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**Total Trihalomethanes Formation Potential of Three  
Wastewater Treatment Plants Effluents in West Bank  
Palestine**

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Wastewater Treatment Plants Effluents in West Bank  
Palestine**

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Plants Effluents in West Bank Palestine**

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Jerusalem- Palestine  
1436 ٠/2015م

## **Dedication**

*To my family and friends for their love and support*

Hadeel Hiasham Ikhmais

## **Declaration**

I certify that the thesis is 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 be submitted for a higher degree to any other university or institution.

Signed:.....

Hadeel Hisham Ikhmais

Date:.....

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## **Abstract**

Wastewater is rich with organic and inorganic precursors that form disinfection by products (DBPs) after chlorination. Therefore, it is important to examine and understand the formation of DBPs in wastewater effluents according to their harm to human health and environment.

The main goal of this study is to investigate trihalomethanes formation potential of treated wastewater effluents from different wastewater treatment plants located in Palestine, after characterization and determination of chlorine demand.

The chosen wastewater treatment plants for the study are Al-Quds University Wastewater Treatment Plant (AQU P), Oasis Hotel Wastewater Treatment Plant (Oasis P) and Al-Auja Wastewater Treatment Plant (Auja P).

For chlorine demand experiments chlorine dosage applied to three wastewater treatment plants samples range from 10 to 2000 mg/L, while measured free chlorine residuals range from 0 to 5mg/L. High concentrations of Activated sludge samples characteristics since AQU P receive large amounts of wastewater from different sources of AQU campus, including laboratories' chemical and organic wastes and kitchens compared to less concentration in oasis P since amount of receiving wastewater depends on visitors of the hotels. Moreover, Auja P receives only grey water which reflected on relatively low ammonia concentration thus less chlorine demand. As a result, the chlorine demand dosages and the patterns of the ammonia are varied among the samples from the three WWTPs due to different characteristics.

Chlorine demand in activated sludge (AS) requires around 1000 mg/L of chlorine which is elevated dose related to concentrated organics and ammonia-N present in wastewater samples from treatment system. However the advanced treatment technologies

Ultrafiltration (UF) and reverse osmosis (RO) required 400 and 20 mg/L respectively. Chlorine demand in Oasis P and Auja P was around 300 mg/L for both.

The distribution of four individual THM compounds investigated by five effluents of three wastewater treatment plants. Chloroform was seen to dominate the THM species in all Wastewater treatment plants effluents. Total trihalomethanes (TTHMs) detected for AS, UF and RO of AQU P were around 740, 372, 96  $\mu\text{g/L}$  respectively after 120 hours of incubation. In Oasis P and Auja P TTHMs after 120 hours of incubation were 1342  $\mu\text{g/L}$  and 1642  $\mu\text{g/L}$  respectively. In all AQU P effluents chloroform occupies 90% of most TTHMs while bromdichloromethane is the minor species with no detection to another species of THMs. In Auja P TTHMs mainly consist from 58% Chloroform and 27% bromodichloromethane however other species as dibromochloromethane and bromoform are detected but with lower percentage 12% and 1.7% respectively. In Oasis P TTHMs mainly consists from Chloroform 69% and bromodichloromethanes 22% however other species as dibromochloromethane and bromoform are detected but with lower concentrations 6% and 1% respectively. Brominated species are detected in Oasis and Auja P due to the presence of bromide in source water of Oasis and Auja P.

Comparing THMs formation potential generated from the chosen wastewater treatment effluents in this study with international studies and for drinking water standards, Palestinian treated wastewater effluents contained high values ranged from 200-1600  $\mu\text{g/L}$  which are considered higher than recommended trihalomethanes for drinking water since there is no specific standards for THMs in wastewater. Significantly higher THMs in wastewater effluents attributed to significant amount of THMs precursors produced after treatment or present in influent and original source of wastewater.



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## Abbreviations

|                 |  |
|-----------------|--|
| AS              | Activated Sludge                             |
| BDCM            | Bromodichloromethane                         |
| BF              | Bromoform                                    |
| BOD             | Biological Oxygen Demand                     |
| Br              | Bromide                                      |
| Ca(OCl)         | Calcium Hypochlorite                         |
| Cl <sup>-</sup> | Chloride Ion                                 |
| Cl <sub>2</sub> | Chlorine                                     |
| COD             | Chemical Oxygen Demand                       |
| CF              | Chloroform                                   |
| CWA             | Clean Water Act                              |
| DBCM            | Dibromochloromethane                         |
| DBPs            | Disinfection by Products                     |
| DBPFP           | Disinfection by Products Formation Potential |
| DOC             | Dissolved Organic Carbon                     |
| DOM             | Dissolved Organic Matter                     |
| DPD             | N,N- diethyl-p-phenylenediamine              |
| DWF             | Drinking Water Facility                      |
| EC              | Electrical Conductivity                      |
| EU              | European Union                               |
| FAC             | Free Available Chlorine                      |
| GC-MS           | Gas Chromatograph-Mass Spectrometer          |
| HAAs            | Haloacetic acids                             |
| HA              | Haloaldehydes                                |
| HF              | Hollow Fiber                                 |
| HK              | Haloketones                                  |
| HNMs            | Halonitromethanes                            |
| HOBr            | Hypobromous Acid                             |
| IC              | Inorganic Carbon                             |
| MCLs            | Maximum Contaminant Levels                   |
| NaOCl           | Sodium Hypochlorite                          |
| NaOH            | Sodium Hydroxide                             |

|                  |   |
|------------------|---|
| NDMA             | Nitrosodimethylamine                          |
| NH <sub>3</sub>  | Ammonium                                      |
| NO <sub>2</sub>  | Nitrite                                       |
| NO <sub>3</sub>  | Nitrate                                       |
| NOM              | Natural Organic Matter                        |
| NTU              | Nephelometric Turbidity Unit                  |
| OBr <sup>-</sup> | Hypobromite Ion                               |
| PCBS             | Palestinian Central Bureau of Statistics      |
| PWA              | Palestinian Water Authority                   |
| RO               | Reverse Osmosis                               |
| SUVA             | Specific Ultraviolet Absorbance               |
| SW               | Spiral Wound                                  |
| TDS              | Total Dissolved Solids                        |
| TSS              | Total Suspended Solids                        |
| THMs             | Trihalomethanes                               |
| TTHMs            | Total Trihalomethanes                         |
| THMFP            | Trihalomethanes Formation Potential           |
| TN               | Total Nitrogen                                |
| TOC              | Total Organic Carbon                          |
| TSS              | Total Suspended Solids                        |
| UF               | Ultrafiltration                               |
| USEPA            | United States Environmental Protection Agency |
| WHO              | World Health Organization                     |
| WWF              | Wastewater Facility                           |
| WWTP             | Wastewater Treatment Plant                    |

# Chapter 1

## Introduction and Objectives

### 1.1 Background

“We have made from water every living thing” Allah says in the Holy Quran. After one and half millennium this view still sensible to people since without water, life doesn't exist.

Based on history, residents gathered, developed and built cities around water sources. For many years human being put standards to their usable water as the clear, with good taste and non odorous. But those standards were totally abandoned after the emerging of water borne diseases which killed thousands of people at that time. Later, the standards changed to maintain safe water which basically chemicals and microbes free (Brown, 1969).

One of the major advancement in public health was achieved after chlorinating and treating of drinking water supply, in the early 1900s (Clark and Sivanganesan, 2002). After that chlorine became the “disinfectant of choice” in drinking water treatment plants. The chlorine glory was disgraced in the 1974, after publishing by Rook (1974) and Bellar et al. (1974) that chloroform result after reaction of chlorine and organics in treatment water supplies. After that, research on water chlorination showed variety of disinfection by products (DBPs) as trihalomethanes (THMs), haloacetic acids (HAAs), haloaldehydes (HAs), haloketones (HKs) (Richardson et al., 2007). Between hundreds of DBPs were reported, trihalomethanes took the attention for their major existence and their health concerns.

The discovery of DBPs led to reconsideration of chlorination by reducing chlorine doses applied to drinking water supply systems or finding alternative disinfectants but the challenge is not to influence the bacteriological safety with minimum DBPs (Gopal et al., 2007; Li et al., 2013)



Water is a resource that is becoming widely scarce and needs to be sustained, locally and globally. One of the most serious problems faced by billions of people today is lacking the availability of fresh water. The accelerating development of industrialization, urbanization and population growth increased water pollution. The deterioration in water quality and scarce in quantity, make wastewater treatment becomes one of the solutions as it reduces pollution of environment and water resources, and provides water alternative resource for continuity and survival (WHO, 2005). Some parts of the world have shown advancement in water supply result in economic benefit, because the minimization in the detrimental health effects and health care costs overcome the costs of undertaking the interventions (WHO, 2005), quoting from the pioneer of water reuse in south Africa Dr. Lucas van Vuuren (1970): “Water should be judged not by its history, but by its quality.” (Brown, 2009)

A water-scarce country has annual supply of renewable freshwater less than 1000 m<sup>3</sup> per capita (Falkenmark and Widstrand, 1992), this scarcity exposes the country to face restrictions in food production, economic development, and stress in natural water systems, and according to the World Health Organization (WHO) (2005) 26 countries with 232 million people are water scarce countries.

To ensure human health protection, wastewater should be disinfected before discharge to environment to prevent waterborne diseases which could be caused after insufficient disinfection of wastewater after the use of the receiving water for human consumption or human contact (Singer, 1999). Over the past century, chlorination was the mostly used method for wastewater disinfection due to the ease of application, proper disinfection capabilities and low costs (Singer, 1999). Major by-product result from chlorination of wastewater are trihalomethanes as well as many halogenated by-products, THMs, are

known animal and suspected human carcinogens also related to low weight births, and abortions (Cantor, 1998; Goel, 2008; Chowdhury and Champagne, 2009).

Despite the positive impact of wastewater reclamation on public health and environment it is still a controversial water supply source (Jimenez and Asano, 2008). The public acceptance and participation is the major barrier for the implementation of wastewater reuse. Many successful wastewater treatment plants were constructed and overcame the economical and technical difficulties but the public acceptance and community support didn't involve in developing the reuse project (Jimenez and Asano, 2008).

## **1.2 History of Wastewater Chlorination**

Wastewater reuse for agriculture was documented before 5000 years ago in the ancient Minoan civilization (Angelakis and Spyridakis, 1996). In the nineteenth century large scale wastewater systems were built to collect wastewater then discharge it to surface waters. In 1840s and 1850s the unplanned reuse of wastewater coupled with outbreak of water borne diseases such as typhoid and cholera (Geiger and Moloney, 1952). The relationship between water and diseases wasn't understood, the dominant thought was that odors cause the disease thus chlorine was used as a deodorant for hiding the smell caused by wastewater; without the understanding of the germicidal capacity of it (White, 1986). The first use of chlorine as a disinfectant was by William Soper of England when he treated the feces of typhoid patients with chlorinated lime before disposal in the sewage system (White, 1986). After that the use of chlorine as a disinfectant was spread widely. In 1958, 30% of all wastewater treatment plants in USA were provided with chlorinators (White, 1986). The twentieth century was considered "the era of wastewater reclamation and reuse" (Jimenez and Asano, 2008). Wastewater reclamation means the treatment of

wastewater to make it reusable, while water reuse means the gainful use of treated wastewater (Rogers et al., 2004).

In the mid-nineteenth century after the development in many aspects in human life, wastewater became more concentrated and polluted also the water bodies which were used for wastewater disposal didn't tolerate more. Contamination and degradation of water quality was noticed. In 1913 the engineers start thinking of treating wastewater by developing the activated sludge (Ohlsson, 2000). After the technological innovation in 1970s which led to water scarcity the significant advances in wastewater reclamation and reuse were born in the USA and around the world (Metcalf and Eddy, 1991). In 1972 the Clean Water Act in USA provided funds and regulations for disposal of treated wastewater.

The advances of recycling technologies and reuse introduce more achievable option for water supply (Postel, 2000). The major three technologies that significantly affect wastewater treatment are biological treatment, disinfection and membrane filtration. Biological treatment is usually the secondary treatment, which is the process of breaking down organic matter by biological activity. Disinfection is applied to prevent water borne diseases before water discharge to environment. Membrane filtration started by traditional filtration methods then progressed to tertiary and advance filters such as microfiltration, ultra filtration, nanofiltration, and reverse osmosis (Metcalf and Eddy, 1991).

### **1.3 Wastewater Situation in Palestine**

Palestine is classified as one of the scarcest countries of renewable water resources per capita; with average domestic water consumption is only 72 Liter per capita per day (L/c/d) in the West Bank, while in Gaza reaches to 90 L/c/d, that is quite below the recommended standards by WHO; which is 100 L/c/d (World Bank, 2004). In some rural communities Palestinians survive on 20 L/c/d which is the minimum amount recommended by the WHO

for emergency situations (World Bank, 2004). Limited water quantity and quality constrains economic development, increasing infrastructure and running costs and lead to health problems. More than half of the available groundwater is used for domestic water supply, which restricts available volume for industrial development and agriculture (PCBS, 2008).

Lack of access to sufficient, sustainable, and safe water has been a long-lasting problem for the Palestinian population (PWA, 2012). Water situation has worsen in the recent years as a result of drought which induced water scarcity, yet the problem exacerbate because of Israeli water policies and practices which violates the Palestinians rights of having adequate living standards (PWA, 2012). Additionally, scarce of water resources and water quality degradation in Palestine are fundamental environmental challenges. Groundwater quality deteriorated because of leakage of untreated wastewater, or wastewater effluent is discharged directly into the environment without treatment (World Bank, 2009).

For many years wastewater management was neglected throughout the Occupied Palestinian Territories and few investments has been made in the wastewater sector since the Oslo Accords (World Bank, 2009). The discharge of untreated wastewater from Israeli settlements has worsened the problem (UNEP, 2003). Wastewater treatment become a priority as a result of water scarcity and pollution of water resources to provide a partial solution to water problem in West Bank and Gaza strip mainly in agricultural irrigation which consumes 70% of water demand in West Bank and Gaza by reuse of treated water for irrigation. However the existing treatment plants in Palestine are not very efficient because of financial and technical obstacles. The reuse of wastewater could be achievable in areas that connected to sewerage systems and treatment plants.

In West Bank, only 30-35 % of the whole population is connected to sewerage networks (PCBS, 2008). The majority of the population uses cesspits for storage of wastewater.

Cesspits vacuumed by tankers who dispose the contents into the environment as wadis, open spaces or solid waste disposal sites (World Bank, 2009). Regardless the low total percentage of access to sewerage, around 70 % of houses in the main cities of West Bank is connected. While, in refugee camps sewage flows through rainwater drains. Most villages have no sewerage system and wastewater is discharged into cesspits or cesspools or infiltration pits (Bursche, 2011).

Irrigation with raw wastewater has been done in many cities in West Bank. Crops and vegetables like parsley, mint, peppers, eggplants, squash, cauliflower, radishes and olive trees are being irrigated with untreated wastewater without any official health control or due consideration to possible health or environmental hazards. Untreated wastewater causes pollution and harms the crops, soil, and groundwater (Abomohor, 2011).

The treated wastewater can be reused successfully in Palestine if it is reused in landscape irrigation, groundwater recharge and in stone cutting (ARIJ, 2009).

The fundamental obstacle in development of wastewater treatment sector is lack of significant investments in wastewater sector thus little or no progress towards solving the heavy environmental issue of water scarcity and pollution (UNEP, 2003). Moreover, within the area of West Bank, available locations for constructing reclamation plants are found only in area C since reclamation plants require large land area which is not far from populated areas. However the construction in area C needs Israeli approval to Palestinians proposals (UNEP, 2003).

