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The Occurrence and Formation Potential of Trihalomethanes  
in Drinking and Recreational water in  
Tulkarm District, Palestine

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Tulkarm District, Palestine

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Recreational water in Tulkarm District, Palestine

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Jerusalem-Palestine  
1426/2005

## **Dedication**

To

My Teachers and my Family

**Declaration:**

I certify that this thesis submitted for the degree of Master is the result of my own research, except where otherwise acknowledged, and that this thesis (or any part of the same) has not been submitted for a higher degree to any other university or institution.

Signed.....

Amer Ateyah Saleem Kan'an

Date: 27 /11/ 2005

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## **Abstract**

Chlorination of drinking water process leads to the formation of a variety of Disinfection By-Products (DBPs) that are considered suspected carcinogenic and mutagenic contaminants and may have adverse health effects on humans. Trihalomethanes (THMs) are a group of compounds that can form when the chlorine, used to disinfect drinking and recreational waters, reacts with the organic matter in the water. The THMs most commonly found in chlorinated water are chloroform, bromodichloromethane, dibromochloromethane and bromoform. THMs are the most frequent Chlorination By-Products (CBPs) and they have been used as surrogates for other CBPs occurrence in drinking water.

Information about the concentrations of THMs in drinking and recreational waters in the West Bank-Palestine is lacking.

A water chemistry evaluation was made for four municipal wells of Tulkarm and Anabta. Nitrate values were 39 mg/L to 141.9 mg/L with mean value 81.9 mg/L, exceeding the Palestinian and the WHO allowable limits.

The average Non-Purgable Organic Carbon (NPOC) in four wells' water samples was 3.6 mg/L and 0.5 mg/L in May and June 2005 respectively.

Free chlorine residual was in the range of 0.01 to 0.43 mg/L in all the samples, with mean value 0.16 mg/L which is far less than the recommended values by the WHO required for efficient drinking water disinfection.

Total trihalomethanes (TTHMs) in tap water were below the MCL of the WHO, EU, and USEPA. The average value of TTHMs in 22 tap water samples was 24.81 µg/L, ranging

from 2.7 µg/L at the chlorination points to 52.7µg/L at the most terminal sampled points of the distribution system.

The travel time effect on THMs formation in the distribution system was clear through the elevated levels of THMs in the samples from extremities points of the distribution system.

THMFP for water samples obtained from three municipal wells, Shwaika (Misnawi) well, Tulkarm municipal well 2 and Anabta municipal well 2 were 153.6 µg/L, 1149.7 µg/L and 290.7 µg/L respectively. THMs formed in the THMFP experiment exceeded the MCL after 6 hours in the sample of Shwaika (Misnawi) well and after 8 hours in the sample of Tulkarm well 2, but after 52 hours in the sample of Anabta well 2.

The pH of the waters of three swimming pools did not comply with the pH recommended by the WHO (6.5-7.6).

The free chlorine determined in the waters of the swimming pools was less than 1 mg/L in three swimming pools and in the other three swimming pools was between 1.44 mg/L and 2.09 mg/L.

The maximum and minimum measured concentration of TTHMs in the swimming pools' waters was 2853.2 µg/L and 405.1 µg/L respectively. Chloroform was the dominant THM occurred in the swimming pools' waters.

The results of this study will be valuable to the Palestinian Water Authority (PWA) in defining the chlorination process efficiency and THMs regulation. Findings are also beneficial for the Palestinian Ministry of Health.



## مُلخَص

يستخدم الكلور في معالجة مياه الشرب والسباحة وذلك من أجل تعقيم المياه والإبقاء على كمية كلور كافية للحد من تلوث المياه أثناء توزيعها في شبكات المياه.

ولكن عملية الكلورة هذه يصاحبها تكون نواتج ثانوية ضارة غير مرغوب بها جراء تفاعل الكلور مع المواد العضوية الموجودة في المياه المكلورة وقد تكون هذه المواد ممرضة ومسرطنة.

وتعتبر مجموعة المركبات ثلاثي هالوجين الميثان (الهالوميثانات) من ابرز المواد الجانبية الضارة التي تنتج عن عملية الكلورة. وأكثر الهالوميثانات توكناً هي الكلوروفورم وبروميد ثنائي كلورو الميثان وثنائي بروميد كلورو الميثان والبرموفورم. ويشير تكون الهالوميثانات الى ان مواد جانبية اخرى ذات أثر سلبي على صحة الانسان تتكون عند كلورة المياه.

ورغم أن عملية الكلورة شائعة لتعقيم المياه في الضفة الغربية- فلسطين إلا أن هذه المواد الناتجة من عملية الكلورة لم يتم قياسها في مياه الشرب والسباحة من قبل، ولا يوجد معلومات عن التراكيز الناتجة لهذه المواد رغم أن هذه النتائج ضرورية لسلطة المياه الفلسطينية ووزارة الصحة لمراقبة وتدقيق فعالية الكلورة في تعقيم المياه ووضع المعايير اللازمة لوجود الهالوميثانات في مياه الشرب والسباحة.

وفي هذا البحث تم تقييم بعض مكونات المياه الجوفية الكيماوية والتي هي مصدر مياه الشرب في منطقة طولكرم وعنتابا والتي بينت ان النيتريت يتراوح بين 39 ملغم/لتر و 141.9 ملغم/لتر وبمعدل 81.9 ملغم/لتر، متجاوزاً المعايير المعتمدة من منظمة الصحة العالمية وسلطة المياه الفلسطينية.

وكذلك تم قياس محتوى المياه من المواد العضوية في نهاية الفصل الماطر لعام 2005 وكانت قيمة هذه المواد في المياه الجوفية (مصدر مياه الشرب) بمعدل 3.6 ملغم/لتر و 0.5 ملغم/لتر في شهري أيار وحزيران على الترتيب.

ولأول مرة تم قياس الهالوميثانات في مياه الشرب وبرك السباحة وكذلك كمية الكلور الحر والفعال في عملية تعقيم المياه اضافة الى إجراء فحص لإمكانية تكون الهالوميثانات في ثلاث عينات مياه جوفية من آبار في طولكرم وعنبتا.

وتراوحت كمية الكلور في 23 عينة مياه شرب تم الحصول عليها من نقاط الكلورة و بيوت موزعة في طولكرم وعنبتا من 0.01 ملغم/لتر الى 0.43 ملغم/لتر وبمعدل 0.16 ملغم/لتر وتقل هذه الكمية عن الكمية المعتمدة من منظمة الصحة العالمية والتي يجب الا تقل عن 0.5 ملغم/لتر.

وأوضحت النتائج أن الهالوميثانات كانت بمعدل 22.8 ميكروغرام/لتر، متراوحة ما بين 2.7 ميكروغرام/لتر عند نقطة الكلورة و 52.7 ميكروغرام في أكثر العينات بعداً عن نقطة الكلورة. وقد أظهرت نتائج قياس الهالوميثانات في شبكات مياه الشرب أن المسافة التي تقطعها مياه الشرب المكلورة داخل شبكة التوزيع تؤدي إلى ارتفاع تركيز الهالوميثانات.

وكانت نتائج فحص إمكانية تكون الهالوميثانات على مدار إسبوع من كلورة المياه: 152.6 ميكروغرام/لتر في مياه بئر عنبتا 2، وكذلك 1149.7 ميكروغرام/لتر في مياه بئر شويكة و 290.7 ميكروغرام/لتر في مياه بئر طولكرم 2. وقد تجاوزت كمية الهالوميثانات الحد الأعلى المسموح به من هذه المواد في مياه الشرب بعد 6 ساعات في مياه بئر شويكة و 8 ساعات في بئر بلدية طولكرم ولكن بعد 52 ساعة في مياه بئر عنبتا 2.

وبسبب وجود تراكيز عالية من البروميد ( 0.72 - 0.94 ملغم/لتر) في المياه الجوفية (مصدر مياه الشرب) في منطقة طولكرم فقد سادت مركبات الهالوميثان الداخل في تركيبها البروميد في مياه الشرب.

وقد تم فحص مياه السباحة في ست برك سباحة في منطقة طولكرم وتبين عند الفحص ان درجة حموضة مياه ثلاث برك لا تتوافق مع توصيات منظمة الصحة العالمية بهذا الشأن، ووجد ايضاً أن

الكلور الفعال يقل عن 1 ملغم /لتر في ثلاث برك وفي البرك الأخرى كان من 1.44 ملغم/لتر إلى  
2.09 ملغم/لتر وبالنسبة لفحص الهالوميثانات في مياه برك السباحة فقد تراوحت كميتها من 455.1  
الى 2853.2 ميكروغرام/لتر وقد ساد من بين هذه الهالوميثانات الكلوروفورم .

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## Abbreviations and Units

<b>Abbreviation:</b>	
Br	Bromide
C	Concentration
CBPs	Chlorine by-products
DBPs	Disinfection By-Products
DOC	Dissolve Organic Carbon
DPD	N,N-Diethyl-p-phenylenediamine
EC	Electric Conductivity
EU	European Union
GC-MS	Gas Chromatograph-Mass Spectrometer
GV	Guideline Value
MAC	Maximum Admissible Concentration
MCL	Maximum Contamination Level
Min.	Minute
NOM	Natural Organic Matter
NPOC	Non-Purgeable Organic Carbon
PA	Palestinian Authority
PCBS	Palestinian Central Bureau of Statistics
PEHD	Polyethylene High Density
PWA	Palestinian Water Authority
SIM	Selective Ion Mode
SPME	Solid Phase Micro Extraction
THM	Trihalomethane
THMFP	Trihalomethane Formation Potential
THMs	Trihalomethanes
TOC	Total Organic Carbon
TTHMs	Total Trihalomethanes
UNEP	United Nations Environment Program
USEPA (EPA)	United States Environmental Protection Agency
WHO	World Health Organization
<b>Unit</b>	
µg/L	Microgram per Liter
µS	Micro Siemens
L	Liter
M	Meter
MCM/yr	Million Cubic Meter per Year
Mg	Milligram
mL	Milliliter
N	Normal (Normality)



# Chapter 1

## Introduction

### 1.1 Background:

Water is the most important natural resource for human being life. Safe and reliable source of water is one of the most vital and essential prerequisites for the community to be stable and safe. The importance of safe water supply was recognized early as civilizations were built. Nowadays rarely we find a community without a piped water source (distribution system) that is available for the daily use and consumption. Water if contaminated has a great potential for causing and transmitting diseases. Microbial contamination of water is one of the major causes for waterborne diseases. This microbial contamination was early discovered to be one of the most important challenges for the authorities responsible for water distribution. According to the statistical information of the World Health Organization (WHO), about 80% of diseases, and more than one third of deaths in developing countries are water-born diseases (Jalal, 1998). Distributing potable water needs pre water treatment actions that ensure high water quality and hygienic parameters before reaching consumers.

Water contamination can arise at four different points in the water supply cycle (Gray, 2002):

1. At the resource
2. During the treatment stage

3. During distribution
4. Within the household plumbing system.

Investment in ensuring access to safe drinking water is valuable and important because its net economic benefit in reducing the costs of the adverse health effect and health cost care; (prevention is better than cure). These economical and social advantages can be achieved by ensuring and maintaining the drinking water quality within the international and national guidelines and standards.

The guidelines for drinking water quality are kept up to date through a process of rolling revision, and they are addressed primarily to water and health regulators, policy makers and their advisors to assist in the development of national standards (WHO, 2004).

The principle of water treatment before and during distribution is to make raw water safe and palatable to drink. World Health Organization (WHO) Guidelines call for uncompromised disinfection of drinking water despite the formation of disinfection by-products (DBPs) with potential health effects (WHO, 2004).

The most important municipal treatment is the destruction of pathogenic microorganisms. For hundreds of years, people died when pathogenic bacteria got into water supplies. This stopped in 1908 when municipal water systems began to add the disinfectant chlorine to the city's water to kill microorganisms (Kelter et al., 1999; Gray, 2002).

A disinfectant is normally used to kill or disable potentially harmful microorganisms. Chlorine is the most disinfectant that is widely used in water disinfection (Gray, 2002).

A disinfectant residual is kept throughout the distribution system in case of any possible microbe contamination or regrowth (Deok-Hee Cho et al, 2003; Gray, 2002). Despite the obvious benefits of adding chlorine and maintaining a disinfectant residual, there are also potential problems and concerns about the safety of chlorine use, because chlorine can combine with Natural Organic Matter (NOM) to form carcinogenic Disinfection By-Products (DBPs). Rook and Bellar et al. reported in 1974 the discovery of the formation of haloforms during chlorination of drinking water (Rathbun, 1997; Jimmy C. Ya and Lai-nor Cheng, 1999; Rodriguez and Serodes, 2001), and after that many halogenated compounds have been reported in chlorinated drinking water and have been assessed for toxicity (Nikolaou et al., 1999; Salameh et al., 2002; WHO, 2004; WHO, 2005). Of these DBPs are trihalomethanes (THMs) which had been proved to be formed and found in waters treated by chlorine (Nikolaou et al., 1999; Golfinopoulos, 2000; Gray, 2002).

Epidemiological studies since the first chlorination by-products (CBPs) were detected in drinking waters early in 1970s have evaluated the probable health effects of those compounds indicating that they are related to cancer (Golfinopoulos, 2000; Villanueva et al., 2003).

In Palestine, Groundwater is the main source for drinking water. Before distributed to the end users, water is chlorinated as a disinfection measure. Palestinian Water Authority (PWA) and other local authorities (Municipalities and local councils); in addition to the

Ministry of Health are the main responsible organizations about water distribution and quality control. PWA was created on 26<sup>th</sup> April 1995, derives its authority from Law No 2 for 1996, issued by the Palestinian Authority (PA). Article 4 of Law 2 sets out the functions of the PWA, they include:

- (1) Guaranty defragmentation of hydrological data collection and archiving and publishing all water resources data and information.
- (2) The monitoring, inspection and management of all Palestinian water resources.

The PWA is the official body which regulates and is responsible for overall water resources in the West Bank and Gaza Strip (PA-PWA, 2000).

Regarding the quality of drinking water the PWA is responsible for imposing a set of regulations on the service providers, which should satisfy the requirements of the various stakeholders including the Ministry of Health (UNEP, 2003).

The monitoring of bulk water is necessary for the improvement of the management of the bulk water system in the West Bank. At the present time, it is considered that the quality of the water coming from wells is good but no organic contaminant, toxic heavy metal, fertilizer or pesticide is analyzed. Also there is no monitoring on the water delivered from Mekorot, reservoirs, and other distributing points. In the small municipalities or villages; analyses are limited (Seureca, 2004).

