature (° C)		
	20	25	30
2.9	0.720	0.690	0.660
8.0	0.680	0.665	0.650
15.0	0.645	0.605	0.575

The results of residual chlorine obtained from the tests conducted under 20ºC, 25ºC, and 30ºC temperature conditions were plotted against time of analysis in Figure 4.14. The figure indicated that the decay of residual chlorine was faster in the test conducted under 30ºC temperature condition as a result of the presence of high chemical reaction rate comparing to the other testes temperature conditions (20ºC and 25ºC).

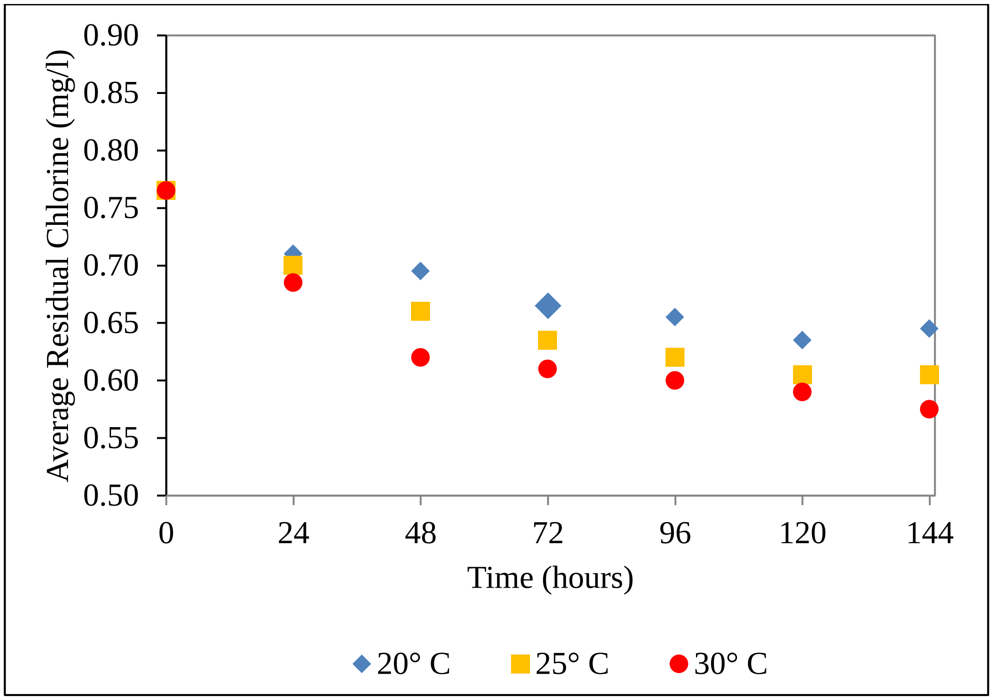


Figure 4.14 Residual chlorine analysis of the water samples comprising 15.0% groundwater for the tests conducted at 20°C, 25°C, and 30°C temp. conditions

4.3.3.3 UV_{254} Absorbance

The result of the UV_{254} absorbance measurements of the synthetic potable water samples conducted taken during the execution of the three simulated residence time tests are presented in Table B13 of Appendix B. The table demonstrates the descriptive statistics for the UV_{254} absorbance measurements obtained from the three experiments. The UV_{254} absorbance measurements for the three tests are plotted against the time of measurements in Figure 4.15. In general, the UV_{254} absorbance values of the water samples decreased with time for the three tests. The decrease in the UV_{254} absorbance is due to the saturation of organic compound ponds which in turn resulted in loss of the molecules' chromophores (Gang et al., 2003), as stated in the previous sections. The result of UV_{254} measurements at the end of all the tests are presented in Table 4.7. In addition, the table demonstrates the effects of temperature and the groundwater percentage utilised in potable water samples on UV_{254} absorbance. The result shows that temperature factors had almost a steady effect on the UV_{254} absorbance values with a slight tendency to decrease the UV_{254} absorbance value as the temperature of the water samples increased. On the other hand, the increase in the percentage of groundwater in the prepared water samples resulted in an increase in the UV_{254} absorbance values.

Table 4.7 UV_{254} absorbance at the end of the tests

Percentage of groundwater in the water samples	Temperature (°C)		
	20	25	30
2.9	0.00255	0.00245	0.00235
8.0	0.00280	0.00290	0.00280
15.0	0.00390	0.00385	0.00380

The results of UV_{254} absorbance measurements for the three tests conducted under 20ºC, 25ºC, and 30ºC temperature conditions were plotted together against the time of analysis (Fig. 4.15). The Figure shows that the UV_{254} absorbance values obtained in the test conducted under 30ºC temperature condition have relatively more decreased than in the other tests as a result of the high temperature condition of the test comparing to the others.

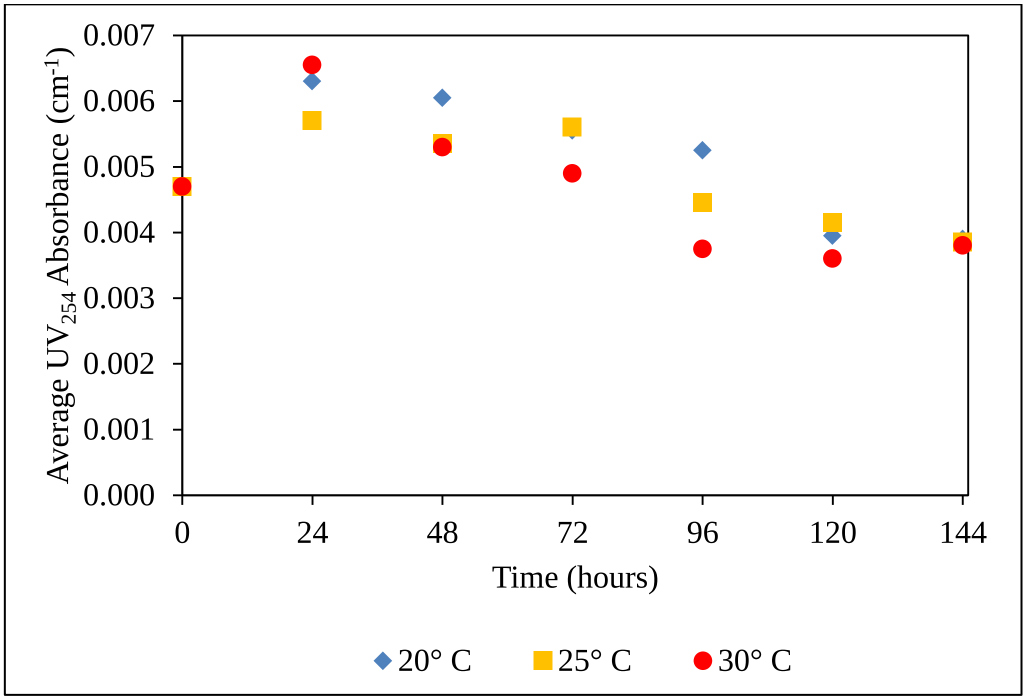


Figure 4.15 UV_{254} absorbance of the water samples comprising 15.0 % groundwater for the tests conducted at 20°C, 25°C, and 30°C temp. condition

4.3.3.4 Salinity

The estimated salinity of the synthetic potable water samples during the simulated residence time tests are presented in Table B14 of Appendix B. The table demonstrates the descriptive statistics of the salinity for the three experiments. The estimated salinity of the synthetic potable water samples for the three experiments was plotted against the time of measurement in Figure 4.16. The result of the estimated salinity for the synthetic potable water samples comprising 15.0% groundwater was higher than from those estimated for the synthetic potable water samples comprising 2.9% and 8.0% groundwater. This increase in the salinity of the water samples is due to the increase in the percentage of groundwater of the synthetic potable water samples. The estimated water salinity at the end of all the tests is presented in Table 4.8. The table shows that temperature has no effect on the salinity in the different temperature conditions. This is due to the fact that the temperature is considered as an external factor and does not affect the salt content of the water samples. However, an increase in the salinity was clearly observed with the increase in the percentage of groundwater.

Table 4.8 The estimated salinity (mg/l) of the water samples at the end of the tests

Percentage (%) of groundwater in the water samples	Temperature (° C)		
	20	25	30
2.9	152.0	151.6	151.6
8.0	309.4	308.8	309.7
15.0	512.1	510.1	509.0

The estimated salinity of the water samples obtained in the three tests conducted under 20ºC, 25ºC, and 30ºC were plotted together against the time of analysis in Figure 4.16. The figure shows that there was no clear difference between the salinity results in the three tests. This is because the tested water samples were prepared with similar groundwater to recarbonated water blending ratio (comprising 15% groundwater and 85% recarbonated water).

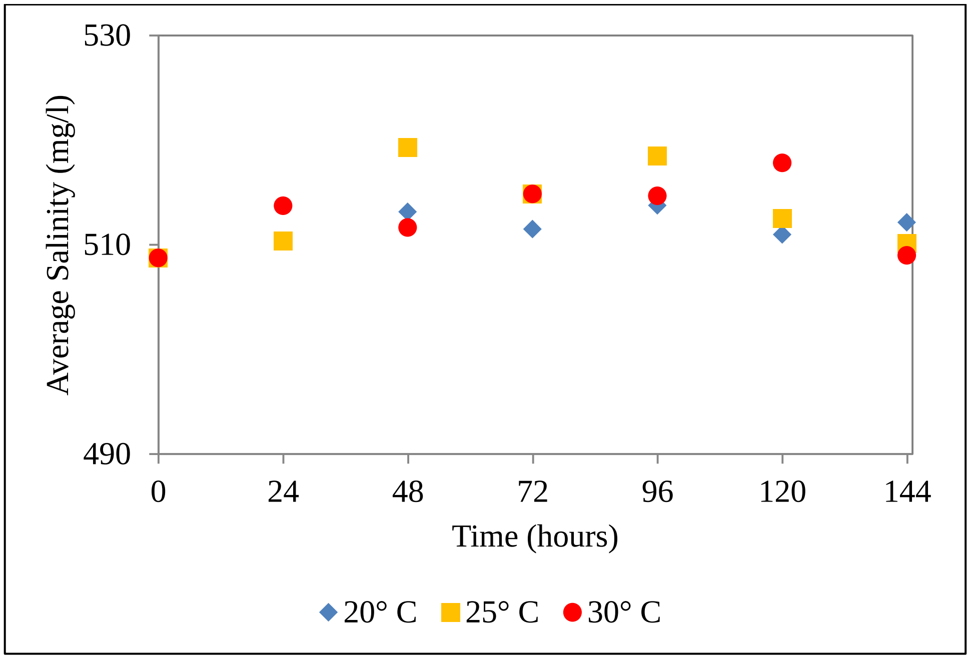


Figure 4.16 Salinity of the water samples comprising 15.0% groundwater for the tests at 20°C, 25°C, and 30°C temp. condition

4.3.3.5 pH of water samples

The results of pH measurements of the synthetic potable water samples comprising 15.0% groundwater which were measured during the execution of the three simulated residence time tests are presented in Table B15 of Appendix B. This table shows the descriptive analysis of the pH measurements for the three experiments. The pH measurements for the three experiments are plotted against the time of measurement in Figure 4.17. In these figures the pH trends showed a slight upward movement during the length of the tests. All the pH measurements at the end of the nine tests are included in Table 4.9. The table shows that both the temperature conditions and the different percentages of groundwater have no significant effects on the pH of the water samples.

Table 4.9 The pH of the water samples at the end of the tests

Percentage of groundwater in the water samples	Temperature (°C)		
	20	25	30
2.9	7.88	7.86	7.88
8.0	7.81	7.86	7.85
15.0	7.80	7.76	7.78

All the pH measurements from the three tests were plotted together against the time of measurement in Figure 4.17 to reveal any difference between such pH measurements. The graph shows no significant difference between the pH measurements of the three tests.

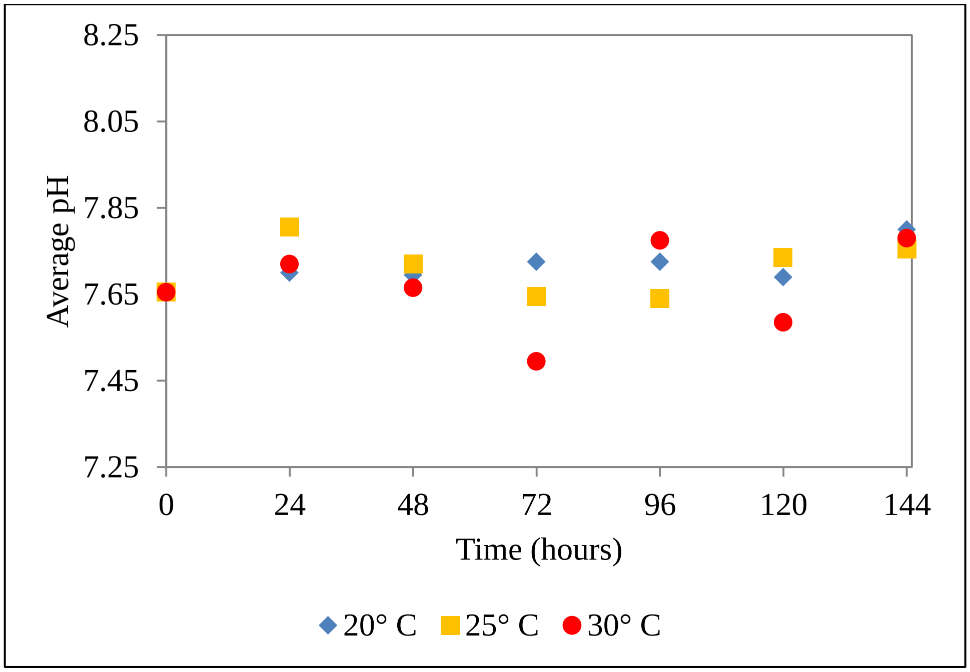
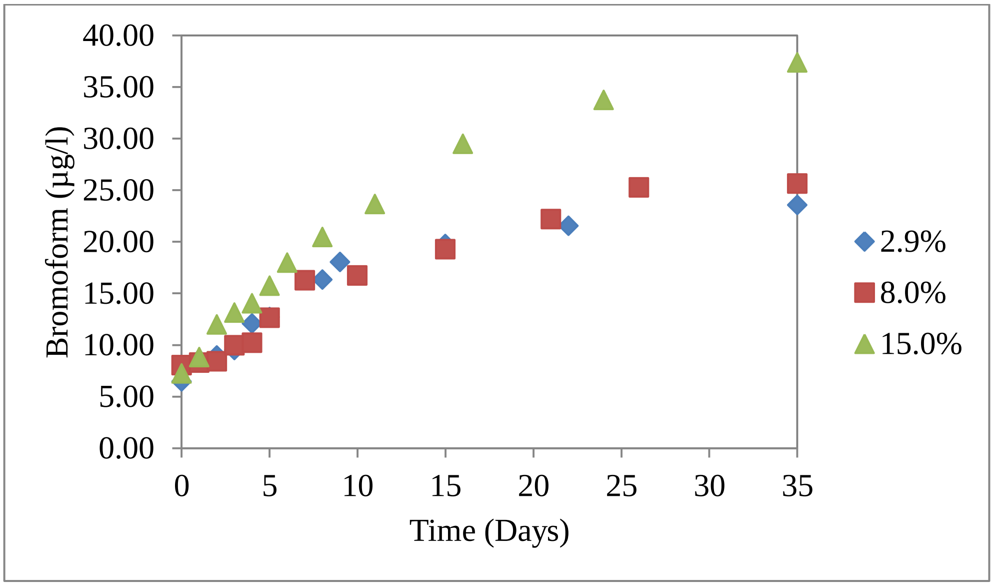


Figure 4.17 The pH of water samples comprising 15.0% groundwater for the tests at 20°C, 25°C, and 30°C temp. conditions

4.3.4 Simulated residence time test for synthetic potable water samples comprising 2.9%, 8.0%, and 15.0% groundwater under extended storage period and 30ºC temp. conditions

The bromoform results of the three simulated residence time tests conducted under extended storage period (> 30 days) and 30ºC temperature conditions is presented in Tables C1 – C3 in Appendix C. the results of bromoform are plotted against the time of analysis for the three tests in Figure 4.18. According to the Figure, a gradual increase in the concentration of bromoform was observed with the progression of time within the three conducted tests. Although bromoform concentration did not exceed the KEPA guideline limit (100 µg/l), the development of bromoform in water samples comprising 15.0% groundwater is relatively higher than the water samples comprising 2.9% and 8.0% groundwater.



4.18 Development of bromoform under extended storage period and 30ºC temperature conditions

4.3.5 Correlation between bromoform, chlorine demand, UV_{254} absorbance and pH of water samples

In this section the correlation analysis between the results of bromoform, chlorine demand, UV_{254} absorbance and pH of the water samples obtained from the simulated residence time tests was carried out to assess the type and strength of the relationship between such variables. A Spearman correlation test (a non-parametric correlation test) was utilised to determine the relationship between the considered variables as the variables were found to be significant (data was not normally distributed) using the normality test of Shapiro-Wilk. In addition, this correlation test was used because the data set of the study meets the test assumptions in which the dataset tested should be measured; for example, on an interval scale (the case of the study dataset) and the relationship between the considered variables should be monotonic i.e. the trend of the relationship between two variables should not be fluctuating. The following subsections demonstrate the results of the Spearman correlation test between the selected study variables.

4.3.5.1 Correlation between bromoform and Δ chlorine

The results of bromoform and Δ chlorine taken during the simulated residence time tests were used in the correlation test. Initially, the bromoform concentrations were plotted against Δ chlorine (Fig. 4.19) to visually inspect the distribution of the points. This graph shows that there is a positive relationship between bromoform and chlorine demand. A Spearman correlation test was run to assess the magnitude of such relationship using SPSS software. The output of the correlation test is as follows

Table 4.10 Spearman's correlation output

	Bromoform (µg/l)	Residual chlorine (mg/l)	UV254 absorbance (cm-1)	pH
Bromoform (µg/l)	1.000	0.914**	0.366**	-0.130
	.	0.000	0.007	0.350
	54	54	54	54

** Correlation is significant at the 0.01 level (2-tailed)

The result shows that there is a strong positive correlation between bromoform and chlorine concentrations which was statistically significant ($r_s(54) = 0.914, p < 0.001$). The positive relationship indicates that as the Δ chlorine increases, more bromoform is formed in the water samples. The chlorine, in the presence of bromide in the water matrix, influence the development of bromoform, in which, more bromoform is expected to be developed in the water samples with higher bromide and organic compounds concentration.

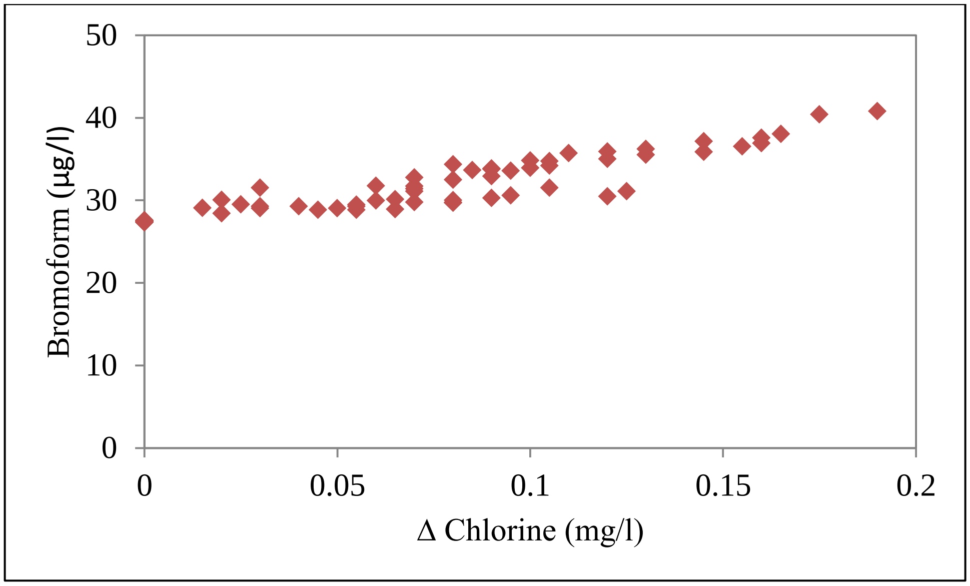


Figure 4.19 Scatter plot of bromoform and chlorine

4.3.5.2 Correlation between bromoform and UV$_{254}$ absorbance

In this section the bromoform and UV$_{254}$ absorbance results obtained from the simulated residence time tests were utilised in the correlation test. The results of bromoform were plotted against UV$_{254}$ absorbance in Figure 4.20 to visualise the distribution of the points. The graph shows a slight positive relationship between the bromoform and the UV$_{254}$ measurements. A Spearman test was run to assess such relationship between the two variables. The result of the test indicated that there was a positive moderate correlation between bromoform and UV$_{254}$ results which was statistically significant ($r_s(54) = 0.366$, $p = 0.007$). The result of the correlation supports the fact that the organic constituents of the water samples represented by UV$_{254}$ absorbance measurements are considered one of the main bromoform precursors (Rodrigues et al., 2007; Chowdhury et al., 2010). Accordingly, the higher the UV$_{254}$ absorbance, the more bromoform would develop in water.