Recently, Palestinian Standards Institute (PSI) and Environment Quality Authority with coordination of Palestinian ministries and universities has established specific wastewater reuse regulation of the wastewater treatment effluent by setting the regulation and standards for physical, chemical and biological parameters of effluent that is not hazardous

if it is used for irrigation or recharge. Table 1.1 illustrates the standards of technical parameters of effluents according to (PSI, 2012).

**Table 1.1.** Palestinian effluents guidelines and standards.

| <b>Effluent parameter</b> | <b>Fodder IRR</b> | <b>Gardens Playground</b> | <b>Industrial Crops</b> | <b>Groundwater Rechargeable</b> | <b>Landscape</b> |
|---------------------------|-------------------|---------------------------|-------------------------|---------------------------------|------------------|
| <b>BOD<sub>5</sub></b>    | 60                | 40                        | 60                      | 40                              | 60               |
| <b>COD</b>                | 200               | 150                       | 200                     | 150                             | 200              |
| <b>DO</b>                 | >0.5              | >0.5                      | >0.5                    | >1                              | >0.5             |
| <b>TDS</b>                | 1500              | 1200                      | 1500                    | 1500                            | 50               |
| <b>TSS</b>                | 50                | 30                        | 50                      | 50                              | 50               |
| <b>pH</b>                 | 6-9               | 6-9                       | 6-9                     | 6-9                             | 6-9              |
| <b>NO<sub>3</sub>-N</b>   | 50                | 50                        | 50                      | 15                              | 50               |

Fodder IRR: feed for live stock irrigation (PSI, 2012).

Wastewater treatment improvement is considered a step toward resolving water scarcity and pollution. However wastewater treatment can be very controversial and can face major opposition when applied in the real word.

#### **1.4 Problem Definition**

Palestine is located in the semi arid climate zone which suffered from water scarcity and water constrains toward water. Wastewater treatment is taking obvious concern as a solution for covering the increasing demand. Before the reuse of wastewater for many aspects in human life such as industrial, agricultural and recreational, or before discharge to environment wastewater should be safe to public health and environment. Disinfection is obligatory before human contact with reused water to avoid water-borne diseases. Unfortunately disinfection of drinking or wastewater with chlorine (as the most applicable

disinfectant) comes with the formation of harmful carcinogenic and mutagenic by products. DBPs come out after the interaction of high load of organic and inorganic that enriches wastewater system. THM is the major class of DBPs and their presence is considered an indicator for other DBPs. The aim of wastewater treatment is to produce an effluent with minimum amount of contaminants, DBPs and their precursors.

Wastewater treatment in Palestine varies in treatment technologies and treated effluent quality. THM formation after wastewater treatment can give indication for the efficiency of treatment technology of wastewater treatment plants (WWTP) in removing organic and inorganic precursor from wastewater, the safety of public health and environment after recharge of wastewater contains these DBPs. Until now THMs weren't investigated in wastewater treatment plants in Palestine therefore it is important to investigate and understand the formation of THMs and compare it to international levels of THMs. To have better understanding of THMs in treated waters, their formation will be evaluated under controlled conditions.

### **1.5 Research Objectives**

The general objective of this study is to investigate trihalomethanes formation potential of treated wastewater from different treatment plants and compare between the different treatment technologies in removing THM precursors.

The specific objectives are:

1. Characterization and description of wastewater treatment plants.
2. Characterization of influents and effluents of wastewater treatment plants.
3. Determination of chlorine demand of each wastewater treatment plant effluent.
4. Assessment of formation potential of THMs of treated wastewater and comparing between different technologies in removing THMs precursors.

5. Investigation of compliance and possible health effects regarding TTHM after chlorination with international levels.



## Chapter 2

### Wastewater Treatment Plants

Reclaimed wastewater is defined as effluents that are exposed to a combination of physical, chemical, and biological treatment technologies to remove suspended solids, dissolved solids, organic matter, nutrients, metals, and pathogens (Glaze et al., 1973). The fundamental objective of wastewater treatment is to eliminate and reduce organic matter under controlled conditions (Rossi et al., 2007). The treatment process for the result of treated water involves four major steps: preliminary, primary, secondary, and tertiary treatment (Wei et al., 2006). Preliminary and Primary treatment involve the physical removal of large solids from the waste stream. Wastewater is then pumped into a sedimentation tank to settle suspended solids and forming primary sludge. Then wastewater is applied to secondary treatment involves a biological process that supplied by aeration tanks that treats the remaining suspended solids and organics by maintain microorganisms alive, Tertiary treatment is a physical-chemical process that concern additional treatment of the effluent from the secondary stage to eliminate chemical and microbial contaminants that passed from secondary treatment. Commonly tertiary treatment involves more advanced treatment process to produce a high quality of treated wastewater. Such as: reverse osmosis, microfiltration, and membrane bioreactor (Maier et al., 2009).

For this study three wastewater treatment technologies were chosen to investigate the role of each specific technology in removal of DBP precursors and decreases DBP concentrations in treated effluents. Different treatment plants were chosen depending on their different treatment technologies which varied between simple and advanced technologies. Moreover, wastewater treatment plants originate from different water resources.

The different wastewater treatment technologies that were used in this research are:

1. Al- Quds University Wastewater Treatment Plant (AQU P) which is located in Al-Quds University in Abu-Dees village.
2. Oasis Hotel Wastewater Treatment Plant (Oasis P) in Oasis Hotel and Resort in Jericho.
3. Auja grey water treatment plant (Auja P) in Jordan Valley Center for Environmental Education and Ecotourism Development.

### **2.1 Al- Quds University Wastewater Treatment Plant (AQU P)**

Wastewater treatment plant constructed at Al-Quds university campus at Abu-Dees in 1998. Wastewater that is produced from many sources as black water, grey water and runoff is collected in a two-stage primary settling basin then pumped to the treatment plant. Preliminary stage comes first to remove coarse solids and large materials. After that primary treatment process is started at the activated sludge with extended aeration that ranges between 16-20 hours hydraulic retention time. The organic matter is oxidized by microorganisms to decrease biological oxygen demand BOD of treated wastewater. Then activated sediment in the clarification tank is pumped to the aeration tank with special pump. The next treatment step is using a coagulating agent to enhance the suspended solid removal before sand filtration. Afterward chlorination of wastewater is applied for disinfection. Then the treated wastewater is gathered in a special pond, part of the secondary activated sludge is joined to ultra-filtration hollow fiber (UF) without chlorination for extra treatment by advanced filtration technologies which are ultra-filtration and reverse osmosis (RO). These 2 scale membrane treatment plants were installed in 2004 and 2006 respectively.

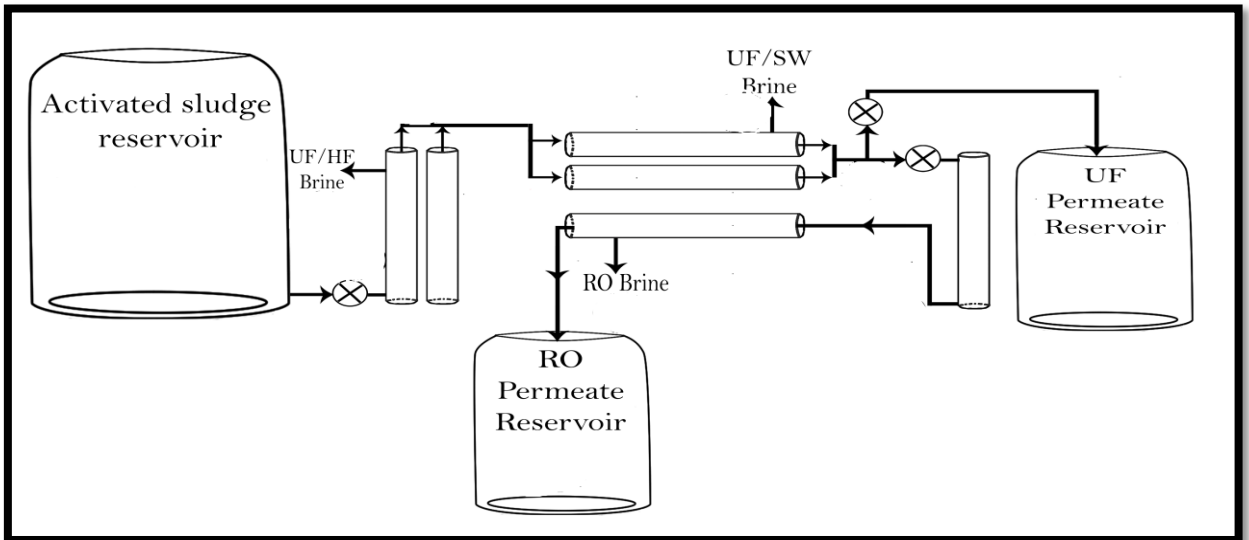
The first UF unit is supplied with 2 pressure vessels that contain the hollow fiber membranes with 100 kD cutoff (Vendor, AST technologies, Model no. 8000-

WWOUT\_IN\_8080). The second UF unit was supplied with 2x4 inch pressure vessels with pressure resistance up to 150 psi. Each vessel holds two separation membranes (spiral wound with 20 kD cutoff which is equivalent to 0.01 micron separation rate). The designed holding capacity of the system is 0.5-0.8 m<sup>3</sup>/h. The advantage of this membrane is its ability to remove bacteria, turbidity agents suspended solids, oil, and emulsions. Hollow fiber and Spiral wound units are designed to deliver 1.5 m<sup>3</sup>/h.

The RO membranes are manufactured from polyamide thin film. It consists of 1x4 inch pressure vessel made from composite material with pressure resistance up to 400 psi. The vessel holds two 4 inches special separation membranes (Manufactured in thin film polyamide with pH range 1-11 model BW30-4040 by DOW Film Tec.). Membrane anti-scaling (Product NCS-106-FG), made of phosphate in water with active ingredient of phosphoric acid disodium salt) are continuously dosed to the RO feed at concentration of 4 mg/L in order to prevent deposition of divalent ions. RO major function is to remove major ions and heavy metals. The designed RO holding capacity of the system is 0.45-0.5 m<sup>3</sup>/h (Khamis et al., 2012).

Schematic diagram of AQU P shows every stage of treatment process including UF-HF, UF-SW and RO stages in Figure 2.1.

The treated wastewater generated from the activated sludge treatment plant at Al-Quds University followed by (part of it) UF and RO systems are monitored all the time by a trained operator under the direct supervision of a specialized technical and research team at Al-Quds University. Treated wastewater generated from this treatment plant is used to irrigate non edible trees and flower plants at the University.



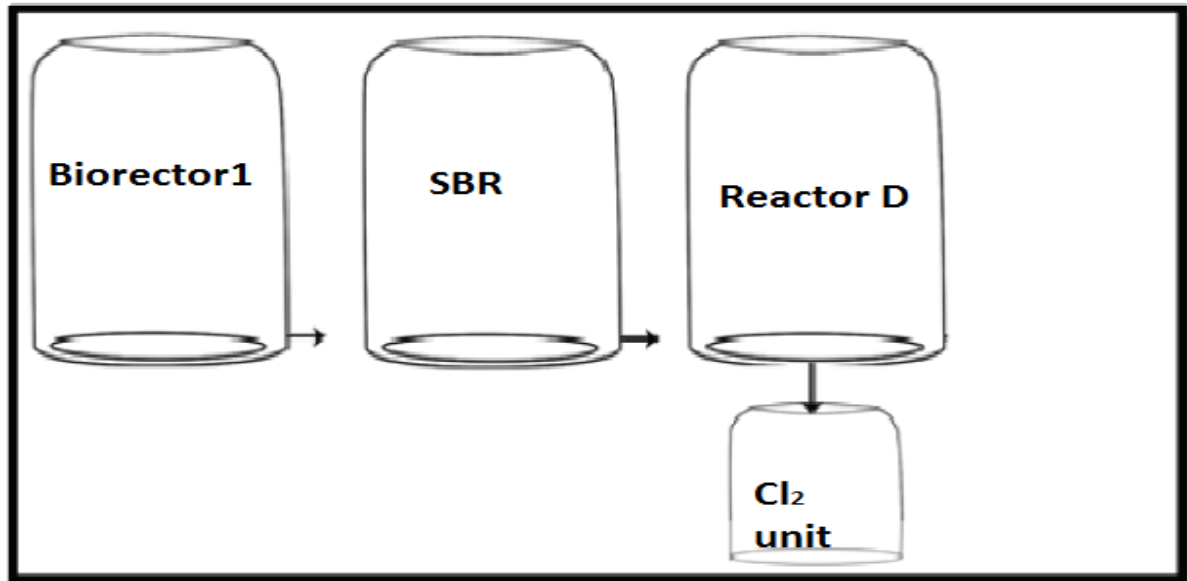
**Figure 2.1.** Schematic diagram of AQU P. (Qurie et al., 2013)

## 2.2 Oasis Hotel Wastewater Treatment Plant (Oasis P) in Jericho.

Oasis hotel and resorts is located on the south of Jericho city. Wastewater treatment plant was built to treat wastewater generated from the casino, hotel rooms, restaurants and kitchens. The recycled water is used then to irrigate ornamental plants. Oasis P was built by TARMAC (1995) LTD, and started working at 1998 to treat around 800 m<sup>3</sup>/day with peak of flow rate around 60 L/sec and 2 cycles per day but because of the closure of the casino the treatment plant treated around 100-120 m<sup>3</sup>/day, during less busy days it works every four days to lower the operational costs.

Preliminary treatment stage includes coarse screening and grit removal to remove large solids and oils, fats and grease. The main operational process is the biological treatment to reduce biological oxygen demand (BOD) of wastewater by introducing bacteria that is already present in wastewater to oxidize the organic matter. Biological treatment of this system is applied by using two bioreactors. The first one is supplied by aerators which is the key factor to maintain the living of bacteria for biodegradation of the organic content, then water pumped to the second bioreactor which is a sequencing batching reactor (SBR) that is based on five steps: filling, reacting with bacteria in the reactor in which most of

carbonaceous BOD is removed in this phase, settling of activated sludge with no mixing or aerating occurs, the sludge that is formed is called the sludge blanket and this step is a critical in determining the effluent quality, decant of clear supernatant effluent after settling by gravity, and idle or disposal of sludge and storage in tanks for converting to fertilizers or use it to keep bacteria alive to reuse in the biodegradation in the bioreactor. After that the effluent travels to reactor D which is a tertiary treatment that includes three sand filters. Chlorination comes in the final stage before going to storage tanks. Figure 2.2 presents all the stages that water passes through. Amount of chlorine applied in this stage is 2 mg/L for two hours. After that the treated water is distributed for irrigation. The treatment process has 2 separated systems one for rainfall, wastewater from hotel rooms, flushing, showering and another line from kitchen alone that is treated by using degreaser to eliminate greases and oils by using skimmers. Reactors are built using permastore glass fused to steel tanks. Bio-oxidation system using fine bubble diffusers and dissolved oxygen control and monitoring, filtration is achieved by using three layers of filtration media; basalt, quartz and anthracite followed by turbidity monitoring. The whole system was carried out by computers with highly developed software but it is no longer available instead manual control is done. (Personal interview with Engineer Tariq Al-Azzah, 13<sup>th</sup> of June\ 2013).