In the West Bank, information about the DBPs concentration or their formation potential is lacking. Concentrations of THMs in the finished drinking water supply systems and recreational water in swimming pools in the West Bank have not been measured before.

This study is addressed to achieve the following aims:

1. Measurement of THMs in the drinking water reaching the end users in Tulkarm and Anabta.
2. Measurement of the THMs in recreational water in the swimming pools in Tulkarm.
3. Determination the THMs formation potential (THMFP) in the groundwater in Tulkarm and Anabta.

## **1.2 Literature Review:**

Rook and Bellar et al. (1974) discovered that chlorination of drinking water leads to the formation of disinfection by-products caused by the reaction of chlorine and naturally occurring organic matter (Rathbun, 1997; Jimmy and Lai-nor Cheng, 1999; Rodriguez and Serodes, 2001). Trihalomethanes are the major disinfection by-products produced, and they were the first detected category of DBPs (Nikolaou et al., 1999; WHO, 2005). THMs are detected in most chlorinated water systems (Golfinopoulos, 2000). THMs formation is a function of organic matter concentration, temperature, pH -increases at high pH-, chlorine dose, contact time (travel time), and bromide ion concentration which alternate the chloro-bromo speciation (Nikolaou, 1999; Kampioti and Stephanou, 2002).

THM formation potential THMFP is a suggested tool for detecting organic contamination of groundwater caused by waste water and landfill leachate. Dissolved Organic Carbon (DOC) can be difficult to quantify. THMs can be an analogue indicator (Stuart et al., 1999; Stuart et al., 2001). The formation potential of DBPs is dependent on the amount of organic matter in the raw water (Sanukida et al., 2001).

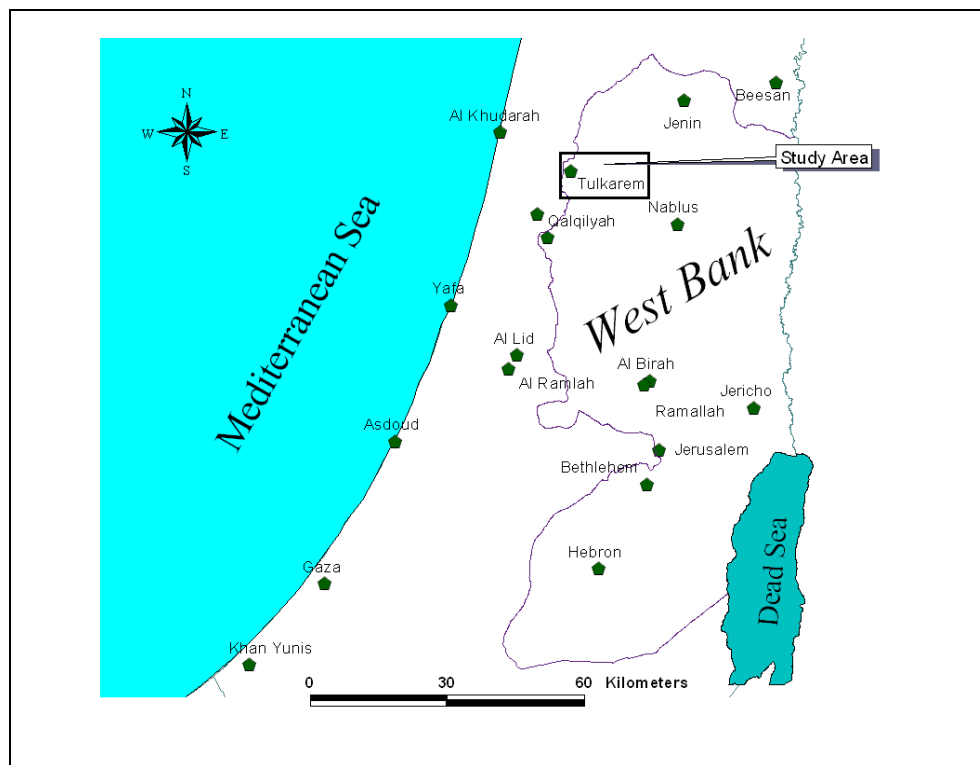
Exposure routes to THMs are ingestion, inhalation and percutaneous absorption (dermal) (Xu Xu et al., 2002; Tsair-Fuh Lin and Shih-Wen Hoang, 2000).

Epidemiological studies suggest that probable health effects of these compounds may be related to cancer (Villanueva et al, 2003; Golfinopoulos, 2000; WHO, 2005). Several studies have suggested that the risk of different cancer cases are increased where chlorinated water have been used (Tokmak et al., 2004). A positive association for growth retardation, small body length and urinary tract defects has been suggested according to several assessment studies concerning the adverse effects and exposure to DBPs (Graves et al., 2001; Calderon, 2000).

A number of analytical methods have been used in THMs analysis, of these; liquid- liquid extraction, static headspace technique, dynamic headspace technique (purge and trap), direct aqueous injection, and solid phase microextraction (SPME). The static headspace method is suitable for the analysis of samples with high content of volatiles, such as THMs (Kuivinen and Johnsson, 1999; Deok-Hee Cho et al., 2003; WHO, 2005; Yuefeng Xie, 2000).

### 1.3 Study Site:

Tulkarm is located in the northwestern part of the West Bank (Fig1.1), very close to the costal plain, 15 km east of the Mediterranean Sea. The population of Tulkarm district is about 134,110 inhabitants (PCBS, 2005). The climate of Tulkarm is subtropical, winter is the raining season, and average temperature in winter ranges from 8 ° C to 16 ° C. In the summer the range is from 17 ° C to 30 ° C (ARIJ, 1996). Tulkarm is within the western mountain basin which is one of the major groundwater basins in the West Bank. The renewable recharge of this basin expected to be 360 MCM/yr. Palestinians abstract only about 20 MCM/yr and the rest flow westwards and trapped by the Israelis (PA-PWA, 2000).



**Fig. 1.1:** Tulkarm, West Bank/Palestine (Study Area)

Water Supply Department of Tulkarm Municipality provides drinking water for 90,000 inhabitants; the other surrounding villages with about 45,000 inhabitants have their own supply systems from private wells (Water Supply Department of Tulkarm Municipality, 2005).

Tulkarm and Anabta Municipalities are responsible for supplying and distributing drinking water from municipal wells; these are six municipal wells in Tulkarm city and two in Anabta. In some limited cases mainly in summertime the water department in Tulkarm gains groundwater from private agriculture wells to compensate water shortage that faced during this period (Water Supply Department of Tulkarm Municipality, 2005). Rameen is a small village located five kilometers to the east of Anabta, receives drinking water from Anabta Municipality wells.

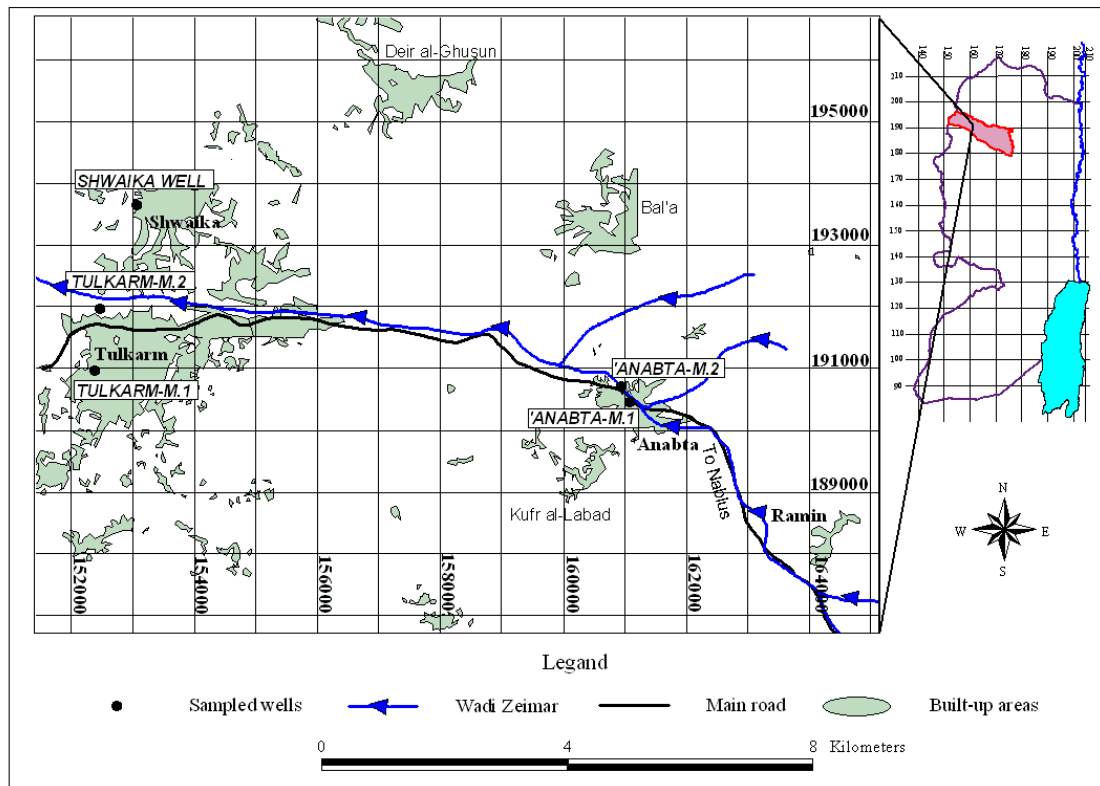
Water chlorination at the point of abstraction from the municipal wells is the only treatment before drinking water enters the distribution system. Additional disinfection or chlorination process does not take place at any point of the system. Most houses use the plastic tanks on the houses' roofs as water temporal storage before using through the tap inside the house.

Five swimming pools distributed in Tulkarm area use groundwater for recreation. All swimming pools are disinfected outdoor pools. Chlorine in different forms (Gas, Sodium or Calcium hypochlorite) is used for disinfecting these pools. The swimming pools are opened for the public of a wide range ages, males and females and kids. These swimming pools are poorly managed to meet the recommended standards either in water disinfection or in



maintaining other chemical, biological and physical water properties (Al-Khatib and Salah, 2003).

Municipal and agriculture wells in Tulkarm and Anabta are close to Wade Zeimar (Fig1.2) which originates from Nablus hills and flows westwards to the west through Anabta.



**Fig. 1.2:** Study Area (Tulkarm District/West Bank)

Nablus, Anabta, refugee camps and other villages along the Wade discharge their sewage in the Wade which continuously flows during the year. Industrial wastewater from food processing, tanning, textile, stone cutting and metal industries is also discharged into the Wade stream at different points along its path from east to west.

There are 19 olive oil mills in the region producing around 1000 m<sup>3</sup> of (zebar) per day (CDM, 2004) discharging their waste "zebar" either directly into the Wade or to cesspits during the olive oil processing period at the beginning of the rain season.

A solid waste site is located to the west of Anabta in the way to Tulkarm in the catchment area of Wade Zeimar. The organic and inorganic leachate from this solid waste site drains directly to the Wade and into the underground.

These pollution sources support the anecdotal stories and much circumstantial information to suggest that groundwater quality in Tulkarm is under significant threat (CDM, 2004). This heavily contaminated surface water has been considered as a pollution source of the surface and groundwater which is the only source of drinking and agriculture water in Tulkarm district (Pfeiffer and Kloss, 2005).

Table 1.1 shows the data of the five municipal wells that were sampled in this study. The depth of the municipal wells in Tulkarm and Anabta ranges between 100 to 200 m representing wells of the aquifer in the area (PA-PWA, 2000; Scarpa, 1998). These wells represent groundwater water from the Upper Cenomanian aquifer which consists mainly from karstic limestone and dolomites (Scarpa et al., 1998).

Table 1.1: Tulkarm and Anabta municipal wells sampled.

Well	Well ID	Aquifer	Coordination		Latitude	Longitude	Well Depth m	Water Use
			E-W	N-S				
<b>Anabta Municipality</b> <b>1</b>	16-19/001	Upper Cenomanian	161,100	190,400	32° 18′	35° 07′	150	Domestic
<b>Anabta Municipality</b> <b>2</b>	16-19/002	Upper Cenomanian	160, 970	190,650	32° 19′	35° 07′	200	Domestic
<b>Tulkarm Municipality</b> <b>1</b>	15-19/017	Upper Cenomanian	152,400	190,920	32° 19′	35° 01′	100	Domestic
<b>Tulkarm Municipality</b> <b>2</b>	15-19/018	Upper Cenomanian	152,480	190,900	32° 19′	35° 01′	118	Domestic
<b>Shwaika (Misnawi) Well</b>	New	Upper Cenomanian	153,200	193,500	32°	35°	120	Domestic

## **Chapter 2**

### **Disinfectants and Disinfection By-Products (DBPs)**

#### **2.1 Disinfectants:**

Microbial hazards and waterborne diseases continue to be a primary concern of the public health (WHO, 2005). Experience has shown the value of a systematic approach towards securing microbial safety. Health based target provide a "benchmark" for water suppliers (WHO, 2004). Primarily ensuring good and safe drinking water can be achieved by the reduction or removal (disinfection) of microbial contaminants through treatment process and the prevention of microbial regrowth during storage, distribution, and end-user consuming of drinking water. This can be achieved by applying disinfectants that are able to disinfect any microbial infection of the source water and maintaining a disinfectant residual throughout the distribution system to limit any possible microbial growth problems (DeSchuytner et al., 2000).

The earliest references to water treatment appear in ancient Sanskrit and Egyptian hieroglyphic writings. As early as the fourth century B. C., the Greek physician Hippocrates recommended straining and boiling water before drinking it. It was not until early 19<sup>th</sup> century that the proper combination of knowledge and technology allowed effective protection of the general public from unsafe water (Garfield, 1985).

A wide range of disinfectants are available, chlorination, ozonation, chloramination, Chlorine dioxide, UV radiation, and advanced oxidation processes. Of these methods chlorination of drinking water is the most used disinfection process (Gray, 2002; USEPA, 2004). Chlorine disinfection is the most widely applied method for potable water disinfection because of its effectiveness and economy (Garfield, 1985; El-Shahat et al., 2001; Gray, 2002). Chlorine has a broad-spectrum germicidal potency and persistence in treated water distributed to the end users; this provides longer protection against microbial regrowth (Christman, 2004).