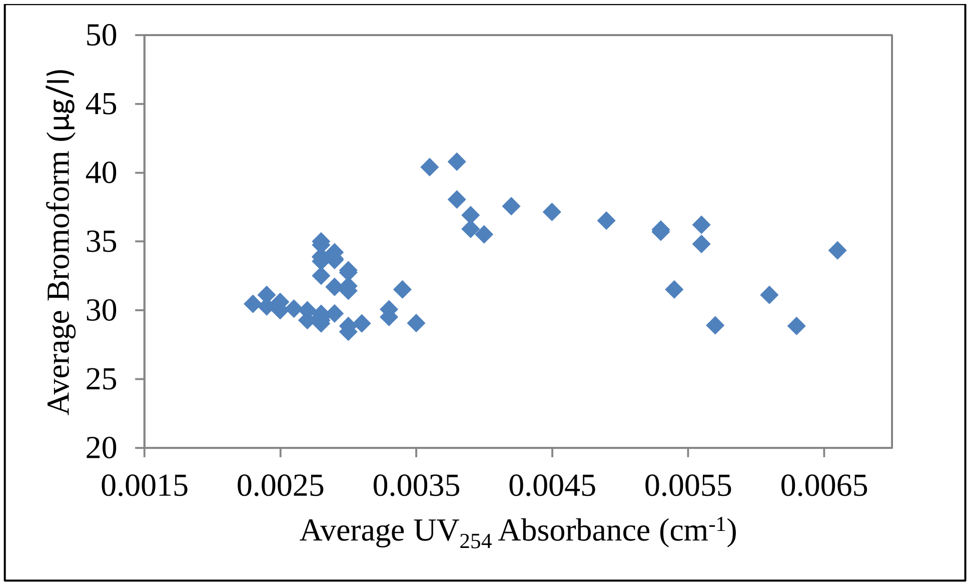


Figure 4.20 Scatter plot of bromoform and UV$_{254}$ absorbance measurements

4.3.5.3 Correlation between bromoform and pH

The results of bromoform and pH obtained from the simulated residence time tests were assessed using a correlation test to unveil the presence of any possible relationship between these two variables. A scatter plot was created for bromoform concentration against the water pH to inspect the distribution of the points (Fig. 4.21). The plot shows that bromoform tends to decrease with the increase in pH of the water samples. A Spearman test was run for the bromoform and water pH results to confirm such observation. The result of the Spearman test indicated that there was a negative weak relationship between the bromoform concentration and pH of the water which was statistically insignificant ($r_S(54) = -0.130, p > 0.05$). The insignificant result is apparently due to the fact that the pH of the water samples in the tests was not altered. However, the negative weak relationship is in agreement with the finding of Chowdhury (2013) in which the author observed a negative relationship between the development of bromoform and pH of the water samples.

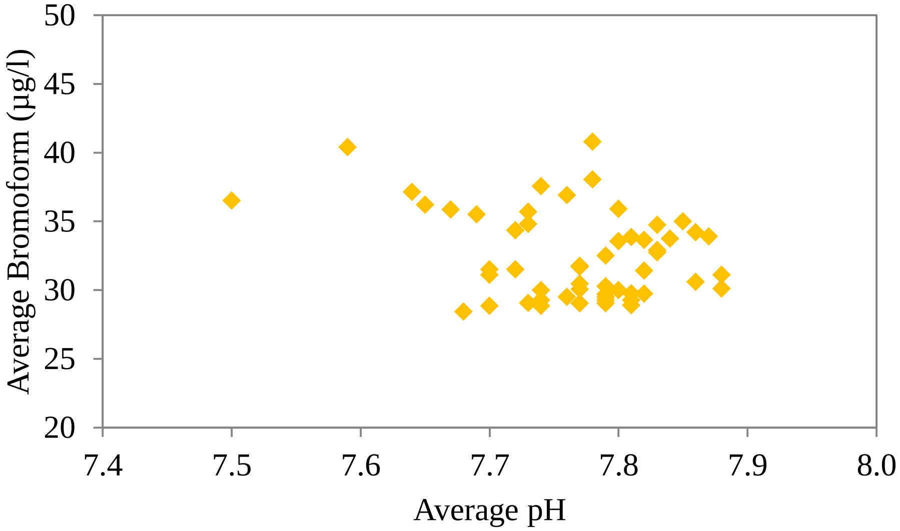


Figure 4.21 Scatter plot of bromoform and pH measurements

4.3.6 Mixed effects model

4.3.6.1 Introduction

In this section the results of bromoform from the nine simulated residence time tests were assessed by using a statistical model called a mixed effects model. This model was utilised to investigate the effect of the preparation method i.e. percentage of groundwater, temperature and storage period factors, on the development of bromoform in the synthetic potable water samples. In addition, the effects of interactions between the three factors on the development of bromoform were also determined. Furthermore, the test that produced the lowest bromoform levels among the other tests was determined by the model. The following subsections demonstrate the results obtained from running the Mixed-effects model.

4.3.6.2 The bromoform results

The bromoform results obtained from the nine simulated residence time tests are presented all together in Table 4.11. This table shows the three levels of preparation methods considered (2.9%, 8.0%, and 15.0%) and temperature factors (20°C, 25°C, and 30°C) in this study. Meanwhile, the storage period factor was represented by the time of analysis including 24 h, 48 h, 72 h, 96 h, 120 h, and 144 h. Moreover, each of the tests consisted of six bromoform measurements in which the top left measurement was the first analysed after 24 h, the top right measurement was the second obtained measurement after 48 h, the second row represented the third and fourth bromoform measurements taken after 72 h and 96 h, respectively, and the third row represented the fifth and sixth bromoform measurements taken after 120 h and 144 h, respectively. Furthermore, the total and average of each of the factors (preparation method and temperature) level are also presented in the table.

Table 4.11 The results of bromoform concentrations (µg/l) for the nine tests

		Preparation Method (groundwater % of synthetic potable water)				
		2.9	**8.0**	**15.0**	**Totals**	**Averages**
Temperature (º C)	**20**	28.4 28.8 29.0 29.3 30.0 30.1	29.1 31.5 31.4 32.5 33.7 33.9	28.9 31.1 34.8 35.7 35.5 35.9	569.6	31.6
	25	29.0 29.3 29.8 29.7 30.3 30.6	30.1 31.8 31.7 33.6 33.9 34.2	28.9 31.5 36.2 37.2 37.6 36.9	582.3	32.4
	30	29.3 29.5 29.7 30.0 30.5 31.1	29.5 32.8 32.9 33.8 34.8 35.0	34.4 35.9 36.5 38.1 40.4 40.8	605.0	33.6
Totals		534.4	586.2	636.3	1756.9	
Averages		29.6	32.6	35.4		32.5

Initially, the table shows an increase in the bromoform total and average concentrations for each level of the preparation methods and temperature factors as the level of those factors were increased. Moreover, the percentage increase of bromoform average from the 20°C to 30°C temperature levels was estimated as 6.3%. Meanwhile, the percentage increase of bromoform average from 2.9 to 15.0 levels of the preparation method was equal to 19.6%. This result indicates that the influence of the preparation methods factor is higher than the temperature factor on the development of bromoform in the synthetic water samples. The result of the investigation into the significance of the effect of the preparation methods and temperature factors and also the storage period factor and all their interactions, using a Mixed effects model, are presented in the proceeding subsections.

4.3.6.3 Assumptions of mixed effects model

The use of the linear mixed effects model requires assumptions of normality and homogeneity of the data to be validated to some degree before running such model. The assumptions of normality and homogeneity of variance were investigated for the bromoform results obtained from the nine tests. The Kolmogorov-Smirnova (K-M) test was used to assess the normality, whereas, the Levene’s test was used to investigate the homogeneity of variance of the data (Field, 2005). The following subsections demonstrate the result of the analysis of normality and homogeneity of variance.

4.3.6.3.1 Test of normality

The results of running the K-M test for the bromoform measurements to assess the normality of the bromoform measurements are presented in Tables 4.12, 4.13, and 4.14, for the preparation method, temperature, and storage period factors, respectively. The three tables show that the results of Kolmogorov-Smirnova tests for all the levels have a *p* value greater than 0.05 except for the level of the 24 hour storage period factor, which indicates normal distribution conditions for the data distribution in those levels. However, with regard to the result of the K-M analysis for the 24 hour level in which the data distribution was found not to be normal, the mixed effects model is considered robust to violation of the normality assumption (Blood et al., 2010).

Table 4.12 Test of normality for preparation method factor

level	Preparation method (GW %)	Kolmogorov-Smirnova		
		Statistic[1]	Df[2]	Sig.[3]
1	2.9%	0.118	18	0.200
2	8.0%	0.161	18	0.200
3	15.0%	0.186	18	0.099

(1) K-M statistic value
(2) Degree of freedom
(3) Significance

Table 4.13 Test of normality for temperature factor

level	Temperature (° C)	Kolmogorov-Smirnova		
		Statistic[1]	Df[2]	Sig.[3]
1	20	0.163	18	0.200
2	25	0.187	18	0.097
3	30	0.138	18	0.200

(1) K-M statistic value
(2) Degree of freedom
(3) Significance

Table 4.14 Test of normality for storage period factor

level	Storage period (hours)	Kolmogorov-Smirnova		
		Statistic[1]	Df[2]	Sig.[3]
1	24	0.326	9	0.007
2	48	0.199	9	0.200
3	72	0.163	9	0.200
4	96	0.179	9	0.200
5	120	0.180	9	0.200
6	144	0.156	9	0.200

(1) K-M statistic value
(2) Degree of freedom
(3) Significance

4.3.6.3.2 Test of homogeneity of variance

The result of Levene’s test undertaken to assess the variance of data in the experiments are presented in Table 4.15. The result shows that the significance values for the temperature and storage periods are more than 0.05, hence, the variances are not significantly different. On the other hand, the result of Levene’s test for the preparation method indicates that the significance value is less than 0.05, which implies that the variance is significantly different; as a result the assumption of homogeneity of variance within the preparation method was not met. However, in the case where the number of measurements is equal in all experiment groups (this is the same as in this research study; six measurements in each test), the model is considered robust against the violation of homogeneity of variance (Kinnear & Gray, 2011).

Table 4.15 Test of homogeneity for preparation method, temperature and storage period factors

Factor	Levene’s Statistic[1]	df1[2]	df2[3]	Sig.[4]
Preparation method	8.901	2	51	0.000
Temperature	0.985	2	51	0.380
Storage period	1.378	5	48	0.249

(1) Levene’s Statistic value
(2) Degree of freedom 1
(3) Degree of freedom 2
(4) Significance

4.3.6.4 Mixed effects model output

A mixed effects model was fitted for the bromoform results obtained from the nine tests. In this model, the bromoform measurements were used as the dependant variable, meanwhile, three independent variables were assigned including the temperature and preparation method as the fixed effects, and the storage period as a random effect. The two-way interactions between the three independent variables including temperature by preparation method, preparation method by storage period, and temperature by storage period were examined. The coefficients of the model (Table 4.16) were used to determine the overall significance of the factors on bromoform development.

Table 4.16 The significance of the main effects and their interactions

Factor		df	Mean Square	F	Sig.
Intercept	Hypothesis	1	57106.421	2075.622	0.000
	Error	5	27.513		
Preparation method (groundwater %)	Hypothesis	2	143.658	31.263	0.000
	Error	10	4.595		
Temperature	Hypothesis	2	17.644	53.423	0.000
	Error	10	0.330		
Storage period	Hypothesis	5	27.513	6.204	0.009
	Error	9.213	4.434		
Temperature * Preparation method	Hypothesis	4	5.529	11.262	0.000
	Error	20	0.491		
Preparation method * Storage period	Hypothesis	10	4.595	9.359	0.000
	Error	20	0.491		
Temperature * Storage period	Hypothesis	10	0.330	0.673	0.737
	Error	20	0.491		

Table 4.16 outlines the significance (e.g. $p > 0.5$ is not significant; $p \leq 0.05$ is significant; $p < 0.01$ is highly significant; $p < 0.001$ is very highly significant) of the main and the interaction effects between the variables. The result indicates that the preparation method, temperature, and storage period have a very highly significant effect ($p < 0.001$ for preparation method and temperature, and $p = 0.009$ storage period) on bromoform development. Furthermore, the interaction effect of the temperature and preparation method, and in addition the interaction effect of the preparation method and storage period have showed a very highly significant effect ($p < 0.001$) on the development of bromoform in the water samples. However, the result shows that there is no significant interaction effect between temperature and storage period on bromoform development i.e. $p = 0.737$. These results are discussed separately in the following sections.

4.3.6.5 Preparation method effects (groundwater %) on bromoform development

The very highly significant effect ($p < 0.001$) of the preparation method on bromoform development reflects the influence of increasing the percentage of groundwater in the synthetic potable water sample. This increase in the groundwater percentage led to an increase in the amount of bromoform precursors including bromide and organic constituents which in turn had encouraged the development of more bromoform in the water samples during the chlorination of water. The development of higher concentrations of bromoform in the water samples has been clearly observed from the result of the average bromoform estimate for the preparation method factor. The model estimates and their corresponding 95% confidence intervals for the average bromoform concentration developed under the effect of preparation method factor across the three temperature conditions and the storage period are presented in Table 4.17. The table shows that the estimate of average bromoform concentration for the level three (35.33 µg/l) of preparation method factor was higher than from those of the level one (29.68 µg/l) and two (32.54 µg/l). Furthermore, the result of estimates of average bromoform concentration (Table 4.17) indicates that the percentage increases were 9.6% and 19.0% for the level two and three of the preparation method factor, respectively. This indicates that the average concentration of bromoform has slightly increased as a result of increasing the percentage of groundwater in the synthetic potable water samples from 2.9% to 15.0%.

Table 4.17 The bromoform estimates of the three levels of preparation method factor

Level	Preparation method (Groundwater%)	Estimate of average bromoform (µg/l)	95% Confidence interval	
			Lower bound (µg/l)	Upper bound (µg/l)
1	2.9	29.68	29.34	30.03
2	8.0	32.54	32.20	32.89
3	15.0	35.33	34.99	35.68

Moreover, the significant difference between the amounts of bromoform developed in the water samples across the three levels of preparation method factor were investigated by conducting a pair comparison test. Table 4.18 shows the *p*-values result for all of the paired comparisons between the three levels (2.9%, 8.0%, and 15.0%) of preparation method factor. The results indicated that the amount of bromoform developed across the levels of preparation method factor concentrations are significantly different ($p < 0.001$). This implies that increasing the percentage of groundwater i.e. in the order of 2.9%, 8.0%, 15.0% in the synthetic potable water samples resulted in a significant increase in the development of bromoform across these levels.

Table 4.18 The differences between preparation method levels represented by p-values

Preparation method (Groundwater %)	**8.0**	**15.0**
2.9	<0.001	<0.001
8.0	-	<0.001

4.3.6.6 Temperature effects on bromoform development

The temperature was also found to have a very highly significant effect i.e. $p < 0.001$ on the development of bromoform in the synthetic potable water (Table 4.16). This is because the fact that the effect of temperature is well documented in the literature as it increases the reaction rate (Chowdhury, 2009), hence it is possible that more reaction product is formed. The model estimates and their corresponding 95% confidence intervals for the average bromoform concentration produced in the executed tests by the effect of the three temperature levels across all the preparation method and storage period levels are presented in Table 4.19. The table shows that the estimate of average bromoform concentration for the level three (33.59 µg/l) of temperature factor was higher than from those of level one (31.64 µg/l) and level two (32.33 µg/l).

Table 4.19 The bromoform estimates of the three levels of temperature factor

Level	Temperature (°C)	Estimate of average bromoform (µg/l)	95% Confidence interval	
			Lower bound (µg/l)	Upper bound (µg/l)
1	20	31.64	31.29	31.98
2	25	32.33	31.99	32.68
3	30	33.59	33.25	33.93

The significant differences between the levels of temperature factor were investigated based on the amount of the developed bromoform in the water samples using a pair comparison test. The results of the pair comparison test conducted between the temperature factor levels are presented in Table 4.20. The results indicated that the differences between all the three levels of temperature factor were highly significant (p = 0.007 between 20° C and 25° C, $p < 0.001$ for both of 20°C and 30°C, and 25°C and 30°C).

Table 4.20 The differences between temperature levels represented by p-values

Temperature (°C)	**25**	**30**
20	0.007	<0.001
25	-	<0.001

4.3.6.7 Storage period effects on bromoform development

The effect of the storage period on the bromoform development was found to be a very highly significant which indicates that the extended storage period time of 144 hours encouraged the development of more bromoform in the water samples. The model estimates and their corresponding 95% confidence intervals for average bromoform concentration produced as a result of the extended storage period across all preparation methods and temperature levels are presented in Table 4.21. The result indicated that the bromoform concentration increased with the increase of the storage period.

Table 4.21 The bromoform estimates of the six levels of storage period factor

Level	Storage Period (hours)	Estimate of average bromoform (μg/l)	95% Confidence interval	
			Lower bound (μg/l)	Upper bound (μg/l)
1	24	29.72	29.23	30.20
2	48	31.34	30.85	31.82
3	72	32.45	31.96	32.93
4	96	33.30	32.81	33.78
5	120	34.05	33.56	34.54
6	144	34.27	33.79	34.76

Table 4.22 represents the significant difference between the six storage period levels, the results of *p*-values indicated a significant difference between most of the six levels of the storage period factor. However, the difference between storage period level 120 and 144 was found to be not significant (*p* = 0.509).

Table 4.22 The differences between storage time levels represented by p-values

Storage period (Hours)	48	72	96	120	144
24	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
48	-	0.003	< 0.001	< 0.001	< 0.001
72	-	-	0.018	< 0.001	< 0.001
96	-	-	-	0.034	0.008
120	-	-	-	-	0.509

4.3.6.8 Interaction effects between preparation method and temperature on bromoform development

The model estimates and their corresponding 95% confidence intervals for average bromoform concentration produced by the combination effect of the three preparation method by the three temperature factors throughout the storage period are presented in Table 4.23. The results showed that the bromoform concentration increased gradually in the water samples as a result of increasing both the temperature level and percentage of groundwater (Figure 4.22).