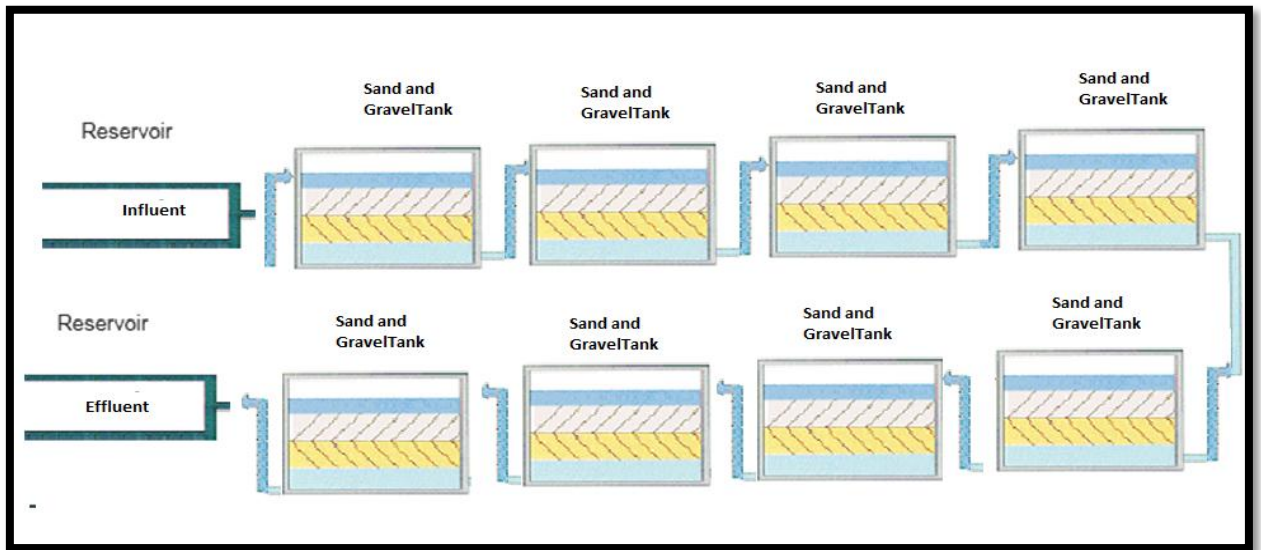
**Figure 2.2.** Schematic diagram of Oasis P

### **2.3 Auja Grey Water Treatment Plant in Jordan Valley Center for Environmental Education and Ecotourism Development (Auja P)**

This treatment plant is located at Al-Auja village, based on collection of grey wastewater result from (showering, bathing, washing machines) in septic tanks followed by gravel filter and sand filter in tanks. The influent is drawn through the gravel as the primary filter media that is portioned into plastic tank. Microorganisms attach themselves to the media in the bed and form a biological film over it, as wastewater trickles through the media; the microorganisms consume and remove contaminants from the influent. Sand filter contains shallow layer of stones, medium gravel, and pea gravel beneath a deep layer of sand. This filter media accomplish treatment through biological processes by consuming organic matter in wastewater, and then constructed wet land that treat grey water in reed bed system and reduces the organic load. Treatment tanks are shown in Figure. 2.3.

Grey water treatment requires simple but specific processes to have safely discharged water. The first step of treatment is the separation of grey water lines from black water that is a heavy source of pollution and kitchen sink which may contain organics, greases and

oils which interfere in the treatment process (Personal interview with Dr. Nader Al-Khateeb, 13<sup>th</sup> of June\ 2013).



**Figure 2.3.** Schematic diagram of AUJA P

## Chapter 3

### Chlorination and Chlorination By-products

#### 3.1 Literature Review

The fetal indices of cholera, typhoid and other water borne diseases were reduced in high rate after the application of water disinfectants. The effectiveness of disinfectants in killing pathogenic microorganisms have given the chance for variety of disinfectants to be applied in water treatment systems as ozone, chlorine dioxide, and chloramines (Anastasi et al., 2013). The disinfection destruct water borne-diseases microorganisms as viruses, bacteria and amoebic cysts. The power of disinfectant is in damaging the cell wall, alteration of cell membranes, protein denaturation of pathogenic microorganisms and the inhibition of the enzyme activity (Buth et al., 2013). The most commonly used disinfectant is chlorine due to its low cost, the ease of application, high germicidal potency and the ability to maintain residuals (Cai et al., 2013). The problem of chlorine disinfectant emerged after the discovery of the carcinogen DBP in the 1970s (Rook, 1974; Bellar et al., 1974). This unwanted side effect of chlorine increased the concern of disinfection process and forced regulations and limitations against the resulted DBPs concentrations. So far there were over 500 DBPs discovered although the United States Environmental Protection Agency (USEPA) has regulated 11 DBPs which are 4 THMs, 5 HAAs, bromate and chlorite (Richardson, 2007).

During chlorination of wastewater, chlorine reacts with dissolved organic matter (DOM) to produce numerous DBPs including THMs as a major by-product (Chang and Her, 2000).

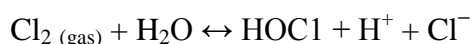
The first time of sewage disinfection was in the year 1892 in Hamburg, Germany (Gascoigne, 1931), and continued since then after noticing the efficiency of chlorine in killing pathogens in wastewater. The application of chlorine to wastewater started with bleaching powder after that liquid chlorine was applied to the effluent of settling tank of



sewage, without any consideration to specific chlorine dose or contact time or quality and quantity of treated water. Later in 1930 the importance of maintaining chlorine residuals in treatment system and variation in chlorine dose started to be appreciated (Gascoigne, 1931).

### 3.2 Chemistry of Chlorine

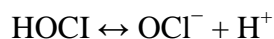
Chlorine is a halogen family member. The halogens are well known for their highly reactive and strongly oxidant ability. Chlorine is always found combined in nature. It exists only as chloride ion  $\text{Cl}^-$ , combined with other elements as a form of soluble chlorides (Geiger and Moloney, 1952). Chlorine properties depend on their physical state. For instance, chlorine gas has a sharp smelling that is irritating to mucous membranes and highly soluble in water (White, 1986). Chlorine owns high electron affinity that contributes to attract electrons towards it, which cause high reactivity with other atoms. Chlorine's oxidizing capacity is based on oxidation-reduction reactivity. Chlorine can be added to water in three common ways: as chlorine gas ( $\text{Cl}_2$ ), sodium hypochlorite ( $\text{NaOCl}$ ), and calcium hypochlorite ( $\text{Ca(OCl)}_2$ ). When added to water as gas, it rapidly hydrolyzes to produce hypochlorous acid ( $\text{HOCl}$ ) according to the following reaction (Inhoffen et al., 1968):



The hydrogen is oxidized and the chlorine gas is reduced (Bedke et al., 2009). At  $18^\circ\text{C}$ , hydrolysis takes a place in a few tenths of a second. Only a few seconds are needed for complete hydrolysis if the temperature decreases to  $0^\circ\text{C}$ . At almost every collision of the chlorine molecule and the hydroxyl ion ( $\text{OH}^-$ ) this reaction occurs (Weiner et al., 2003).

The hypochlorous acid then easily dissociates into hypochlorite ions ( $\text{OCl}^-$ ) and hydrogen ions ( $\text{H}^+$ )

Follows this reaction:



Free available chlorine has powerful germicidal potency as well high combination ability with organic and inorganic compounds in water and wastewater. One of the main competing reactions, when chlorine enters wastewater, is the reaction of free chlorine with ammonia (Leggat, 1949).

### **3.3 Chlorine Forms**

Three forms of chlorine are usually applied to disinfect water systems. The gaseous chlorine, which is a greenish-yellow toxic gas, applied in large treatment facilities in developed countries. Chlorine gas can be lethal at low concentrations (0.1%) by volume and therefore must be handled only by highly trained personnel (Chang and Her, 2000).

Sodium hypochlorite is a water-based solution containing sodium hydroxide and chlorine (CEPIS, 2001). It is favored to be used in small scale water systems and in households. It contains 10-14% available chlorine, sodium hypochlorite is highly toxic and hazardous (Skinner, 2001). It has the potential to be corrosive, gives off gas, and loses 10% of available chlorine in 10 days and it shouldn't be stored for more than 4-6 months (Sedlak, 2011).

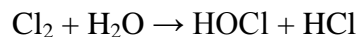
Calcium hypochlorite, or bleaching powder, is not as much dangerous as gaseous chlorine yet it is highly corrosive if directly contacted with skin or inhaled. In solid form, calcium hypochlorite is more stable than sodium hypochlorite, but once dissolved in solution, its half life becomes limited (Hopkins, 1946).

### 3.4 Chemistry of Chlorine in Wastewater Treatment System

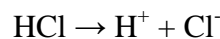
Wastewater chemistry is considered highly complicated; it contains a mixture of chemical and biological matters (Fukushima et al., 2014). In the disinfection process the chemical mixture of wastewater is very critical since their reaction with disinfectants in wastewater will lower the disinfection efficiency (Glaze et al., 1973).

Chlorine is a strongly reactive oxidizing agent that reacts with inorganic and organic compounds in wastewater. Such as; iron, manganese, hydrogen sulfide, organic nitrogen and ammonia (Fukushima et al., 2014). When chlorine reacts with the previous compounds, it exhausts its disinfecting properties to satisfy the demand of chlorine. The effective chlorine dosage is the dose that exceeds the demand of wastewater, which is different in every wastewater treatment system yet it could be different in the same wastewater system from day to day (Fiorentino et al., 2015). In order to assure the disinfection ability of chlorine in treatment water system, the chlorine dose should exceed the demand dose, by subtracting the demand from the dosage, the chlorine concentration will be given.

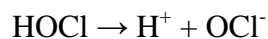
Immediately upon chlorine enters the treatment water system as chlorine gas or hypochlorite salts, reactions with the oxidizing agents initiated. As shown in the following reactions (Griffin and Chamberlin, 1941)



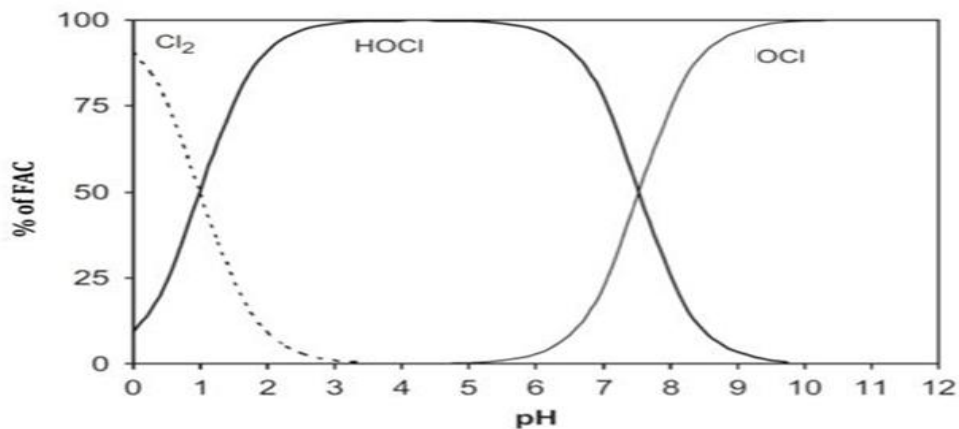
Actually, the HCl completely dissociates into hydrogen and chloride ions:



The hypochlorous acid only partially dissociates (because it is a weak acid) into hydrogen and hypochlorite ions:



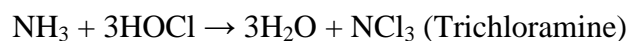
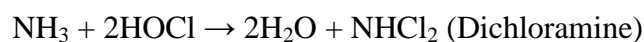
The degree of the previous dissociation and free available chlorine (FAC) is pH dependent, which means in slightly alkaline solution (pH 7.5) the chlorine is equally divided between the two forms (Fig. 3.1). As the water system shifts to be more alkaline, extra hypochlorite is formed. At pH 10 all chlorine exists as hypochlorite ions. In the contrary as solutions become more acidic (pH below 7) there is increasing amounts of hypochlorous acid being formed. At (pH 5) chlorine exists entirely as HOCl.



**Figure 3.1.** Effect of pH on the distribution of hypochlorous acid and hypochlorite ion (Metcalf and Eddy, 1991)

In the case of chlorination of wastewater supplementary compounds are formed called chloramines. These chloramines result as the heavy presence of ammonia in wastewater systems. In aqueous solutions with pH 7.0 to 8.5, HOCl reacts rapidly with ammonia to form inorganic chloramines in a series of competing reactions (Haat et al., 2013)

The desirable reactions between HOCl and ammonia are as follows:



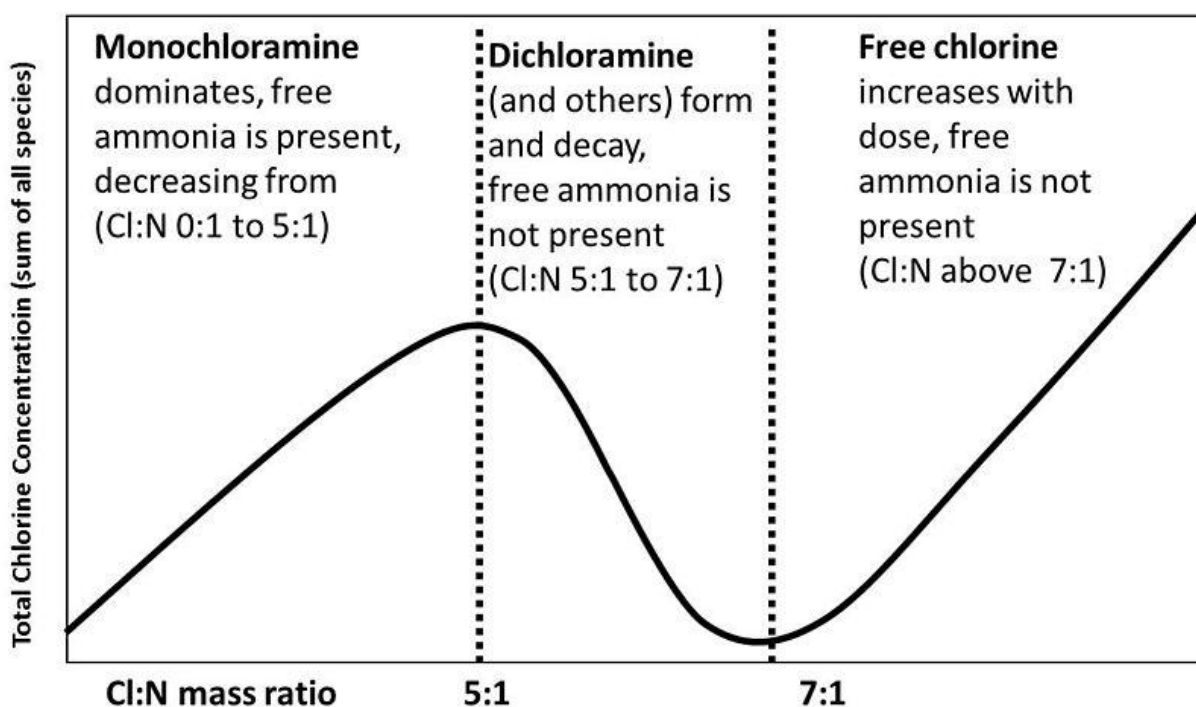
These reactions occur instantly and are pH dependent. At pH levels above 8.5 only monochloramines are formed, below 8.5, mixtures of mono and dichloramine result, and below pH 4.2 only trichloramine exists. Chloramines are known as combined chlorine residual (Haas, 1999). If high chlorine dosage enters water system contains ammonia or ammonia compounds destruction of ammonia and the formation of free chlorine residuals started after reaching the breaking point (Pant and Mittal, 2007). Chlorine is consumed rapidly after added to water containing ammonia, organics and metals, to satisfy water demand. If ammonia is highly present in water, combined chlorine residual will start to form as (chloramines, dichloramine, and trichloramine) (McDonald, 2003). As more chlorine is added to the system chloramines will start to consume until the breaking point occurs and the first free chlorine residual is obtained. All water systems that chlorinate their water will develop breakpoint chlorination (Chamberlin, 1949).