Chlorination of drinking water started for the first time in the United States in 1908 (Garfield, 1985; DeSchuytner et al., 2000) and then chlorination became one of the most important and widely used method in developed and developing countries. During the treatment process, chlorine is added to drinking water as elemental chlorine (chlorine gas), sodium hypochlorite solution, dry calcium hypochlorite or chlorine dioxide. Chlorine has the advantage of ensuring clean water reaching the tap, whereas other disinfectants -such as ozone, UV light and ultra filtration- are unable to prevent the regrowth of biological contaminants (Wijk, 2002; Gray, 2002). In addition to the controlling disease-causing organisms, chlorination offers a number of benefits including:

- Reduces many disagreeable tastes and odors;
- Eliminates slime bacteria, molds and algae that commonly grow in water supply reservoirs, on the walls of water mains and in storage tanks;
- Removes chemical compounds that have unpleasant tastes and hinder disinfection

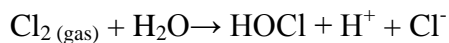
- Helps remove iron and manganese from raw water (Chlorine Chemistry Council and Canadian Chlorine Coordinating Committee, 2003).

Chlorine replacement with alternative disinfectants is still not the choice. Although they help in minimizing the THMs formation they have other undesirable problems. Ozone has not the ability to prevent regrowth in the distribution system and is cost; chloramines have less efficiency and toxic, chlorine dioxide produce chlorite and chlorate which are inorganic pollutants (Jimmy C. Yu and Lai-nor Cheng, 1999; Gray 2002).

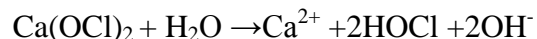
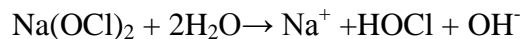
## **2.2 Chlorine and Chlorine Chemistry:**

In 1774, a Swedish pharmacist Carl W. Scheel discovered chlorine (Wijk, 2002). Chlorine is a common nonmetallic element belonging to the halogens, which is best known as a heavy greenish yellow, irritating, and toxic gas of disagreeable odor. Chlorine is a strong oxidizing agent and disinfectant. As an oxidizing agent, it has a strong tendency to withdraw electrons from other atoms or molecules. Chlorine can be liquefied under pressure at room temperature, making it easy to store and transport. Chlorine is also highly soluble in water, making it easy to add to water supplies in carefully controlled amounts (Webelements, 2005; The Chlorine Institute, Inc. 1999).

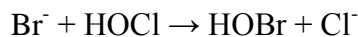
Chlorine gas reacts rapidly with water to form hypochlorous acid (HOCl) and hydrogen and chloride ions (Christman, 1998). Hypochlorous acid, in turn, reacts instantaneously and reversibly with water to form hypochlorite (OCl<sup>-</sup>) and hydrogen ions (Garfield, 1985; Harp, 1995).



In the same way sodium and calcium hypochlorite hydrolyze as the following



Bromide present in the chlorinated water produces hypobromous (HOBr) acid and hypobromite ( $\text{OBr}^-$ ) ion in a substitution reaction (Harp, 1995; Stuart et al., 1999) this interference leads for the formation of brominated disinfection by-products (Stuart et al., 1999).



When chlorine dissolves in water hypochlorous acid (HOCl) and hypochlorite ion ( $\text{OCl}^-$ ) are formed referred to as free chlorine residuals consisting of applying chlorine and hypochlorites, but combined chlorine residuals are chloramines produced by combining hypochlorites with ammonia and other nitrogen-containing contaminants, total chlorine is the sum of both free available and combined chlorines (Water Quality and Health Council, 2004). Combined chlorines last longer than free forms but less effective in disinfecting (Chlorine chemistry council and Canadian Chlorine coordinating Committee, 2003; Healthy Buildings international, Inc).

Both hypochlorous and hypochlorite are effective oxidants that disinfect bacteria, viruses and protozoa that may be in the source drinking water. The  $\text{OCl}^-$  ions are able to disrupt

cell walls and enter the cell, interfering with cellular respiration and intracellular transport. Hypochlorite also has the ability to destroy the viral nucleic acid inactivating any viruses in the water supply (DeSchuytner et al., 2000).

Chlorination eliminates bacteria, molds and algae that can grow in water storage tanks and mains (Chlorine Chemistry Council and Canadian Chlorine coordinating Committee, 2003; DeSchuytner et al., 2000; Harp, 1995).

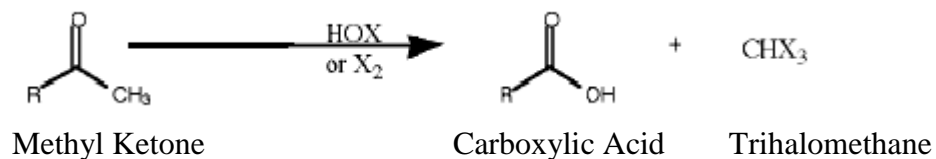
It is essential to balance the benefit gained from chlorination in saving and protecting public health and the possible or probable adverse effects result from the different possible carcinogenic disinfection by-products. This can be achieved by optimizing the concentration of chlorine in both free (residual) and combined forms and the contact time. To achieve disinfection with the minimal harm, effective chlorine and contact time can be estimated at a given water temperature by multiplying the final free chlorine (mg/L) by minimum contact time (minutes). Consequently if the chlorine concentration is to be minimized the contact time must be lengthened and visa versa (Chlorine chemistry council and Canadian Chlorine coordinating Committee, 2003). Chlorine dosing rate depends on the flow rate and the residual required, normally 0.2-0.5 mg/L after 30 minutes (Gray, 2002).



### 2.3 Disinfection By-Products (DBPs):

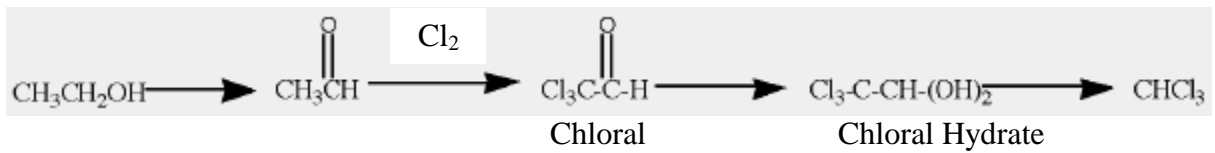
Drinking water chlorination dramatically decreased the rates of waterborne diseases (Christman, 1998). Nevertheless, a growing number of investigators have been finding evidence that chlorine may have adverse effects as well. The adverse effects of chlorination result both from chlorine and from a wide range of chlorination by-products (CBPs) formed by the reactions of chlorine with natural organic matter and chemicals found naturally in water. Chlorine reacts with the naturally occurring organic compounds (humic and fulvic substances) producing THMs and other DBPs (Stack et al., 2000).

Chlorination by-products formation continues as long as there is a residual free chlorine concentration and precursor organic material (Rathbun, 1997). Of the mechanisms that are suggested to explain the reaction of chlorine with the natural organic matter is haloform reaction. Haloform reaction involves the conversion of Methyl Ketone to a carboxylic acid and a trihalomethane molecule (DeSchuytner et al., 2000).



X: is Cl or any other halogen atom

Another proposed reaction mechanism is transformation of an alcohol (ethanol) to chloral which produces chloral hydrate that generates a molecule of chloroform (one of the trihalomethanes) (DeSchuytner et al., 2000).



In 2002 Richardson identified more than 600 water disinfection byproducts including trihalomethanes, haloaceticacids, haloaldehydes, haloketones, haloacetotnitriles, chloropicrin, chlorophenols and chlorinated ethylene (Nikolaou et al., 1999; DeSchuytner et al., 2000). The major class of disinfection byproducts in drinking water is trihalomethanes (Stack et al., 2000; Nikolaou et al., 2002; Thacker et al., 2002).

#### 2.4 Trihalomethanes (THMs):

All disinfectants produce DBPs that may be of concern (Nikolaou et al., 2002; Gray, 2002). Trihalomethanes (THMs) are simple halogen-substituted single-carbon compounds with the general formula  $\text{CHX}_3$ , where X may be any halogen atom or combination of them (Stack et al., 2000; WHO, 2005). The prominent halogens that are found in THMs are chlorine and bromine (Stack et al, 2000). The principal DBPs formed during chlorination are trihalomethanes (THMs). Trihalomethanes that are most commonly found in drinking water are a group of four chemicals (Nikolaou et al., 2002; www.cdc.gov; Stack et al, 2000):

- Trichloromethane (Chloroform) which has the formula  $\text{CHCl}_3$
- Bromodichloromethane (BDCM) which has the formula  $\text{CHBrCl}_2$
- Dibromochloromethane (DBCM) which has the formula  $\text{CHBr}_2\text{Cl}$
- Tribromomethane (Bromoform) which has the formula  $\text{CHBr}_3$

The four major THMs (Chloroform, Bromodichloromethane, Dibromochloromethane and Bromoform) are liquids at room temperature. They are volatile and slightly soluble in water, with solubilities less than 1 mg/mL at room temperature (WHO, 2005).

When chlorine is introduced to water, hypochlorous acid (HOCl) is produced, and hypobromous acid (HOBr) is also formed as a result of a substituting reaction with bromide which is naturally present in the chlorinated raw water (Kampioti and Stephanou, 2002). Both hypochlorous and hypobromous react with naturally occurring organic matter to create four compounds of THMs.

Trihalomethanes do not normally found in raw groundwater (Chlorine chemistry council and Canadian Chlorine coordinating Committee, 2003). They are generated principally as by-products of the chlorination of the drinking water. Hypochlorous acid oxidized bromide ion to form hypobromous acid (Stuart et al., 2001), which together with chlorine reacts with natural organic matter in the chlorinated drinking water forming different THMs. The THM formation is dependent on the temperature, pH, chlorine and bromide concentration, the natural organic matter in the raw water and travel time (contact time) of water within the system (Rodriguez and Serodes, 2001). THMs can be taken in by ingestion, inhalation, and by dermal absorption when showering, bathing and swimming, even during other activities such as washing dishes, clothes and cleaning the house (Tsair-Fuh Lin and Shih-Wen Hoang, 2000; Xu Xu et al., 2002; Villanueva, 2003).

## **2.5 Health Effects:**

After drinking water chlorination, levels of mutagenic activity increases, and the epidemiologic evidence suggests that chlorination by-products pose a cancer risk to humans (Wigle, 2000; WHO, 2005). Many epidemiological studies on chlorination and chlorination by-products had show that these substances are animal carcinogenic and highly linked to many adverse health impacts on humans at long term exposure (Walker and Olle, 2002; Gray et al., 2001; Pegram et al., 1997). From a public health aspect, they are suspected to be carcinogenic and thus exposure to them should be minimized (Stack et al., 2000; Stuart et al., 2001). Several studies have suggested that their existence increases the risks of bladder, stomach, large intestine and rectal cancer in areas where chlorination is used as a disinfection treatment before water distribution (Fawell, 2000; Tokmak et al., 2004). Some toxicological studies suggest an association between DBPs and reproductive and developmental effects; such as low and very low birth weight, preterm delivery, spontaneous abortion or miscarriage (Graves et al., 2001; Chlorine chemistry council and Canadian Chlorine coordinating Committee, 2003; WHO, 2005).

Trihalomethanes have hepatotoxic and nephrotoxic effects (Patrick et al., 1997; WHO, 2005) in addition to genotoxic effect in the liver and kidney (Stuart et al., 2001).

Risk of carcinogenic compounds is a statement of probability which means that no lower value for the risk existence (Stuart et al., 2001). Even THMs are in concentrations lower than the regulated limits they could cause cancer from daily water intake (Tokmak et al.,

2004). The risk of cancer from consuming THMs species is not the same, but the risk increases by consuming tap water or exposure from swimming pool having the four species (Ching-Hung Hsu et al., 2001).

## **2.6 Factors Influencing the Formation of Trihalomethanes:**

There are main physical and chemical factors affecting THMs formation in treated water by chlorine. These are pH, contact time, temperature and season, natural organic material, chlorine dose and bromide concentration (Nikolaou et al., 1999; DeSchuytner et al., 2000; El-Shahat et al., 2001).

1. Increasing pH increases the Hypochlorous dissociation and thus increases trihalomethane formation
2. Contact time (travel time) increases the formation of trihalomethanes
3. Temperature and season: At higher temperature chlorine reacts faster with natural organic matter and this leads to a seasonal variation in trihalomethane formation.
4. Natural organic matter: concentration and properties of natural organic matter has a role in increasing the formation of trihalomethanes.
5. Chlorine dose: trihalomethane formation increase as free chlorine dose increases, also more chlorinated than brominated species are formed.
6. Bromide: Natural or anthropogenic bromide increases the brominated halomethnes. In cases of high bromide concentration the bromodichloromethane, dibromochloromethane and bromoform are the major (dominant) trihalomethanes formed.

## **2.7 Trihalomethanes Formation Potential (THMFP):**

Chlorinated drinking water is usually stored temporarily in special tanks and then distributed for the end users. This means that chlorine dose should be in excess for effective disinfection (Stuart et al., 1999). The excess free chlorine can react with organic compounds present in the water during storage or distribution (Stack, 2000). For this reason it is common to measure trihalomethane formation potential (THMFP) as a standard test (Stuart et al, 1999; Stuart et al 2001).

In the 19<sup>th</sup> edition of standard methods for examination of water and wastewater, a method is detailed for this test, in which samples of water under standard conditions are buffered at pH  $7.0 \pm 0.2$ , chlorinated with an excess of free chlorine, and stored at  $25 \pm 2^\circ\text{C}$  for 7 days (APHA, 1995). THMFP is the concentration of THMs formed in water tested in the described method. The THMFP test can be useful in evaluating water treatment or drinking water source or for the prediction of THM concentrations in a distribution system (Thacker et al., 2002). Also THMFP test can be considered as an analogue indicator for organic matter in water (Stuart et al., 1999). The need for an analogue indicator arises because of the wide range of organic matter that may be in water either from natural or anthropogenic sources, and the difficulty in quantifying this organic load due to low stability, reproducibility and facilities (Stuart et al, 2001). The formation potential of THMs and other disinfection by-products can be a tool for detecting groundwater contamination either by sewage effluent or domestic drainage (Sanukida et al., 2001; Stuart et al., 1999).

Dissolved organic carbon in polluted water can be estimated from the THMFP test (Stuart et al., 2001).

## **2.8 Swimming Pools:**

Swimming pools of all types should be maintained at satisfactory physical, chemical and biological conditions (WHO, 2000). Different choices of disinfectants are used for pool water disinfection. Disinfection by-products have been detected in swimming pools varies with the disinfectant used (WHO, 2000; Fantuzzi et al., 2001). Disinfectant residual level must be maintained to ensure disinfection, but the optimization of disinfectant concentration and the proper time and method of disinfection used must be regulated, because disinfectants themselves are harmful and their adverse health effects have been reported (WHO, 2000).