Table 4.23 The bromoform estimates based on the effects of preparation method and temperature

Preparation method (groundwater%)	Temperature (° C)	Estimate of average bromoform (µg/l)	95% Confidence Interval	
			Lower bound (µg/l)	Upper bound (µg/l)
2.9%	20	29.28	28.68	29.87
	25	29.77	29.17	30.37
	30	30.00	29.41	30.60
8.0%	20	31.99	31.40	32.59
	25	32.53	31.93	33.12
	30	33.11	32.51	33.71
15.0%	20	33.64	33.05	34.24
	25	34.70	34.10	35.30
	30	37.66	37.06	38.26

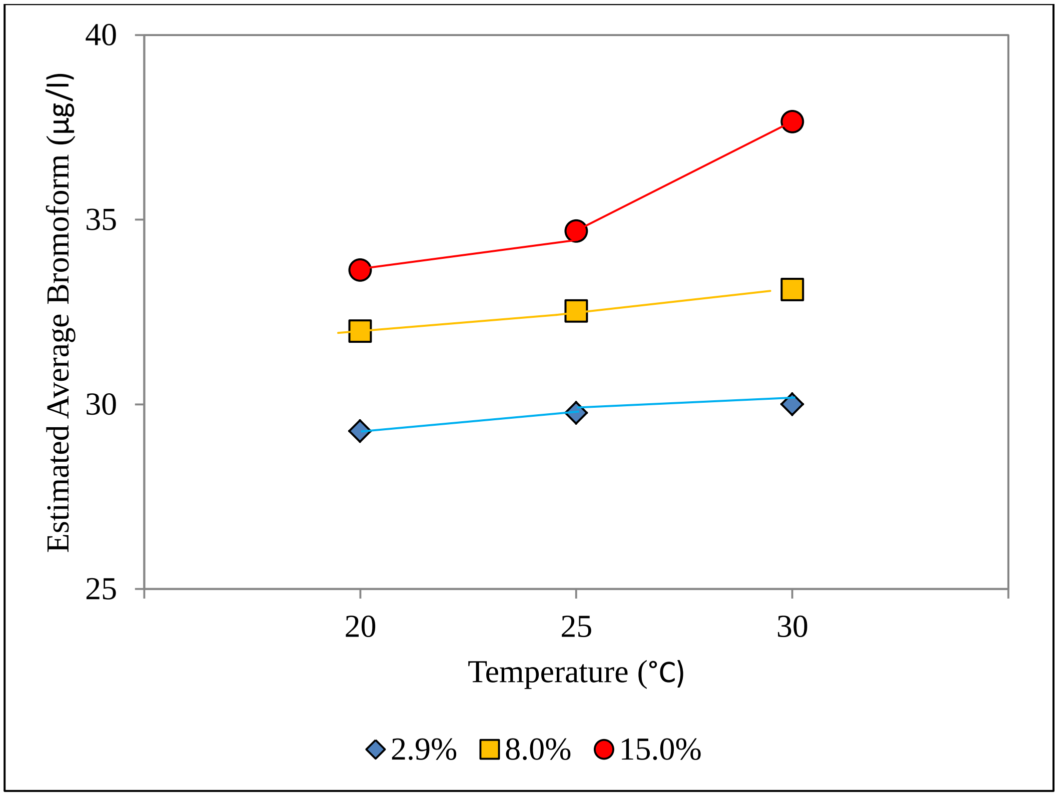


Figure 4.22 The interaction effect of preparation method (groundwater %) and temperature on bromoform development

Table 4.24 shows *p*-values results for all of the paired comparisons between the combination effect of the preparation method and temperature. The result indicated that the bromoform concentration is significantly different between all three temperature levels for the 15% preparation method level. On the other hand, it is only significantly different between 20°C and 30°C for the 8.0% preparation method level. Finally, the bromoform concentration is not significantly different between the three temperature levels for the 2.9% preparation method level.

Table 4.24 The differences between temperature levels according to preparation method levels represented by p-values

Preparation method (groundwater%)	**Temperature (° C)**	**25**	**30**
2.9%	**20**	0.237	0.088
	25	-	0.571
8.0%	**20**	0.201	0.012
	25	-	0.166
15.0%	**20**	0.017	<0.001
	25	-	<0.001

4.3.6.9 Interaction effects between preparation method and storage period on bromoform development

The model estimates and their corresponding 95% confidence intervals for average bromoform concentration produced by the combination effect of the three preparation methods by the storage period levels across the three temperature levels are presented in Table 4.25. The result showed that the bromoform concentration increased in water samples by increasing the percentage of groundwater and storage period duration (Figure 4.23).

Table 4.25 The bromoform estimates of combination effect of preparation method and storage period

Preparation method (groundwater %)	Storage period (hours)	Average bromoform concentration for 20°C, 25°C, and 30°C tests (µg/l)	95% Confidence interval	
			Lower bound (µg/l)	Upper bound (µg/l)
2.9%	24	28.91	28.07	29.76
	48	29.19	28.35	30.03
	72	29.51	28.66	30.35
	96	29.66	28.81	30.50
	120	30.23	29.39	31.08
	144	30.60	29.76	31.44
8.0%	24	29.53	28.69	30.38
	48	32.00	31.16	32.85
	72	32.00	31.16	32.84
	96	33.27	32.42	34.11
	120	34.10	33.26	34.94
	144	34.35	33.51	35.19
15.0%	24	30.70	29.86	31.54
	48	32.82	31.97	33.66
	72	35.83	34.99	36.68
	96	36.97	36.12	37.81
	120	37.82	36.97	38.66
	144	37.87	37.02	38.71

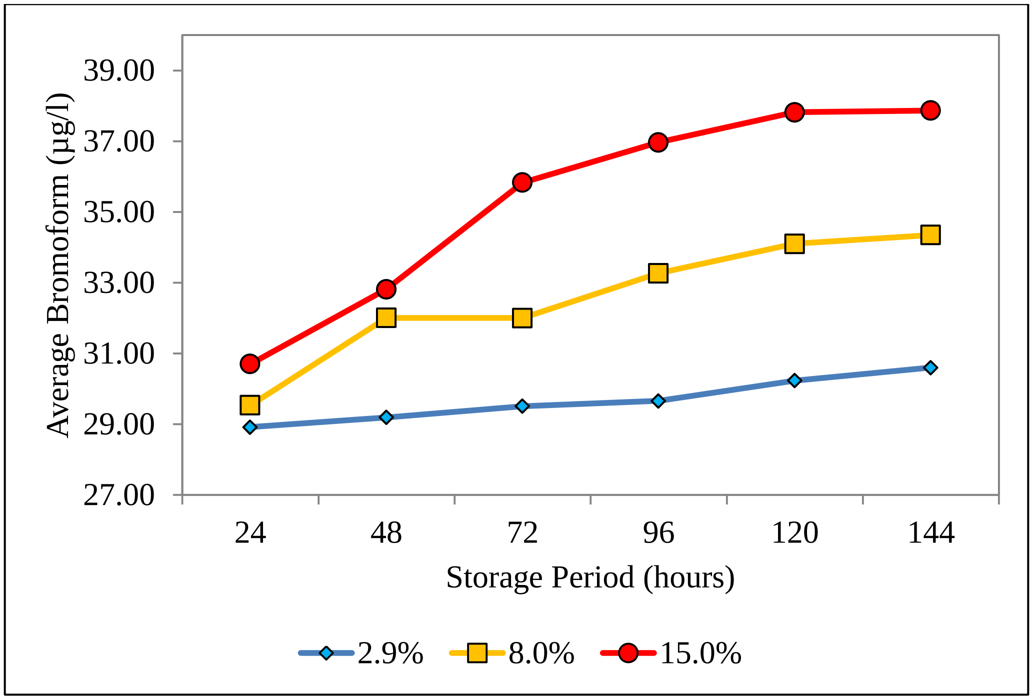


Figure 4.23 The combination effect of preparation method (groundwater %) and storage period on bromoform development

The maximum bromoform concentration as a result of the three preparation method levels was achieved on a storage period of 144 hours which is the end of the test duration (Table 4.26). The table shows that the highest average bromoform concentration was formed across the tests conducted on synthetic potable water comprising 15.0% groundwater at the end of the tests i.e. at 144 hours. Meanwhile, the lowest average bromoform concentration was formed across the test conducted on the water samples comprising 2.9% groundwater.

Table 4.26 The bromoform estimates based on storage period factor at 144 hours across the preparation method levels

Storage period (Hours)	Preparation method (groundwater %)	Average bromoform (µg/l)	95% Confidence interval	
			Lower bound (µg/l	Upper bound (µg/l)
144	2.9%	30.60	29.76	31.44
	8.0%	34.35	33.51	35.19
	15.0%	37.87	37.02	38.71

Table 4.27 shows *p*-values results for the paired comparisons between the combination effect of the preparation method at a storage period of 144 hours. The results indicated that the bromoform concentration is significantly different between the three preparation method levels at this storage period.

Table 4.27 The differences between preparation method levels at a storage period of 144 hours

Storage period (Hours)	**Preparation method (groundwater%)**	**8.0%**	**15.0%**
144	**2.9%**	<0.001	<0.001
	8.0%	-	<0.001

4.4 Bromoform predictive model

4.4.1 Linear bromoform model

4.4.1.1 Introduction

The predictive modelling is a technique often used in the field of drinking water quality to predict the probability of a disinfection by-product developing in drinking water. In this study, a multiple regression analysis was used to formulate a bromoform predictive model. The purpose of the model is to forecast the concentration of bromoform in potable water based on the measurements taken during the implementation of the simulated residence time tests. The data obtained from nine simulated residence time tests (experimental conditions: synthetic water comprising 2.9%, 8.0% and 15.0% of groundwater under 20°C, 25°C, and 30°C temperatures) were employed in building a bromoform predictive model. Thereafter, the bromoform predictive model created was used to predict bromoform concentration in fresh potable water samples collected at the Doha blending facility by utilising a separate data set obtained from conducting simulated residence time tests on fresh potable water samples. Finally, an assessment of the bromoform predictive model was conducted by estimating the mean absolute deviation (MAD) and the root mean of the squared prediction errors (RMSPR).

4.4.1.2 Model parameters

The measurements of storage period, residual chlorine, UV_{254} absorbance, water pH, and bromide obtained during the execution of three simulated residence time tests for the synthetic potable water samples comprising 2.9%, 8.0% and 15.0% of groundwater were used in building a bromoform predictive model based on the assigned temperature for each experiment (20°C, 25°C, and 30°C). The measurements of storage period, residual chlorine, UV_{254} absorbance, water pH, temperature and bromide parameters, in addition, to the interactions between temperature*blending ratio, storage period*blending ratio, and storage period*temperature were used as independent variables; whereas, bromoform was used as a dependent variable in building the predictive model. A multiple regression analysis was conducted using SPSS software to obtain the coefficient of each dependent variable. The output of the analysis including correlation between the model variables, model summary, ANOVA, residual plot, model coefficients are presented in the following subsections.

4.4.1.3 Descriptive statistics

The first table in the output of the regression analysis is a table of the descriptive statistics for each variable included in the developed bromoform predictive models (Table 4.28). The average, standard deviation, and number of the measured variables are presented.

Table 4.28 Descriptive statistics of the model variables

No.	Variable	Mean	Std. Deviation	N
1	bromofom	31.81	3.46	63
2	bromide	0.0113	0.0064	63
3	temperature	25	4	63
4	storage period	72	48	63
5	residual chlorine	0.698	0.054	63
6	UV_{254} absorbance	0.0036	0.0011	63
7	pH	7.77	0.07	63
8	temp*blending ratio	215.83	131.54	63
9	storage*blending ratio	621.60	601.41	63
10	storage period*temperature	1800.00	1260.97	63

4.4.1.4 Correlation between the model variables

Table D1 of Appendix D shows the pair wise correlations between the bromoform and each of the independent variables in one hand and the pair wise correlations among the independent variables in the other hand. The correlation matrix shows that bromoform is correlated with all of the independent variables, however, only four of the independent variables (i.e. residual chlorine, storage period, blending ratio, and bromide) are correlated with bromoform at a 0.05 significant level, whereas, temperature and UV_{254} absorbance are correlated with bromoform at 0.116 significant level. On other hand, the correlation matrix shows that there is a perfect collinearity between blending ratio and bromide (r = 1), consequently, only one of these two independent variables included in the bromoform predictive model (i.e. bromide), and hence, six independent variables were utilised in development of bromoform predictive model of this study. In addition, the result of the correlation matrix indicated that there is a relatively high correlation between storage period and residual chlorine (r = 0.72). This situation may cause the presence of the problem of multicollinearity; two or more of the explanatory variables are highly correlated which leads to unpredictable change of the coefficient estimates if a small change occurs with model data. However, the multicollinearity issue does not affect the forecast power or reliability of the predictive models (Funica, 2009).

4.4.1.5 Model summary

Table 4.29 shows the multiple correlation coefficient (R) which is a measure of the prediction power of the model was 0.97. Furthermore, the coefficient of determination (R^2) which is the proportion of variance of bromoform that can be explained by the independent variables – storage period, residual chlorine, UV254 absorbance, bromide, ph, and temperature was 0.942 which means that the independent variables explain 94.2% of the variability of bromoform.

Table 4.29 Model Summary

Model	R	R^2	Adjusted R^2	Std. Error of the Estimate
1	0.970^a	0.942	0.932	0.9028797

4.4.1.6 ANOVA

Table 4.30 shows ANOVA output of the multiple regression analysis. The result indicated that model is significant (p = 0.001). This means that the independent variables (storage period, residual chlorine, UV254 absorbance, bromide, pH, and temperature) statistically significantly predict bromoform in the model and that the relationship found in the model between bromoform and the independent variables was not due to mere chance.

Table 4.30 ANOVA

Model	Sum of Squares	df	Mean Square	F	Sig.
Regression	698.088	9	77.565	95.150	0.000[a]
Residual	43.205	53	0.815		
Total	741.293	62			

4.4.1.7 Regression assumptions

The appropriateness of the linear regression model for the study data was evaluated by examining residual histogram and plots of the developed bromoform model. Figures 4.24, 4.25 and 4.26 shows the histogram of residuals, normal probability-probability plot, plot of standardised predicted values against standardised residuals, respectively. Figure 4.24 shows histogram of residuals which provide a visual assessment for the normality assumption. The figure demonstrates that the measurement errors in the response variables are normally distributed (bell shape).

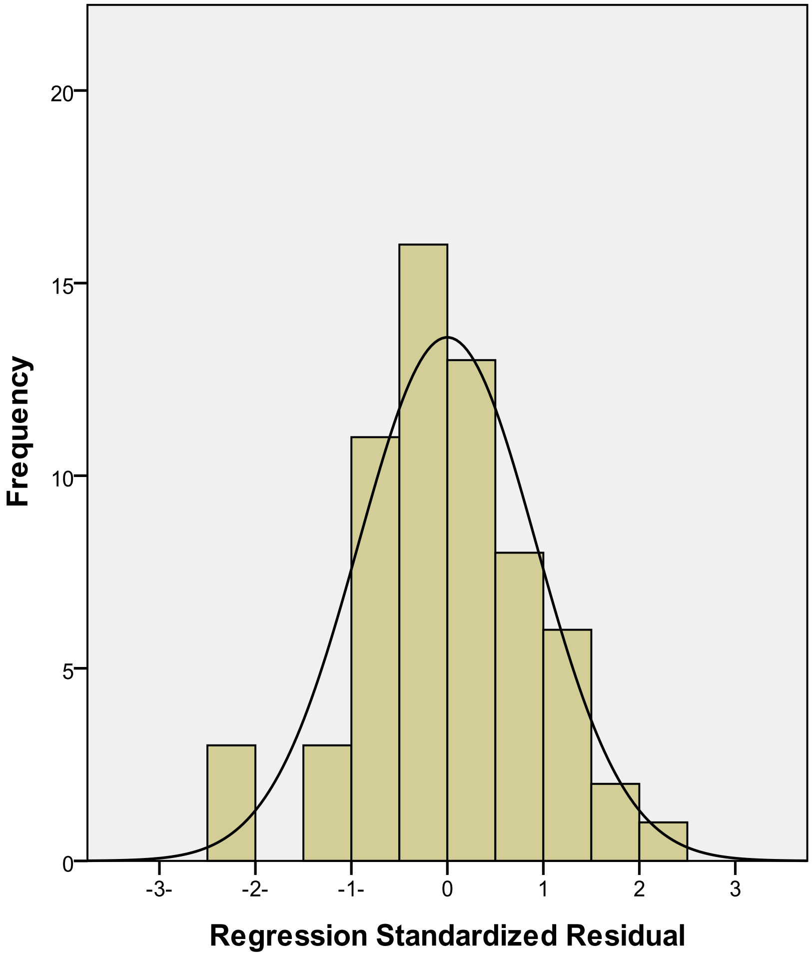


Figure 4.24 Histogram of residuals

Figure 4.25 shows the normal probability-probability (P-P) plot which based on the standardised residuals of the model. The points on the normal probability plot falls along the straight diagonal line, which indicates the residuals are normally distributed, hence, normality assumption is satisfied.

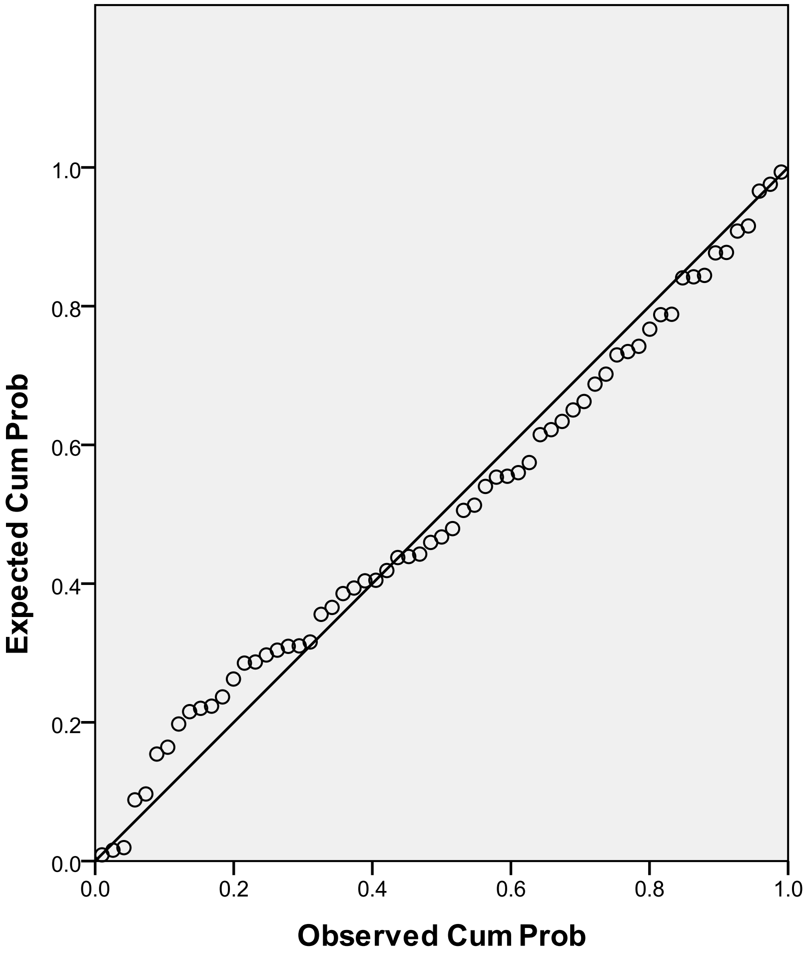


Figure 4.25 Normal probability-probability plot

Figure 4.26 shows the residuals on the vertical axis and the predicted values on the horizontal axis. The points on the residual plot are randomly dispersed and there is no clear pattern for the points (U-shaped or inverted U), therefore, the linear regression model utilised is appropriate for the data.