The major factors of disinfecting wastewater system are first, achieving enough chlorine concentrations to maintain free chlorine residuals in the treated system, and then bacteria should be come in contact with the disinfectant solution for a specific contact time (McDonald, 2003). Many factors influence breakpoint chlorination as initial ammonia nitrogen concentration, pH, temperature and demand by some inorganic as Iron, Manganese, H<sub>2</sub>S (Yang et al., 2005).

### **3.5 The Breaking Point Curve**

The germicidal potency of any chlorine dose depend mainly on the chlorine demand of wastewater treatment system, the extent of free chlorine residual and the combined available chlorine (Pignata et al., 2012). The competing reactions of ammonia, metals, and several others, are primarily dependent on pH and controlled to a large extent by the chlorine to ammonia nitrogen ratio (Cl<sub>2</sub>: N). Temperature and contact time have important role (Haas, 1999). Figure 3.2 shows the essential relationships between the chloramines

species at various  $\text{Cl}_2$ : N ratios. Monochloramine is mainly produced when the applied  $\text{Cl}_2$ : N ratio is less than 5:1 by weight. As the applied  $\text{Cl}_2$ : N ratio increases from 5:1 to 7.6:1, breakpoint reaction occurs, reducing the residual chlorine level to a minimum. Breakpoint chlorination results in the formation of nitrogen gas, nitrate, and nitrogen chloride. At  $\text{Cl}_2$ : N ratios above 7.6: 1, free chlorine and nitrogen trichloride are present (March and Gual, 2007).



**Figure 3.2.** Chlorine residual curve for breakpoint chlorination (Metcalf and Eddy, 1991)

The indication of breakpoint experiment to the disinfection of wastewater is that: Firstly, the chlorine disinfection power is dependent on its chemical form; as free chlorine is being more powerful than the combined chlorine. Secondly, if only disinfectant in the wastewater treatment system is chlorination, the dose should be exceeding the breaking point for active disinfection. Thirdly as all chloramines consumed, the free residual chlorine will increase proportionally to increased chlorine dose. Finally the shape of breakpoint curve is different from each wastewater treatment system to another depend on the variation of wastewater

characteristics, pH, ammonia concentration, temperature and treatment technology of removing organics (Arana et al., 1999; Balkrishna et al., 2014; Bayo et al., 2009).

### **3.6 Chlorine Demand**

Domestic wastewater contains heavy organic nitrogen compounds. These compounds come from proteinaceous substances, urine and organic proteins (Chambers, 1971). The chlorine interaction with organic nitrogen is distinct from reaction with ammonia. The production of reaction of chlorine with organic nitrogen is organic chloramines compounds that are more stable than ammonia chloramines and they consume chlorine without interfere with disinfection process but they interfere with the chemical analysis of residual chlorine and appear as dichloramine (Chang et al., 2013).

In wastewater system, the nitrogen species are found as contaminants. All nitrogen present in wastewater present in the form of organic nitrogen (Ivanov, 2010). By time organic nitrogen converts to ammonia nitrogen. As the aerobic conditions continue in wastewater system, oxidation of ammonia into nitrite and nitrate take place (Chen et al., 2010). The sanitary quality uses the previous knowledge as indicator. For instance, Water systems that contains mostly organic and ammonia nitrogen are considered to be recently polluted and contains great potential danger (Bhupinder and Baker, 1983).

In 1940 it was found that drinking waters with high nitrate content often caused Methemoglobinemia infants so regulations by USEPA were determined. Level of the nitrate-nitrogen concentration shouldn't exceed 10 mg/L, while nitrite-nitrogen concentration should not exceed 1 mg/L in public water supplies (WHO, 2005).

Methemoglobinemia results from the interaction of nitrite with hemoglobin, for this reason, a maximum contaminant level for drinking water has been determined for nitrite as well as nitrate. Nitrite can also interact with amines after chlorination to form nitrosamines, which are carcinogen DBPs. The formation of N-nitrosodimethylamine (NDMA) by these

processes has been found to result during wastewater treatment. Ammonia reacts with chlorine to form chloramines, which are slower and less efficient disinfectant than free chlorine (Hatt et al., 2013).

### **3.7 Disinfection By- Products**

The positive side of chlorine introduction in drinking water systems in eliminating pathogenic microorganisms has come with risk of forming carcinogen DBPs. THMs and HAAs are two major groups of DBPs found in drinking water (Liang and Singer, 2003). The concentrations of THMs and other DBPs in drinking water can be reduced at the treatment plant by removing organic matter from water before chlorine is added, by improving the disinfection process or using alternative disinfection methods (Mayer et al., 2015). It is critical that any method used to control THMs levels must protect the effectiveness of water disinfection (Sirivedhin and Gray, 2005).

Trihalomethanes (THMs) are halogen-substituted single-carbon compounds with the general formula  $CHX_3$ , where X represents a halogen which may be chlorine, bromine, fluorine, or iodine or combinations (Nikolaou et al., 2004).

THMs most commonly present in chlorinated water are Chloroform ( $CHCl_3$ ), Bromoform ( $CHBr_3$ ), Bromodichloromethane ( $CHCl_2Br$ ), and Chlorodibromomethane ( $CHClBr_2$ ). THMs are produced when hypochlorous acid reacts with organic matter in source waters (Novikov and Noarov, 1984).

Several organizations balanced the positive effects with the negative sequences of the DBPs by emphasizing any potential health risks from DBPs should be carefully weighed against the known health effects of microbial contaminated drinking water supplies. The US Center for Disease Control and Prevention makes the following statement about trihalomethanes in chlorinated drinking water: “Research suggests that, over a lifetime, the risk of bladder cancer increases with chronic consumption of trihalomethanes. In



populations in developing countries, however, the risk of death or delayed development in early childhood from diarrhea transmitted by contaminated water is far greater than the relatively small risk of bladder cancer in old-age” (CDC, 2001).

WHO supports this view, making the following statement about disinfection by-products in their Guidelines for Drinking Water Quality: “Where local circumstances require a choice be made between meeting microbiological guidelines or guidelines for disinfection byproducts such as chloroform, the microbiological quality must always take precedence. Efficient disinfection must never be compromised” (WHO, 2005).

DBPs appear when a disinfectant, such as chlorine, reacts with natural organic matter (NOM), in water system (Singh et al., 2012). NOM is the major organic precursor with which halogens react to form byproducts (Waller et al., 1998).

After treatment of drinking water with disinfectants a wide range of DBPs of health concern were regulated. New studies on DBPs have shown emerging DBP which could be more harmful than regulated analogues such as iodinated THMs, haloacetonitriles, halonitromethanes (HNMs), haloacetaldehydes, and nitrosamines (Yang et al., 2015). Those emerging DBPs may result as polluted drinking water supplies, polluted by wastewater, algae, or iodide, or due to secondary or alternative disinfectant to chlorine such as chlorine dioxide, ozone, ultraviolet; that basically used to minimize regulated DBPs instead they give rise to new species of DBPs (Mitch et al., 2003).

Since the discovery of DBPs in mid-1970s the awareness of their side effects weren't ignored. Toxicological studies presented their danger in causing liver, kidney, large intestine, cancer or other adverse reproductive imparities in laboratory animals, or abortion (Grazuleviciene et al., 2011).

Epidemiological studies shown an increasing risk for bladder or colon cancer after exposure of many years (Kuo et al., 2009), other studies combined between the

consumption of chlorinated water and birth defects or spontaneous abortion (Kronberg and Christman, 1989; Chowdhury and Champagne, 2009).

As a result many countries give guidance for DBPs as THMs and HAAs in drinking water (Ling et al., 2008). The basis for regulating THMs and HAAs are using them as surrogates for the toxicity of other species of DBPs and minimizing their concentrations to have less concentration of other DBPs (Reckhow et al., 1990). The studies of finding alternative disinfectants for chlorine have discovered new DBPs. This increased the challenge of achieving highly disinfectant level along with minimum concentration of DBPs.

Most of THMs formation potential studies were focused on drinking water facilities (DWF) but recent works start using wastewater treatment facilities (WWF) to study their DBPs formations and reactions. The same major types of DBPs (THMs and HNMs) are found at drinking water supplies as well as wastewater treatment supplies since most influent of WW originates from treated DW (Liu et al., 2013). The difference between formations of DBPs of both DWF and WWF is the different characteristics of precursors found in them. NOM is the primary precursor for DWF but not the dominant for WWF (Sun et al., 2009). Nitrification condition is another factor in DBP formation. If the plant is well nitrified, the ammonia nitrogen values will be low, thus more free available chlorine (FAC) to react with precursors thus more DBPs will be formed (Bond et al., 2014). In low nitrified facilities higher concentration of ammonia will be formed thus high chlorine demand and lower FAC left to form DBPs (Sun et al., 2009).

### **3.8 Factors Influence Trihalomethanes Formation**

The general reaction lead to the formation of THMs during chlorination can be expressed as follows:



The presence of each species of THMs will be different depending on water source, the treatment processes and conditions operated at water treatment works (Hong et al., 2007).

The key factors that can influence THMs formation are pH, organic concentration, bromide concentration, free chlorine concentration and contact time (Sun et al., 2009).

The four THMs compounds are liquid at room temperature, classified as relatively to extremely volatile. The vapor pressure at 25°C ranges from 80 kilo Pascal (K Pa) for bromoform to 23.33 k Pa for chloroform. The THMs are slightly soluble in water with solubility less than 1mg/mL at 25°C (Sun et al., 2009).

### **3.8.1 pH Influence**

High pH increases the rate of formation and concentration of THMs (Rook, 1974). At higher pH the hydrolysis step that leads to THMs formation is facilitated (Liang and Singer, 2003). Usually, the increase in THMs related to high pH is associated with decrease in other DBPs as HAAs (Carlson and Hardy, 1998).

### **3.8.2 Organic Carbon Influence**

DBPs appear when a disinfectant, such as chlorine, reacts with dissolved organic matter (DOM), in water system (Cantor, 1994). DBPs formation is strongly dependant on DOM concentration (Yang et al., 2014). Studies have shown that the physical and chemical properties of organics effect DBP formation (Reckhow et al., 1990). In the presence of bromide ion ( $\text{Br}^-$ ), the free chlorine ( $\text{HOCl}$ ) reacts with the DOM to form mixed chloro-bromo byproducts while in the absence of  $\text{Br}^-$  only chlorinated by-products emerge (Sun et al., 2009).

The DOM is measured as dissolved organic carbon (DOC) or total organic carbon (TOC). Another measure commonly applied is the specific ultraviolet absorbance (SUVA), which

is equal to the UV absorbance divided by the dissolved organic carbon concentration (Hua et al., 2015).

The relative quantities of chlorinated and brominated THM species formed are dependent on the ratios of chlorine to bromide, chlorine to TOC and TOC to bromide (Chowdhury et al., 2010). THMs species depend on the precursor material and the treatment to which wastewater is subjected to. The decline in chlorine concentrations at the contact tank over the time, or an increase in the amount of bromide in water system, will also result in a shift in the chlorine to bromide ratio, leading to a subsequent shift in the ratio of chlorinated to brominated THM species (Amy et al., 1987; Clark et al., 1997), since bromide uses chlorine substitution sites, the formation of chlorinated species is reduced. However, if chlorine is in excess, or the amount of bromide is low, chlorinated species will be dominant.

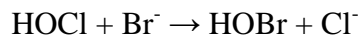
### **3.8.3 Temperature**

In general at higher temperatures the rate of reaction increases. Higher temperatures also mean a higher rate of hydrolysis which leads to faster break up of aromatic bonds, resulting for further halogenations and a higher formation of DBPs (Singh et al., 2013; Zhang et al., 2015).

Also, the effect of temperature on THM formation has investigated not only for the treatment systems, but also in customers' houses. The formation of THMs studied after water was heated for a 35 minute. The samples revealed a significant increase in THM concentrations from 104 to 211 $\mu\text{g}/\text{L}$  and 115 to 386  $\mu\text{g}/\text{L}$  in water samples with an initial free chlorine residual concentration of 0.1 mg/L and 1.2 mg/L respectively (Zhang et al., 2015).

### 3.8.4 Bromide Concentration

Hypochlorous acid or hypochlorite ion oxidizes the available bromide in the water to form hypobromous acid (HOBr) or hypobromite ion ( $\text{OBr}^-$ ) (Watanabe et al., 1984) as follows:



HOBr and  $\text{OBr}^-$  react with NOM to form a mixture of brominated and mixed chloro-bromo by-products. Chlorine is more electronegative thus more reactive than bromide, but HOBr is 25 times more reactive than HOCl (Chowdhury et al., 2010). The formation of brominated THMs is a function of the  $\text{Br}_2$ : NOM ratio and  $\text{Br}_2$ :  $\text{Cl}_2$  ratio (Cowman and Singer, 1996; Singer, 1999).

Recently the researchers are more interested in the reactions of bromide with chlorine because the brominated organic by-products are expected to be more harmful to health than chlorinated analogues (Sun et al., 2009). Moreover, bromodichloromethane has been reported to cause a higher cancer risk than chloroform (Rodrigues et al., 2007). The risk of rectal cancer has been shown recently to be associated with levels of bromoform (Sun et al., 2009).

### 3.9 Controlling Trihalomethanes in Wastewater

The precursors in drinking water systems are the natural organic matter (NOM) while in wastewater treatment systems the dissolved organic matters are much complicated (DOM) and consist of proteins, carbohydrates and oils (Wang et al., 2013).

Many empirical models have been found to estimate the formation of THMs. One of these models is done by (Westerhoff, 2006):

$$\text{THMs} = 0.0412[\text{TOC}]^{1.098}[\text{Cl}_2]^{0.152}[\text{Br}^-]^{0.068}[\text{Temp}]^{1.069}[\text{pH}]^{0.263}$$

This model suggests that THMs concentration increases with increasing total organic carbon (TOC), chlorine dose, bromide ion concentration, temperature, pH and reaction time.

THMs precursor removal was determined in drinking water treatment facilities. Several methods have been used to control DBP precursors as enhanced coagulation, granular activated carbon (GAC), ion exchange, membrane filtration (Westerhoff et al., 2004). However these precursor control technologies may not be effective for wastewater as much as it is for drinking water since the application of these technologies for THM precursor removal in wastewater will cause a significant financial burden for many wastewater utilities and require high operation and maintenance costs (Hsu et al., 2012).

Optimize chlorine dose and contact time is another control to reduce THM formation in wastewater treatment plants. Another suggested method that can be done in wastewater treatment plant is using multiple chlorine injection points based on plant flow to reduce the contact time and chlorine consumption (Janzen and Beier, 2006).

Most wastewater treatment plant use uncovered chlorine contact basin for disinfection to enable wastewater to be exposed to ultraviolet irradiation from sunlight but this process can cause loss of chlorine in contact basin thus the chlorine dose will be increased to maintain residuals. Moreover, UV irradiation may act as a catalyst and increase THM formation. Fitzpatrick (2005) studied the effect of sunlight irradiation during wastewater disinfection on THM formation. His study showed that in closed basin the free residual concentration is higher and THM formation is lower when compared to open chlorination basins. Many wastewater treatment plants that using sodium hypochlorite solution for chlorination experience increase in pH level because of hydrolysis of hypochlorite solution. In order to lower THM level during chlorination, controlling pH is very important since THM formation is favored at high pH levels. The chlorine dose and temperature of reaction have significant impact. When chlorine dose increase the increase in THM concentration is nearly linearly (Wu et al., 2013).