Chlorine residual recommended in swimming pool water in UK is 1-2 mg/L, USA 1-3 mg/L, Germany 0.3-0.6 mg/L and Italy 0.6-1.2 mg/L (WHO, 2000). In general, if chlorine in the pool environment smells, it is dangerously high (Rushall and Weienthal, 2003).

Construction of swimming pools in the West Bank has increased in the last few years. Pools may be private, semi-public (hotel, health club) or public. Pools may be located indoors or outdoors. In the West bank groundwater is the source of water that is used in the swimming pools. Chlorine in its different forms (gas, sodiumhypchlorite and

calciumhypochlorite) is used to disinfect the swimming pools water in the West Bank (Al-Khatib and Salah, 2003).

Users of the swimming pools vary in their ages, sex, and education and awareness. Swimmers entering a pool contribute in the contamination of the water with a rich mixture of organic compounds, saliva, urine, skin scales, hair, dirt, fecal matter, sweat, and body oils. Parasites and microbes are added to the water (Healthy Buildings International, Inc.; WHO, 2000; Fantuzzi et al., 2001).

The risk of illness or infection associated with swimming pools has been linked to faecal contamination because of improper disinfection or not at all applied (WHO, 2000). The pool water if not filtrated and disinfected continuously becomes a sever health risk to the swimmers. Al-Khatib and Salah (2003) have reported that all the 46 pools in the West Bank/Palestine they tested during summer 2000 are microbiologically contaminated.

The WHO decided to develop guidelines to recreational water in 1994. In 2000 the final draft was achieved and published for consultation to develop the final guidelines for safe recreational water environments. In the WHO guidelines draft disinfectants and disinfection by-products have been discussed as one of the chemical hazards in the swimming pools waters. According to the WHO draft, there are three main roots of exposure to chemicals in swimming pools; Inhalation, dermal contact and direct ingestion.



THMs are the main DBPs in swimming pools that have been studied due to their high concentrations, frequency of occurrence, and possible toxicity (WHO, 2000; Aggazzotti et al., 1998).

DBPs that are produced in pools disinfection are at levels that are at least comparable to those produced in drinking water disinfection, but DBPs found in pool waters easily exceed these levels because of recycling water in swimming pools and continuous addition of organic precursors by bathers and disinfectants by operators (Stack, 2000; Fantuzzi et al., 2001). Regular swimmers' blood plasma chloroform (one of the four main THMs) has been proved to be highly elevated (Healthy Buildings International, Inc.; Aggazzotti et al., 1998).

Total and individual species of THMs have been determined in swimming pools water and in the air above the pool water surface in different countries and the values were in a wide range from few micrograms per liter to about one thousand microgram per liter in the pool water, but the range in the air (measured in microgram per cubic meter) is less although it increase in indoor pools (WHO, 2000; Fantuzzi et al., 2001). Chloroform is the prevalent among THMs studied in swimming pool waters show mean values from 14 to 198 $\mu\text{g/L}$ , while for the other THMs lower values were observed (Fantuzzi et al., 2001; Aggazzotti et al., 1998).

## 2.9 Trihalomethanes Guidelines:

Trihalomethanes are rarely found in groundwater before treatment by chlorine (WHO, 2004). The first time THMs were discovered to be in treated drinking water was in 1974 (Kuivinen and Johnsson 1999; Nikolaou, 1999; WHO, 2005). Accordingly after that their health impact was intensively studied and explored as carcinogenic materials. WHO international standards for drinking water did not refer to THMs before 1984 and after that until 1993 chloroform was the only to be regulated. After 1993 guideline values were established separately for all four THMs. In the 2004 3rd edition guidelines for drinking water quality WHO established the guidelines for the individual and total trihalomethanes TTHMs (WHO, 2004). Table 2.1 shows the individual and total guideline values. Total trihalomethanes is calculated either by normal summation of the individual THMs values or by a ratio fractionation and summation that should not exceed 1. The following equation illustrates the ratio fractionation summation for establishing total THMs standards to account for additive toxicity (WHO, 2004):

$$\frac{C_{\text{bromoform}}}{GV_{\text{bromoform}}} + \frac{C_{\text{dibromochloromethane}}}{GV_{\text{dibromochloromethane}}} + \frac{C_{\text{Bromodichloromethane}}}{GV_{\text{bromodichloro}}} + \frac{C_{\text{bromoform}}}{GV_{\text{bromoform}}} \leq 1$$

Where: C= Concentration in the sample and GV= Guideline value

Table 2.1: Guideline Values for THMs (WHO, 2004)

<b>Disinfection by-product (DBPs)</b>	<b>Guideline values (µg/liter)</b>
Chloroform	200
Bromodichloromethane	60
Dibromochloromethane	100
Bromoform	100
Total Trihalomethanes (TTHMs)	The sum of the ratio of the concentration of each to its respective guideline value should not exceed 1

The United States Environmental Protection Agency (USEPA) rule that regulates DBPs was implemented first in 1979 (Nikolaou et al., 1999). The initial regulation of TTHMs allowable annual average level was 100 µg/L, and no individual trihalomethane was regulated (Nikolaou et al., 1999); after that it was reduced to 80 µg/L since 31/12/2003, and individual four trihalomethanes were regulated; chloroform (zero), bromodichloromethane (zero), dibromochloromethane (60 µg/L), and bromoform (zero) (USEPA, 2005).

The EU countries have established either a Maximum Admissible Concentration (MAC) for total trihalomethanes-comparable to Maximum Contaminant Levels (MCL) in the United States-or a guide value-similar to U.S. Maximum Contaminant Level Goal. For various European countries MAC ranges from 30 to 100µg/L. Some EU like Sweden set the guide value at 1 µg/L (Golfinopoulos and Arhonditsis, 2002; Salameh et al., 2002). In Jordan the limit was raised in 1997 from 100 to 150 µg/L (Salameh et al., 2002). In the Palestinian standards (second draft of drinking water modified standards) DBPs were not mentioned (Seureca, 2004).

## **Chapter 3**

### **Methods and Materials**

#### **3.1 Materials:**

Glassware was scrupulously cleaned by tap water and a detergent, and then rinsed with distilled water, for several times and finally with hydrochloric acid solution three times before rinsing again with distilled water. The glassware was dried at 50°C inside an incubator to avoid any contamination and dust.

Distilled water was distilled in the Environmental Lab using Barnstead distillater. The resulting distilled water was of high quality and did not have any measurable organic impurities when analyzed by the multi N/C 2000 analyzer for organic carbon.

Polyethylene high density (PEHD) one litter bottles with a screw cap was used for the collection of water samples for the THMFP test and the routine chemical analyses. PEHD bottles were rinsed thoroughly with distilled water and after that with hydrochloric acid before allowed to dry at 50°C inside an incubator to avoid any dust or any other contaminants.

30 mL glass vials with Teflon lined caps purchased from Supelco were used for the collection of water samples for the total organic carbon (TOC) analysis.

40 mL brown vials with Teflon lined screw caps purchased from Supelco were used for the collection of water samples for the THMs analysis.

One liter brown glass reagent bottles with fit cap were used for the THMFP experiment.

THMs standards were purchased from Supelco (Cat. No 48746). These THMs standards were a mixture of four compounds (Chloroform, Bromdichloromethane, Dibromochloromethane, and Bromoform). A series of THMs dilutions from 5 to 200 µg/L were prepared from the standard solution.

Chlorine stock solution (dose solution) was prepared in the Environmental Lab at Al-Quds University by dissolving Calciumhypochlorite in one liter of distilled water to have available chlorine 4-20%.

Sodium Hydroxide 1 N and Phosphate buffer (6.81 g potassium dihydrogen phosphate and 1.17 g sodium hydroxide dissolved in 100mL distilled water) were prepared to use in maintaining the pH at  $7 \pm 0.2$  during the THMFP experiment.

Ascorbic Acid as a neat material (10 mg for 10 mL sample) was used as a dechlorination reagent in quenching to prevent further formation of THMs.

### **3.2 Sampling:**

At the end of the raining season in 19<sup>th</sup> May 2005 raw ground water samples from the source points of drinking water were collected from five sampling points (wells). The five sampled municipal wells were: Anabta 1 and 2, Tulkarm 1 and 2 and Shwaika (Misnawi) well. Samples from prechlorination points were collected in one liter PEHD bottles. The prechlorination tap was allowed to run 5 minutes, and then PEHD bottles were rinsed with the raw water from the sampling point three times. Samples were transferred to the lab inside an ice box at 4°C and then stored in the refrigerator at 4°C.

Routine chemical analysis for major cations and anions of the samples was achieved within few days in the Environmental Lab at Al-Quds University.

Samples for TOC analysis (Non-purgeable Organic Carbon-NPOC) were collected in 30 mL glass vials with screw Teflon lined caps from the prechlorination taps at the site of abstraction, they were preserved and transferred at 4°C in an ice box and stored overnight in the refrigerator. TOC analysis was achieved in the second day of sampling using multi N/C 2000 analyzer from Analytikajena AG.

23 tap water samples were collected at representative points, 5 samples from the taps at the chlorination points of the wells before water pumping into the distribution system, resembling the lowest travel time (also denoted contact time), 8 samples from houses in Tulkarm (distributed in different locations in the city with variation in the distance from the

distribution points), 6 samples from houses in Anabta (resembling different distances from the distribution point, 3 samples from houses in Rameen (at the extremity point of the distribution system, but vary in their distance from the concrete reservoir that receives chlorinated water from Anabta and distribute it through a local distribution mains).

Tap water samples for THMs analyses were collected in 40 mL brown vials. 40 mg of quenching reagent (Ascorbic acid neat material) was added to the vial before sampling (10mg for 10 mL sample), the tap was allowed to run for 3-5 minutes after which the vials were carefully half filled to add 3 drops of 1 N HCl (to prevent biodegradation and dehydrohalogenation (Golfinopoulos, 2000) and then the vials were completely filled avoiding any air bubbles. Vials were closed tightly with their screw Teflon lined caps and transferred to the lab inside an ice box at 4°C. Samples were stored in refrigerator at 4°C not more than 14 days before analysis.

On 18<sup>th</sup> June 2005 water samples from swimming pools for THMs analyses were collected in 40 mL brown vials of the same type used for tap water collection. Pool water samples were obtained from the inside water body at depth not less than 30 cm using a narrow neck bottle to transfer the water sample into the brown vials in which the same quenching reagent (Ascorbic acid) used in tap water samples was used, three drops of 1 N HCl were added to the vial before filling it completely. Samples were preserved and transferred in the same conditions of the tap water samples.

### **3.3 Measurements and Analyses:**

Electric conductivity (EC), Acidity (pH) and temperature were determined at the sampling sites using a multi WTW meter.

Free chlorine (residual chlorine) was determined at the sampling site using a portable spectrophotometer from HACH. N, N-diethyl-p-phenylenediamine (DPD) colorimetric method was applied for the free chlorine determination (HACH, 1997).

N/C 2000 analyzer from Analytikajena AG with an autosampler was used in the TOC analysis. Non purgeable organic carbon (NPOC) was determined in the water samples after acidification of the water sample with 2 N HCl and then purged with nitrogen gas (99.999%) to remove carbon dioxide.

$\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were determined by titration with 0.01 N EDTA. Anions  $\text{NO}_3^-$ ,  $\text{PO}_4^{2-}$ , and  $\text{SO}_4^{2-}$  were determined by colorimetric method using a spectrophotometer from HACH.  $\text{HCO}_3^-$  and  $\text{Cl}^-$  were determined by titration with 0.1 N HCL and 0.01 N  $\text{AgNO}_3$  respectively. Bromide was determined by ion selective electrode.

### **3.4 Trihalomethanes Formation Potential (THMFP):**

Water samples for the purpose of THMFP determination were obtained from three source points: Anabta well 2, Tulkarm well 2, and Shwaika (Misnawi) well, on the 18<sup>th</sup> June 2005.



One liter of raw water from each well was transferred into a brown reagent bottle in the lab; 5 mL of the chlorine dosing solution was transferred into the sample in the reagent bottle and the free (residual) chlorine reached was  $4 \pm 0.5$  mg/L. The pH was Adjusted to  $7 \pm 0.2$  using NaOH 1N and the phosphate buffer. The dosed and buffered samples were incubated at  $25^\circ\text{C} \pm 0.5$  using an incubator. From each bottle a series of samples (0, 2, 4, 6, 8, 22, 28, 52, 76, 100, 149, 173hr) were obtained for THMs analysis in the same sampling method used in tap water. Samples were stored at  $4^\circ\text{C}$  in refrigerator and then transferred for the GC analysis within 14 days.

### **3.5 Trihalomethanes Extraction and Analysis:**

The headspace method was used; it has the advantages of being rapid with good repeatability and minimum of solvent handling and waste production (Kuivinen and Johnsson, 1999, Nikolaou et al., 2002). Headspace method is suitable for samples with high contents of THMs and it has an acceptable detection limit without contamination risk from the solvent (Ru-song Zhao et al, 2004; Nikolaou et al, 2002; Deok-Hee Cho et al, 2003). Five milliliter of the water sample was transferred quantitatively into a 10 mL headspace vial and the vial was immediately sealed with a stainless steel crimp top cap equipped with PTFE-lined septa. The vials were statically incubated at  $95^\circ\text{C}$  for 20 minutes in a CombiPal autosampler (CTC Analytics AG, Switzerland). An aliquot (1000  $\mu\text{L}$ ) of the headspace was subsequently withdrawn and injected into the injector of a 6890N Agilent GC/MS at 300  $\mu\text{L/s}$ . Separation was performed on a J&W-VRX column. The column oven temperature was held at  $40^\circ\text{C}$  for 4 min, ramped to  $45^\circ\text{C}$  at  $0.5^\circ\text{C}/\text{min}$ , held for 2 min, ramped to  $70^\circ\text{C}$

at 2.0°C/min, and ramped to 150°C at 10°C/min. The injections were done in split mode (split ratio 2.0), with injector temperature at 220°C, transfer line temperature at 280°C and ion source temperature at 230°C.

SIM method was developed for 4 compounds (chloroform, bromodichloromethane, dibromochloromethane, bromoform) following USEPA method No. 501. Quantification and method validation were performed with external standard calibration. Calibration curves in the concentration range from 5 to 200 µg/L were prepared from standard solution (Supelco Cat. No 48746).