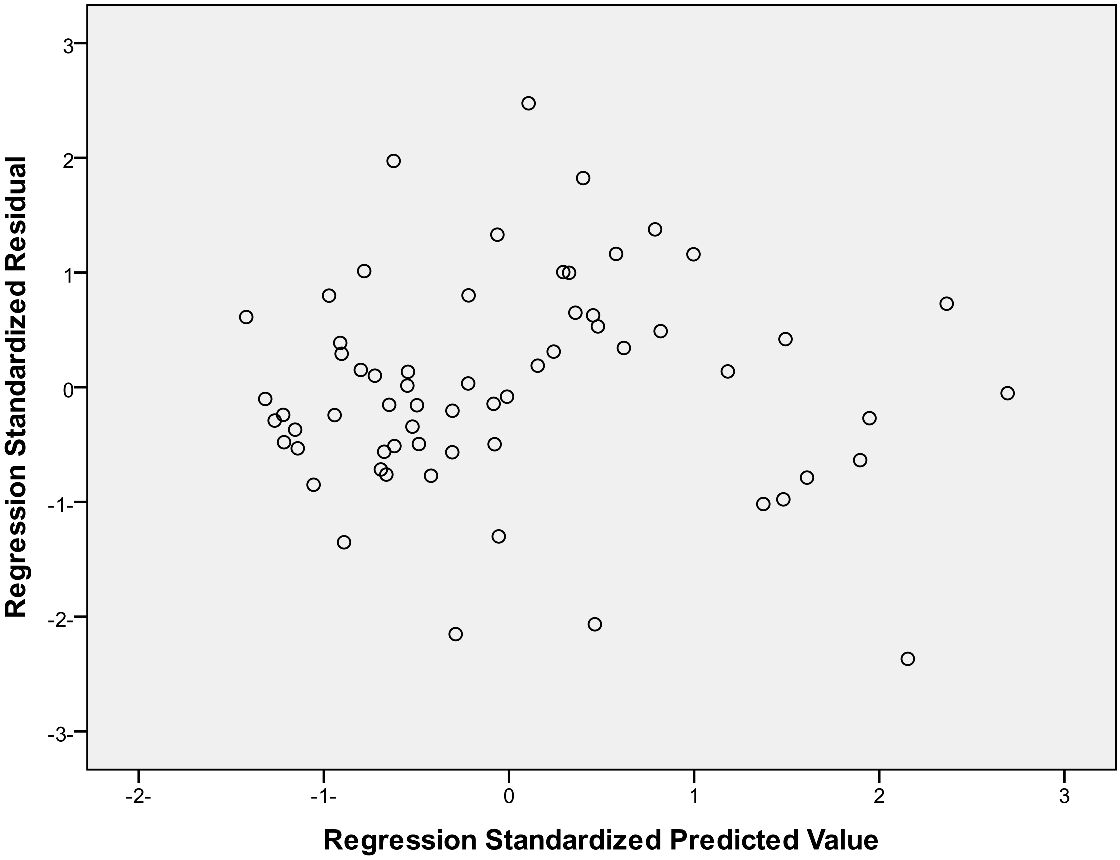


Figure 4.26 Plot of standardised predicted values against standardised residuals

4.4.1.8 Model coefficients

The values of the regression coefficients in the model are presented in Table 4.31 (column B). The model regression coefficients indicate how much bromoform varies with an independent variable if all the other independent variables are kept constant. The coefficients were used to build the bromoform predictive model.

Table 4.31 Coefficients of the predictive model

Model	Unstandardized Coefficients		Standardized Coefficients	t	Sig.
	B	Std. Error	Beta		
(Constant)	68.935	16.365		4.212	0.000
temperature	-0.085-	0.072	-0.101-	-1.184-	0.242
bromide	-355.389-	130.681	-0.659-	-2.720-	0.009
UV_{254}	-233.193-	276.730	-0.073-	-0.843-	0.403
pH	-1.063-	2.206	-0.022-	-0.482-	0.632
storage period	-0.005-	0.015	-0.075-	-0.345-	0.731
residual chlorine	-38.257-	8.363	-0.597-	-4.575-	0.000
temperature* blending ratio	0.017	0.006	0.665	2.945	0.005
storage period* blending ratio	0.003	0.001	0.542	5.148	0.000
storage period * temperature	0.0003	0.001	-0.109-	-0.471-	0.639

The coefficient table shows that there were four independent variables that found to be significant in the model, namely, bromide, residual chlorine, the interaction between temperature and blending ratio, and the interaction between storage period and blending ratio. The other variables were found to be insignificant in the presence of these four variables in spite of the fact that they were found pair wise correlated with bromoform; this can be explained by the correlation found among the independent variables. The most influential explanatory variables in the model are the ones with high absolute standardized coefficient (Beta), namely, the interaction between temperature and blending ratio, bromide, residual chlorine, and the interaction between storage period and blending ratio, respectively.

4.4.1.9 Bromoform predictive model

The bromoform predictive model developed in this study upon residual chlorine, UV_{254} absorbance, storage period, pH, temperature, bromide, the interactions between temperature with blending ratio, storage period with blending ratio and storage period with temperature is as follows (**Equation 1**):

$$\begin{aligned}\hat{B} &= 68.935 - (0.085 \times temperature) - (355.389 \times bromide) - (233.193 \times UV_{254}\,absorbance) \\ &- (1.063 \times pH) - (0.005 \times storage\ period) - (38.257 \times residual\ chlorine) \\ &+ (0.017 \times temperature * blending\ ratio) + (0.003 \times storage\ period * blending\ ratio) \\ &+ (0.0003 \times storage\ period * temperature)\end{aligned}$$

In comparison between the bromoform predictive model formulated in this study and those created in the previous studies (Malcolm Pirnie Inc., 1993; Montgomery Watson, 1993; Siddiqui et al., 1994; Rathbun, 1996; Rodrigues et al., 2007) the previous models were built based on parameters obtained from experiments conducted on river water samples; whereas, the created bromoform model in this study is based on experiments conducted on synthetic potable water samples comprising of groundwater and recarbonated water. Furthermore, Rathbun (1996) and Rodrigues et al., (2007), in their experiments, have added bromide solution in the water samples to promote the development of bromoform during chlorination. The addition of bromide in river water samples does not reflect the concentration of bromide in such natural raw water. Therefore, the formulated predictive bromoform models based on such experiments could not be used to forecast bromoform or even other disinfection by-products in a real situation. In contrast, in this research study, the chemical characteristic of the tested raw water was almost similar to the one utilised at potable water production facility (Doha blending facility). Furthermore, the storage period factor is important and has a strong effect on the development of bromoform. This factor was included in the developed bromoform model of this study, however, the factor was not presented in the Rathbun (1996) and Rodrigues et al., (2007) models.

4.4.1.10 Model prediction performance

In this research study, the performance of the developed bromoform predictive model was assessed by estimating the mean absolute deviation (MAD) and the root mean of the squared prediction errors (RMSPR) which are two measures of predictive effectiveness indicated by Sittikariya (2006). The expressions of MAD and RMSPR are as follows

$$MAD = \frac{1}{n^*}\sum_{i=1}^{n^*} | y_i - \hat{y}_i |$$

$$RMSPR = \sqrt{\frac{\sum_{i=1}^{n*} (Y_i - \hat{Y}_i)^2}{n*}}$$

where:

Y_i = the value of bromoform concentration in the i^{th} validation case,

$\hat{Y}_i$ = the predicted value of bromoform concentration for the i^{th} validation case based on the validation data set, and,

n* = the number of cases in the validation data set.

The mean absolute deviation was considered to be the mean of the absolute differences between the measured bromoform concentrations obtained from the tests conducted on fresh potable water samples comprising 2.9% groundwater which were collected from the Doha blending facility (NB the fresh water dataset has not been used in the model development and was considered as the model validation dataset), and the predicted bromoform which was estimated by fitting the independent parameters measured in the tests (i.e. residual chlorine, storage period, pH, UV_{254} absorbance, temperature, and bromide). The estimated absolute error between the measured and predicted bromoform results are presented in Table 4.32. In addition, the measured and predicted bromoform results are plotted in Figure 4.27. According to the results, the absolute error ranged between 0.06 and 2.04. The mean absolute deviation, as calculated by the following equation, was found to be MAD = 0.99 which indicates that the model has a good prediction ability of for the concentration of bromoform in water. In addition to the mean absolute deviation MAD, the root mean of the squared prediction errors (RMSPR) was also calculated to assess the validity of the model. It is found that the root mean of the squared prediction errors value of RMSPR = 1.18 , is close to its corresponding root mean squared errors value of RMSE = 0.903 for the same predictive model. This means that the RMSE statistic was not seriously biased and it provided an appropriate indication of the predictive ability of the derived models (Kutner et al., 2005).

Table 4.32 Comparison between measured and predicted bromoform concentrations using a separate dataset not used in the model development

bromide	temp.	storage period	residual chlorine	UV_{254} absorbance	pH	blending ratio	measured bromoform	predicted bromoform	RMSPR*	MAD**
0.004	20	0	0.660	0.0033	7.99	2.9	30.25	32.29	4.17	2.04
0.004	20	24	0.625	0.0038	8.00	2.9	32.45	33.59	1.29	1.14
0.004	20	48	0.630	0.0035	8.00	2.9	33.20	33.55	0.13	0.35
0.004	20	72	0.625	0.0036	8.00	2.9	33.45	33.81	0.13	0.36
0.004	20	96	0.620	0.0032	8.00	2.9	33.90	34.19	0.08	0.29
0.004	20	120	0.615	0.0024	8.00	2.9	35.60	34.65	0.90	0.95
0.004	20	144	0.615	0.0016	8.00	2.9	36.00	34.93	1.15	1.07
0.004	25	0	0.660	0.0033	7.99	2.9	30.25	32.11	3.47	1.86
0.004	25	24	0.625	0.0036	7.99	2.9	32.80	33.47	0.45	0.67
0.004	25	48	0.620	0.0034	8.02	2.9	33.70	33.76	0.00	0.06
0.004	25	72	0.620	0.0033	8.03	2.9	34.10	33.86	0.06	0.24
0.004	25	96	0.615	0.0035	8.02	2.9	34.55	34.11	0.19	0.44
0.004	25	120	0.610	0.0023	8.12	2.9	36.00	34.57	2.06	1.43
0.004	25	144	0.605	0.0014	8.01	2.9	36.35	35.17	1.39	1.18
0.004	30	0	0.660	0.0033	7.99	2.9	30.25	31.94	2.84	1.69
0.004	30	24	0.625	0.004	8.08	2.9	33.45	33.10	0.12	0.35
0.004	30	48	0.620	0.0036	8.03	2.9	34.00	33.53	0.22	0.47
0.004	30	72	0.620	0.0032	8.09	2.9	34.65	33.65	1.00	1.00
0.004	30	96	0.610	0.0033	7.97	2.9	36.00	34.22	3.15	1.78
0.004	30	120	0.605	0.0022	8.07	2.9	36.30	34.65	2.71	1.65
0.004	30	144	0.600	0.0012	8.02	2.9	37.10	35.22	3.55	1.88

* root mean of the squared prediction errors
** mean absolute deviation

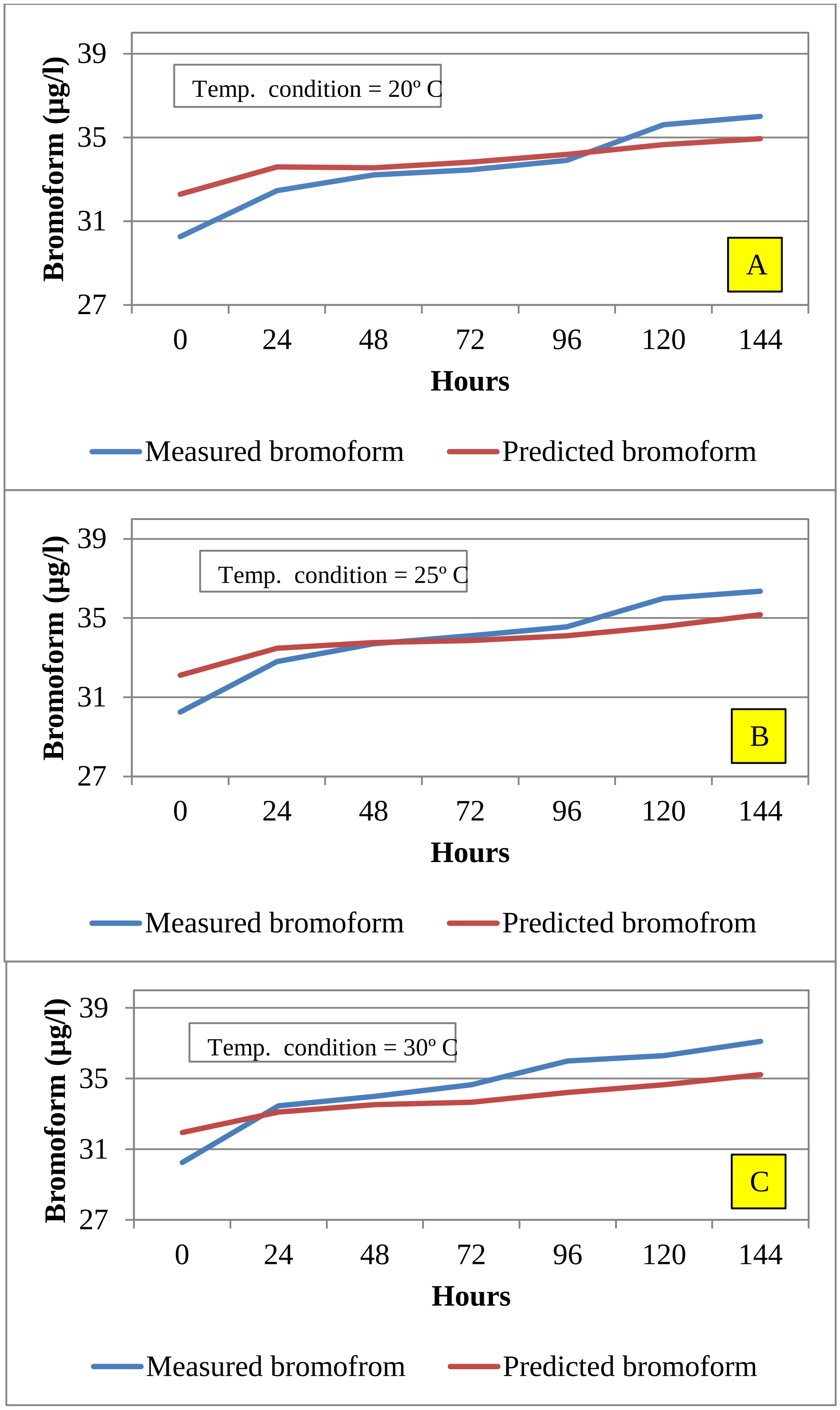


Figure 4.27 The prediction performance of the model against the measured result under three different temperature conditions: A=20 °C, B=25 °C and C=30 °C

4.4.1.11 Sensitivity analysis

The result of SA conducted to assess the effect of the parameters of the linear model on bromoform development is presented in Table 2 and Figure 1. The table shows the highest, average and lowest bromoform concentration obtained from manipulating each of the model parameters for 1000 iterations. The lowest (34.47 µg/l) and the highest (59.10 µg/l) bromoform concentrations were obtained during manipulating storage period parameter (Figure 1). The result shows the importance of the water storage period in encouraging the development of bromoform in which a positive relationship exists. The lowest bromoform concentration developed at time equal zero whereas the highest concentration found around time equal to 840 hours. The residual chlorine has the second most significant effect on development of bromoform in which the highest and lowest bromoform concentrations were obtained as 54.42 µg/l and 39.17 µg/l, respectively. The bromide comes in the third rank, in terms of the most significant factors that influence the development of bromoform. The highest and lowest bromoform obtained were 49.59 µg/l and 44.10 µg/, respectively. The temperature and UV_{254} absorbance parameters resulted in relatively similar highest and lowest concentration of bromoform and ranked fourth and fifth, respectively. The least model parameter that influence the bromoform development is pH. The sensitivity analysis results suggested that storage period, residual chlorine and bromide, respectively, were the most significant factors that influence the bromoform development.

Table 4.33 The statistics of the SA conducted on the parameters of the linear model (Equation 1), represented by bromoform concentration (µg/l)

Statistic	pH	Residual chlorine	UV_{254} absorbance	Temperature	Bromide	Storage period
Highest	43.48	54.42	47.33	47.73	49.59	59.10
Average	42.94	46.61	46.77	46.78	46.84	46.96
Lowest	42.41	39.17	46.21	45.80	44.10	34.47

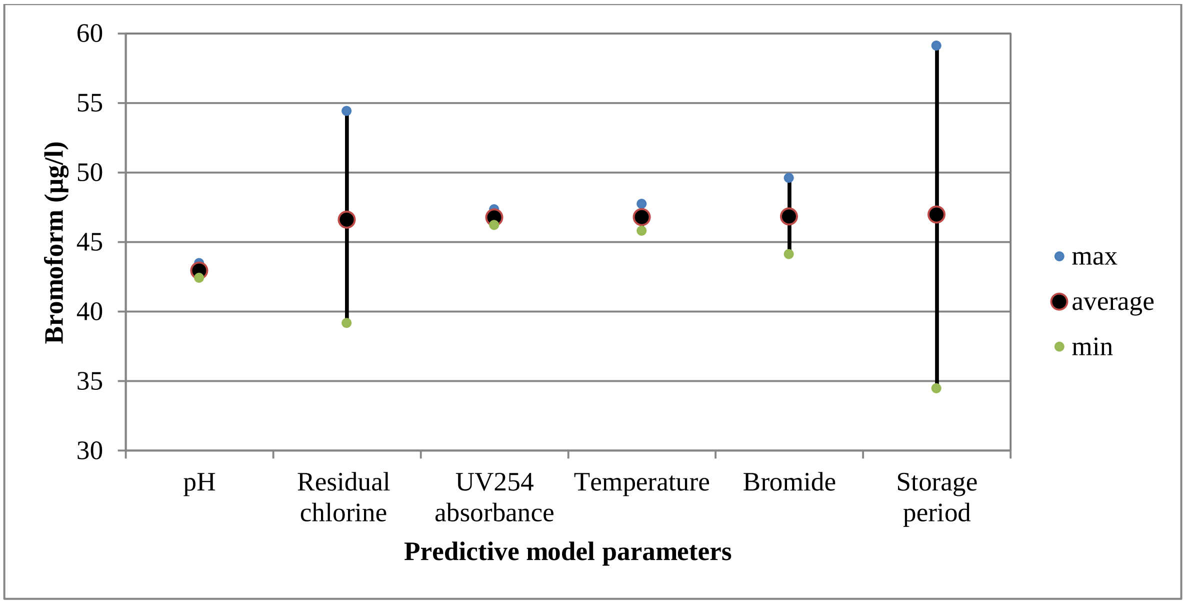


Figure 4.28 The parameters that have the most influence on the concentration on bromoform ranked in the following order: storage period, residual chlorine, bromide, temperature, UV_{254} absorbance and pH

4.4.1.12 Model validation for the 35 days duration

The second validation test of the bromoform predictive model (Equation 1) was carried out using dataset obtained from the three tests conducted over 35 days. The results of predicted bromoform is presented in Table 4.34. The result shows that there is a wide variation between all the predicted and measured bromoform. The predicted bromoform in some cases is higher four folds from the measured one. Although the first validation test which was conducted on fresh water samples showed a slight difference between the predicted and measured bromoform values. This is because that the dataset which was used for the development of the bromoform predictive model (Equation 1) has similar characteristics (water chemistry in terms of initial bromoform and duration of the test) to the individual dataset used in the first validation test. Meanwhile, in the second validation test, the concentration of initial bromoform was lower and the duration of the tests was short in the first validation test and long in the second validation test. The outcome of the second validation test emphasize the need of including a new parameter in bromoform predictive model which is the initial bromoform. Therefore, a new bromoform predictive model which includes initial bromoform concentration was develop as presented in the next section.