In some wastewater treatment plants re-aeration tank is used to increase dissolved oxygen before discharge to wastewater. The re-aeration tank is also beneficial in reducing THM since THMs are volatile. THMs removal by aeration is a function of initial THM concentration water flow rate and air flow rate (Tarquin, 2005). The removal depends on the chemical properties of the THM. For example, Henry's law constant (KH) is an indicator of the solubility of a gas at a certain pressure; the higher the KH the lower the solubility of a gas. The order of the solubility of the four THMs is  $\text{CHBr}_3 > \text{CHBr}_2\text{Cl} > \text{CHBrCl}_2 > \text{CHCl}_3$ . The reverse order is true for the volatility of the THMs therefore, the removal efficiency of THMs by aeration is expected to be in the order of  $\text{CHCl}_3 > \text{CHBrCl}_2 > \text{CHBr}_2\text{Cl} > \text{CHBr}_3$ . THM removal by aeration is a function of the initial THM concentration (Tarquin, 2005).

### **3.10 Disinfection By- Products Regulations**

The concern of DBPs started in 1970 immediately after their discovery. After wards, in 1979 the regulation starts to be considered. The first was the United States Environmental Protection Agency (USEPA) assigned the maximum level of THMs 100  $\mu\text{g/L}$  (USEPA, 2007). After that the EPA regulations continued to set more DBPs maximum contaminant levels (MCLs) as THMs, HAAs, Bromate and Chlorite (AWWA, 2008). However, since the discovery of THMs, about 500 DBPs were determined. The priority of DBPs for regulation depends on their available toxicity data (Abbas et al., 2015; Abda et al., 2015).

Ways of exposure by people include inhalation since THMs are highly volatile at room temperature or after evaporation by boiling water, the absorption of skin to water during showering or bathing and the ingestion of water or food (Pignata et al., 2012).

THMs were classified as possible human carcinogens (Zhao et al., 2004). The use of chlorinated treated water for agricultural application and human consumption to crop foods irrigated by chlorinated reclaimed water, is a potential route of exposure to DBPs (WHO,

2006). The toxicity of THMs led to maintain regulations to control total THMs (TTHMs) in drinking water. WHO regulated 200 µg/L for chloroform. USEPA assigned 80µg/L for TTHMs. The European Union (EU) determined 100 µg/L for TTHMs (WHO, 2005). Unfortunately, specific standards are not available for treated wastewater used for agriculture irrigation, except for the maximum permissible chloroform concentration in soils receiving untreated municipal wastewater which approximately 0.47 mg/kg (WHO, 2006). In Australia a study to investigate wastewater disinfection by product was conducted, TTHMs formation occurred between 46 to 279 µg/L for the final post chlorination effluent which exceeds Australian drinking water guideline (Watson et al., 2012). Some municipal wastewater treatment plants in New Jersey established limits for trihalomethanes after wastewater chlorination; for chloroform 221, BDCM 3.3, DBCMB 2.4 and bromoform 26 µg/L (Patoczka et al., 2011).

In a study for trihalomethanes formation potential in denitrification wastewater treatment plant done by Pregeant (1992), the highest THM concentration formed was 200 µg/L.



## Chapter 4

### Materials and Methods

#### 4.1 Glassware, Chemical Reagents, and Stock Solutions

Glassware was scrupulously cleaned by tap water and a detergent, then rinsed with distilled water for five times and finally with hydrochloric acid solution three times before rinsing again with deionized distilled water (DDW). The glassware was dried at 80 °C inside an oven to avoid any contamination and dust.

One liter brown glass reagent bottles with fit cap were used for chlorine demand test. 40 mL glass vials with Teflon lined caps were used for collection of water samples for total organic carbon (TOC), inorganic carbon (IC), total nitrogen (TN). 130 mL brown glass reagent bottles with screw caps were used for THMFP experiments. 10 mL glass vials with Teflon lined septa caps for THMs analysis.

Reagent water used in the experiments was distilled deionized water (DDW) produced by a Millipore water purification system. Reagents of ammonia test: Phenol reagent for 250 mL: 7.5 g Sodium phosphate ( $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ) (Sigma, catalog No. 5778), 7.5 g Sodium citrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) (sigma, catalog No. 54641), 0.75 g EDTA, (Sigma catalog No. E9884), 15.75 g phenol crystals. (Sigma, catalog no. p 5566), 0.05 g Sodium nitroprusside ( $\text{Na}_2\text{FeCN}_5\text{NO} \cdot 2\text{H}_2\text{O}$ ) (Sigma, catalog no.0501) were dissolved in 250 mL DW, and were mixed very well. Finally the reagent was stored in dark bottles for only two weeks.

Sodium hydroxide (NaOH) 1N: 4 g of NaOH (Sigma, catalog No. 30620) was dissolved in 100 mL of DW.

Hypochlorite reagent: 100 mL of NaOH 1N was added to 100 mL of D.W, then 6 mL of 11% sodium hypochlorite was added, (catalog No. 48481) and mixed very well, the total volume should be 206 mL. Finally the reagent was stored in dark bottles for only two weeks.

Standards prepared from ammonia stock solution of 1000 mg/L. DPD Free Chlorine Powder Pillows, for 10 ml catalog number 21055-69. Sodium hydroxide and Phosphate buffer were used to maintain pH during THMFP test. Ascorbic acid (10 mg for 10 mL sample) was used as a quenching reagent to stop chlorine reaction before THM analysis.

#### **4.2 Wastewater Samples**

Wastewater samples were taken from three wastewater treatment plants, Al-Quds University Wastewater Treatment Plant (AQU P), located in Abu-Dees village, Oasis Hotel Wastewater Treatment Plant (Oasis P), located in Jericho, Al- Auja Grey Water Treatment Plant in Jordan Valley Center for Environmental Education and Ecotourism Development (Auja P). Samples were collected from the influents of the reclamation plants (raw wastewater samples) and after conventional treatment processes (activated sludge, sedimentation and filtration). The plants were selected because they use different treatment technologies in wastewater treatment with different influent sources and characteristics. Ammonium occurs extensively in wastewater thus conducting ammonia analysis is important before chlorinating the sample (Espigares et al., 2013). In this study wastewater breakpoint were generated from unchlorinated effluents from AQU P, Oasis P and Auja P. AQU P sample was taken from secondary effluent from a conventional activated-sludge process, and other samples from two types of Ultra-filtration membrane and reverse osmosis (RO).

The samples were taken at 2/11/2013, 1/12/2013, 11/10/2014, 8/11/2014, 13/12/2014, 18/1/2015, 28/2/2015, 11/3/2015 and 4/4/2015.

The effluents were characterized by measuring the following parameters: pH, electrical conductivity (EC), turbidity and total suspended solids, Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), nitrate, nitrite, the second stage is chlorine demand experiments and THMs analysis as the final stage.

### 4.3 Wastewater Characterization

Summary of the parameters, analytical methods and instruments used in the study are presented in Table 4.2. The detailed information about these methods is provided in this section. The majority of these methods were developed following Standard Methods for the examination of water and wastewater (Eaton et al., 1995).

**Table 4.2.** Summary of characterization parameters

| parameter | Unit  | Instrument    |
|-----------|-------|---------------|
| pH        |       | pH meter      |
| EC        | μS/Cm | EC meter      |
| TDS       | mg/L  | TDS meter     |
| TSS       | mg/L  | HACH          |
| TURBIDITY | NTU   | HACH          |
| BOD       | mg/L  | Oxi- meter    |
| COD       | mg/L  | UV Absorbance |
| AMMONIUM  | mg/L  | UV Absorbance |
| NITRATE   | mg/L  | UV Absorbance |
| NITRITE   | mg/L  | HACH          |

**4.3.1 pH measurement:** In this study the pH meter used was Thermo Scientific Orion Star plus meter. Calibration was done daily by purchased certified buffers.

**4.3.2 Temperature:** Test was done in the wastewater characterization field by thermometer probe.

**4.3.3 Electrical Conductivity (EC) and Total Dissolved Solids (TDS):** These two parameters were measured by the same device. EC- TDS meter M 201 portable HANNA instrument.

**4.3.4 Turbidity and Total Suspended Solids (TSS):** These measurements took place by HACH portable data logging spectrophotometer DR/2010. The instrument was set by dialing specific wavelength nanometer to each test. Results were shown as mg/L for TSS 810 nm and NTU for turbidity 860 nm.

**4.3.5 Biochemical Oxygen Demand (BOD):** Samples for BOD analysis were tested immediately after collection to minimize the reduction of BOD. Preparation of dilution water: 5mL of sample was placed in BOD bottle and 1 mL each of phosphate buffer, MgSO<sub>4</sub>, CaCl<sub>2</sub>, and FeCl<sub>3</sub> solutions/L of D.W were added. The initial dissolved oxygen (DO) was determined immediately after filling BOD bottle with diluted sample. Water blank was prepared as a check on quality of dilution water. After 5 days of incubation DO was determined in sample and blanks.

**4.3.6 Chemical Oxygen Demand (COD):** Is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. 2.5 mL of sample were added to 3.5 mL sulfuric acid and 1.5 mL digestion solution then test tubes were covered by aluminum foil for 2 hours in oven then were measured by UV absorbance at 600 nm.

**4.3.7 Nitrate:** Spectrophotometer measurement read absorbance against samples by using a wavelength of 220 nm to obtain NO<sub>3</sub> reading and a wavelength of 275 nm to determine interference due to dissolved organic matter.

**4.3.8 Nitrite:** The contents of one (NitriVer 2) Nitrite Reagent powder pillow were filled to sample and measured by HACH portable data logging spectrophotometer DR/2010.

#### **4.4 Chlorine Demand Experiments**

First the ammonia level in non-chlorinated water was evaluated before starting the test, and then the chlorine stock of 5% available chlorine was purchased. After that the strength of the chlorine stock was checked. In ten brown one-liter bottles, 500 mL of wastewater to be tested were placed, without filtration of the samples. Then chlorine solution was added to each bottle according to the dose calculated and assigned before to achieve breakpoint. After chlorination, 30 minutes of incubation in dark was done. The results of free chlorine and ammonia were obtained and graphed.

**4.4.1 Ammonium:** 25  $\mu$ L of sample were taken then 0.5 mL of phenol reagent, 0.75 mL hypochlorite reagent and 1.25 mL D.W were added to the sample and mixed very well, the sample were read on spectrophotometer after 1 hour and a calibration curve was prepared, the best fit was used by finding linear least square algorithm. From the graph and fitted algorithm the concentration of the samples were calculated.

#### **4.4.2 Free Chlorine Residual Experiment**

Chlorine stock solutions were prepared by dilution of a sodium hypochlorite solution (5% available chlorine). Free available Chlorine was determined using the N, N-diethyl-p-phenylenediamine (DPD) free chlorine test method. The samples were used to establish chlorine demand curves for each reclamation plant by setting up jar tests and plotting the chlorine residuals resulted by HACH DR1890 Colorimeter, after the reaction with DPD powder kit with 10 mL sample after one minute of reaction. Curves of each wastewater

treatment plant samples formed different shapes because of different organics, metals and ammonia present in each wastewater as shown in the characteristics

On Hach instrument the stored program number was entered, the cell was pre- cleaned and dried and wiped, the 10 mL sample was filled in the sample cell, then it was hold in the cell holder and covered tightly by the instrument cap, the zero button was pressed after that the powder pillow kit content was added to the cell, the sample was capped and swirled to dissolve the powder for about 20 seconds. Immediately the cell placed in the instrument to read after 1 minute of reaction with the DPD (Hach, 2013). Chlorine demand curves were plotted versus ammonia concentration after disinfection and incubation of 30 minutes.

#### **4.5 Total Organic Carbon (TOC), Inorganic Carbon (IC), and Total Nitrogen (TN)**

##### **Analysis**

Simultaneous analysis of the total organic carbon (TOC), total nitrogen (TN) and inorganic carbon (IC) in wastewater samples was performed on Shimadzu TOC-VCPN coupled with TNM-1 module.

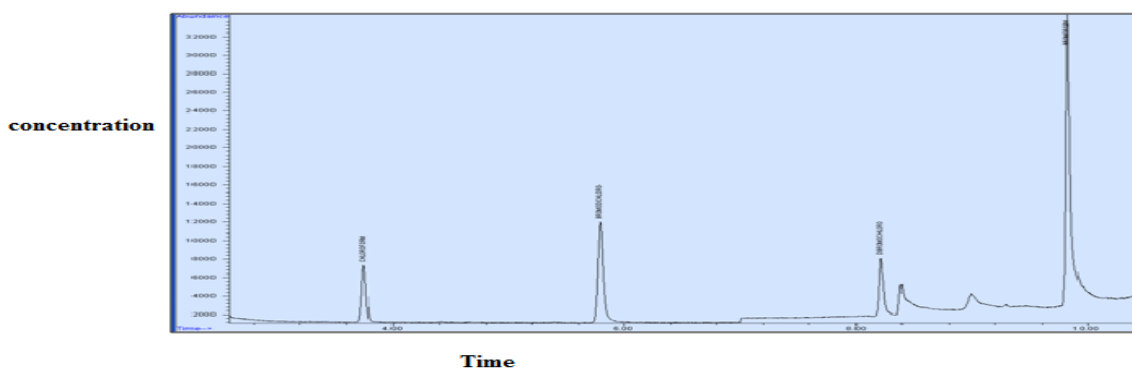
#### **4.6 Trihalomethanes Formation Potential (THMFP)**

Wastewater samples were obtained from three different wastewater treatment plants from each effluent source samples were transferred to 130 mL brown glass bottles chlorinated to maintain chlorine residuals and incubated for 1, 2, 4, 8, 24, 48, 72, 96, 120 hours at the end of each specific incubation period samples were quenched by ascorbic acid to prevent further THMs formation. pH was adjusted to  $7 \pm 0.3$  using NaOH and HCl. Samples were kept under 25°C in incubator under dark. Samples were preserved in the refrigerator at 4°C until analysis took place.

#### 4.7 Trihalomethanes GCMS Analysis

Five milliliter of wastewater samples was transferred into a 10 mL headspace vial which was immediately sealed with a stainless steel screw cap with PTFE-lined septum. Vials were statically incubated at 95 °C for 10 minutes in a COMPIPAL auto sampler (CTC Analytics AG, Switzerland). An aliquot 1 mL of the headspace gas was subsequently withdrawn and injected into a 6890N Agilent GC combined with 5973 Agilent MS. Separation was performed on a Varian Factor Four™ capillary column (VF-5ms, 30 m, 0.25 mm, 0.25 µm). The column oven temperature was held at 35 °C for 5 min then ramped to 60 °C at 10 °C/min and finally ramped to 200 °C at 25 °C/min. Injections were done in a pulsed split mode (split ratio 10 after 0.05 min of injection) with injector temperature at 220 °C. The transfer line and the ion source temperatures were maintained at 280 °C and 230 °C respectively.

Selected ion mode (SIM) method was developed for four compounds (chloroform, bromodichloromethane, dibromochloromethane, bromoform) following USEPA 501 trihalomethane method. Quantification ions and method validation were performed with external standard calibration. Calibration curves in the concentration range from 2 to 100 µg/L were prepared from standard solution (Restek, Catalog # 30211). Wastewater samples were diluted according to THM calibration curve.



**Figure 4.1.** GCMS-chromatogram of trihalomethanes mix (chloroform, bromodichloromethane, chlorodibromomethane and bromoform).