## Chapter 4

### Results and Discussion

#### 4.1 Groundwater Properties in Tulkarm and Anabta Municipal wells:

The Physical properties of the sampled Municipal wells that represent drinking water source are presented in Table 4.1. The pH of the water samples ranged between 7.29-7.62, the average being 7.43. These pH values are affected by the buffering effect of carbonate rocks (limestone and dolomites) in the area (Scarpa et al., 1998). Increasing pH causes an increase in THM formation with all species either brominated or not (Nikolaou et al., 1999).

Electric Conductivity (EC) also has relatively high values range from 864 to 1098 $\mu$ S/cm. The EC values are a function of high ionic composition (Table 4.2) that will affect the THM positively. The average temperature of the samples from the municipal groundwater wells is 23.9 reflecting the temperature of groundwater of the shallow aquifer during summer period. In general, reactions are faster at higher temperatures, which apply for the THM formation reactions also (Nikolaou et al., 1999).

Table 4.1: Physical properties of groundwater of some Municipal wells in Tulkarm and Anabta

Date			Well	EC Us/cm	pH	Temp °C
19	5	2005	Shwaika (Misnawi) Well	898	7.51	23.5
19	5	2005	Hamadallah Well	993	7.39	25.3
19	5	2005	Anabta Municipality 1	1098	7.34	23.6
19	5	2005	Anabta Municipality 2	864	7.29	23
19	5	2005	Tulkarm Municipality 2	1070	7.62	23.9

The concentration of the major anions and cations in some drinking water source wells in Tulkarm are presented in Table 4.2. The ionic abundance in the collected water samples shows the following trend:  $\text{Cl}^- > \text{HCO}_3^- > \text{NO}_3^- > \text{SO}_4^{2-} > \text{Br}^- > \text{PO}_4^{3-}$  for the anions and  $\text{Ca}^{2+} > \text{Mg}^{2+}$ . The high values of Ca and Mg ions also confirm the dissolution of the carbonate in the aquifer and surface rocks in the area.

Table 4.2: Ionic Concentration of groundwater of some Municipal Wells in Tulkarm and Anabta

Date			Well	Cl <sup>-</sup> mg/l	NO <sub>3</sub> <sup>-</sup> Mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l	HCO <sub>3</sub> <sup>-</sup> mg/l	PO <sub>4</sub> <sup>3-</sup> mg/l	Br <sup>-</sup> mg/l	Ca <sup>2+</sup> mg/l	Mg <sup>2+</sup> mg/l	NH <sub>4</sub> <sup>+</sup> mg/l
19	5	2005	Shwaika (Misnawi) well	92.2	74.6	28	360	0.19	0.72	91.4	36.9	0
19	5	2005	Anabta Municipality 1	127.6	141.9	44	305	0.11	0.94	106.6	33.5	0.03
19	5	2005	Anabta Municipality 2	99.3	68.3	30	317	0.07	0.78	90.5	25.8	0
19	5	2005	Tulkarm Municipality 2	113.4	39	40	384	0.21	0.82	101.8	39.4	0

The Nitrate values range widely between 39 to 141.9 mg/L; the mean value is 81.9 mg/L which is more than the Palestinian and WHO maximum allowable limit for drinking water of 50 mg/L for short term exposure (WHO, 2005; Seureca, 2004). Nitrate in excess in drinking water affects the infants below the age of six months; it causes shortness of breath and blue-baby syndrome (USEPA, 2005). Sulfate which is considered as a secondary health factor that affects the taste of drinking water when the concentration is more than 250 mg/L (USEPA, 2005) is lower than the guideline values of both WHO and USEPA.

Bromide which present generally in low concentrations in groundwater has shown relatively high values in the sampled wells in Tulkarm district ranged from 0.72 to 0.94 mg/L. The bromide source could be anthropogenic from either methylbromide that has

been used widely in agriculture activities in the area, or from the waste water which is draining all the year in Wade Zeimar that reach the groundwater reservoir. Another source of bromide in groundwater is the rain water originates from Mediterranean Sea (15 kilometers to the west of the study area). Bromide in the drinking water allows the formation of brominated trihalomethanes.

Total Organic Carbon (TOC) concentrations in the groundwater used for drinking purposes in Tulkarm and Anabta wells are presented in Table 4.3. TOC was determined for samples collected in May/2005 and in June/2005. The values show big differences between the two sample sets.

Table 4.3: TOC Content of Groundwater from Tulkarm and Anabta Municipal Wells

Well	TOC* (mg/L)	
	19/05/2005	18/06/2005
Shwaika (Misnawi) Well	4.85	0.652
Anabta Municipal Well 1	4.37	**
Anabta Municipal Well 2	3.16	0.462
Tulkarm Municipal Well 1	2.13	0.439
Tulkarm Municipal Well 2	**	0.454

\* TOC was measured as NPOC

\*\* Not measured

During May the end of the raining season but the recharge is still taking place, the TOC level is higher than in June the beginning of summer where the recharge rate is at low level. The highest level of TOC was 4.85 mg/L in Shwaika (Misnawi) municipal well in the mid of May, but this level decreased to 0.652 mg/L in the mid of June. The lowest TOC concentration was 2.13 mg/L in Tulkarm municipal well 1 in May, and this level decreased to 0.439 mg/L in June.

TOC content in the groundwater in Tulkarm and Anabta municipal wells is from two different sources: The natural source which is from the soil horizon located above the rock formation, and from the waste water which reach the groundwater through the karstic aquifer. The precursor of trihalomethanes formation is the organic carbon in the drinking water disinfected by chlorine. There is a significant positive correlation between trihalomethane formation and TOC concentration (Salameh et al, 2002; Nikolaou et al, 1999) which will be discussed further in section 4.4.

#### **4.2 Free (Residual) Chlorine in Drinking water in Tulkarm and Anabta:**

The results of free (residual) chlorine concentration at the chlorination points of the source point wells and at the end points in the users' tap water are presented in Table 4.4.

Table 4.4: Free (residual) chlorine in the drinking water in Tulkarm and Anabta

No.	Sample Site	Water type and source	Free Cl (mg/L)	
			19/05/2005	18/06/2005
1	Anabta municipal well 2	Point of chlorination	0.13	0.3
2	Anabta municipal well 2	Point of chlorination (dose increased)	0.41	*
3	Anabta municipal well 1	Point of chlorination	0.43	*
4	Ateyah Kanan home	Tapwater/Anabta (before plastic tank)	0.65	*
5	Ateyah Kanan home	Tapwater/Anabta (after plastic tank)	0.07	0.01
6	Tulkarm municipal well 1	Point of chlorination	0.38	0.33
7	Shwaika (Misnawi) well	Point of chlorination	0.19	0.34
8	Shwaika Clinic	Tapwater/Shwaika	0.05	0.04
9	Abdalkareem Mur'eb home	Tapwater/Shwaika	0.03	0.03
10	Khadoore College	Tapwater/Tulkarm	0.02	0.14
11	Fawaz Yones home	Tapewater/Tulkarm	0.16	0.21
12	Al'amore Mosque	Tapwater/Tulkarm	0.03	0.03
13	Alhatab home	Tapwater/Tulkarm	0.08	0.11
14	Yaser M. Abu Abed home	Tapwater/Tulkarm	0.07	0.13
15	Subhee Cofee	Noor shams refugee camp	0.24	*
16	Abdala Barakat home	Tapwater/Anabta	0.18	*
17	Jamal Jadala home	Tapwater/Anabta	0.14	*
18	Farhan Sabube home	Tapwater/Anabta	0.08	*
19	Ahmad Fareed home	Tapwater/Rameen	0.02	0.03
20	Abdala Thabet home	Tapwater/Rameen	0.02	0.02
21	Jawdat Sulayman home	Tapwater/Rameen	0.06	0.03
22	Abu Ali Resturant	Tapwater/Anabta	0.43	*
23	Tulkarm municipal well 2	Point of chlorination	*	0.41

\* Not measured

The average free chlorine measured in the two sampling campaigns is 0.16 mg/L. These values are less than the recommended values by the WHO. The free chlorine residual concentration recommended by WHO for effective disinfection is  $\geq 0.5\text{mg/L}$  after at least 30 minutes contact time (WHO, 2004). The maximum value of free chlorine was 0.65 mg/L at a household tap water in Anabta which exceeded the value of free chlorine measured at the same day at the chlorination point at Anabta; this may be due to the variation of chlorine dose input in different days.

The free chlorine concentration was very low in the most far user points such as Rameen and Khadoore points (0.02-0.14 mg/L). All the values of free chlorine measured were lower than the WHO maximum allowable value 5 mg/L (WHO, 2004). No chlorination is implemented at any point of the network rather than the chlorination point at the source point's wells.

There is a need to investigate the chlorine demand for the groundwater so to adjust the chlorine dose at the chlorination points that will maintain the required free chlorine in the distribution system. Additional chlorination at different points in the distribution network is recommended especially in the part delivering water to Rameen from Anabta.

During the sampling campaigns, low technical skills were noticed among the technicians who are responsible about chlorination process at the wells. Technicians have no means to optimize or monitor the chlorine dose and the free chlorine residual.

#### **4.3 Trihalomethanes Concentrations in Drinking water in Tulkarm and Anabta**

THMs in drinking water sampled from different end users points are presented in table 4.5. Total trihalomethanes for all measured samples complies with the recommended guidelines of WHO and USEPA. All the measured values for individual species of trihalomethanes and total trihalomethanes are less than the maximum guidelines of WHO, but exceeding the USEPA maximum contamination level (zero) for bromodichloromethane and bromoform.



The measured values of dibromochloromethane and chloroform are less than the maximum values by both WHO and USEPA.

Table 4.5: Concentration of THMs in chlorinated drinking water in Tulkarm and Anabta 19/5/2005

point	Sample Site	Water type and source	CHCl <sub>3</sub> µg/L	CHCl <sub>2</sub> Br µg/L	CHClBr <sub>2</sub> µg/L	CHBr <sub>3</sub> µg/L	TTHMs µg/L
1	Anabta municipal well 2	Point of chlorination	0.2	0.1	0.2	0.2	0.7
2	Anabta municipal well 2	Point of chlorination (dose increased)	0.2	0.2	0.3	0.1	0.8
3	Anabta municipal well 1	Point of chlorination	12.9	0.3	3.1	6.7	23
4	Ateyah Kanan home	Tapwater/Anabta (before plastic tank)	1.7	3.3	10.3	16.1	31.4
5	Ateyah Kanan home	Tapwater/Anabta (after plastic tank)	1.1	2.4	9	29.7	42.2
6	Tulkarm municipal well 1	Point of chlorination	0.8	0.3	0.3	0.3	1.7
7	Shwaika (Misnawi) well	Point of chlorination	0.1	0.2	0.1	0.3	0.7
8	Shwaika Clinic	Tapwater/Shwaika	0.2	0.3	0.4	21.8	22.7
9	Abdalkareem Mur'eb home	Tapwater/Shwaika	0.2	0.2	0.6	8.9	9.9
10	Khadoore College	Tapwater/Tulkarm	1.3	0.2	1.6	7.6	10.7
11	Fawaz Yones home	Tapwater/Tulkarm	0.7	0.2	0.9	6.5	8.3
12	Al'amore Mosque	Tapwater/Tulkarm	0.2	0.4	0.5	19.97	21.07
13	Alhatab home	Tapwater/Tulkarm	0.2	0.1	0.8	9.2	10.3
14	Yaser M. Abu Abed home	Tapwater/Tulkarm	0.1	0.3	0.3	2	2.7
15	Subhee Cofee	Noor shams refugee camp	0.1	0.5	0.2	2.3	3.1
16	Abdala Barakat home	Tapwater/Anabta	3.1	1	8.5	34.8	47.4
17	Jamal Jadala home	Tapwater/Anabta	20.1	0.4	3	8.5	32
18	Farhan Sabube home	Tapwater/Anabta	0.9	0.6	1.6	6.1	9.2
19	Ahmad Fareed home	Tapwater/Rameen	0.2	0.4	3.2	38	41.8
20	Abdala Thabet home	Tapwater/Rameen	0.1	0.3	5.5	36.9	42.8
21	Jawdat Sulayman home	Tapwater/Rameen	0.2	0.7	6.8	45	52.7
22	Abu Ali Resturant	Tapwater/Anabta	20.2	1	4.3	7.8	33.3

The average of the measured TTHMs at the end user tap water points reaching the houses is 24.81µg/L and the maximum and the minimum values measured were 52.7µg/L and 2.7µg/L respectively.

The average chloroform, bromodichloromethane, dibromochloromethane and bromoform measured at the end user tap water points were 3 µg/L, 0.7 µg/L, 3.4 µg/L, 17.7 µg/L respectively.

The brominated trihalomethane species are the prominent in 87% of the measured samples, in the others chloroform was the prominent trihalomethane. This prominence of brominated trihalomethanes is the result of high bromide content of the groundwater. The high bromide level comes from the interaction of the polluted surface water and groundwater. The main source of bromide in the groundwater is the sewage and industrial waste that flow around the year in Wade Zeimar and from the usage of methyl bromide in agriculture.

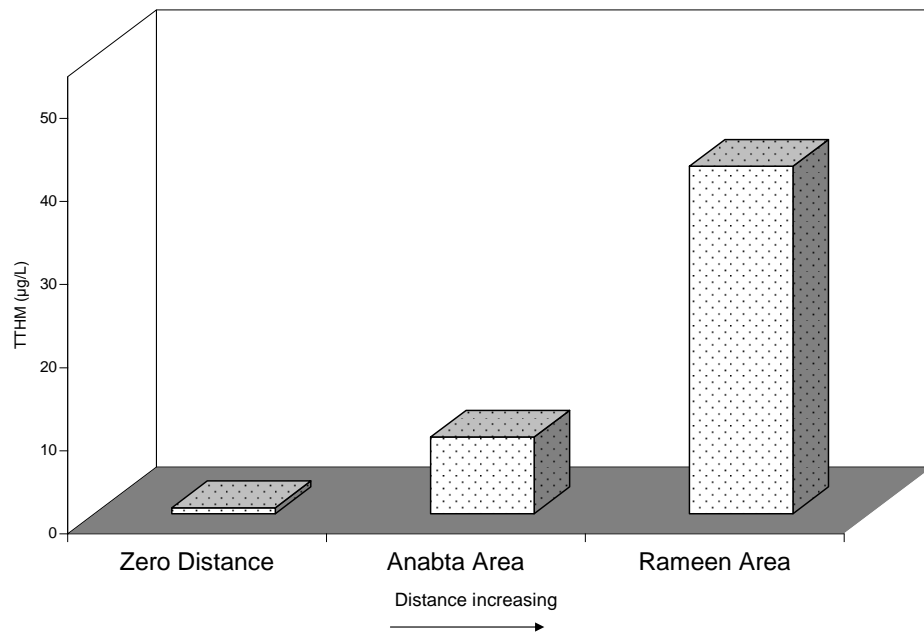
The maximum values for total trihalomethanes were measured in Rameen (52.7, 42.8, 41.8 µg/L) where the contact time (travel time) is the most. The minimum values of trihalomethanes (0.07-1.7 µg/L) were measured at the chlorination points where the contact time was ignorable.