Table 4.34 Predicted bromoform by the linear model (Equation 1) against the measured bromoform for the three tests conducted over 35 days

Storage period (hours)	Measured bromoform (µg/l)	Predicted bromoform (µg/l)
0	6.46	27.71
24	8.59	30.26
48	8.97	31.58
72	9.52	32.34
96	11.15	34.59
120	12.69	35.57
192	16.33	37.18
216	18.05	38.42
360	19.76	42.65
528	21.55	47.43
840	23.55	51.77
0	8.04	28.70
24	8.28	31.24
48	8.42	32.21
72	9.97	33.22
96	10.21	36.61
120	12.65	38.05
168	16.27	41.95
240	16.74	44.43
360	19.29	48.59
504	22.21	53.81
624	25.29	58.78
840	25.63	65.53
0	7.25	29.72
24	8.83	32.27
48	11.99	35.49
72	13.15	37.09
96	14.03	38.94
120	15.75	40.88
144	17.97	42.44
192	20.47	47.50
264	23.64	51.85
384	29.51	59.32
576	33.75	69.50
840	37.37	83.98

4.4.2 Nonlinear bromoform model

The prediction results of the linear model (Equation 1) show considerable deviation from the measured concentration of bromoform, therefore, further investigations were carried out to develop a nonlinear model. A nonlinear bromoform predictive model was developed using four independent variables (i.e. residual chlorine, UV_{254} absorbance, storage period and pH measured during conducting the simulated residence time tests) and three interaction terms (i.e. storage period x temperature, storage period x blending ratio and initial bromoform x bromide x storage period). The employed dataset were divided into two individual datasets. The first dataset (model development dataset) included data obtained from tests conducted on synthetic potable water samples. The second dataset (model validation data set) included data obtained from the tests conducted on fresh water samples and from the extended storage period tests (35 days). The developed nonlinear bromoform predictive model is as follows (**Equation 2**):

$$\begin{aligned} Bromoform = {} & \boldsymbol{\beta 1}\, residual\ chlorine^{\boldsymbol{\beta 2}} + \boldsymbol{\beta 3}\, UV\ absorbance_{254}{}^{\boldsymbol{\beta 4}} \\ & + \boldsymbol{\beta 5}\, storage\ period^{\boldsymbol{\beta 6}} + [\boldsymbol{\beta 7} + (\boldsymbol{\beta 8} \times pH)] \\ & + \left[\boldsymbol{\beta 9}\, (storage\ period \times temperature)^{\boldsymbol{\beta 10}}\right] \\ & + \left[\boldsymbol{\beta 11}\, (storage\ period \times blending\ ratio)^{\boldsymbol{\beta 12}}\right] \\ & + \left[\boldsymbol{\beta 13}\, (initial\ bromoform \times bromide \times storage\ period)^{\boldsymbol{\beta 14}}\right] \end{aligned}$$

4.4.2.1 Model coefficients

The introduction of the interaction terms in the bromoform predictive model was carried out to include the interactive effect between independent variables in the model. The best fit function was obtained using the Curve Estimation Regression tool in the SPSS software. Table 4.35 shows the coefficients value of the predictive model (Equation 2).

Table 4.35 The coefficients of bromoform predictive model (Equation 2)

Coefficients	**Model value**
β1	-617.364
β2	0.051
β3	2.410
β4	-0.267
β5	-0.585
β6	0.500
β7	-805.520
β8	1.675
β9	-429.881
β10	-2.678E-6
β11	1534.142
β12	-0.012
β13	378.517
β14	0.047

The measured vs. predicted bromoform concentrations as a result of the execution of the nonlinear model (Equation 2) is presented in Table 4.36. Additionally, the plot of measured bromoform vs. predicted bromoform is presented in Figure A. The plot compares the predicted and measured data of bromoform. As can be seen from the plot, the points are closely distributed around the line of perfect correlation which visually indicates a good predictive model. Moreover, the figure shows an aggregate of two groups of data points. This is due to the variation in the initial and subsequently on the final concentrations of bromoform in water in the tests conducted, in which the bottom left data points represent the test conducted on water samples which had relatively lower initial bromoform concentration than the data points located on the upper right of the figure.

Table 4.36 Predicted vs. measured bromoform for the nonlinear model (Equation 2)

Test conditions	**Measured bromoform**	**Predicted bromoform**
6 days, 20 °C, 2.9%	29.04	28.91
	29.27	29.27
	29.98	29.32
	30.10	29.73
6 days, 25 °C, 2.9%	29.75	30.00
	29.70	30.31
	30.27	31.08
	30.60	31.13
6 days, 30 °C, 2.9%	29.73	30.56
	30.00	30.69
	30.45	32.54
	31.10	32.67
6 days, 20 °C, 8.0%	29.10	28.55
	31.50	29.47
	31.40	31.95
	32.50	32.70
	33.70	32.95
	33.90	33.33

Table 4.36 (continued).

6 days, 25 °C, 8.0%	30.10	29.00
	31.80	31.24
	31.70	31.98
	33.60	33.39
	33.90	33.83
	34.20	33.99
6 days, 30 °C, 8.0%	29.50	29.19
	32.80	31.78
	32.90	32.86
	33.80	33.12
	34.80	33.99
	35.00	34.79
6 days, 20 °C, 15%	28.90	30.18
	31.10	31.69
	34.80	33.82
	35.70	34.78
	35.50	36.69
	35.90	36.67
6 days, 25 °C, 15%	28.90	31.05
	31.50	33.62
	36.20	35.10
	37.20	36.75
	37.60	38.12
	36.90	38.57
6 days, 30 °C, 15%	34.40	31.20
	35.90	35.50
	36.50	36.43
	38.10	38.46
	40.40	39.08
	40.80	40.23

Table 4.36 (continued).

35 days, 30 °C, 2.9% (only the first 6 days)	8.59	8.88
	8.97	9.10
	9.52	9.13
	11.15	11.04
	12.69	11.91
	16.33	12.82
35 days, 30 °C, 8.0% (only the first 6 days)	8.28	8.57
	8.42	8.82
	9.97	9.00
	10.21	12.25
	12.65	13.34
	16.27	16.99
35 days, 30 °C, 15.0% (only the first 6 days)	8.83	10.13
	11.99	12.74
	13.15	13.51
	14.03	14.60
	15.75	15.73
	17.97	16.43

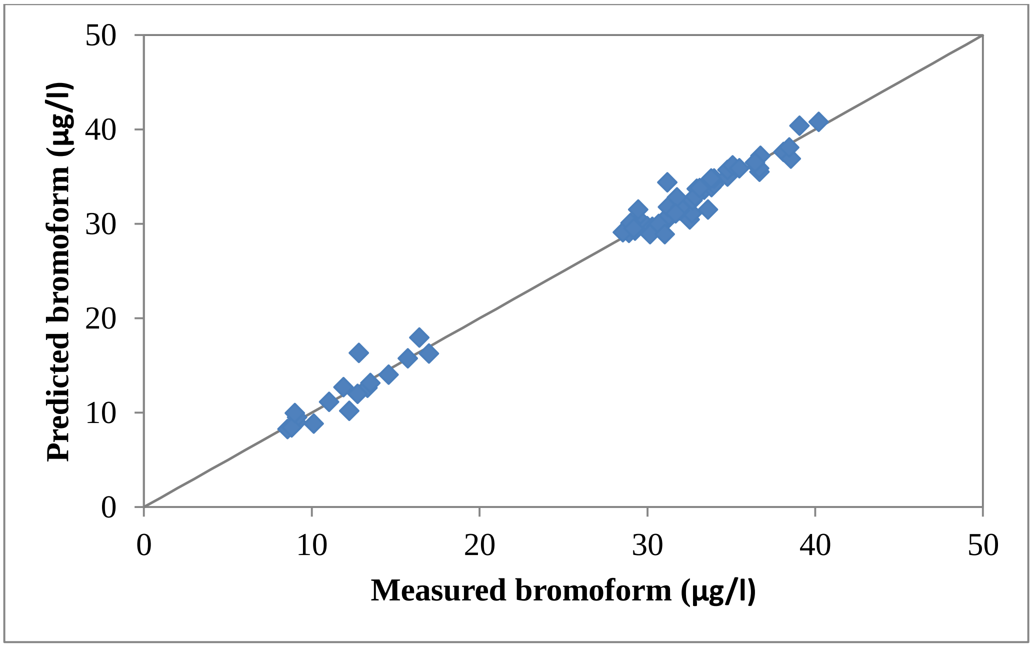


Figure 4.29 Predicted vs. measured bromoform for the nonlinear model (Equation 2)

4.4.2.2 Model prediction performance

The performance of the bromoform predictive model (Equation 2) was assessed by Mean Prediction Bias (MPB) and Mean Absolute Deviation (MAD). The MPB method is used to estimate the direction and magnitude of the predictions average bias. A high positive value of MPB is an indication of model over-prediction whereas a low value of MPB indicates the predictive model performs well in comparison to measured data. The MAD is often employed to assess the average dispersion of a predictive model. The estimate of MAD provides an indication of model prediction of the measured values; a value close to zero means that the predictive model forecasts the measured values well.

$$MPB = \frac{\sum_{i=1}^{n}(Y_i - \hat{Y}_i)}{n}$$

$$MAD = \frac{\sum_{i=1}^{n}|Y_i - \hat{Y}_i|}{n}$$

For both equations 1 and 2, $Y_i = measured\ data$, $\hat{Y}_i = predicted\ data$

The results of the estimated MPB and MAD are 0.0002 and 0.81, respectively. The MPB result which is close to zero indicates that the bromoform predictive model (Equation 2) could predict bromoform well. Meanwhile, the MAD result suggests that the bromoform model predicts the measured values well.

4.4.2.3 Model validation

The validation of the developed nonlinear bromoform predictive model (Equation 2) was conducted by utilizing a separate dataset. The separate data set was obtained from the three tests conducted on fresh potable water samples collected from Doha blending facility. In addition, these datasets were part of the three extended storage tests (35 days) conducted on synthetic potable water samples. It should be noted that the data obtained from the first six days of the tests was excluded because it was used in the model development. The result of the measured vs. predicted bromoform is presented in Table 4.37. The distribution of the data points (Figure 4.30) of the predicted vs. measured bromoform and the 95% confidence bands. In Figure 4.30, most of the data points of the predicted vs. measured bromoform are within the confidence interval. The two points that were not within the limits of the 95% interval represent the predicted at long time of 576 hours and 840 hours for the extended storage test (35 days) conducted on synthetic potable water comprising 15% groundwater. This indicates that the predictive model could underestimate bromoform concentration beyond a specific time (576 hours) under the given conditions. Nevertheless, model prediction was good for the rest of the used dataset in the validation.

Table 4.37 The performance of the nonlinear model (Equation 2) by using the validation dataset

Test conditions	Measured bromoform	Predicted bromoform
Freshwater, 6 days, 20° C, 2.9%	32.45	33.59
	33.20	32.92
	33.45	33.00
	33.90	33.16
	35.60	34.28
	36.00	35.52
Freshwater, 6 days, 25° C, 2.9%	32.80	33.60
	33.70	33.53
	34.10	33.44
	34.55	33.24
	36.00	34.85
	36.35	36.29
Freshwater, 6 days, 30° C, 2.9%	33.45	33.53
	34.00	33.46
	34.65	33.63
	36.00	33.54
	36.30	35.09
	37.10	37.46
Synthetic water, 35 days, 30° C, 15%	20.47	20.33
	23.64	21.54
	29.51	23.91
	33.75	24.78
	37.37	27.00
Synthetic water, 35 days, 30° C, 8.0%	16.74	17.20
	19.29	17.86
	22.21	19.24
	25.29	21.47
	25.63	22.51
Synthetic water, 35 days, 30° C, 2.9%	16.33	12.24
	18.05	13.23
	19.76	15.62
	21.55	18.99
	23.55	20.31

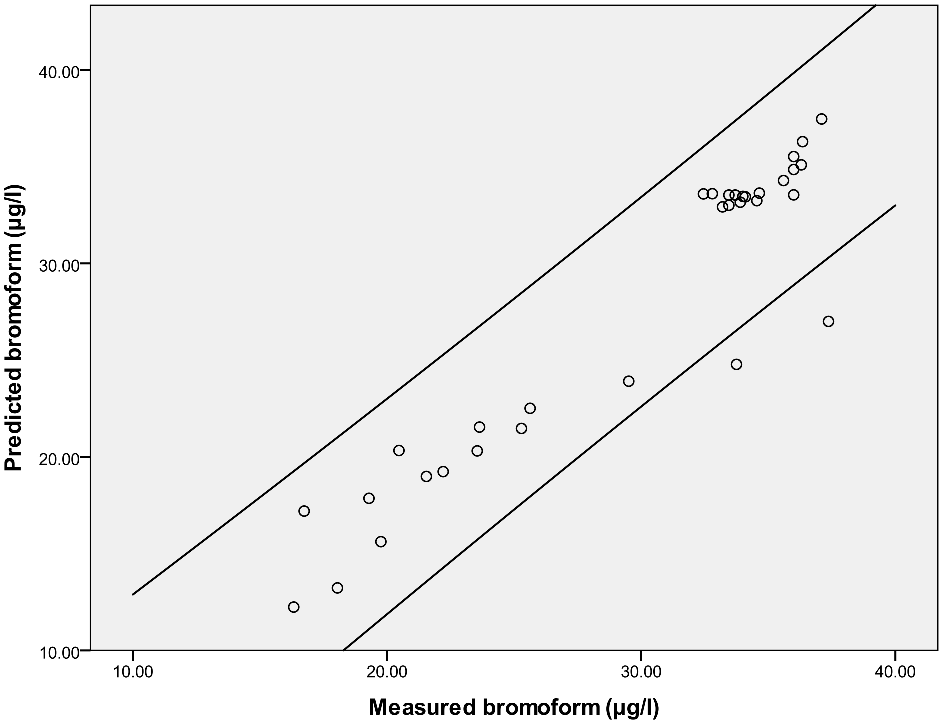


Figure 4.30 Distribution of the most data points of the predicted vs. measured bromoform within 95% confidence intervals

4.4.2.4 Sensitivity analysis

The sensitivity analysis was conducted for the nonlinear predictive model to evaluate the effect of the parameters of the predictive model (Equation 2) on the development of bromoform. Table 4.38 shows the parameters of the nonlinear predictive model and their assigned minimum, maximum and average values utilized in the sensitivity analysis. It is worth to be mentioned that the assigned values of the model parameters are similar to those used in the sensitivity analysis conducted on the linear predictive model (Equation 1) in the previous section except the addition of the initial bromoform and blending ratio parameters in the nonlinear predictive model.

Table 4.38 The values of parameters of nonlinear model used in the sensitivity analysis

Model Parameter	Unit	Minimum	Maximum	Average
Residual chlorine	mg/l	0.40	0.80	0.60
Bromide	mg/l	0.004	0.020	0.012
Temperature	° C	20	30	25
Initial bromoform	µg/l	6.00	27.00	16.50
UV_{254} absorbance	cm^{-1}	0.0018	0.0066	0.0042
Storage period	hrs	0	840	420
pH	-	7.00	8.00	7.50
Blending ratio	%	2.9	15	8.95

The sensitivity analysis was performed to assess the effect of each of the model parameters individually on the development of bromoform by using random values (1000 iterations). Table 4.39 shows the result of the sensitivity analysis conducted on the model parameters.

Table 4.39 The statistics of the SA conducted on the parameters of the nonlinear model and represented by bromoform concentration (µg/l)

Statistic	**pH**	**Residual chlorine**	**UV_{254} absorbance**	**Temp.**	**Bromide**	**Storage period**	**Initial bromoform**	**Blending ratio**
Highest	30.69	42.15	32.49	29.86	40.61	58.02	40.72	48.75
Average	29.85	30.33	30.10	29.86	28.01	29.63	27.75	31.44
Lowest	29.02	20.98	28.67	29.86	6.42	28.69	8.50	21.28

The highest bromoform concentration (58.02 µg/l) was achieved at time equal 840 hours during manipulating of the storage period parameter. The second highest bromoform concentration (48.75 µg/l) was achieved at blending ratio equal to 15.0%. This is followed by residual chlorine, initial bromoform, bromide, UV_{254} absorbance, pH and finally temperature. A graphical demonstration of the most influential parameters on the concentration of bromoform is presented in Figure 4.31.

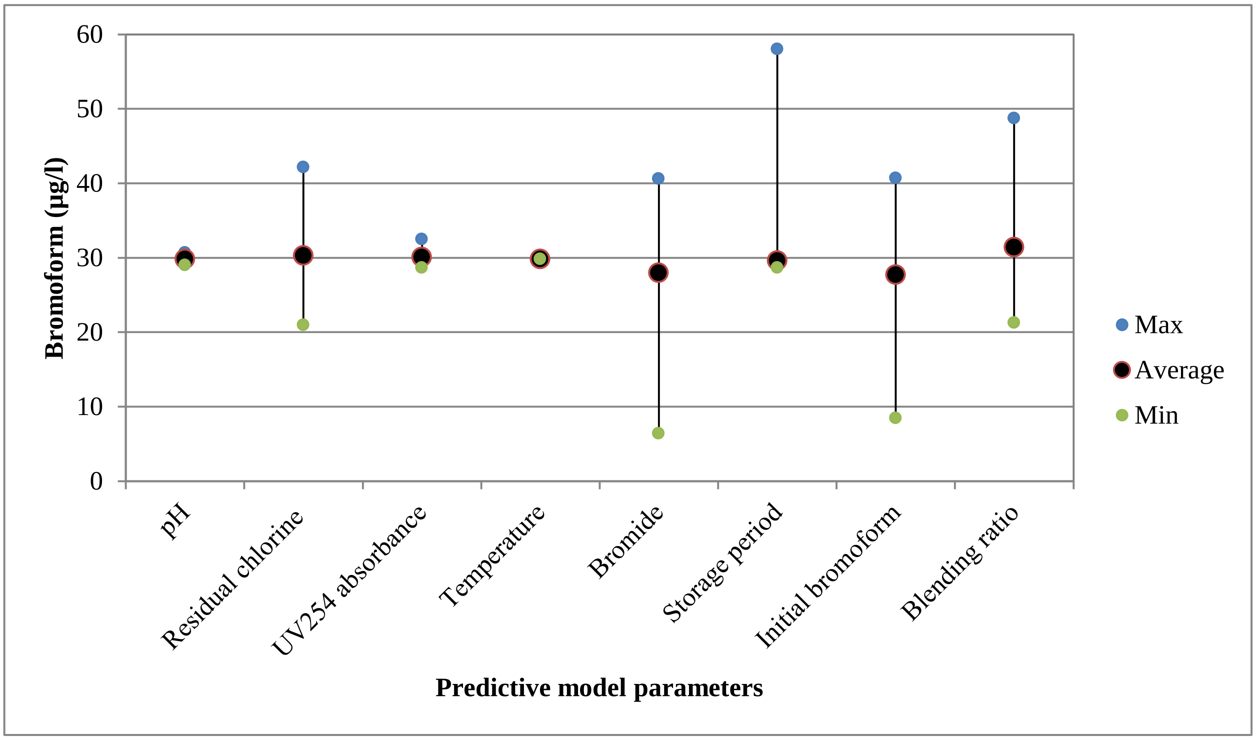


Figure 4.31 The parameters that have the most influence on the concentration of bromoform ranked in the following order: storage period, blending ratio, residual chlorine, initial bromoform, bromide, UV_{254} absorbance, pH and temperature

4.5 Comparison between bromoform predictive models

The performance of the bromoform predictive models of the study (Equations 1 & 2) and two bromoform models published in the literature (Montgomery Watson's model published in Chowdhury et al., 2009; Rathbun's model published in Rathbun, R.E. et al., 1996) was carried using a separate dataset which was not used in the development of bromoform models of the current study. The selection of the two published models was based on the availability of data to run these models. As for Rathbun's model, the parameters required to evaluate the model includes pH, chlorine, dissolved organic compound and bromide, meanwhile, Montgomery Watson's model requires total organic carbon, bromide, chlorine and time. It should be noted that all the parameters used in the models comparison were measured during the tests conducted except of total organic compound. However, the total organic compound was assumed to be equal to the dissolved organic compound as the organic contents of drinking water in Kuwait is low. The results of the measured bromoform concentrations in addition to the predicted bromoform by the four models are presented in Table 4.40. In addition, the distribution of predicted vs. measured data points for the four bromoform models is presented in Figure 4.32. The table shows that the linear model has predicted bromoform very well in the first three validation dataset and failed to predict bromoform concentration in the rest of the datasets. The reason of the prediction failure is possibly due not including the initial bromoform parameter in the linear predictive model. The nonlinear model has predicted bromoform concentrations very well for the first three of the validation dataset and to relatively less accurate for the rest of the dataset. The Rathbun's model has severely underestimated bromoform concentrations in all the validation dataset. Finally, Montgomery Watson's model has poorly estimated bromoform concentration except for the first three bromoform concentrations in the last validation dataset (No. 6). The nonlinear model of the study showed a better bromoform prediction than the other models.