## **Chapter 5**

### **Results and Discussion**

#### **5.1 Wastewater Characterization**

Three wastewater treatment plants were chosen for this study based on their different technology of treatment and different characteristics. For Each wastewater sample biological, chemical and physical parameters are presented in the tables 5.1 AQU P, which includes activated sludge (AS), Ultra filtration-Hollow Fiber (UF-HF), Ultra filtration-Spiral Wound (UF-SW) and Reverse Osmosis (RO). Oasis P and Auja P.



**Table 5.1.** Biological, chemical and physical characteristics of treated wastewater from AQU P Oasis P and Auja P

| Sample               | AQU Raw   | AQU AS    | AQU UF HF | AQU UF SW | AQU RO    | Oasis Raw | Oasis Final | Auja Raw  | Auja Final | US EPA | Weak | Medium | Strong | PS   |
|----------------------|-----------|-----------|-----------|-----------|-----------|-----------|-------------|-----------|------------|--------|------|--------|--------|------|
| TEMP °C              | 28.5 ±1   | 28.3 ±1   | 26.2 ±1   | 25.1 ±1   | 24 ±1     | 27.9 ±0.4 | 28.8 ±0.5   | 28.6 ±0.3 | 28.4 ±0.3  | 6-9    | -    | -      | -      | -    |
| pH                   | 8.15 ±0.2 | 7.5 ±0.3  | 7.65 ±0.3 | 7.4 ±0.4  | 7.14 ±0.1 | 8.2 ±0.3  | 8.01 ±0.2   | 8.64 ±0.2 | 8.13 ±0.1  | -      | -    | -      | -      | -    |
| EC uS/Cm             | 1.98 ±0.5 | 1.72 ±0.3 | 0.84 ±0.3 | 0.61 ±0.4 | .04 ±0.2  | 1.47 ±0.6 | 1.07 ±0.4   | 1.23 ±0.5 | 0.70 ±0.5  | -      | -    | -      | -      | -    |
| TDS mg/L             | 970 ±100  | 880 ±150  | 43 ±250   | 340 ±200  | 22 ±10    | 730 ±50   | 500 ±50     | 640 ±40   | 330 ±40    | 1000   | 250  | 500    | 850    | 1500 |
| TSS mg/L             | 492 ±20   | 145 ±20   | 76 ±20    | 55 ±20    | 5 ±10     | 187 ±50   | 37 ±43      | 295 ±45   | 59 ±40     | 45     | 100  | 220    | 350    | 50   |
| TS mg/L              | 1462 ±50  | 1025 ±50  | 506 ±30   | 395 ±20   | 27 ±10    | 917 ±50   | 537 ±40     | 935 ±45   | 389 ±50    | -      | -    | -      | -      | -    |
| TUR NTU              | 698 ±15   | 187 ±15   | 55 ±10    | 33 ±10    | 0 ±3      | 287 ±30   | 128 ±40     | 361 ±50   | 103 ±50    | -      | -    | -      | -      | -    |
| NH <sub>3</sub> mg/L | 900 ±20   | 750 ±20   | 475 ±15   | 11 ±15    | 8 ±3      | 127 ±20   | 10 ±20      | 89 ±15    | 50 ±15     | -      | 12   | 25     | 50     | 15   |
| NO <sub>2</sub> mg/L | 125 ±16   | 52 ±16    | 33 ±15    | 14 ±10    | 3 ±0.5    | 18 ±15    | 13 ±15      | 63 ±10    | 15 ±10     | 10     | 0    | 0      | 0      | 0    |
| NO <sub>3</sub> mg/L | 12.7 ±5   | 8.4 ±6    | 4.7 ±4    | 5 ±0.3    | 2.3 ±0.2  | 70 ±20    | 40 ±15      | 50 ±15    | 20 ±10     | 10     | 0    | 0      | 0      | 0    |
| BOD mg/L             | 850 ±50   | 600 ±50   | 154 ±50   | 75 ±25    | 15 ±5     | 74 ±20    | 68 ±20      | 178 ±15   | 120 ±15    | 45     | 110  | 220    | 400    | 40   |
| COD mg/L             | 1853 ±100 | 1000 ±30  | 300 ±25   | 210 ±25   | 20 ±5     | 250 ±20   | 50 ±10      | 453 ±10   | 287 ±10    | 200    | 250  | 500    | 1000   | 150  |

AQU= Al-Quds University, AS= activated sludge, UF.HF= ultrafiltration hollow fiber, UF.SW=ultrafiltration spiral wound, RO= reverse osmosis, PS= Palestinian standards.

Raw wastewater characteristics of AQU P are classified as strong wastewater with BOD<sub>5</sub> 850 mg/L concentration, COD 1853 mg/L, TS 1492 mg/L, TDS 970 mg/L, TSS 492 mg/L

and free ammonium 900 mg/L this classification according to USEPA (2003) standards as shown in table 5.1. Palestinian wastewater classified as strong wastewater (PWA, 2012) and AQU P wastewater included in this category. The secondary effluent for AQU P has BOD<sub>5</sub> 600 mg/L, TSS 145 mg/L, pH 7.5.

The quantity and quality of wastewater is determined by many factors; the amount of contaminants and constituents which are different in each WWTP due to differences in the characteristics of each influent that depends on source of wastewater, amounts of wastewater, technical design and treatment process used.

Raw wastewater characteristics of Oasis P are classified as weak wastewater with BOD<sub>5</sub> 74 mg/L concentration, COD 250 mg/L, TS 917 mg/L, TDS 730 mg/L, TSS 187 mg/L and free ammonium 127 mg/L according to USEPA (2003) standards.

Raw wastewater characteristics of Auja P are classified as weak wastewater with BOD<sub>5</sub> 178 mg/L concentration, COD 453 mg/L, TS 935 mg/L, TDS 640 mg/L, TSS 295 mg/L and free ammonia 89 mg/L according to USEPA (2003) standards.

According to Memorandum of understanding (MOU) on guidelines and technical criteria for sewerage projects signed between Israel and PWA for treated effluents, has determined 20 mg/L of BOD and 30 mg/L TSS for secondary treatment but for tertiary treatment TSS 10 mg/L and BOD 10 mg/L (World Bank, 2004) in this study only RO effluents of AQU P achieved the guideline.

Measurement of these wastewater quality parameters are important to determine the magnitude of the difference between each treatment processes before allowing the chlorine disinfection stage.

The secondary treatment stage of AQU P is AS with extended aeration ranges between 16-20 hours hydraulic retention time. After AS stage effluent parameters reduced such as BOD 600 mg/L, COD 1000 mg/L, NH<sub>3</sub> 750 mg/L. The difference between UF and RO

membranes in designation resulted in differences in removal efficiency. The first UF unit is supplied with 2 pressure vessels that contain the hollow fiber membranes. The second UF unit supplied with 2x4 inch pressure vessels with pressure resistance up to 150 psi. RO membranes are manufactured from polyamide thin film. It consists of 1x4 inch pressure vessel made from composite material with pressure resistance up to 400 psi. The vessel holds two 4 inches separation membranes. Thus RO effluent with less pore size and more pressure than UF produces the least contaminant parameters among all effluents as shown in table 5.1.

Oasis P main operational process is the biological treatment that is applied by using two bioreactors and sand filters while Auja P based on collection of grey water result from (showering, bathing, washing machines) in septic tanks followed by gravel filter and sand filter tanks. Auja P has the simplest treatment process lead to the least removal efficiency. According to different treatment schemes wastewater samples from the AQU P, Auja P, Oasis P show a large fluctuation in wastewater quality as displayed in table 5.1

## **5.2 Chlorine Demand**

Chlorine dosage applied to three WWTPs samples ranges from 10 to 2000 mg/L, while measured free available chlorine (FAC) residuals ranges from 0 to 5mg/L.

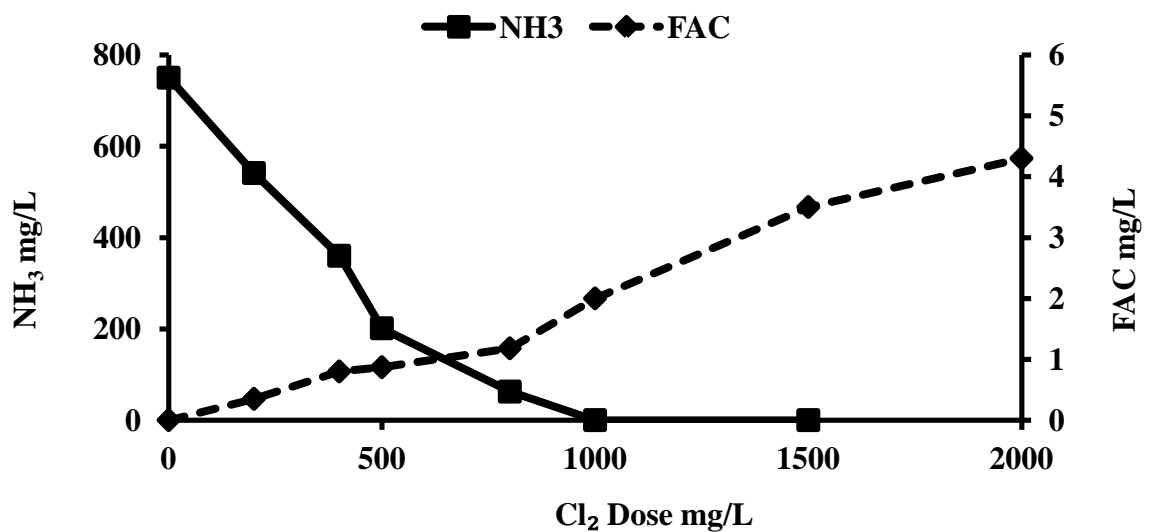
Ammonium concentrations of the samples are plotted in figures 5.1 to 5.10. The decline in Ammonium concentration after each treatment stage is noted. Ammonium concentration declined proportionally after satisfying chlorine demand (Leggat, 1949). Chlorine demand is calculated by subtracting the residual measured on site from the daily chlorine dose (White, 2010).

This study focuses mostly on ammonium's interaction with chlorine; however other compounds contribute to chlorine demand such as (TOC, Nitrite, Iron, Manganese, and Organic N). The varying concentrations of other parameters increase chlorine demand

(Taras, 1950). The reactions between chlorine and ammonium are easy to understand when chlorine dosage and residuals are plotted (Spon, 2008).

### 5.2.1 AQU P Cl<sub>2</sub> Demand

In figure 5.1 chlorine demand in AS requires around 1000 mg/L of chlorine which is an elevated dose related to concentrated organics and ammonia-N present in wastewater samples from treatment system.

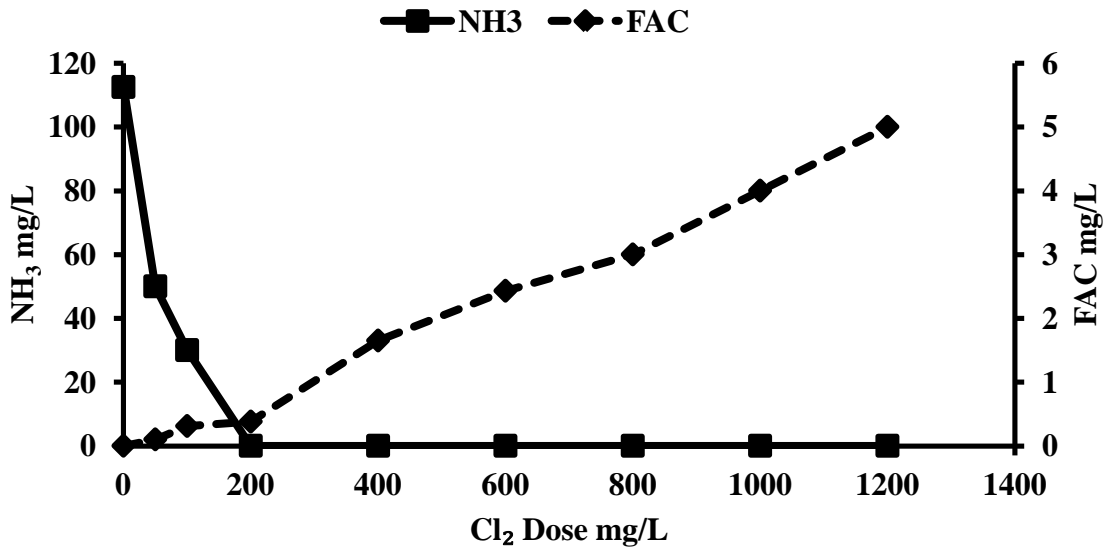


**Figure 5.1.** Chlorine demand and ammonium concentration for Activated Sludge samples

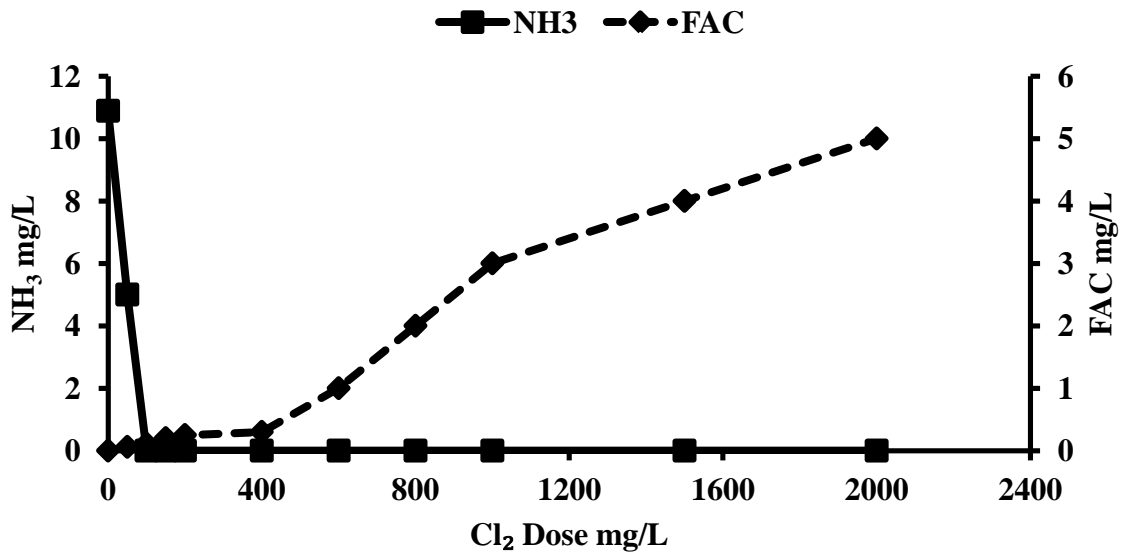
The raw samples of AQU P have ammonium concentration approximately 900 mg/L which reduces after AS treatment to reach approximately 750 mg/L.

The chlorine demand in AS is considered a very high comparing to WHO standards (2006) which required 20 mg/L of chlorine for activated sludge effluent. However, the presence of large concentration of ammonium in wastewater has resulted in the need to super-chlorinate in order to eliminate and satisfy the demand. Thus AS unit needs more improvement in treatment to eliminate more ammonia concentration and organics.

Figures 5.2, 5.3, represent the first stage of advanced treatment membranes which are ultra filtration hollow fiber and ultra filtration spiral wound respectively.