THMs were measured for one sample before and after the plastic tank (sampling points 4 and 5) at Kanan's home in Anabta. The results of these two samples show that the TTHMs increased after the tank by 25.6%, and the increase was in dibromochloromethane and bromoform, while chloroform and bromodichloromethane were slightly decreased.

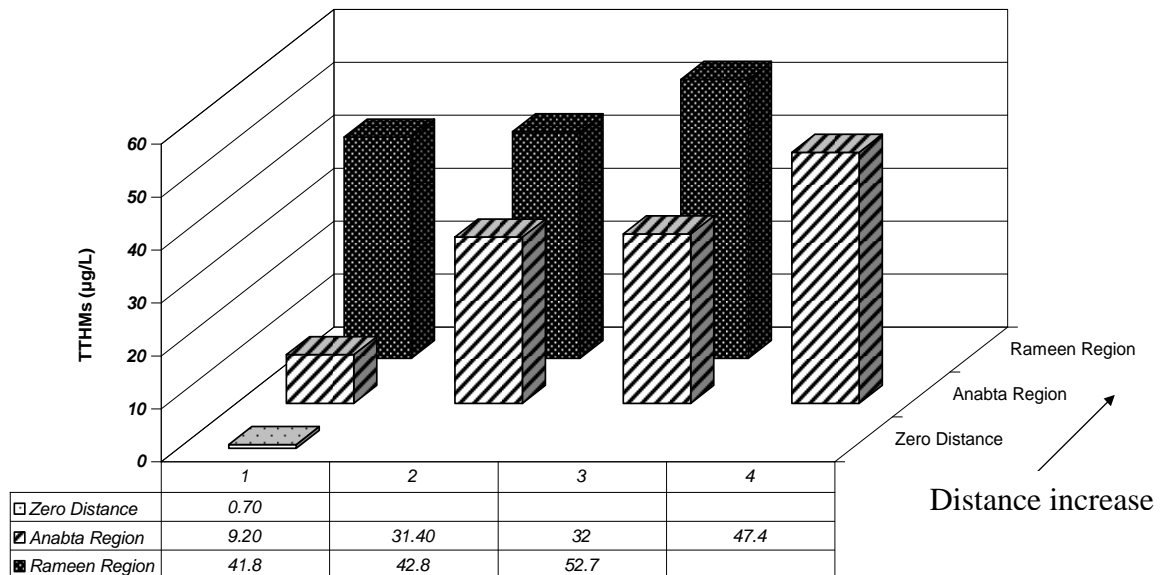
Figures 4.1 and 4.2 show the relation between the trihalomethane concentration and the distance from the chlorination points for the tap water samples of Anabta and Rameen.

Rameen tap water samples which are the most far points (5 to 6 km) from the chlorination point present in Anabta contained the higher total trihalomethane content. In the contrast, Anabta tap water samples have less trihalomethane content.

In Fig 4.2 the different samples of Anabta and Rameen are presented according to their relative distance from the chlorination point. The variation in total trihalomethane measured content is clearly related to the distance from the chlorination point.



**Fig. 4.1:** Relationship between TTHMs concentration and the distance from chlorination point

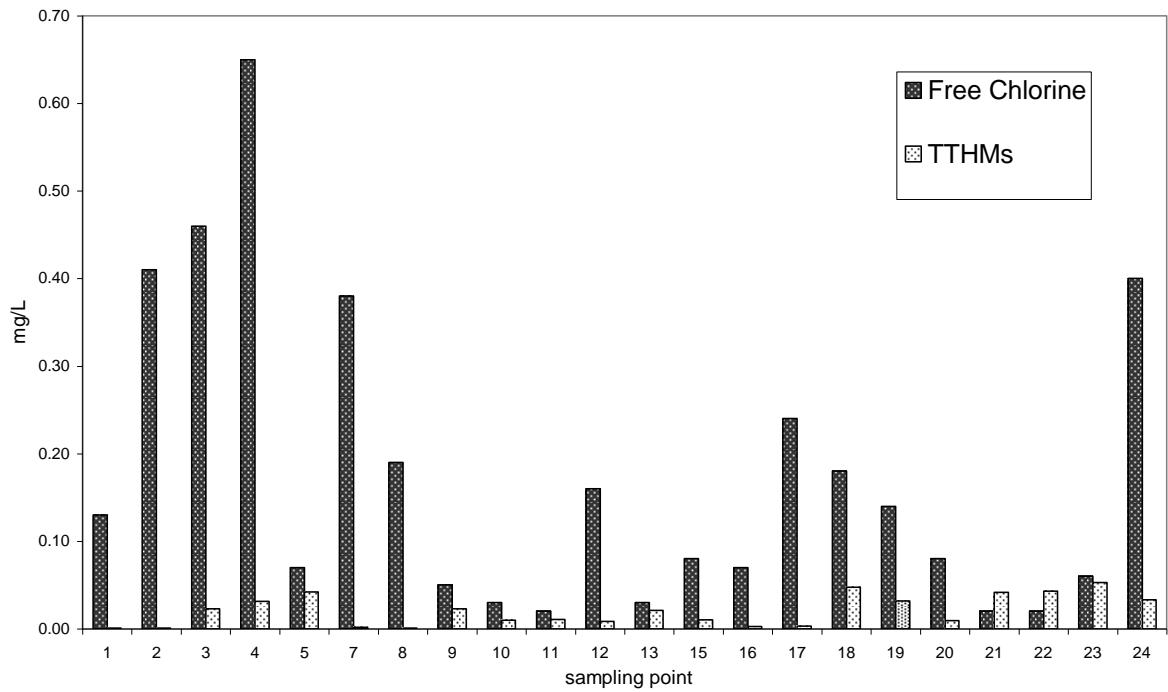


**Fig. 4.2:** TTHMs measured at different distances from the chlorination points

The increase of THMs in the water is due to the long contact time that increases the reaction time between chlorine residual and organic material to produce more trihalomethanes.

The total trihalomethanes concentration in tap water samples and the measured free chlorine residual are shown in Fig. 4.3. Free chlorine residual is higher at the chlorination points but the total trihalomethanes is in very trace amount at these chlorination points (points 1, 2, 6, 7). At the end user points the free chlorine residual is lower than 0.5 mg/L in all points except point 4 in which the free chlorine residual was 0.65 mg/L exceeding the same day chlorination dose at the source point indicating that it is coming from the chlorination dose a day before the sampling day. The free chlorine residual decreased

continuously through the network of the distribution system, at the same time the total trihalomethane concentration increased. At sampling point 22 which is a sample from a restaurant very close to the chlorination point at Anabta municipal well 1, both free chlorine residual and total trihalomethanes are relatively high compared with other samples from Anabta.



**Fig. 4.3:** Free Chlorine and TTHMs concentration in Drinking water

The high free chlorine residual at point 22 caused the formation of high total trihalomethanes although the distance from the chlorination point is very short (few meters) compared to the other sampling points that at more far distances.

#### **4.4 Trihalomethanes Formation Potential (THMFP) in Groundwater from some Municipal Wells of Tulkarm and Anabta**

The trihalomethane formation potential test was performed using three different groundwater samples from three municipal wells of Tulkarm district. The samples were collected from Anabta municipal well 2, Shwaika (Misnawi) well and Tulkarm municipal well 2. The three groundwater samples were chlorinated with calcium hypochlorite  $\text{Ca}(\text{OCl})_2$  solution until 4 mg/L free chlorine residual was reached. The samples were incubated at  $25^\circ\text{C} \pm 0.5$  and buffered using phosphate buffer to maintain the pH at  $7 \pm 0.2$ . Sampling at consequent time intervals was carried.

The results of trihalomethanes measured in the formation potential experiment for Anabta well 2, Shwaika (Misnawi) well and Tulkarm well 2 are presented in table 4.6, table 4.7 and table 4.8 respectively. The total trihalomethanes exceeded the WHO guideline ( $100\mu\text{g/L}$ ) and the maximum contamination level of USEPA ( $80\mu\text{g/L}$ ) after 6 hours of incubation for Shwaika (Misnawi) well sample and after 8 hours of incubation for Tulkarm well 2 sample. Anabta well 2 sample exceeded the guideline value after 52 hours (more than two days). After one week of incubation the TTHMs formed were  $153.6\mu\text{g/L}$  in Anabta well 2, and  $1149.7\mu\text{g/L}$  in Shwaika (Misnawi) well, and  $290.7\mu\text{g/L}$  in Tulkaem well 2.

The prominent trihalomethanes formed are the brominated trihalomethanes (As was found in the tap water samples) due to the relatively high bromide concentration in the raw

groundwater of the three wells. Dibromochloromethane was the highest trihalomethane species formed in Anabta well 2 and Shwaika (Misnawi) well, but bromoform dominated in Tulkarm well 2 where bromide concentration is more in the raw water sample (Table 4.2).

Table 4.6: THMFP in Anabta well 2

Time (hr)	CHCl <sub>3</sub> µg/L	CHCl <sub>2</sub> Br µg/L	CHClBr <sub>2</sub> µg/L	CHBr <sub>3</sub> µg/L	TTHMs µg/L	Fractionation Summation**
0	0.7	0.2	0.2	2.1	3.2	0.03
2	1.6	0.1	5.1	5.1	12	0.11
4	3	4.8	10	8.7	26.5	0.28
6	3.3	5.8	12.1	10.1	31.4	0.34
8	3.6	6	11.9	9.6	31.1	0.33
22	6.5	13.6	25.5	18.1	63.7	0.70
28	6.8	14.6	28.2	19.2	68.7	0.75
52	9.7	21.9	40.3	25	96.9	1.07
76	9.3	26.1	49	31.5	115.9	1.29
100	11.6	31.5	62.3	42.9	148.3	1.64
149	14.4	39	71	42.5	166.8	1.86
173	10.1	32.8	67.6	43.2	153.6	1.71

Table 4.7: THMFP in Shwaika (Misnawi) well

Time (hr)	CHCl <sub>3</sub> µg/L	CHCl <sub>2</sub> Br µg/L	CHClBr <sub>2</sub> µg/L	CHBr <sub>3</sub> µg/L	TTHMs µg/L	Fractionation Summation**
0	2.2	3.4	10.7	8.3	24.7	0.26
6	11.1	21.2	49.3	33.1	114.8	1.23
28	39.8	69	148.3	85.2	342.2	3.68
76	80.5	128.5	287.2	159.2	655.4	7.01
149	126.1	198.3	428	231.3	983.7	10.53
173	138.9	225.6	503.9	281.3	1149.7	12.31

Table 4.8: THMFP in Tulkarm well 2

Time (hr)	CHCl <sub>3</sub> µg/L	CHCl <sub>2</sub> Br µg/L	CHClBr <sub>2</sub> µg/L	CHBr <sub>3</sub> µg/L	TTHMs µg/L	Fractionation Summation**
0	2.1	1.1	7.1	55	65.3	0.65
2	3.1	2.9	10.7	56.8	73.5	0.74
8	4.7	7.3	18.9	72.4	103.3	1.06
22	7.4	13	27.3	68.3	115.9	1.21
52	13.2	28	55	89.7	185.9	1.98
100	14.6	35.4	72.5	90.2	212.7	2.29
173	18.2	51.4	108.4	112.7	290.7	3.16

\*\* The sum of the ratio of the concentration of each to its respective guideline value.

According to the equation of the WHO standards to account for additive toxicity which should not exceed 1:

$$\frac{C_{\text{bromoform}}}{GV_{\text{bromoform}}} + \frac{C_{\text{dibromochloromethane}}}{GV_{\text{dibromochloromethane}}} + \frac{C_{\text{Bromodichloromethane}}}{GV_{\text{bromodichloro}}} + \frac{C_{\text{bromoform}}}{GV_{\text{bromoform}}} \leq 1$$

Where: C= Concentration in the sample and GV= Guideline value

The fractionation summation for each sample was calculated and the values are presented in tables 4.6, 4.7, and table 4.8. The additive fractionation formed for trihalomethanes exceeded one after 6 hours in Shwaika (Misnawi) well, and after 8 hours in Tulkarm well 2, and after 52 hours in Anabta well 2. The high formation potential of trihalomethanes measured in the Shwaika (Misnawi) well can be explained by the high organic material content measured in the groundwater (Table 4.3) since the organic material is the precursor of the trihalomethane formation when water is chlorinated.

In Fig 4.4, Fig 4.5 and Fig 4.6 the Trihalomethanes formation potential rate for each of the three wells Anabta well 2, Shwaika (Misnawi) well and Tulkarm well 2 are plotted. The trihalomethanes formation potential occurred at high rate in the first two days and then the rate of their formation decreased and trended to become constant as time proceeding and the organic material is consumed. The trihalomethane potential deterrent factor is the organic material present in each sample and thus the formation potential reflected the amount of organic material present in each sample. In this way the formation potential of trihalomethanes can be used as an analogue test of organic material in water.