Table 4.40 Comparison between bromoform predictive models

No.	Validation dataset	Measured bromoform (µg/l)	Estimated bromoform (µg/l)			
			Predictive models of the current study		Predictive models from lierature	
			Linear	Nonlinear	Rathbun, R.E.	Montgomery Watson
1	dataset obtained from the tests conducted over 6 days on fresh water samples comprising 2.9% groundwater under 20 ºC temperature condition.	32.45	33.59	33.59	0.05	13.81
		33.20	33.55	32.92	0.04	15.31
		33.45	33.81	33.00	0.05	16.04
		33.90	34.19	33.16	0.04	16.54
		35.60	34.65	34.28	0.05	16.90
		36.00	34.93	35.52	0.05	17.33
2	dataset obtained from the tests conducted over 6 days on fresh water samples comprising 2.9% groundwater under 25 ºC temperature condition.	32.80	33.47	33.60	0.04	13.81
		33.70	33.76	33.53	0.05	15.05
		34.10	33.86	33.44	0.05	15.90
		34.55	34.11	33.24	0.05	16.40
		36.00	34.57	34.85	0.05	16.76
		36.35	35.17	36.29	0.05	17.03
3	dataset obtained from the tests conducted over 6 days on fresh water samples comprising 2.9% groundwater under 30 ºC temperature condition.	33.45	33.10	33.53	0.05	13.81
		34.00	33.53	33.46	0.05	15.05
		34.65	33.65	33.63	0.05	15.90
		36.00	34.22	33.54	0.04	16.26
		36.30	34.65	35.09	0.05	16.61
		37.10	35.22	37.46	0.05	16.88
4	dataset obtained from the tests conducted over 35 days on synthetic water samples comprising 2.9% groundwater under 30 ºC temperature	20.47	47.50	20.33	0.65	50.74
		23.64	51.85	21.54	0.65	50.83
		29.51	59.32	23.91	0.67	48.98
		33.75	69.50	24.78	0.68	49.38
		37.37	83.98	27.00	0.71	47.00
5	dataset obtained from the tests conducted over 35 days on synthetic water samples comprising 8.0% groundwater under 30 ºC temperature	16.74	44.43	17.20	0.21	38.00
		19.29	48.59	17.86	0.21	38.55
		22.21	53.81	19.24	0.22	37.85
		25.29	58.78	21.47	0.22	35.54
		25.63	65.53	22.51	0.24	35.23
6	dataset obtained from the tests conducted over 35 days on synthetic water samples comprising 15.0% groundwater under 30 ºC temperature	16.33	37.18	12.24	0.04	17.55
		18.05	38.42	13.23	0.04	17.21
		19.76	42.65	15.62	0.04	16.44
		21.55	47.43	18.99	0.04	14.86
		23.55	51.77	20.31	0.04	15.46

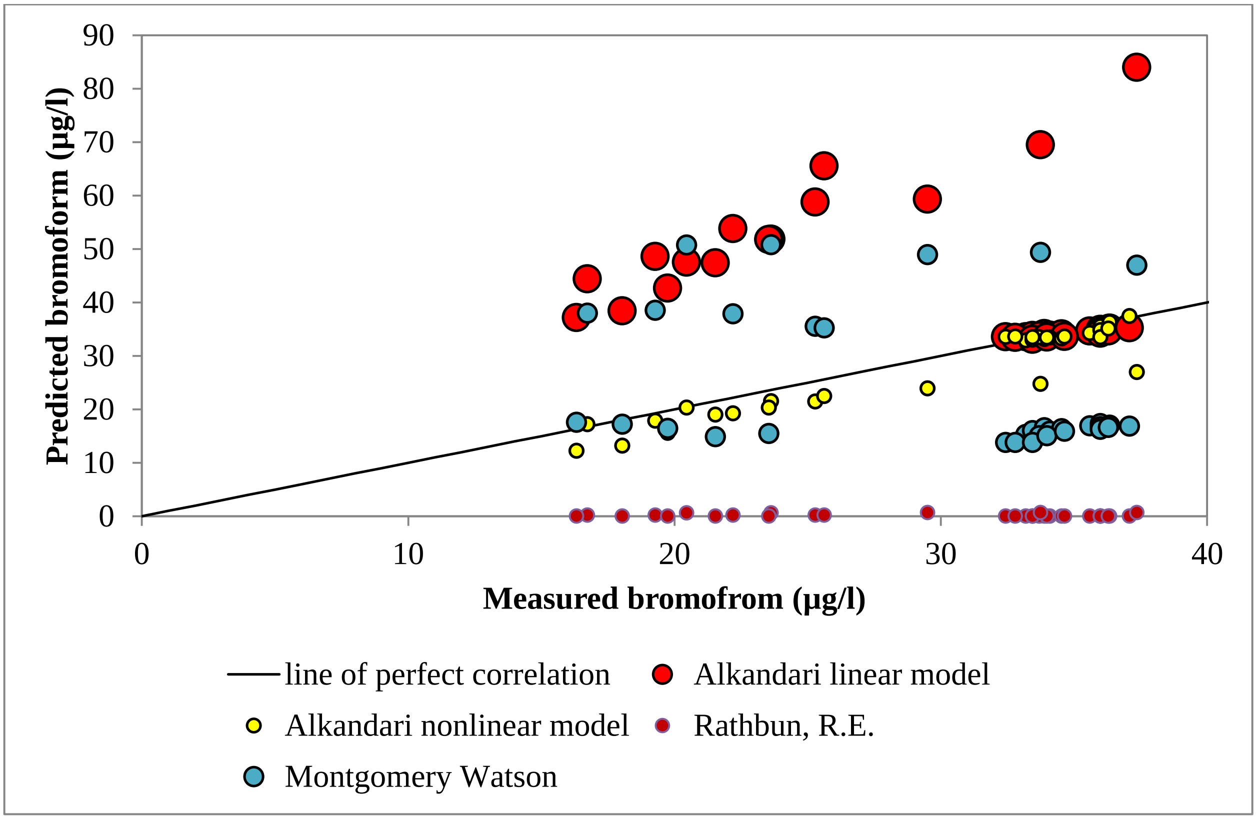


Figure 4.32 The distribution of the predicted vs. measured bromoform data points around the line of perfect correlation

4.6 Bromoform regulatory failure test

The possibility of failure of the KEPA guidelines for bromoform concentration in drinking water (100 µg/l) was investigated individually for each of the parameters of the nonlinear bromoform model (Equation 2). A random values outside the actual range (above the maximum and below the minimum values) of model parameters was used to identify the condition at which bromoform concentration in drinking water would exceed the guideline level. The analysis was conducted by assigning an average values for the model parameters except of the tested parameter. The result of the test conducted showed that at a given bromide concentration equal to 0.240 mg/l, the bromoform concentration has reached to 100 µg/l on condition that the values of the other model parameters are as shown in Table 4.41. The assigned value of residual chlorine in which bromoform concentration reached to 100 µ/l was 0.05 mg/l. As for the pH parameter, pH random values between 6 and 9 was tested and the results showed that bromoform concentrations were below the guidelines level. The UV_{254} absorbance at almost zero level (0.0004) resulted in bromoform concentration equal to 110 µg/l. The tested range of the blending ratio (2.9% - 15.0%) showed the concentration of bromoform below the regulatory target. The temperature parameter was tested between 10°C and 50°C and the bromoform result was below the guideline limit. Finally, the bromoform concentration has not reached the guideline limit during manipulating the initial bromoform parameter.

Table 4.41 The values of water quality and operational conditions in which failure of the regulatory target of bromoform would be expected

No.	Bromide (mg/l)	Residual chlorine (mg/l)	UV254 absorbance (cm^{-1})	Storage period (hours)	Initial bromoform (µg/l)	pH	Blending ratio (%)	Temp. (° C)	Bromoform (µg/l)
1	0.240	0.60	0.0042	420	16.5	7.5	8.95	25	100
2	0.012	0.05	0.0042	420	16.5	7.5	8.95	25	100
3	0.012	0.05	0.0004	420	16.5	7.5	8.95	25	110

Chapter 5

Bromoform management strategy

5.1 Introduction

A reduction in the amount of bromoform in the potable water of Kuwait could be achieved by implementing a bromoform management strategy. This study proposes that a management strategy consists of several actions aimed at minimising the presence of bromoform in potable water. The suggested actions are based on the findings of the regulatory failure test (section 4.6) and works published in this field. The experiences of neighbouring countries, such as Israel (Richardson et al., 2003), which had the same potable water quality issue has to be considered and benefited from. The establishment of a bromoform management strategy requires a knowledge and preliminary information with regard to the bromoform compound and its precursors in source water. Moreover, information relating to the potable water production cycle is necessary to help develop such a strategy. The required knowledge was gathered by conducting the theoretical and experimental activities of this study. Therefore, this chapter briefly discusses the proposed bromoform management strategy. This strategy consists of several suggested actions designed for each stage of the potable water production cycle in Kuwait. The production cycle includes source water production (i.e. recarbonated water and groundwater), potable water production, the disinfection of the potable water, and finally the distribution of the potable water. The following sections discuss the proposed actions associated with the bromoform management strategy.

5.2 Guidelines toward water quality and operational conditions

The development of bromoform in drinking water of Kuwait above the guideline limit could occur under certain water quality and operational conditions. The “regulatory failure” test conducted in section 4.6 indicated that several parameters of the model could encourage the development of bromoform to a level above the guideline limit. The parameters that were identified including bromide, residual chlorine and UV_{254} absorbance. As for the bromide, the concentration of bromide should be monitored and not to exceed 0.24 mg/l (in the presence of the water quality and operational conditions relevant to such bromide value, Table X) as it might encourage the development of bromoform to a level equal to KEPA guideline (100 µg/l) as it was shown in the regulatory failure test. The residual chlorine has a negative relationship with bromoform as more bromoform would develop during the decay of chlorine in the presence of sufficient organic content and bromide in water. The regulatory failure test conducted to assess the effect of residual chlorine on the development of bromoform showed that during the decay of chlorine to a level equal to 0.05 mg/l, a bromoform concentration equal to 100 µg/l was observed (in the presence of the water quality and operational conditions relevant to such residual chlorine value, Table X). Accordingly, the development of bromoform could be minimized to a level below the guideline level either by lowering the residence time of water to less than 420 hours or by reducing the blending ratio to below 8.95%. Finally, the UV_{254} absorbance at a level near to (0.0004 cm^{-1}) was led to the development of bromoform concentration equal to 110 µl during performing the regulatory failure test. This situation could be resolved by the reduction of both of the residence time of water to below 420 hours and blending ratio to less than 8.95%.

5.3 Stage one: source water management

The production of potable water in Kuwait depends on seawater and groundwater. The seawater contains significant amounts of bromide and natural organic compounds which are considered to be the main precursors for the development of bromoform. On the other hand, the groundwater has significant amounts of the bromide compound and a relatively low concentration of natural organic compounds. Although the use of such types of water in association with the current disinfection practice in the production of potable water influences the development of bromoform, the utilisation of seawater and groundwater in Kuwait is crucial because they are the only natural sources of water that are available in sufficient quantities that can be utilised in the production of potable water. There are several actions that could be considered during the production of recarbonated water and groundwater to lower the chances of bromoform developing in the potable water in Kuwait. These actions are discussed separately in the following subsections for recarbonated water and groundwater.

5.3.1 Recarbonated water

A concentration around 27.0 μg/l of bromoform was detected in the recarbonated water tested. This amount of the bromoform compound represents 27% of the KEPA guideline limit (i.e. 100 μg/l) adopted for such a compound. The presence of the bromoform compound in recarbonated water is due to the pre-treatment practice as it is applied to seawater. The pre-treatment practice includes the addition of chlorine to seawater in order to inhibit biofouling inside the distillation units. The biofouling issue affects the carrying capacity and speed of flow inside water lines, reducing the performance of the heat exchanger tubes, and leads to corrosion. The estimated annual expenditure for controlling biofouling issues rose to 10 billion pounds in 2003 (Abdul Azis et al., 2003). Chlorination is widely used as an antifouling method to minimise biofouling growth in the desalination industry. As in the case of Kuwait, the chlorination practice is applied in the Doha distillation plant. Usually, a chlorine solution of 2.0 mg/l is injected into the seawater at the intake of the distillation plant which is located 200m offshore. Just before the seawater enters the distillation unit, an intermittent chlorine shock dose of 6.0 mg/l is applied to the seawater to eliminate the presence of any marine microorganisms (Ali and Riley, 1989). As a result, this chlorination practice is clearly responsible for the presence of the bromoform compound in the water produced by the distillation plant (i.e. recarbonated water). At this preliminary stage of the potable water production cycle, the amount of the bromoform compound forms a challenge for the Ministry of Electricity and Water, because the amount would increase and may exceed the guideline limits during the further stages involving the disinfection and distribution of potable water.

A key solution to reducing the development of the bromoform compound at this early stage of the potable water production cycle is to change the antifouling method used. Nowadays, many antifouling technologies are available such as chlorine dioxide, ultra violet radiation, hydrogen peroxide, and ozone (Abdul Azis et al., 2003; Lopez-Galindo et al., 2010). In one study conducted by Petrucci and Rosellini (2005), the authors found that chlorine dioxide effectively prevented biological growth in the Sidi Krir power plant located in Egypt. Furthermore, additional benefits from using chlorine dioxide was reported including safety, annual cost and, more importantly, a failure to react with the bromide compound to form brominated compounds. In fact, the authors claimed that chlorine was less effective when compared to chlorine dioxide in terms of controlling biofouling, and promoted the development of brominated compounds.

In another study, Penru et al. (2012) examined the disinfecting performance of ultra violet (UV) radiation, and UV radiation coupled with hydrogen peroxide (H_2O_2) on seawater. The authors stated that both methods achieved full disinfection. Moreover, an improvement in the reduction of natural organic matter (measured by UV_{254} absorbance) was attained (up to 55%) by using the UV/H_2O_2 method. In addition, no chlorate, bromate, trihalomethanes, and haloacetic acids were detected during the application of such methods. A promising application in the form of UV and H_2O_2 in terms of seawater disinfection was addressed by the study.

Another way to remove the bromoform compound from recarbonated water is by the addition of a final treatment stage at the desalination plant. Uyak et al. (2008) have examined two types of nanofiltration (NF) technologies, including NF-DS5 and NF-200 membranes for the removal of trihalomethanes. The study revealed that both NF membranes effectively remove trihalomethanes, especially brominated trihalomethanes, due to their higher molecular weight and size. The removal efficiency of NF-DS5 and NF-200 membranes for chloroform, bromodichloromethane and dibromochloromethane, respectively, were between 81 – 88 %, 84 – 94 %, and 93 – 96 %. Moreover, Lou et al. (2009) conducted a laboratory investigation using an advanced water treatment system (i.e. ozonation combined with biologically activated carbon) for trihalomethanes and haloacetic acid (HAA_5) removal. The treatment system employed reduced the concentrations of THMs and HAA_5 in the fully treated water, respectively, to 13.97 µg/l and 17.67 µg/l.

Singer et al., (2007) evaluated the effectiveness of utilising magnetic ion exchange (MIEX) for the removal of organic compound and bromide from a source water. The authors found that the MIEX removed substantial amount of organic carbon from water as a reduction in dissolved organic carbon and UV_{254} absorbance was achieved. In Addition, bromide was removed from source water to some degree by MIEX. Accordingly, THM was decreased in water as a result of employing MIEX treatment method.

Overall, the previous studies showed that the presence of the bromoform compound can be eliminated in recarbonated water by simply changing the disinfection practice applied, removal of DBP precursors from source water, or the compound could be minimised, in the case of the application of chlorination practice, by the addition of a final treatment stage.

5.3.2 Groundwater

Groundwater is the other source water used in the production of potable water in Kuwait. In addition to the production of potable water, groundwater is used for landscape irrigation, farming, industrial, and is delivered to residential areas by a network system mainly for watering gardens. As a result, the rate of using groundwater (i.e. 220 m^3/y/p) exceeds the natural groundwater replenishment rate (i.e. 8 m^3/y/p) (Darwish et al., 2008). This intensive abstraction of groundwater has led to the quality of groundwater deteriorating over time (Al-Senafy and Abraham, 2004). Al-Zubari (1998) pointed out that the deterioration of the quality of groundwater is due to connate water (groundwater entrapped in the sedimentary rocks during the time of rock deposition where the water becomes naturally saline) up-flow and seawater intrusion as a result of groundwater over pumping. The entrapped groundwater is a possible source of bromide. The deterioration of groundwater quality is clearly observed in many groundwater fields around the country as in the increase of groundwater salinity (Alhumoud et al., 2010). Therefore, the protection of groundwater from further deterioration is an urgent need in order to allow the continuation of the use of groundwater in the production of potable water.

A protective action has been proposed in several studies in order to sustain groundwater by the use of treated wastewater for non-potable activities. In one of these studies, Suleiman and Abdal (2002) carried out a study to investigate alternative water sources in Kuwait for agricultural applications. The authors addressed the importance of using wastewater in agricultural and landscape developments in the light of the scarcity of natural fresh water resources.

In another study, a laboratory investigation was conducted by Al-Shammiri et al. (2005) to assess the suitability of secondary wastewater effluent treated with microfiltration technology for greenery purposes in Kuwait. The result showed that the use of secondary treated water led to a significant reduction in biological oxygen demand, chemical oxygen demand, total suspended solids, and total bacterial count, when filtered using microfiltration. In addition, the trace elements in the filtered water were found to be below the guidelines limit. Nonetheless, the authors argued that the accumulation of such elements may occur over time in the irrigated soil. Overall, the study suggested that water produced by microfiltration could be used in landscaping.

The previous studies showed that the treated wastewater is an important resource that should be used in non-potable activities. Therefore, the application of treated wastewater in Kuwait for farming, landscaping, and watering gardens would reduce the pressure on the demand for groundwater. At the present time, treated wastewater in Kuwait is of a high quality as a result of using sophisticated treatment technologies. Kuwait has built one of the world's largest wastewater plants which uses membrane technologies ("Sulaibiya water project a first for GE," 2005). The plant uses ultrafiltration and reverse osmosis to treat 375,000 m^3/day of municipal effluent. The quality of the treated water is comparable to potable water. Unfortunately, the treated water is only used for farming, and to a lesser degree in landscape irrigation, from when the plant started operations in December, 2004. The expansion in terms of using the treated wastewater for non-potable activities would result in reduction in the use of groundwater. As a consequence, the recovery of the groundwater in terms of quality and quantity could be achieved.

Another way to minimise the presence of bromoform in potable water is by utilising the type of groundwater that has the lowest concentration of inorganic precursors for the production of potable water. Al-Ruwaih et al. (2010), demonstrated that the groundwaters used in the production of potable water have different degrees of salinity in terms of the related groundwater production fields, ranging from 2,330 mg/l from the Um-Qudair groundwater field to 6,366 mg/l from the Al-Atraf groundwater field. The difference is also observed with regard to the concentration of bromide in the groundwater. Therefore, relatively low quality groundwater could be used for non-potable activities, while the high quality groundwater water should be only utilised in the production of potable water. However, there are infrastructure issues which prevent the application of such an action. The issue is represented by the fact that the groundwater network system responsible for the delivery of groundwater to the potable water production facility, the irrigation system, and to residential areas is connected. The separation of the groundwater network into two separate networks for the production of potable water and for other purposes, is suggested in order to utilise the best quality of groundwater in the production of potable water, hence minimising the chance of bromoform being developed.

5.4 Stage two: potable water production

The production of potable water is carried out through blending groundwater and recarbonated water in a certain ratio. Based on the experimental results of this study, it was found that the utilised groundwater contains significant amounts of the bromide compound (0.710 mg/l). Therefore, it is suggested that the groundwater percentage should be at a minimum during the blending of both groundwater and recarbonated water for the production of potable water. The higher the percentage of groundwater used in the production of potable water, the more bromoform would be developed in the finished water.

5.5 Stage three: disinfection practice with regard to potable water

The chlorination method is used to disinfect potable water in Kuwait. This disinfection method is not desirable when it comes to disinfecting water that contains a significant amount of bromide. In Kuwait, the type of source water used in production of potable water is bromide source-water. Consequently, as a result of chlorination, the bromoform compound in potable water samples is frequently detected in concentrations above the guideline limits. In this study, during the collection of water samples at the Doha blending facility, the bromoform levels in a fresh chlorinated potable water sample was measured as 100.1 µg/l due to a out of control increase in the residual chlorine from around 0.65 mg/l to 0.85 mg/l. This incident indicated that the water produced has the potential to form bromoform above the guideline limits, though the facility has used the groundwater at the lowest percentage (i.e. 2.9%). Therefore, the investigation of other alternative disinfection methods for the disinfection of potable water is a necessary step in terms of controlling the level of bromoform in potable water in Kuwait. Although chlorination is used widely by water companies to disinfect potable water, many such companies are replacing chlorine with other disinfectant agents as a result of the chlorinated by-products (Richardson et al., 2003).