**Figure 5.2.** Chlorine demand and ammonium concentration for Ultrafiltration Hollow Fiber samples

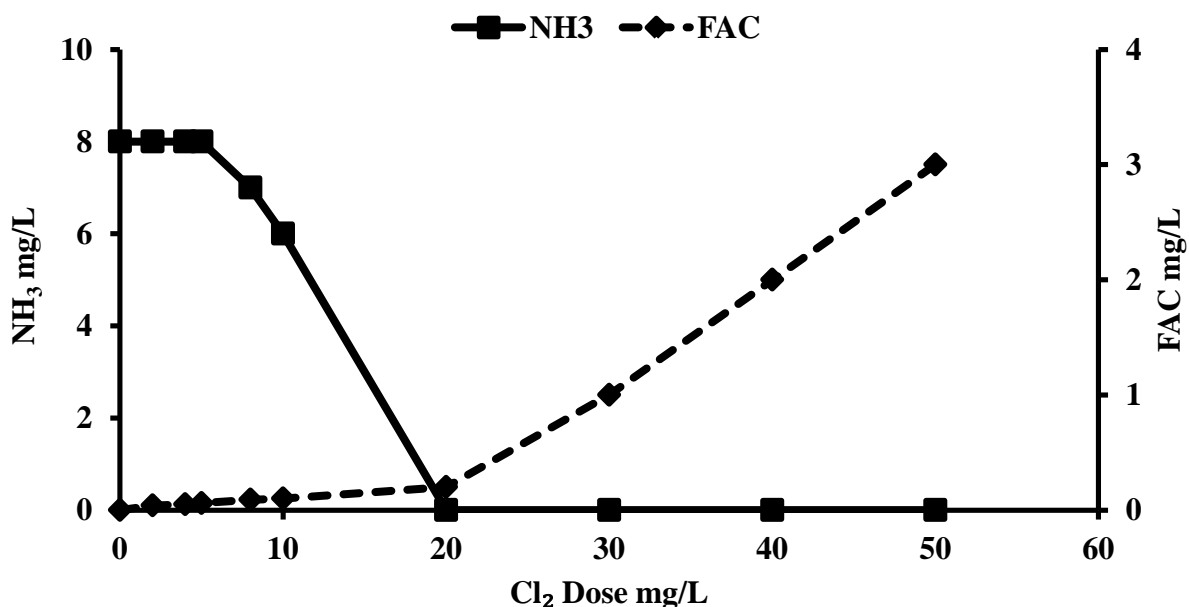


**Figure 5.3.** Chlorine demand and ammonium concentration for Ultrafiltration Spiral Wound samples

The results show reduction of ammonium concentration from 750 mg/L to around 113 mg/L in the effluent of UF-HF after passes through UF membranes which reduced

chlorination demand as well. After the completion of the UF treatment stage the  $\text{Cl}_2$  demand is reached to 150 mg/L and ammonium concentration of 11 mg/L related to more efficient treatment than AS stage.

Figure 5.4 presents the final stage of advanced membrane technology RO in AQU P with the minimal concentration of  $\text{Cl}_2$  demand reached to 20 mg/L.

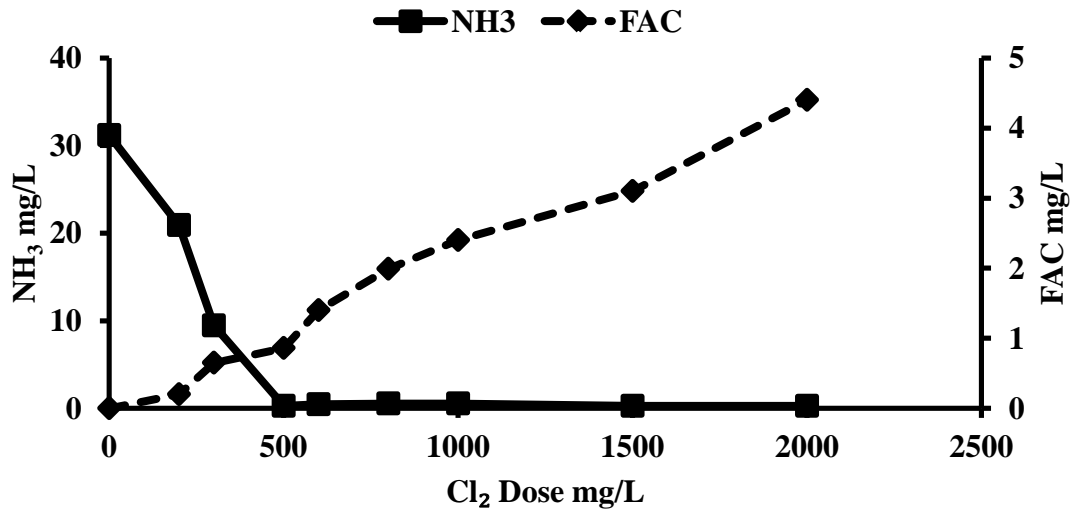


**Figure 5.4.** Chlorine demand and ammonium concentration for Reverse Osmosis samples. Membrane processes applications have more efficiency in nitrogen compounds removal from water and wastewater (Hsu et al., 2012). The efficiency of RO systems in removal of ammonium, organic and nitrite nitrogen is varying in the range of 60–90% (Chen and Westerhoff, 2011). RO has high efficiency in removing all ions of nitrogen (Metcalf and Eddy, 1999). Several researches have been conducted for an application of RO to remove nitrogenous compounds (Agus and Sedlak, 2010). In AQU P RO effluents have the minimum ammonia concentration.

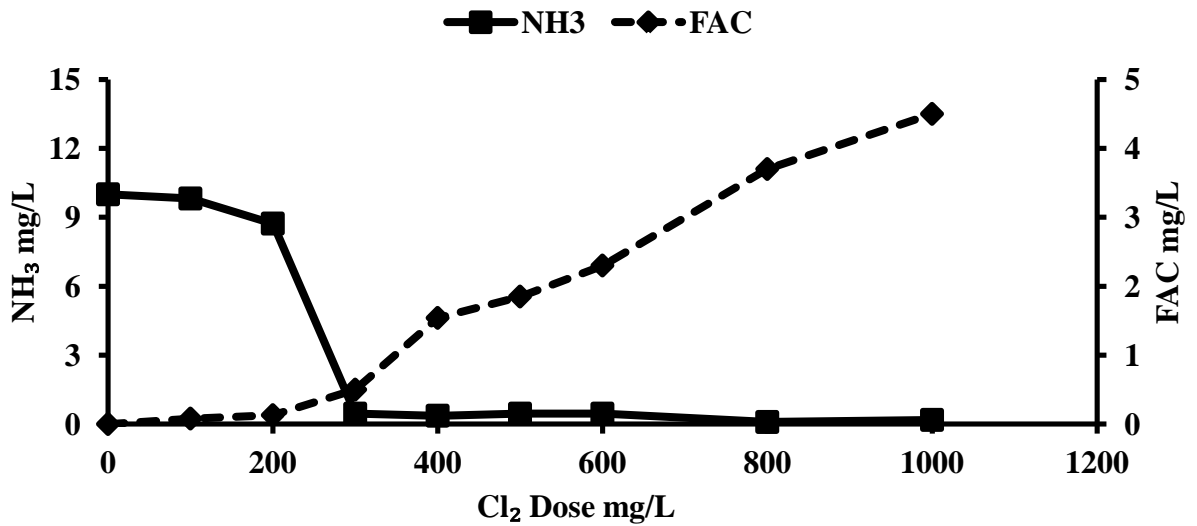
### 5.2.2 Oasis P $\text{Cl}_2$ Demand

Raw water source concentration does change, thus chlorine dosage need to meet the changing levels of ammonia. Figures 5.5 and 5.6 have shown the relationships between

ammonium and free chlorine, in Oasis P bioreactors 1 and 2. The initial ammonium concentration in Oasis P is approximately 32 mg/L which reduces after the bioreactor 2 stage of treatment to reach approximately 10 mg/L.



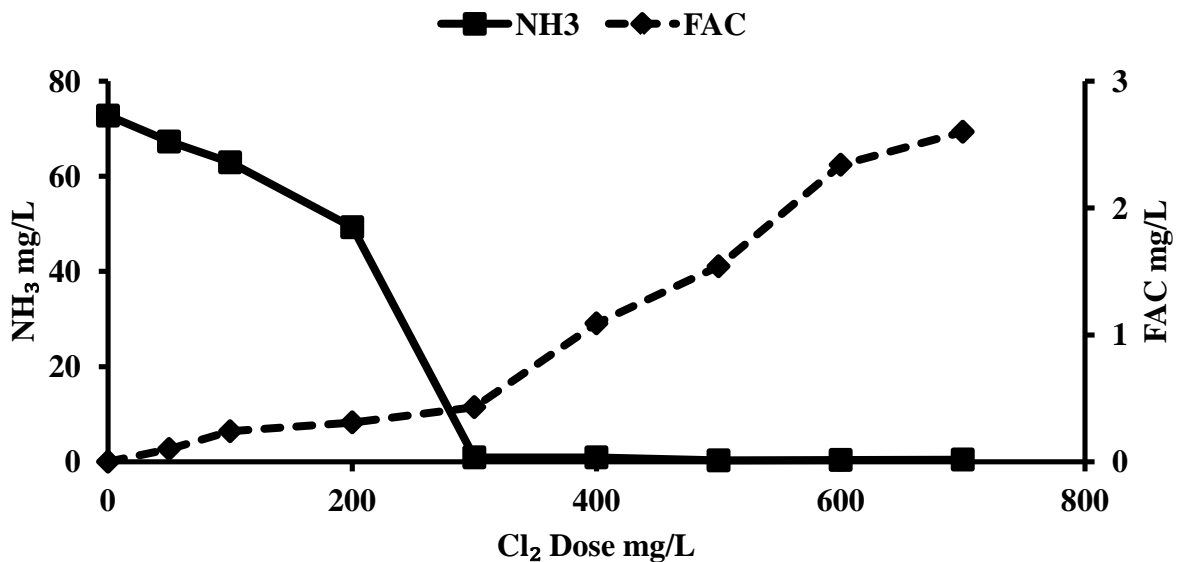
**Figure 5.5.** Chlorine demand and ammonium concentration for Oasis bioreactor 1 samples



**Figure 5.6.** Chlorine demand and ammonium concentration for Oasis bioreactor 2 samples

### 5.2.3 Auja P Cl<sub>2</sub> Demand

Figures 5.7, 5.8, 5.9, 5.10 present Auja P ammonia and chlorine inverse relationship. The initial concentration of ammonium in tank 3 is approximately 75 mg/L and ends in the effluent to be 50 mg/L in the final tank, with chlorine demand around 300 mg/L in both influent and effluent. Hence no obvious treatment and reduction in ammonium concentration is noticed in this treatment system. A study stated that the smaller the concentration of ammonium in wastewater before chlorination, the more free chlorine that could be generated for a fixed dose of chlorine (Pant and Mittal, 2007) this occurred in Auja tank 7 and final tank with FAC reaches to around 5mg/L.



**Figure 5.7.** Chlorine demand and ammonium concentration for Auja tank 3 samples



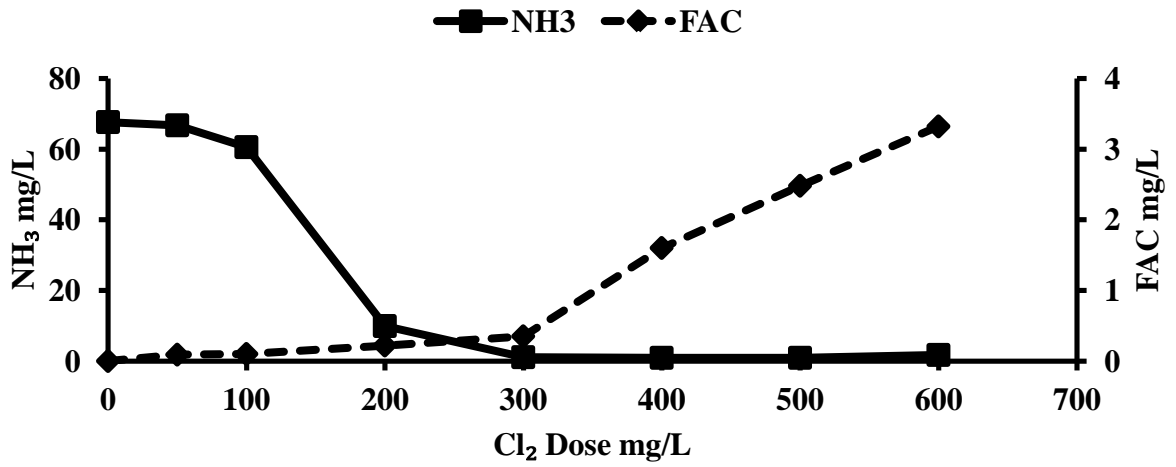


Figure 5.8. Chlorine demand and ammonium concentration for Auja tank 5 samples

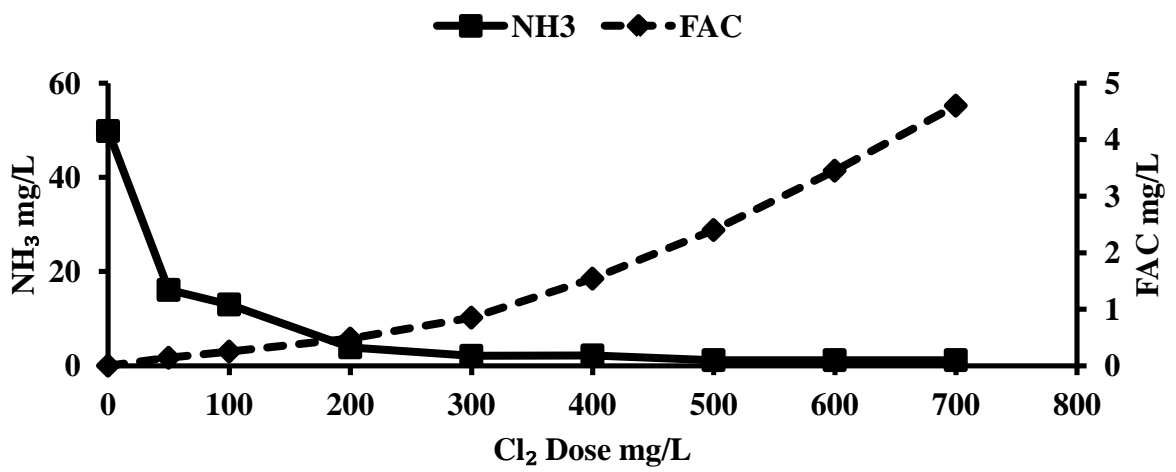
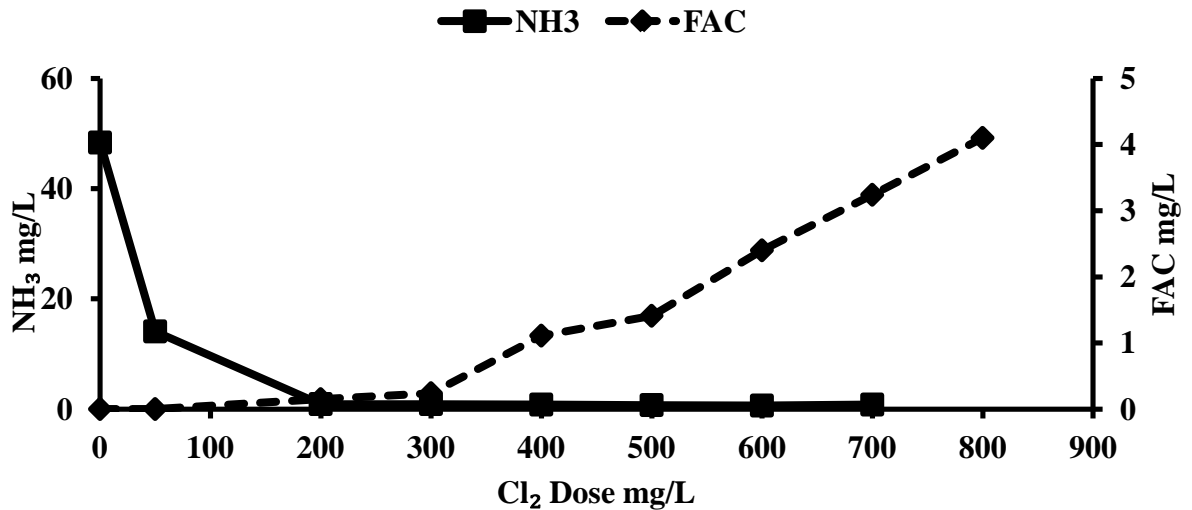


Figure 5.9. Chlorine demand and ammonium concentration for Auja tank 7 samples



**Figure 5.10.** Chlorine demand and ammonium concentration for Auja final tank samples

Some references provide a guideline stating when free residual chlorine is a 93-95% of total residual chlorine then breakpoints are achieved but such principles can be misleading (White et al., 1986). To assure the chlorination is beyond breakpoint ammonium should be zero or very near to zero (Connell, 1999). In this study all wastewater samples, ammonium was removed by chlorine and reached to zero mg/L. When chlorine is added, FAC start showing up gradually in small concentrations less than 1 mg/L, until ammonia reached to zero mg/L at this point FAC increases proportionally and reaches to 5 mg/L.