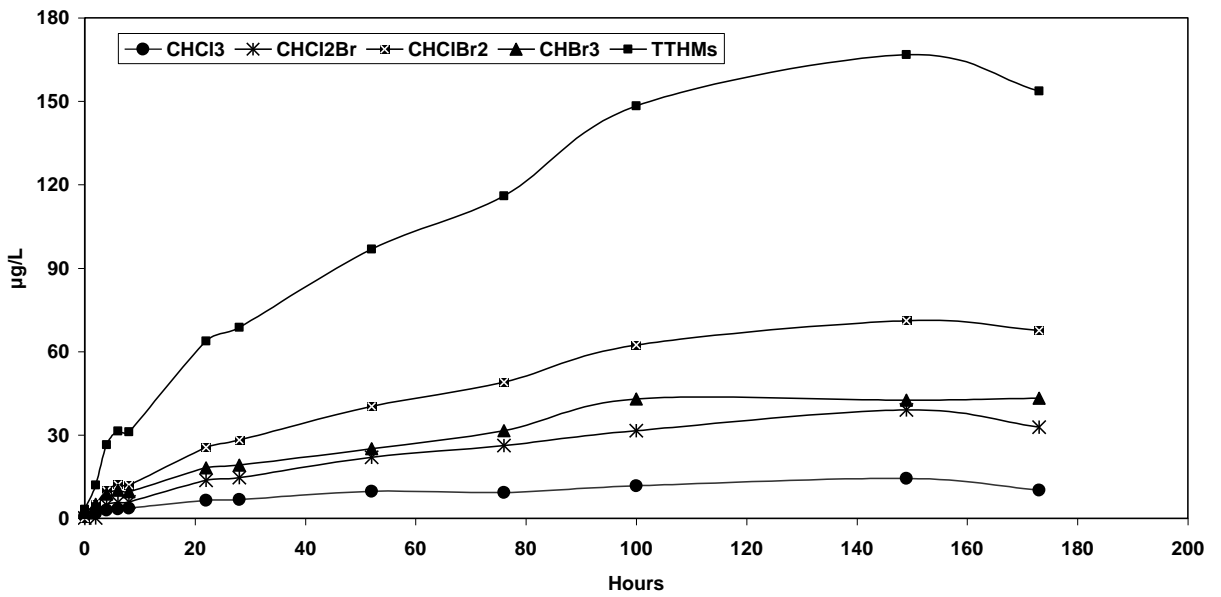


Fig. 4.4: THMFP rate in Anabta well 2 (sampled at 18 June 2005)

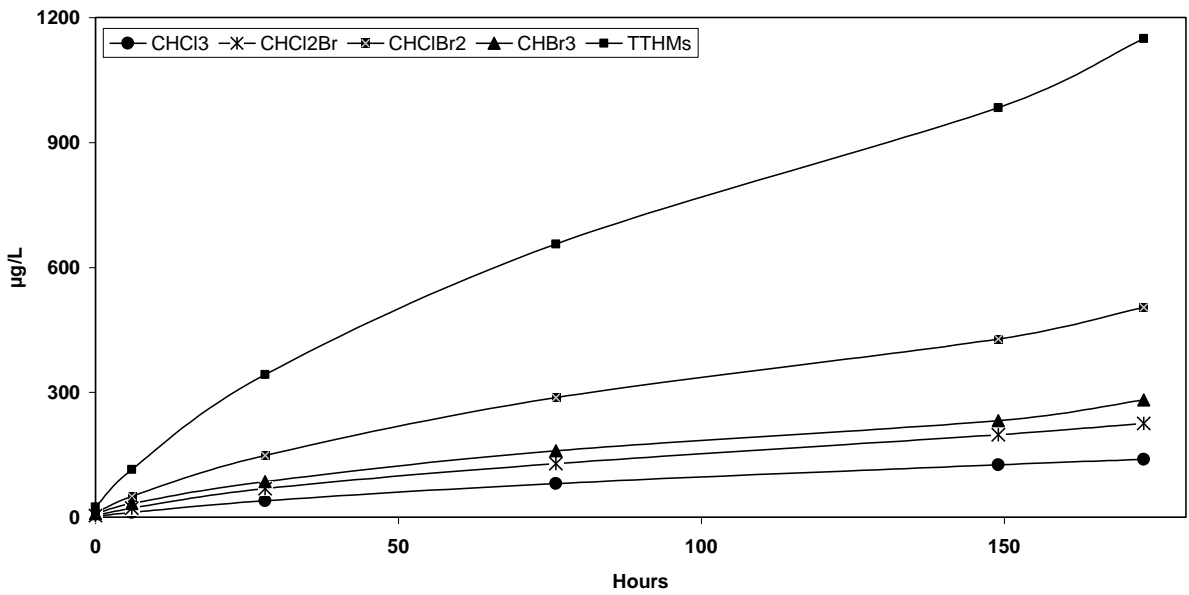
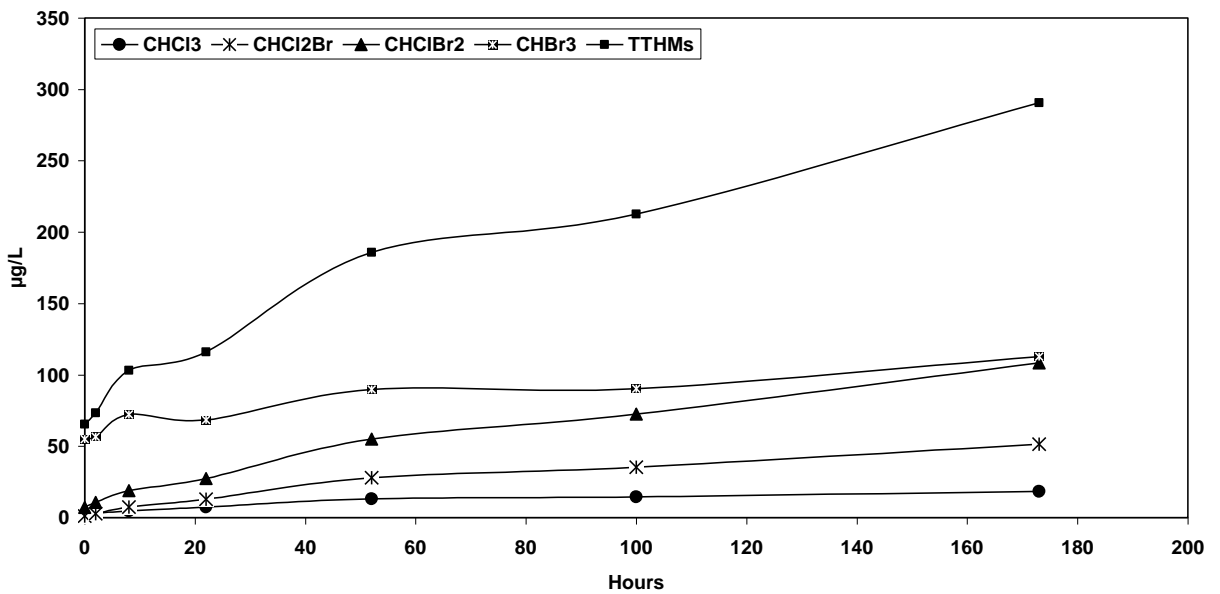
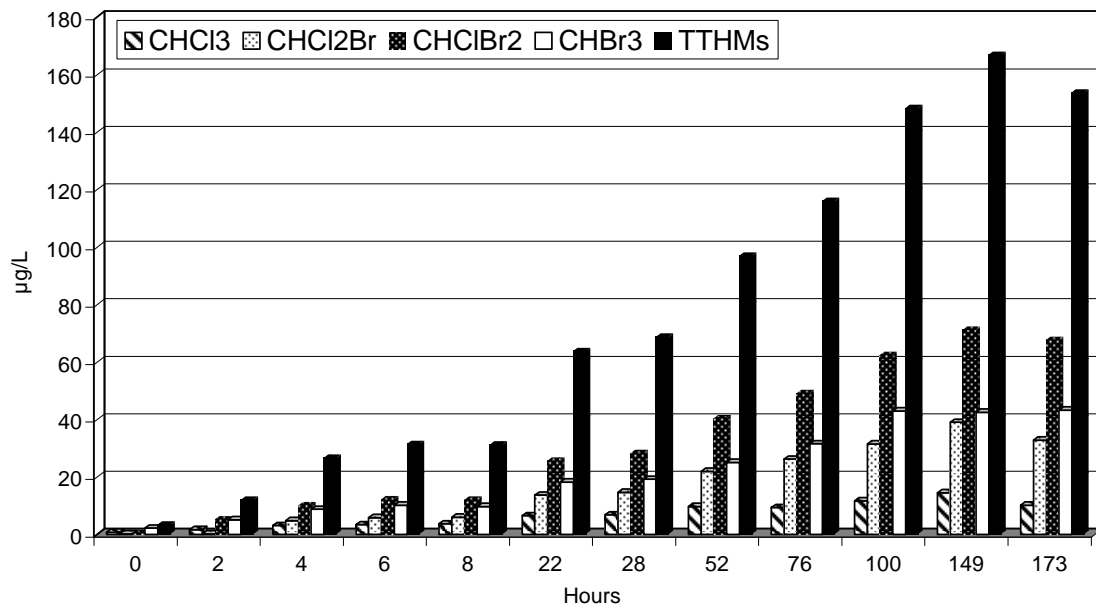


Fig. 4.5: THMFP rate in Shwaiqw (Misnawi) well (sampled at 18 June 2005)



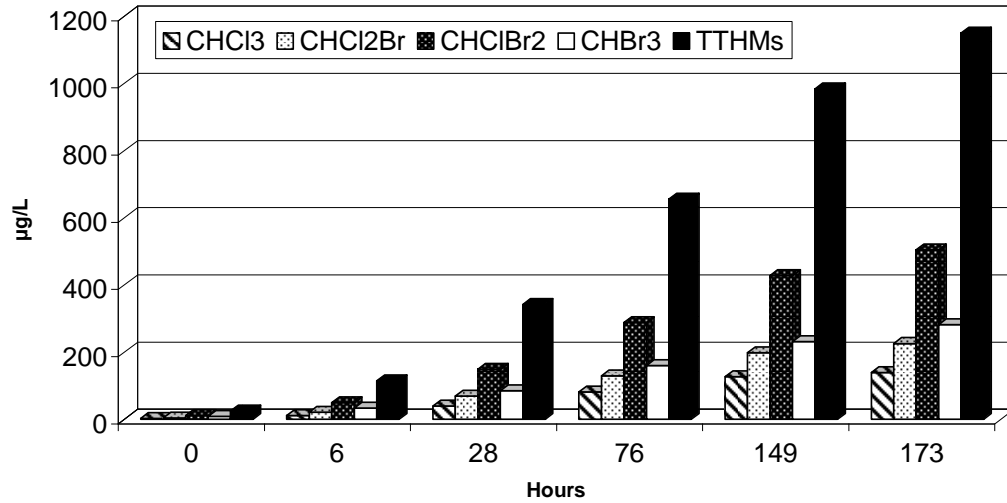
**Fig. 4.6:** THMFP rate in Tulkarm well 2 (sampled at 18 June 2005)

In Figures 4.7, 4.8 and 4.9 the different species of trihalomethanes and total trihalomethanes are shown. Dibromochloromethane is prominent in Anabta well 2 and Shwaika (Misnawi) well, where chloroform is the minor trihalomethane formed in the water of all the three wells' samples.

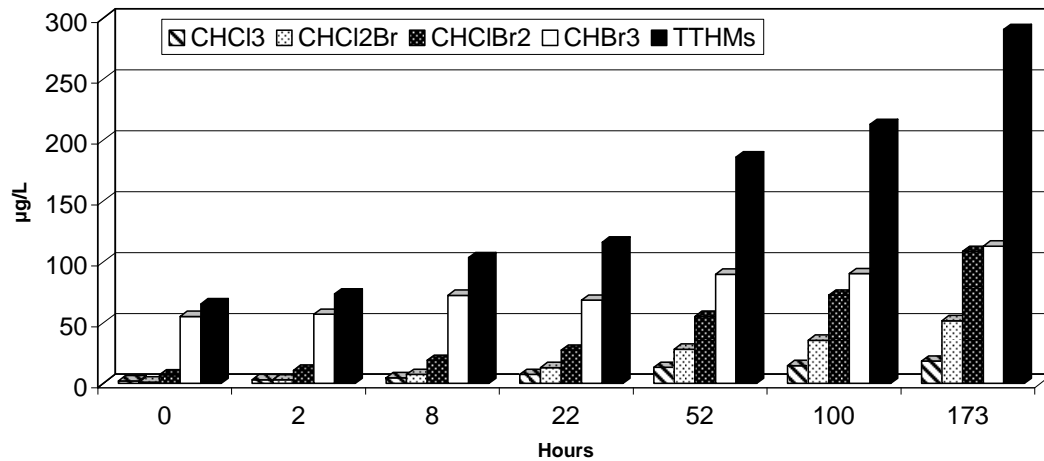


**Fig. 4.7:** THMs formed in Anabta well 2 (sampled at 18 June 2005)

In Tulkarm well 2 the prominent trihalomethane species is bromoform, dibromochloromethane is the second species formed in Tulkarm well 2 as shown in Fig. 4.9.

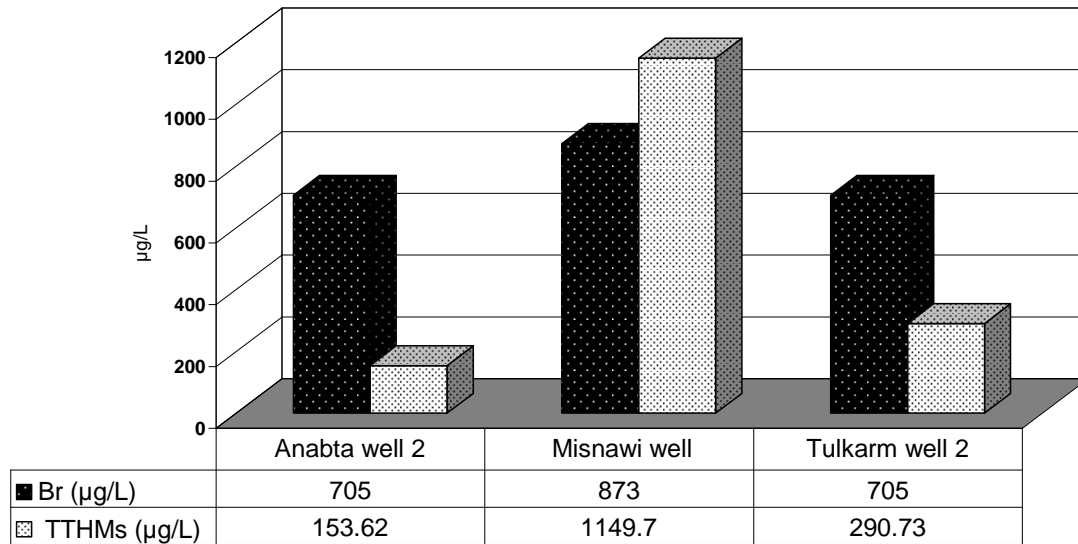


**Fig. 4.8:** THMs formed in Shwaika (Misnawi) well (sampled at 19 June 2005)



**Fig. 4.9:** THMs formed in Tulkarm well 2 (sampled at 19 June 2005)

The effect of bromide concentration and organic carbon on the potential formation of trihalomethanes in the raw water from the three wells is shown in Fig 4.10 and Fig 4.11 respectively.