At the present time, water companies are using disinfection methods, either solely or in combination, to disinfect potable water including chlorine dioxide, chloramines, ultraviolet, and ozone (Chowdhury et al., 2009). The selection of the disinfection method is based on disinfection costs, efficiency, stability, the chemistry of the source water, and other factors. For example, Israel is one of the first countries in the region to switch from chlorine to chlorine dioxide and chloramines, as a result of the occurrence of high bromoform levels (100 µg/l) in the chlorinated potable water in the middle of the 1970s (Richardson et al., 2003). Meanwhile, neighbour countries such as Saudi Arabia, Qatar and the United Arab Emirates, have evaluated the chlorine dioxide systems as a replacement for chlorination for the disinfection of potable water (Gazette, 2011).

In the literature, Belluati et al. (2007) have examined the effect of utilising chlorine dioxide as a disinfecting agent with regard to potable water produced from the desalination of seawater. The authors found that the disinfection by-product of chlorine dioxide, namely, chlorate, was detected in very low concentrations and below the WHO guideline level. In addition, the other main disinfection by-product of chlorine dioxide, chlorate, was suggested by the study to be minimised by using a high purity of chlorine dioxide (i.e. 98%) during the disinfection of potable water. Moreover, no bromate was detected in the study because chlorine dioxide does not react with bromide compound. To sum up the previous studies, the investigation of alternative disinfection methods is considered the optimal solution for the bromoform problem in potable water.

5.6 Stage four: water distribution systems

The concentration of disinfection by-products in the potable water found in a consumer's tap is often found to be two to three times higher from its concentration at a water treatment works (Rossman et al., 2001; EPA, 2008). Usually, this increase in disinfection by-products occurs during the transition of potable water in water distribution systems. The factors that influence the development of disinfection by-products during the transition of potable water within water distribution systems are the age of the water, the concentration and the type of disinfection by-product precursors, the type and dose of disinfectant and the concentration of disinfectant residuals (EPA, 2008). In terms of the age of the water, the disinfectant residual often continues to react with natural organic compound while travelling within the water distribution system. Therefore, the longer the residence time of the potable water (i.e. the age of the water) in a water distribution system, the higher the eventual development of disinfection by-products. Furthermore, potable water located at dead ends or in stagnant zones within a water distribution system has the highest levels of disinfection by-products. However, there are several actions that could be considered in order to minimise the hydraulic residence time in a water distribution system, such as looping of dead ends, managing valves (e.g. using isolation valves), replacing oversized pipes, and installing blow-offs for removing sediments and biofilms (EPA, 2008).

Furthermore, the characteristic of the high hydraulic residence time of potable water reservoirs is probably presented in Kuwait. This situation occurs as a result of the absence of the readily available natural fresh water resources for the production of potable water. As a result, the Ministry of Electricity and Water has built water reservoirs to store potable water before delivering it to the consumers. At the same time, the stored water represents a strategic reserve for emergency purposes. The capacity of all the potable water reservoirs around the country is around 11.9 million cubic meters. The largest reservoirs can hold nearly 0.5 million cubic meters of potable water, whereas the capacity of the smallest reservoir is around 500 cubic meters (MEW, 2010). Frequently, the large amount of chlorinated potable water stored in reservoirs with high hydraulic residence time and poor mixing, promotes the development of disinfection by-products (EPA, 2008). Several actions have been suggested by the environmental public authority – office of water to minimise the effect of such factors. For example it has been suggested that there is a need to reduce the age of finished water inside reservoirs by maintaining adequate volume turnover, and applying scheduled maintenance activities including repairs, sediment removal, and the replacement of reservoir coatings.

5.7 Bromoform reduction strategies at Hawali city

The problem of the occurrence of bromoform in potable water in Hawali city could be resolved through modification of the potable water production processes, and maintenance of the related water distribution system. The suggested actions include application of alternative disinfection methods other than chlorination of the seawater and the finished water, management of groundwater that is utilised in the production of potable water, and organising maintenance schedule for water distribution system of Hawali city.

The disinfection of bromide containing-water with chlorine would result in the formation of bromoform (as it was seen in the bromoform results obtained in the tests). In addition, a strong correlation was found between chlorine demand and bromoform. These findings suggest that chlorination is not the preferable disinfection method to be used in the disinfection of such type of water. Therefore, other water disinfection alternative such as chlorine dioxide is suggested to be tested and used in the pretreatment of seawater and the finished potable water produced by Doha blending facility. The chlorine dioxide is successfully tested and to disinfect potable water around world.

The groundwater of Doha blending facility was found to have a significant amount of bromide (0.710 mg/l). Such groundwater once utilised in the production of potable water mean the produced water has the potential to develop bromoform during chlorination. Therefore, exploration of other groundwater fields that do not contain significant amounts of bromide is suggested in order to overcome the problem of bromoform development in the potable water. Furthermore, restriction of the groundwater with good quality (i.e. limited bromoform precursors) to be used only in the production of potable water.

The development of bromoform in water is possibly continued during transition of water along the water distribution system of Hawali city. An organised maintenance schedule is suggested to control the presence of bromoform in water which include analysing water samples more frequently for pinpointing the locations with a high concentration of bromoform, routine system flushing of such locations, removing dead-ends within the water distribution system, and minimising water residence time.

5.8 Benefits from implementing the bromoform management strategy

The reduction of the bromoform compound in the potable water of Kuwait can be achieved through implementing a bromoform management strategy. The proposed strategy consists of many actions suggested for each stage of the potable water production cycle. These actions include, generally, the protection of the quality and the quantity of groundwater by retaining groundwater for the production of potable water only, the adoption of disinfectant methods other than chlorination for the pretreatment of seawater, minimising the percentage of groundwater used during the production of potable water, considering alternative disinfection methods for the disinfection of potable water, and finally minimising the hydraulic residence time in potable water storage facilities and in the piping of the distribution system. However, these actions may incur operational and infrastructure costs for the Ministry of Electricity and Water. Nonetheless, the protection of the consumers’ health is an important issue, and the return on expenditure (cost of the modification of the potable water production processes and distribution) would result in lowering the health issues related to the exposure to the bromoform compound, hence, saving on the medical treatment costs associated with overcoming such health issues (Chowdhury et al., 2011).

Chapter 6

Conclusions and future works

6.1 Introduction

The study was designed to assess the development of bromoform in the potable water of Kuwait. In this study the focus was only on bromoform and not on the other trihalomethane compounds as the compound represents between 48 and 100% of the trihalomethane compounds found in the potable water of Kuwait. The study has identified the role of the source water, i.e. the utilized groundwater and recarbonated water, in the development of bromoform compound in potable water. Moreover, several simulated residence time tests were carried out under controlled conditions to identify which of those conditions, if considered, would result in the reduction of bromoform in water. The correlation between the presence of bromoform and several selected water quality parameters (residual chlorine, UV254 absorbance, and pH of the water samples) were investigated. In addition, the effect of several factors on the development of bromoform including the preparation method, temperature and storage period of the water samples were determined. The study also developed a bromoform predictive model which could be used to forecast the concentration of bromoform in potable water. Finally, a bromoform management strategy was proposed at the end of this research study aimed to minimise the chance of occurrence of bromoform in the potable water of Kuwait. The following sections provide answers to the study objectives separately and in addition, the proposed future works related to this research field.

6.2 Conclusions

The research objectives consisted of four main parts which were stated in the introduction chapter (section 1.5). In the following subsections, the conclusions are provided separately for each research objective in turn.

Assessment of bromoform, bromide, and natural organic compounds present in the sources (groundwater and recarbonated water) of potable water, and their ultimate concentration levels in the synthetic potable water samples.

In terms of bromoform, the results of the analysis of bromoform carried out on the recarbonated water samples collected from the Doha blending facility plant indicated the presence of bromoform (WHO and KEPA guideline for bromoform is 100 µg/l) value in these water samples. The detected concentrations were around 30 µg/l. As for bromide, the results of bromide analysis for the groundwater and recarbonated water samples collected at the Doha blending facility indicated that the groundwater consisted of a significant amount of bromide (0.710 mg/l) whereas, the bromide was found below the analytical method detection limit (25 µg/l) for the recarbonated water samples. Furthermore, the results of bromide analysis for the synthetic potable water samples prepared in the laboratory reveal that increasing the percentage of groundwater in potable water during the potable water production would result in an increase in bromide concentration in potable water.

Moreover, the results of the analysis of the dissolved organic compound and UV_{254} absorbance for the sources of potable water including the groundwater and recarbonated water were 0.291 mg/l and 0.080 mg/l for the dissolved organic carbon, respectively, whereas, the UV_{254} absorbance values were 0.0119 cm^{-1} and 0.0016 cm^{-1}, for the groundwater and recarbonated water samples, respectively. As for the synthetic water samples, the results of analysis of dissolved organic carbon and UV_{254} absorbance indicated that increasing the percentage of groundwater i.e. in the order of 2.9%, 8.0%, 15.0% in the synthetic potable water samples resulted in an increase in the dissolved organic compound in the order of 0.083 mg/l, 0.098 mg/l, 0.132 mg/l, respectively, and for the UV_{254} absorbance values the increase were in the order of 0.0020 cm^{-1}, 0.0025 cm^{-1}, 0.0039 cm^{-1}, respectively.

Investigation of the effects of the water preparation method, temperature, storage period, and the interactions between these on bromoform formation, using a simulated residence time tests, and a mixed effects model

The simulated residence time tests (i.e. nine tests) under controlled laboratory conditions (preparation method, temperature and storage period) followed by statistical analysis of a mixed effects model were carried out to assess the effects of such conditions, whether or not they are significance (e.g. $p > 0.5$ is not significant; $p \leq 0.05$ is significant; $p < 0.01$ is highly significant; $p < 0.001$ is very highly significant), on the development of bromoform. The model results were as follows.

To determine the significance of the following main factors affecting bromoform formation in water

- **Preparation method**
- **Temperature**
- **Storage period**

The results of the statistical analysis of the mixed effects model indicated that the preparation method, temperature, and storage period factors have a very highly significant effect ($p < 0.001$) on the development of bromoform in the potable water samples.

To determine the significance of the following interacting factors for bromoform formation in water

- **Preparation method and temperature**
- **Preparation method and storage Period**
- **Storage Period and temperature**

The results showed that the interaction between preparation method and temperature, and preparation method and storage period, have a very highly significant effect ($p < 0.001$) on the development of bromoform in the synthetic potable water samples. Meanwhile, there was no significant interaction effect ($p = 0.737$) between temperature and storage period on the development of bromoform.

Comparison between the results of average bromoform concentration developed in the nine simulated residence time tests conducted on different synthetic potable water samples comprising 2.9%, 8.0% and 15.0% groundwater.

The comparison between the average bromoform concentrations of the simulated residence time tests indicated that the lowest average bromoform concentration i.e. 29.28 µg/l was formed in the test conducted on the synthetic potable samples comprising 2.9% groundwater with temperature conditions equal to 20º C; whereas, the highest average bromoform concentration i.e. 37.66 µg/l was formed in the test conducted on the synthetic potable water samples comprising 15% groundwater with temperature conditions equal to 30º C.

Overall, to determine the preparation methods and temperature conditions which would minimise bromoform development in potable water produced by Doha blending facility.

The preparation method level of 2.9% groundwater with temperature level equal to 20º C both proved to develop the minimum bromoform concentration i.e. 29.28 µg/l in water samples among all the tested levels. Nonetheless, although the maximum bromoform concentration detected in all the nine tests has not reached the guideline level (100 µg/l), other factors should be put into consideration (e.g. higher chlorine dose, conditions of water distribution systems, water residence time in the related distribution system) in order to keep the bromoform concentration below the guideline level at the extremities of the water distribution system.

Assessment of the correlation between bromoform compounds, chlorine demand, UV_{254} absorbance and pH of the water samples.

The results of correlation analyses showed that there was a strong positive relationship between bromoform and chlorine demand (r_s (54) = -0.902, $p < 0.01$), a positive moderate relationship between bromoform and UV_{254} absorbance (r_s (54) = 0.366, $p < 0.01$), and a negative weak relationship between bromoform and pH (r_s (54) = -0.130, $p = 0.350$) of the water samples.

Development of a predictive model to forecast the formation of bromoform in potable water produced by the Doha blending facility

Bromoform predictive models (four models) were assessed in which two of these models were developed in this study (linear and nonlinear models) and compared against two models published in the literature. The nonlinear predictive model developed in this study showed a good prediction capability than the other models in terms of forecasting bromoform in drinking water.

Development of a strategic management plan for controlling bromoform formation in the potable water of Kuwait.

A bromoform management plan was proposed to control the occurrence of bromoform in the potable water of Kuwait. The plan is based on regulatory failure test conducted in this study and other suggested actions designed for each stage of the potable water production cycle.

6.3 Future works

The current work has focused on the presence of bromide in sources of potable water and the development of bromoform during chlorination of such source water. Further work is required to assess the presence of iodide which is another halogenated compound present in seawater and groundwater in significant amounts (Agus et al., 2007). The chlorination of water consisting of iodide would result in the formation of disinfection by-products such as iodo-THMs and iodo-acids. These types of disinfection by-products are more carcinogenic than the chlorinated analogs (Richardson et al., 2003).

Chlorination is the sole disinfection practice employed by the water authority in Kuwait to disinfect potable water. The use of such a method for water which contains bromide in significant amounts is considered problematic as it leads to development of brominated disinfection by-product compounds. Further work is suggested to assess the suitability of employing other potable water disinfection methods such as chlorine dioxide and chloramines. Consideration should be given to selection of a disinfection method that would not eventually produce disinfection by-product compounds above the guideline limits.

The created bromoform predictive model in the current research study is based on laboratory data. Further work is suggested to test the predictive models on actual water distribution systems for operational purposes (e.g. forecast concentration of disinfection by-products along water networks).

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Appendix

Appendix A. Mixed effects model Syntax

```
UNIANOVA Bromoform BY Temperature Prep_Method Storage_Period
  /RANDOM=Storage_Period
  /METHOD=SSTYPE(3)
  /INTERCEPT=INCLUDE
  /POSTHOC=Temperature Prep_Method(LSD)
  /PLOT=PROFILE(Storage_Period*Prep_Method)
  /EMMEANS=TABLES(Prep_Method) COMPARE ADJ(LSD)
  /EMMEANS=TABLES(Prep_Method*Storage_Period) COMPARE (Prep_Method)
  /CRITERIA=ALPHA(.05)
  /DESIGN=Prep_Method Temperature Storage_Period Prep_Method*Temperature Prep_Method*Storage_Period
Temperature*Storage_Period.
```

Appendix B. The laboratory results of bromoform and water quality parameters

Table B1. Bromoform analysis of the synthetic potable water samples comprising 2.9% groundwater for the three tests conducted under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	Bromoform measurement (µg/l)		Average (µg/l)	Standard deviation	Bromoform measurement (µg/l)		Average (µg/l)	Standard deviation	Bromoform measurement (µg/l)		Average (µg/l)	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	27.3	27.4	27.3	0.07	27.3	27.4	27.3	0.07	27.3	27.4	27.3	0.07
24	28.5	28.4	28.4	0.07	28.9	29.2	29.0	0.21	29.3	29.2	29.3	0.07
48	27.9	29.8	28.8	1.34	28.4	30.2	29.3	1.27	28.4	30.5	29.5	1.48
72	29.1	29.0	29.0	0.07	29.6	29.9	29.8	0.21	29.8	29.7	29.7	0.07
96	29.4	29.1	29.3	0.21	28.8	30.6	29.7	1.27	29.8	30.2	30.0	0.28
120	29.4	30.5	30.0	0.78	30.1	30.4	30.3	0.21	30.2	30.7	30.5	0.35
144	29.8	30.4	30.1	0.42	30.5	30.7	30.6	0.14	28.9	33.3	31.1	3.11

Table B2. The result of residual chlorine analysis of the synthetic water samples comprising 2.9% groundwater obtained in the simulated residence time tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	Residual chlorine measurement (mg/l)		Average (mg/l)	Standard deviation	Residual chlorine measurement (mg/l)		Average (mg/l)	Standard deviation	Residual chlorine measurement (mg/l)		Average (mg/l)	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	0.78	0.79	0.785	0.007	0.78	0.79	0.785	0.007	0.78	0.79	0.785	0.007
24	0.77	0.76	0.765	0.007	0.75	0.76	0.755	0.007	0.75	0.76	0.755	0.007
48	0.74	0.74	0.740	0.000	0.75	0.74	0.745	0.007	0.73	0.73	0.730	0.000
72	0.74	0.73	0.735	0.007	0.72	0.71	0.715	0.007	0.71	0.70	0.705	0.007
96	0.73	0.73	0.730	0.000	0.72	0.69	0.705	0.021	0.71	0.70	0.705	0.007
120	0.73	0.72	0.725	0.007	0.69	0.70	0.695	0.007	0.66	0.67	0.665	0.007
144	0.73	0.71	0.720	0.014	0.69	0.69	0.690	0.000	0.67	0.65	0.660	0.014

Table B3. The result of UV_{254} absorbance measurements of the synthetic water samples comprising 2.9% groundwater obtained in the simulated residence time tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	UV_{254} absorbance measurement (cm^{-1})		Average (cm^{-1})	Standard deviation	UV_{254} absorbance measurement (cm^{-1})		Average (cm^{-1})	Standard deviation	UV_{254} absorbance measurement (cm^{-1})		Average (cm^{-1})	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	0.0031	0.0032	0.00315	0.00007	0.0031	0.0032	0.00315	0.00007	0.0031	0.0032	0.00315	0.00007
24	0.0030	0.0029	0.00295	0.00007	0.0026	0.0030	0.00280	0.00028	0.0026	0.0029	0.00275	0.00021
48	0.0032	0.0028	0.00300	0.00028	0.0027	0.0027	0.00270	0.00000	0.0028	0.0029	0.00283	0.00004
72	0.0030	0.0031	0.00305	0.00007	0.0031	0.0027	0.00290	0.00028	0.0028	0.0027	0.00275	0.00007
96	0.0027	0.0028	0.00275	0.00007	0.0028	0.0027	0.00275	0.00007	0.0026	0.0024	0.00250	0.00014
120	0.0025	0.0028	0.00265	0.00021	0.0025	0.0023	0.00240	0.00014	0.0024	0.0022	0.00230	0.00014
144	0.0025	0.0026	0.00255	0.00007	0.0024	0.0025	0.00245	0.00007	0.0024	0.0023	0.00235	0.00007

Table B4. The result of the estimated salinity of the synthetic water samples comprising 2.9% groundwater obtained in the simulated residence time tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	Salinity measurement		Average (mg/l)	Standard deviation	Salinity measurement		Average (mg/l)	Standard deviation	Salinity measurement		Average (mg/l)	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	151.5	151.5	151.5	0.0	151.5	151.5	151.5	0.0	151.5	151.5	151.5	0.0
24	152.1	151.9	152.0	0.2	151.6	151.2	151.4	0.3	151.5	151.3	151.4	0.1
48	151.0	150.8	150.9	0.2	151.5	151.5	151.5	0.0	152.7	151.5	152.1	0.9
72	152.1	151.3	151.7	0.6	152.6	151.6	152.1	0.7	152.9	151.4	152.2	1.1
96	150.8	151.1	150.9	0.2	151.7	151.1	151.4	0.5	153.6	151.1	152.4	1.8
120	152.0	151.5	151.8	0.4	152.7	151.7	152.2	0.7	153.9	151.8	152.8	1.5
144	152.2	151.8	152.0	0.3	151.7	151.5	151.6	0.2	151.3	151.9	151.6	0.4

Table B5. The result of pH measurements of the synthetic water samples comprising 2.9% groundwater obtained in the simulated residence time tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	pH measurement		Average	Standard deviation	pH measurement		Average	Standard deviation	pH measurement		Average	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	7.81	7.84	7.83	0.02	7.81	7.84	7.83	0.02	7.81	7.84	7.83	0.02
24	7.72	7.64	7.68	0.06	7.74	7.80	7.77	0.04	7.75	7.82	7.79	0.05
48	7.71	7.76	7.74	0.04	7.66	7.81	7.74	0.11	7.76	7.81	7.79	0.04
72	7.79	7.79	7.79	0.00	7.82	7.80	7.81	0.01	7.78	7.85	7.82	0.05
96	7.82	7.79	7.81	0.02	7.77	7.80	7.79	0.02	7.77	7.82	7.80	0.04
120	7.73	7.74	7.74	0.01	7.79	7.79	7.79	0.00	7.76	7.78	7.77	0.01
144	7.86	7.89	7.88	0.02	7.84	7.88	7.86	0.03	7.84	7.91	7.88	0.05

Table B6. The result of bromoform concentration in the synthetic water samples comprising 8.0% groundwater obtained in the simulated residence time tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	Bromoform measurement (µg/l)		Average (µg/l)	Standard deviation	Bromoform measurement (µg/l)		Average (µg/l)	Standard deviation	Bromoform measurement (µg/l)		Average (µg/l)	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	27.6	27.3	27.5	0.21	27.6	27.3	27.5	0.21	27.6	27.3	27.5	0.21
24	28.7	29.4	29.1	0.49	30.2	29.9	30.1	0.21	29.7	29.3	29.5	0.28
48	31.9	31.2	31.5	0.49	31.1	32.4	31.8	0.93	32.7	32.8	32.8	0.07
72	31.6	31.2	31.4	0.28	31.5	31.9	31.7	0.28	33.2	32.6	32.9	0.42
96	32.8	32.2	32.5	0.42	33.9	33.2	33.6	0.49	34.3	33.2	33.8	0.78
120	34.2	33.1	33.7	0.78	33.6	34.2	33.9	0.42	35.3	34.2	34.8	0.78
144	33.5	34.2	33.9	0.49	34.9	33.5	34.2	0.99	34.8	35.2	35.0	0.28

Table B7. The result of residual chlorine concentration of the synthetic water samples comprising 8.0% groundwater obtained in the simulated residence time tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	Residual chlorine measurement (mg/l)		Average (mg/l)	Standard deviation	Residual chlorine measurement (mg/l)		Average (mg/l)	Standard deviation	Residual chlorine measurement (mg/l)		Average (mg/l)	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	0.760	0.780	0.770	0.014	0.760	0.780	0.770	0.014	0.760	0.780	0.770	0.014
24	0.760	0.750	0.755	0.007	0.750	0.750	0.750	0.000	0.750	0.740	0.745	0.007
48	0.730	0.750	0.740	0.014	0.700	0.720	0.710	0.014	0.690	0.710	0.700	0.014
72	0.710	0.690	0.700	0.014	0.700	0.700	0.700	0.000	0.690	0.670	0.680	0.014
96	0.690	0.690	0.690	0.000	0.670	0.680	0.675	0.007	0.680	0.680	0.680	0.000
120	0.680	0.690	0.685	0.007	0.680	0.660	0.670	0.014	0.670	0.660	0.665	0.007
144	0.680	0.680	0.680	0.000	0.660	0.670	0.665	0.007	0.660	0.640	0.650	0.014

Table B8. The result of UV_{254} absorbance measurements of the synthetic water samples comprising 8.0% groundwater obtained in the simulated residence time tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	Average UV_{254} absorbance measurement (cm^{-1})		Average (cm^{-1})	Standard	Average UV_{254} absorbance measurement (cm^{-1})		Average (cm^{-1})	Standard	Average UV_{254} absorbance measurement (cm^{-1})		Average (cm^{-1})	Standard
	1st	2nd			1st	2nd			1st	2nd		
0	0.0038	0.0037	0.00375	0.0001	0.0038	0.0037	0.0038	0.0001	0.0038	0.0037	0.00375	0.0001
24	0.0038	0.0032	0.00350	0.00042	0.0032	0.0033	0.0033	0.00007	0.0034	0.0031	0.00325	0.00021
48	0.0034	0.0033	0.00335	0.00007	0.0030	0.0030	0.0030	0.00000	0.0030	0.0030	0.00300	0.00000
72	0.0030	0.0030	0.00300	0.00000	0.0028	0.0029	0.0029	0.00007	0.0031	0.0029	0.00300	0.00014
96	0.0028	0.0027	0.00275	0.00007	0.0027	0.0028	0.0028	0.00007	0.0029	0.0028	0.00285	0.00007
120	0.0029	0.0028	0.00285	0.00007	0.0027	0.0029	0.0028	0.00014	0.0028	0.0028	0.00280	0.00000
144	0.0027	0.0029	0.00280	0.00014	0.0029	0.0029	0.0029	0.00000	0.0027	0.0029	0.00280	0.00014

Table B9. The result of the estimated salinity of the synthetic water samples comprising 8.0% groundwater obtained in the simulated residence time tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	Salinity measurement (mg/l) 1st	2nd	Average (mg/l)	Standard deviation	Salinity measurement (mg/l) 1st	2nd	Average (mg/l)	Standard deviation	Salinity measurement (mg/l) 1st	2nd	Average (mg/l)	Standard deviation
0	308.0	310.2	309.1	1.6	308.0	310.2	309.1	1.6	308.0	310.2	309.1	1.6
24	309.1	306.9	308.0	1.6	308.0	306.4	307.2	1.2	308.0	306.9	307.5	0.8
48	309.7	306.9	308.3	1.9	310.8	308.0	309.4	1.9	308.6	307.5	308.0	0.8
72	306.4	306.9	306.6	0.4	306.9	307.5	307.2	0.4	307.5	306.9	307.2	0.4
96	306.4	306.4	306.4	0.0	306.9	306.4	306.6	0.4	308.6	307.5	308.0	0.8
120	308.0	307.5	307.7	0.4	310.2	308.0	309.1	1.6	309.7	309.1	309.4	0.4
144	309.7	309.1	309.4	0.4	309.1	308.6	308.8	0.4	310.2	309.1	309.7	0.8

Table B10. pH measurements of the synthetic water samples comprising 8.0% groundwater obtained in the tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	pH measurement		Average	Standard deviation	pH measurement		Average	Standard deviation	pH measurement		Average	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	7.80	7.79	7.80	0.01	7.80	7.79	7.80	0.01	7.80	7.79	7.80	0.01
24	7.74	7.71	7.73	0.02	7.74	7.80	7.77	0.04	7.75	7.76	7.76	0.01
48	7.63	7.77	7.70	0.10	7.76	7.77	7.77	0.01	7.81	7.84	7.83	0.02
72	7.82	7.82	7.82	0.00	7.74	7.80	7.77	0.04	7.83	7.82	7.83	0.01
96	7.76	7.82	7.79	0.04	7.80	7.79	7.80	0.01	7.82	7.86	7.84	0.03
120	7.79	7.84	7.82	0.04	7.86	7.87	7.87	0.01	7.84	7.82	7.83	0.01
144	7.79	7.83	7.81	0.03	7.84	7.87	7.86	0.02	7.84	7.86	7.85	0.01

Table B11. Bromoform concentration of the synthetic water samples comprising 15.0% groundwater obtained in the tests conducted under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	Bromoform measurement (µg/l)		Average (µg/l)	Standard deviation	Bromoform measurement (µg/l)		Average (µg/l)	Standard deviation	Bromoform measurement (µg/l)		Average (µg/l)	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	27.9	27.2	27.6	0.5	27.9	27.2	27.6	0.5	27.9	27.2	27.6	0.5
24	29.4	28.3	28.9	0.8	30.0	27.8	28.9	1.6	33.4	35.3	34.4	1.3
48	30.8	31.4	31.1	0.4	31.9	31.1	31.5	0.6	35.9	35.8	35.9	0.1
72	34.6	35.0	34.8	0.3	35.3	37.1	36.2	1.3	36.2	36.8	36.5	0.4
96	36.1	35.3	35.7	0.6	37.3	37.0	37.2	0.2	38.3	37.8	38.1	0.4
120	35.8	35.2	35.5	0.4	37.3	37.8	37.6	0.4	39.5	41.3	40.4	1.3
144	36.0	35.8	35.9	0.1	36.9	36.9	36.9	0.0	40.9	40.7	40.8	0.1

Table B12. Residual chlorine concentration of the synthetic water samples comprising 15.0% groundwater obtained in the tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	Residual chlorine measurement (mg/l)		Average (mg/l)	Standard deviation	Residual chlorine measurement (mg/l)		Average (mg/l)	Standard deviation	Residual chlorine measurement (mg/l)		Average (mg/l)	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	0.78	0.75	0.765	0.021	0.78	0.75	0.765	0.021	0.78	0.75	0.765	0.021
24	0.71	0.71	0.710	0.0	0.70	0.70	0.700	0.0	0.68	0.69	0.685	0.007
48	0.71	0.68	0.695	0.021	0.67	0.65	0.660	0.014	0.61	0.63	0.620	0.014
72	0.67	0.66	0.665	0.007	0.64	0.63	0.635	0.007	0.63	0.59	0.610	0.028
96	0.66	0.65	0.655	0.007	0.61	0.63	0.620	0.014	0.59	0.61	0.600	0.014
120	0.64	0.63	0.635	0.007	0.61	0.60	0.605	0.007	0.59	0.59	0.590	0.0
144	0.64	0.65	0.645	0.007	0.61	0.60	0.605	0.007	0.57	0.58	0.575	0.007

Table B13. The result of UV_{254} absorbance measurements of the synthetic water samples comprising 15.0 % groundwater obtained in the simulated residence time tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	Average UV_{254} absorbance measurement (cm^{-1})		Average (cm^{-1})	Standard	Average UV_{254} absorbance measurement (cm^{-1})		Average (cm^{-1})	Standard	Average UV_{254} absorbance measurement (cm^{-1})		Average (cm^{-1})	Standard
	1st	2nd			1st	2nd			1st	2nd		
0	0.0047	0.0047	0.0047	0.00000	0.0047	0.0047	0.0047	0.00000	0.0047	0.0047	0.0047	0.00000
24	0.0064	0.0062	0.0063	0.00014	0.0058	0.0056	0.0057	0.00014	0.0066	0.0065	0.00655	0.00007
48	0.0059	0.0062	0.00605	0.00021	0.0054	0.0053	0.00535	0.00007	0.0053	0.0053	0.0053	0.00000
72	0.0055	0.0056	0.00555	0.00007	0.0054	0.0058	0.0056	0.00028	0.0049	0.0049	0.0049	0.00000
96	0.0051	0.0054	0.00525	0.00021	0.0042	0.0047	0.00445	0.00035	0.0038	0.0037	0.00375	0.00007
120	0.0040	0.0039	0.00395	0.00007	0.0042	0.0041	0.00415	0.00007	0.0037	0.0035	0.0036	0.00014
144	0.0039	0.0039	0.0039	0.00000	0.0039	0.0038	0.00385	0.00007	0.0038	0.0038	0.0038	0.00000

Table B14. The result of the estimated salinity of the synthetic water samples comprising 15.0% groundwater obtained in the simulated residence time tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	Salinity measurement		Average (mg/l)	Standard deviation	Salinity measurement		Average (mg/l)	Standard deviation	Salinity measurement		Average (mg/l)	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	510.0	507.5	508.7	1.8	510.0	507.5	508.7	1.8	510.0	507.5	508.7	1.8
24	510.5	510.1	510.3	0.3	509.7	510.9	510.3	0.8	513.9	513.6	513.7	0.2
48	513.5	512.8	513.2	0.5	519.4	519.1	519.3	0.2	510.8	512.4	511.6	1.1
72	511.9	511.1	511.5	0.6	513.3	516.3	514.8	2.1	514.0	515.7	514.9	1.2
96	514.0	513.5	513.8	0.4	519.0	517.9	518.5	0.8	515.7	513.6	514.7	1.5
120	511.8	510.1	511.0	1.2	513.0	511.9	512.5	0.8	513.6	522.0	517.8	5.9
144	511.8	512.4	512.1	0.4	509.7	510.6	510.1	0.6	509.7	508.3	509.0	1.0

Table B15. The pH measurement of the synthetic water samples comprising 15.0% groundwater obtained in the simulated residence time tests under three different temperature conditions

Time (Hours)	Incubation temperature 20° C				Incubation temperature 25° C				Incubation temperature 30° C			
	pH measurement		Average	Standard deviation	pH measurement		Average	Standard deviation	pH measurement		Average	Standard deviation
	1st	2nd			1st	2nd			1st	2nd		
0	7.56	7.75	7.66	0.13	7.56	7.75	7.66	0.13	7.56	7.75	7.66	0.13
24	7.72	7.68	7.70	0.03	7.82	7.79	7.81	0.02	7.72	7.72	7.72	0.00
48	7.64	7.75	7.70	0.08	7.73	7.71	7.72	0.01	7.72	7.61	7.67	0.08
72	7.69	7.76	7.73	0.05	7.60	7.69	7.65	0.06	7.37	7.62	7.50	0.18
96	7.66	7.79	7.73	0.09	7.57	7.71	7.64	0.10	7.76	7.79	7.78	0.02
120	7.65	7.73	7.69	0.06	7.74	7.73	7.74	0.01	7.49	7.68	7.59	0.13
144	7.78	7.82	7.80	0.03	7.74	7.77	7.76	0.02	7.76	7.80	7.78	0.03

Appendix C

Table C1 The water quality parameters obtained from the tests (duration: 35 days) conducted on water samples comprising 2.9% groundwater under & 30ºC temperature conditions

Initial bromoform (µg/l)	bromide (µg/l)	temp. (°C)	storage period (hours)	residual chlorine (mg/l)	ultra violet absorbance 254 (cm^{-1})	pH	blending ratio (%)	bromofom (µg/l)
9.08	0.004	30	0	0.78	0.0045	7.38	2.9	6.46
9.08	0.004	30	24	0.73	0.0033	7.33	2.9	8.59
9.08	0.004	30	48	0.70	0.0036	7.39	2.9	8.97
9.08	0.004	30	72	0.69	0.0031	7.43	2.9	9.52
9.08	0.004	30	96	0.64	0.0030	7.42	2.9	11.15
9.08	0.004	30	120	0.62	0.0029	7.53	2.9	12.69
9.08	0.004	30	192	0.60	0.0028	7.61	2.9	16.33
9.08	0.004	30	216	0.58	0.0025	7.52	2.9	18.05
9.08	0.004	30	360	0.52	0.0022	7.49	2.9	19.76
9.08	0.004	30	528	0.45	0.0021	7.54	2.9	21.55
9.08	0.004	30	840	0.44	0.0018	7.61	2.9	23.55

Table C2 The water quality parameters obtained from the tests (duration: 35 days) conducted on water samples comprising 8.0% groundwater under & 30ºC temperature conditions

Initial bromoform (μg/l)	bromide (μg/l)	temp. (°C)	storage period (hours)	residual chlorine (mg/l)	ultra violet absorbance 254 (cm^{-1})	pH	blending ratio (%)	bromoform (μg/l)
9.33	0.0104	30	0	0.76	0.005	7.36	8	8.04
9.33	0.0104	30	24	0.72	0.0037	7.33	8	8.28
9.33	0.0104	30	48	0.71	0.0036	7.43	8	8.42
9.33	0.0104	30	72	0.7	0.0037	7.45	8	9.97
9.33	0.0104	30	96	0.63	0.0035	7.46	8	10.21
9.33	0.0104	30	120	0.61	0.0033	7.50	8	12.65
9.33	0.0104	30	168	0.54	0.0034	7.59	8	16.27
9.33	0.0104	30	240	0.53	0.0032	7.56	8	16.74
9.33	0.0104	30	360	0.51	0.0031	7.55	8	19.29
9.33	0.0104	30	504	0.48	0.0029	7.56	8	22.21
9.33	0.0104	30	624	0.44	0.0027	7.52	8	25.29
9.33	0.0104	30	840	0.42	0.0024	7.65	8	25.63

Table C3 The water quality parameters obtained from the tests (duration: 35 days) conducted on water samples comprising 15.0% groundwater under & 30ºC temperature conditions

Initial bromoform (μg/l)	bromide (μg/l)	temp. (°C)	storage period (hours)	residual chlorine (mg/l)	ultra violet absorbance 254 (cm^{-1})	pH	blending ratio (%)	bromofom (μg/l)
9.67	0.0195	30	0	0.73	0.0064	7.49	15	7.25
9.67	0.0195	30	24	0.70	0.0053	7.52	15	8.83
9.67	0.0195	30	48	0.65	0.0048	7.51	15	11.99
9.67	0.0195	30	72	0.64	0.0045	7.53	15	13.15
9.67	0.0195	30	96	0.62	0.0046	7.60	15	14.03
9.67	0.0195	30	120	0.60	0.0045	7.62	15	15.75
9.67	0.0195	30	144	0.59	0.0043	7.66	15	17.97
9.67	0.0195	30	192	0.52	0.0042	7.66	15	20.47
9.67	0.0195	30	264	0.50	0.004	7.65	15	23.64
9.67	0.0195	30	384	0.46	0.0038	7.64	15	29.51
9.67	0.0195	30	576	0.44	0.0037	7.65	15	33.75
9.67	0.0195	30	840	0.40	0.0035	7.68	15	37.37

Appendix D

Table D1 The correlation between the parameters of bromoform model

		bromoform	residual chlorine	temperature	storage period	UV$_{254}$	pH	blending ratio	bromide
bromoform	Pearson Correlation	1	-0.938-**	0.200	0.647**	0.201	-0.235-	0.580**	0.580**
	Sig. (2-tailed)		0.000	0.116	0.000	0.115	0.064	0.000	0.000
	N		63	63	63	63	63	63	63
residual chlorine	Pearson Correlation		1	-0.236-	-0.721-**	-0.212-	0.205	-0.550-**	-0.551-**
	Sig. (2-tailed)			0.063	0.000	0.095	0.106	0.000	0.000
	N			63	63	63	63	63	63
temperature	Pearson Correlation			1	0.000	-0.095-	0.046	0.000	0.000
	Sig. (2-tailed)				1.000	0.459	0.722	1.000	1.000
	N				63	63	63	63	63
storage period	Pearson Correlation				1	-0.342-**	0.260*	0.000	0.000
	Sig. (2-tailed)					0.006	0.040	1.000	1.000
	N					63	63	63	63
UV$_{254}$	Pearson Correlation					1	-0.594-**	0.814**	0.817**
	Sig. (2-tailed)						0.000	0.000	0.000
	N						63	63	63
pH	Pearson Correlation						1	-0.580-**	-0.583-**
	Sig. (2-tailed)							0.000	0.000

	N							63	63
blending ratio	Pearson Correlation							1	1.000**
	Sig. (2-tailed)								0.000
	N								63
bromide	Pearson Correlation								1
	Sig. (2-tailed)								
	N								

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Appendix E

Table E1 The model variables for the fresh potable water samples taken during the tests

Experimental temperature condition (°C)	Storage period (hrs)	Bromoform (µg/l)	Residual chlorine (mg/l)	UV_{254} absorbance (cm^{-1})	pH
20	0	30.25	0.660	0.0034	7.99
	24	32.45	0.625	0.0039	8.07
	48	33.20	0.630	0.0035	7.98
	72	33.45	0.625	0.0036	8.07
	96	33.90	0.620	0.0032	7.93
	120	35.60	0.615	0.0025	8.09
	144	36.00	0.615	0.0016	8.06
25	0	30.25	0.660	0.0034	7.99
	24	32.80	0.625	0.0037	7.99
	48	33.70	0.620	0.0035	8.02
	72	34.10	0.620	0.0033	8.03
	96	34.55	0.615	0.0035	8.02
	120	36.00	0.610	0.0023	8.12
	144	36.35	0.605	0.0015	8.01
30	0	30.25	0.660	0.0034	7.99
	24	33.45	0.625	0.0040	8.08
	48	34.00	0.620	0.0036	8.03
	72	34.65	0.620	0.0032	8.09
	96	36.00	0.610	0.0034	7.97
	120	36.30	0.605	0.0022	8.07
	144	37.10	0.600	0.0012	8.02