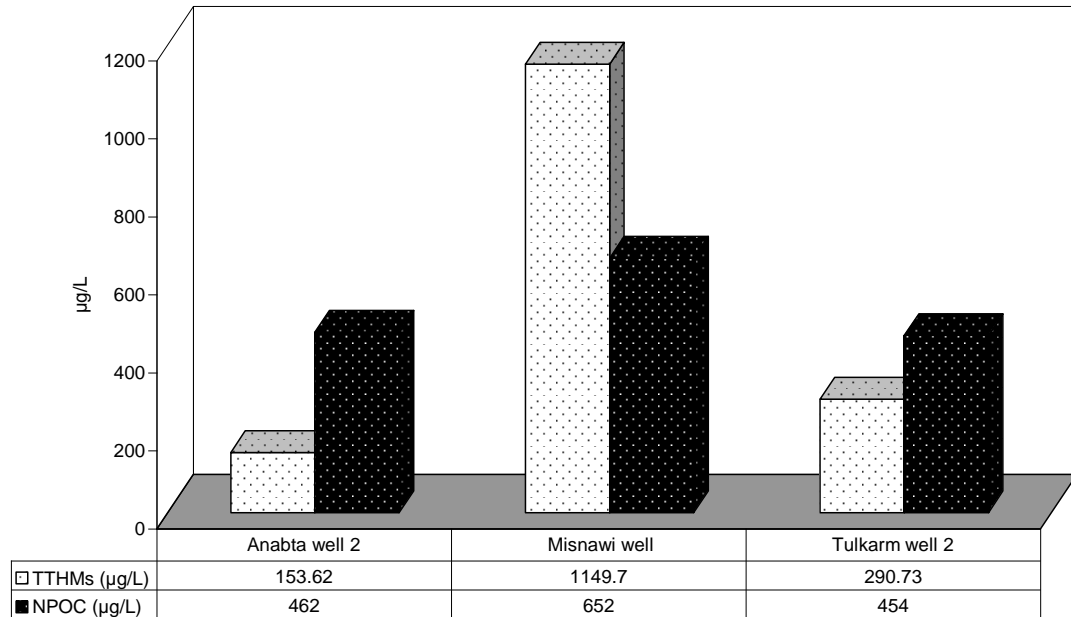
**Fig. 4.10:** Bromide effect on trihalomethane formation

The organic material which is the precursor of trihalomethane formation could be from the natural organic material that reach the groundwater through the karstic system of the aquifer or from anthropogenic pollutants. Bromide also increases and alternates the trihalomethane formation.

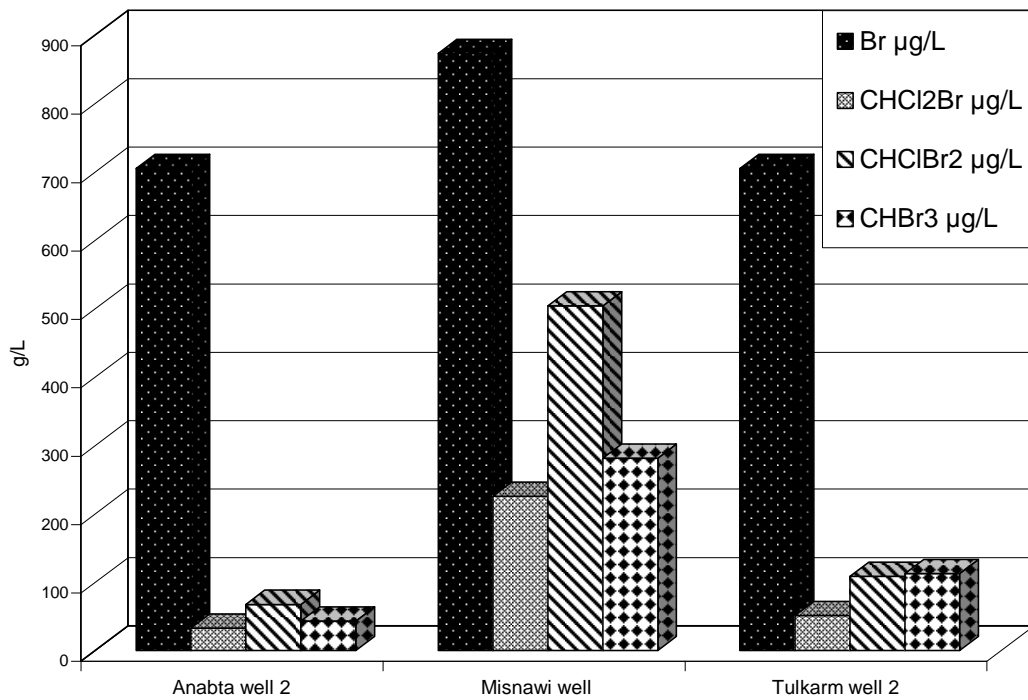
Shwaika (Misnawi) well has the higher bromide and organic material content which increases the trihalomethane formation in the water sample of this well as can be seen from Fig 4.10 and Fig 4.11.

Increase bromide level in the water causes the formation of higher level of brominated trihalomethane species. In Fig 4.12 the formation of brominated trihalomethanes and

bromide content in each well are shown. Shwaika (Misnawi) well has the highest bromide value and the highest brominated trihalomethanes formation potential.



**Fig. 4.11:** Organic carbon effect on Trihalomethane formation



**Fig. 4.12:** Bromide effect on brominated trihalomethanes formation

#### 4.5 Properties of Swimming Pools' water in Tulkarm

The physical properties and the free chlorine residual for six swimming pools water from Tulkarm are presented in Table 4.9.

Table 4.9 Physical properties and free chlorine residual of swimming pools' water in Tulkarm

<b>Date of Sampling</b>	<b>Swimming Pool</b>	<b>pH</b>	<b>EC (µs/cm)</b>	<b>Temp °C</b>	<b>Free Chlorine mg/L</b>
18/06/2005	Janat Al tefel	7.21	1212	26.4	1.72
18/06/2005	Wade Al sham	8.12	722	26	0.09
18/06/2005	Al sahel	6.82	1453	28.7	0.65
18/06/2005	Al waha (small)	7.83	3540	28.7	0.84
18/06/2005	Al waha (large)	7.39	3100	29	2.09
18/06/2005	Tal Al rabee'	7.68	2200	27.5	1.44

To obtain the maximum disinfection effect the pH of the water in a swimming pool must be in the range of 6.5-7.6, and chlorine is considered ineffective at pH 8 and above (WHO, 2000). The pH of 50% of the swimming pools' water did not comply with this pH guideline.

The free chlorine residual in swimming pools' waters recommended by the United Kingdom is 1-2 mg/L and American National standard institute 1-3 mg/L (WHO, 2000). The free chlorine residual measured in Tulkarm swimming pools' waters did not achieve these values in 50% of the pools. The lowest amount of free chlorine residual (0.09 mg/L) is noticed in Wade Al sham pool which has the highest pH (8.12). This low free chlorine residual is a result of low dissociation rate of disinfectant due to the high pH and/or because of low dose of chlorination.

The EC of the water of some swimming pools was elevated compared to the groundwater that is used to fill the swimming pools. This EC elevation is due to the heavy bathing load and the delay in the water turnover.

#### **4.6 Trihalomethanes Concentrations in Recreational water in Swimming Pools in Tulkarm.**

The results of the trihalomethanes measured in the water of six swimming pools in Tulkarm are presented in Table 4.10.

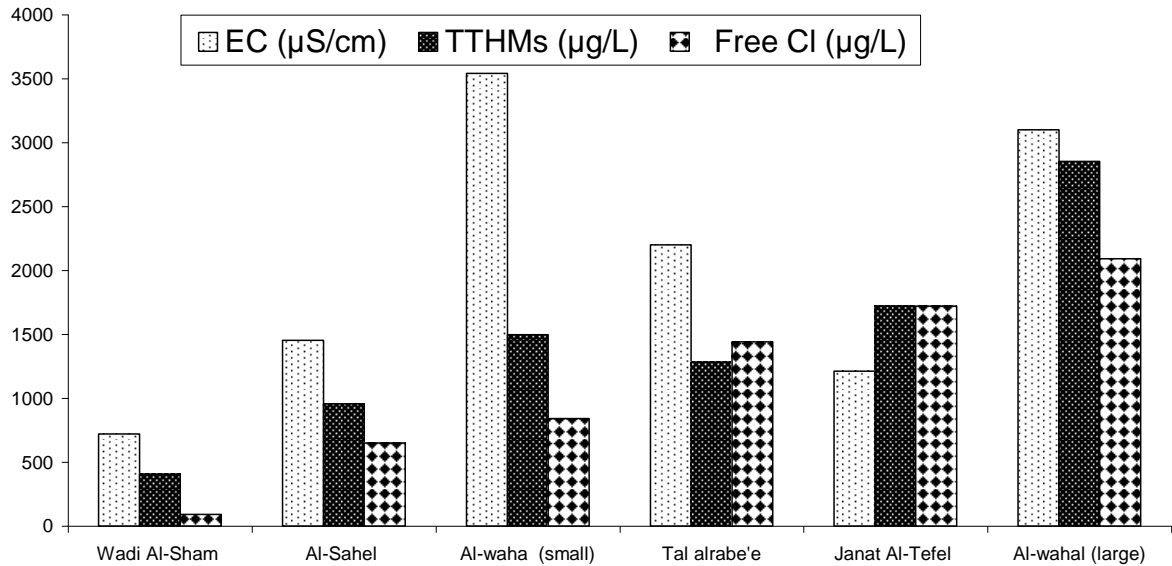
Table 4.10 THMs in recreational water in swimming pools in Tulkarm

<b>Date of Sampling</b>	<b>Swimming Pool</b>	<b>CHCl<sub>3</sub> µg/L</b>	<b>CHCl<sub>2</sub>Br µg/L</b>	<b>CHClBr<sub>2</sub> µg/L</b>	<b>CHBr<sub>3</sub> µg/L</b>	<b>TTHMs µg/L</b>
18/06/2005	Janat Al tefel	1461.3	187.7	61.5	9.3	1719.7
18/06/2005	Wade Al sham	67.8	87	147.4	102.9	405.1
18/06/2005	Al sahel	787	126.1	40.9	2.6	956.6
18/06/2005	Al waha (small)	1163.8	248.9	74.7	10	1497.4
18/06/2005	Al waha (large)	2094.9	561.3	179	18	2853.2
18/06/2005	Tal Al rabee'	979.5	226.9	69.9	6.9	1283.1

Chloroform is the abundant trihalomethane and bromoform is the minor trihalomethane measured in five pools. In Wade Al sham pool the brominated trihalomethanes were the prominent trihalomethane species. Wade Al sham swimming pool when sampled was new pool and still not opened for the public; the physical water properties of this pool (Table 4.9) indicate fresh water properties. The other pools are heavily used with high bathing load and low water turnover (Personal communications). The swimmers always contribute in adding organic material to the water of the swimming pools. This high organic content and continuous chlorination produced a high concentration of trihalomethanes especially chloroform in the five swimming pools.



In Fig 4.13 the different concentration of total trihalomethanes, free residual chlorine and the EC measured in the water of each pool are shown. Proportionality of free chlorine and trihalomethane formation is obvious through the increasing of trihalomethanes by increasing the free chlorine residual.



**Fig. 4.13:** TTHMs, Free chlorine and EC in swimming pools in Tulkarm

Also the water samples with higher EC measurements produced high level of trihalomethane. The maximum total trihalomethane was measured is 2853.2 µg/L at Al waha (large) pool and the minimum was measured at Wade Al sham 405.5 µg/L. The average of the total trihalomethanes measured in the swimming pools in Tulkarm is 1452.5 µg/L. These values are very high compared to what has been reported in swimming pools waters in different countries. The ranges reported by the WHO for different countries are lower than 500 µg/L in most cases (WHO, 2000). The chloroform concentrations in swimming pool waters mean values are from 14 to 198 µg/L; while other trihalomethanes

were lower (Fantuzzi et al., 2001). Taking this in consideration, more management and monitoring is required to make the swimming pool waters more safe and with the minimum adverse health effect on the swimmers.

#### **4.7 Conclusion and Recommendations**

Drinking water treatment (disinfection by chlorine) and distribution in Tulkarm district promote the formation of disinfection by-products. Trihalomethanes occurrence in tap water and in swimming pool waters indicates that also other disinfection by-products are produced. The high formation potential of trihalomethanes results in the groundwater which is the main source of drinking water in Tulkarm district impose the necessity for reviewing and continuous monitoring and auditing the drinking water quality concerning the organic pollutants and the disinfection by-products that is highly related to the public health.

The high and dominant occurrence of brominated halomethanes in drinking water containing high levels of bromine results in iodinated (iodine- containing) DBPs which are known to be more toxic to cells than other DBPs (c3.org-chlorine issues, 2004).

Water chlorination is the only treatment measure that takes place before distributing water for the domestic use needs more attention for the optimization of chlorine dose and residual concentrations that should be maintained in the distribution system according to the contact time (travel time) and the other chemical and physical properties of drinking water. The

chlorine demand for effective and safe disinfection should be estimated according to the source water quality and the organic material content.

As it is well known "No one size fits all", solutions and plans should consider the available resources and facilities. PWA and other responsible partners with the help of researchers in the field must characterize all DBPs resulting from drinking water chlorination so that to build the data base of complex information on DBPs. Their challenge is to map out the optimum course of managing these compounds without any compromise of eliminating waterborne pathogens.

The polluted surface water in Tulkarm area is affecting the groundwater quality causing it less palatable and increasing the risk on the public health in the area. Special treatment and management of the waste water in the area is recommended to minimize the pollution effect and the negative ecological impact on the whole area.

Technical persons and workers involved in water chlorination need more qualification and training on monitoring and optimizing the chlorination process. At the same time instrumentation and necessary chemicals and materials for monitoring the chlorination process are required. Maintenance of the chlorination pumps at the chlorination points is important and vital.

Swimming pools in Tulkarm are mismanaged and their water turnover and maximum bathers load are to be reviewed by the stakeholders responsible for such activities. The high

results of DBPs in the swimming pools waters refer to their high content of organic matter - mainly added by bathers themselves- and continuous chlorination.

Chlorination of swimming pools waters which is the only disinfection process is not compromised but a combination of two disinfection processes –such as chlorine and ozone- may be the choice, so to minimize the required optimum chlorine dose (Rushall and Weisenthal, 2003).

It is crucial to implement an over year monitoring program for THMs occurrence in the Palestinian drinking water so to verify the compliance of the values of THMs with the standards and guidelines recommended by the WHO and other international agencies.

PWA and Palestinian Health Ministry are encouraged to intensive their auditing and supervising the swimming pools that are increasing in the West Bank.

Training and education of swimming pools' owners and operators on the optimum operational (physical and chemical) parameters is highly recommended.

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