The difference in ammonium levels affects breakpoint results (Janzen and Beier, 2006). This happens in chosen wastewater samples from three wastewater treatment plants that shows different ammonium concentrations and varied in chlorine demand as indicated earlier.

The purpose of breakpoint chlorination is to ensure effective disinfection by satisfying the chlorine demand of wastewater. In wastewater that contains ammonium, breakpoint chlorination is a mean of eliminating ammonium to achieve true free chlorine residual (McDonald, 2003). The amount of chlorine consumed during these reactions is referred to

as the chlorine demand that must be added to achieve a specific chlorine residual and good disinfection (Palin, 1974).

High concentrations of AS characteristics since AQU P receive large amounts of wastewater from different sources of AQU campus, including laboratories' chemical and organic wastes and kitchens due to large population of the campus and from rain water, compared to less concentration in Oasis P since amount of receiving wastewater depends on visitors of the hotels during the study the hotel wasn't in the high season. Moreover Auja P receives only grey water which reflected on relatively low ammonia concentration. As a result, the breakpoint chlorine dosages and the patterns of the breakpoint curves are varied among the samples from the three WWTPs.

Figures from 5.1 to 5.10 show the general inverse relationships between ammonium and free chlorine, ammonium in wastewater react with free chlorine, generates more chloramines (or combined chlorine residual). Thus, the smaller the concentration of ammonia in wastewater treatment system prior to chlorination, the more free chlorine that could be generated for a fixed dosage of chlorine (Arana et al., 1999).

To sum up chlorine is a non-selective oxidant and will therefore react with both organic and inorganic substances in wastewater in different degrees (White, 2010). Chlorine consumption is controlled essentially by the type and quantities of these constituents mainly ammonia concentration, and variations in raw water quality and treatment processes described earlier justifies the variation in chlorine demand results (Chen et al., 2011).

In Palestine the level of chlorine residuals in drinking water must be maintained in the range 0.2-1 mg/L to prevent microbial contamination of distribution system (PWA, 2012) but no specific values for chlorine residual in wastewater.

### 5.3 THM Precursors Analysis

In order to gain some insight about the precursors involved in THMs formation in wastewater effluents. THM formation depends on several factors; primarily, chlorine dose, temperature, wastewater quality (pH, organic and inorganic content) (Chang et al., 2013). Therefore, the management of THMs involves the assessment and reduction of factors contributing to their formation.

The main objective of this section is to introduce analysis and comparison of THM formation in three wastewater treatment plants, relating the differences to WWTP operational and source water characteristics and to define the major trihalomethanes factors in the three wastewater treatment plants.

Table 5.2 summarizes the mean values of measured raw water quality parameters in 5 wastewater effluents.

**Table 5.2.** Characteristics of five wastewater effluent samples

| Sample    | TEMP<br>°C | pH      | Cl <sub>2</sub><br>mg/L | TOC<br>mg/L | IC<br>mg/L | TN<br>mg/L | TUR<br>NTU | TDS<br>mg/L |
|-----------|------------|---------|-------------------------|-------------|------------|------------|------------|-------------|
| AQU<br>AS | 28±0.2     | 7.8±0.2 | 200                     | 17.2±10     | 147.3±20   | 107.0±10   | 187±15     | 880±150     |
| AQU<br>UF | 27±0.2     | 7.6±0.2 | 100                     | 10.75±10    | 65±5       | 49.5±15    | 33±10      | 340±200     |
| AQU<br>RO | 25±0.1     | 7.2±0.2 | 50                      | 2.2±0.4     | 11.6±5     | 9.7±10     | 0±3        | 22±100      |
| Oasis     | 27±0.1     | 7.5±0.2 | 100                     | 6.6±0.2     | 73.0±10    | 18.0±17    | 128±40     | 500±50      |
| Auja      | 28±0.2     | 7.8±0.2 | 100                     | 9.2±1       | 93.6±12    | 31.7±10    | 103±50     | 330±40      |

TOC =total organic carbon, TN= total nitrogen), IC =inorganic carbon, AQU= Al-Quds University, AS= activated sludge, UF.HF= ultrafiltration hollow fiber, UF.SW= ultrafiltration spiral wound, RO= reverse osmosis

Many empirical models have been found to estimate the formation of THMs. One of these models is done by Westerhoff, (2006):

$$\text{THMs} = 0.0412[\text{TOC}]^{1.098}[\text{Cl}_2]^{0.152}[\text{Br}^-]^{0.068}[\text{Temp}]^{1.069}[\text{pH}]^{0.263}$$

This model suggests that THMs concentration increases with increasing total organic carbon (TOC), chlorine dose, bromide ion concentration, temperature, pH and reaction time.

**5.3.1 TOC effect on THM formation:** Dissolved organic matter (DOM) is considered as the primary precursor to DBP in wastewater (Cho et al., 2003). Dissolved organic carbon DOC or TOC has known as precursors for DBPs and they were considered as a surrogate parameter for disinfection by products formation potential (DBPFP) (Rodriguez and Serodes, 2005). These parameters are used for water assessment quality and are known for their ease of application and costs (Rodriguez, et al., 2004).

The greatest TOC measured is in the Activated sludge of AQU P 17.2 mg/L. The advanced membrane of AQU P RO shows the least TOC concentrations 2.2 mg/L.

TOC is used as indicator for organics and DBP precursor removal effectiveness. The USEPA regulation assigned water treatment plants using chemical disinfectants to reduce levels of TOC as an introduction of reducing DBP precursors. USEPA accepts enhanced coagulation as the best available technology for achieving DBP precursor's removal (USEPA, 1998). In this study enhanced coagulation has been done after AS and before UF in advanced membrane treatment of AQU P which minimized TOC to 10.75 mg/L.

To investigate the organics removal through AQU P, TOC samples has the greatest removal of TOC. RO stage removes around 87% TOC after AS stage. Generally, RO membranes are manufactured from polyamide thin film that shown the least contaminant and THMs precursors. TOC removal across the oasis biological process is around 12% reduction in final effluent concentrations. Auja P TOC removal is around 4% this would be

resulted since filtration (sand and gravel) is known to remove only a small portion of NOM (Westerhoff and Chowdhury, 1996) and due to simple technology used in treatment.

AS samples are shown the richest parameters due to heavy load of wastes generated from many sources in AQU campus. Oasis P and Auja P final effluents contain relatively high concentrations of TOC, IC and TN, comparing to advanced treatment of UF and RO of AQU P. Oasis P contains TOC of 6.6 mg/L, while Auja P contains 9.9 mg/L TOC.

**5.3.2 Chlorine dosage:** The increase in DBP precursors increases DBP formation. However, DBP formation increases also due to the increase in chlorine demand resulted by the NOM (Pregeant, 1992). The increase in chlorine demand requires a higher chlorine dose to maintain the required chlorine residual which will result in an increase in DBP formation (Xie, 2004). Through oxidation of NOM with chlorine intermediate compounds could form; these intermediates are oxidized by chlorine, or bromine, to form DBPs (Pregeant, 1992). In this study the applied chlorine dose for AS of AQU P is 200 mg/L with TOC 17.2 mg/L which is expected to have greatest THMs formation comparing to other effluents receive less doses and lesser TOC.

**5.3.3 Temperature:** The temperatures range throughout the study period between 25-28 °C as the initial temperature after collection from WWTPs. After that, temperature was constant during the incubation period of the experiment 25°C. In general at higher temperatures the rate of reaction increases. Higher temperatures also mean a higher rate of hydrolysis, which leads to a faster break up of aromatic bonds, resulting for further halogenation and a higher formation of DBPs (White, 2010).

**5.3.4 pH:** High pH increases the rate of formation and concentration of THMs (Liang and Singer, 2003; Rook, 1974). At higher pH the hydrolysis step that leads to THMs formation is facilitated (Carlson and Hardy, 1998). After samples collection of AQU P pH decline

after each treatment stage raw, AS, UF, RO as follows 8.15, 7.5, 7.4, 7.14 although after Oasis and Auja Ps pH remains high 8.01 and 8.13 respectively but pH maintained constant during the incubation period.

There are other contribution factors in THMs such as turbidity and total dissolved solids.

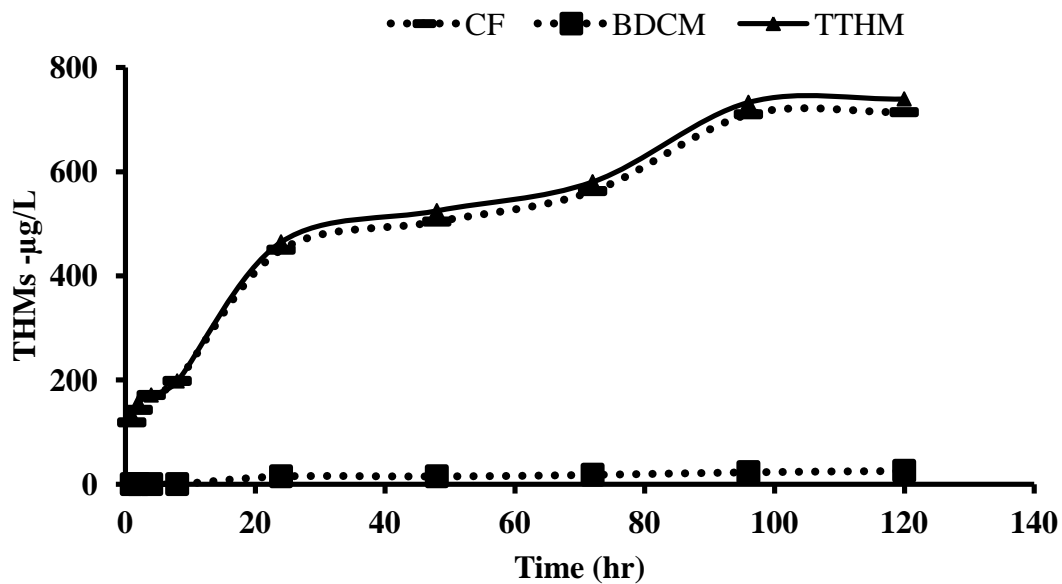
**5.3.5 Turbidity:** In AQU P the removal efficiency of turbidity is approximately 82%, 100% by UF and RO advanced membrane treatment, respectively. The turbidity of finished wastewater from RO of AQU P is reduced to 0 NTU. Therefore UF/RO membrane treatment processes have satisfactory turbidity removal. Oasis P and Auja P turbidity efficiency removal is 55%, 71% respectively that provides better chances for increased THMs in these effluents. Turbidity is considered THMs precursors, the more efficient removal of turbidity, less THMs formation (Yang et al., 2014).

**5.3.6 Total Dissolved Solids:** TDS is considered as THM precursor. Therefore reducing TDS concentration can reduce the amount of produced THMs (Yang et al., 2014). Table 5.2 is shown the mean concentration of TDS in every effluent. However UF/RO membrane treatment process was more efficient in reducing TDS which result in 61%, 97%. The advantages of UF/RO membranes are their ability to remove bacteria, turbidity agents and suspended solids (Gopal et al., 2007). However Oasis P and Auja P effluents contain TDS 300 and 500 mg/L and with removal efficiency 30% and 48% respectively which could expect to result in higher THMs formation than advanced treatment of UF and RO of AQU P.

#### 5.4 THMs Results

THMs include chloroform ( $\text{CHCl}_3$ ), bromodichloromethane ( $\text{CHBrCl}_2$ ), chlorodibromomethane ( $\text{CHBr}_2\text{Cl}$ ) and bromoform ( $\text{CHBr}_3$ ), the sum of them is known as total THMs (TTHMs) (Adams, 2005).

Variations in TTHM depend on the quantity and characteristics of organic matter, chlorine dose and contact time, pH, and temperature. Higher THMs arise from higher precursor's levels, temperatures, dosage rates, reaction times.

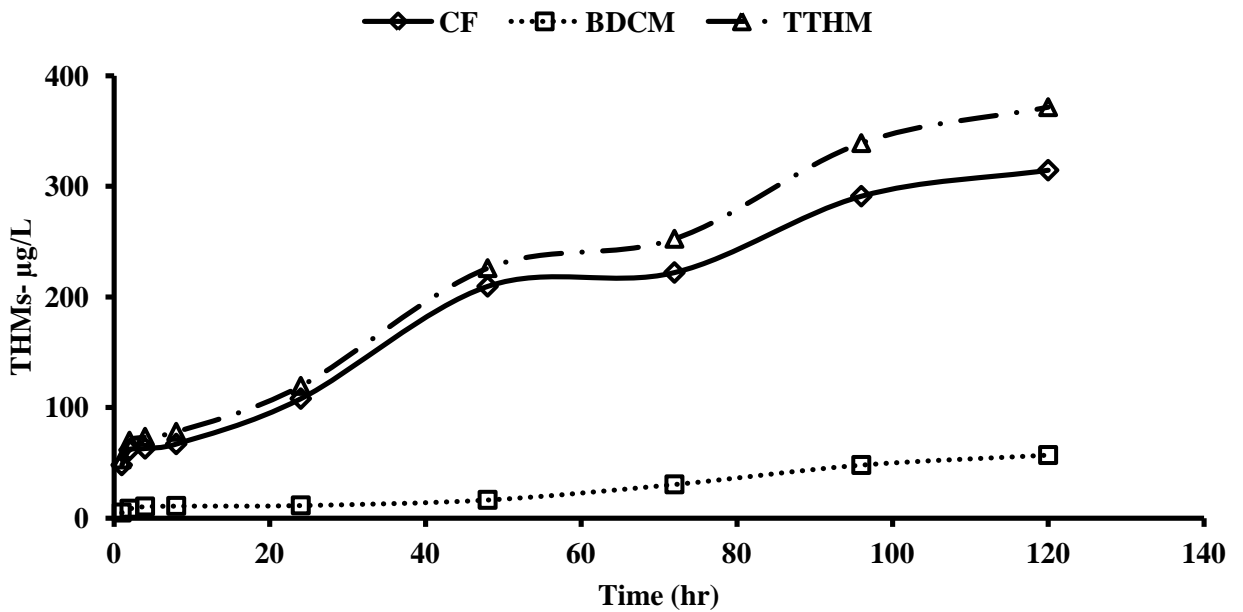


**Figure 5.11.** Chloroform (CF), Bromodichloromethane (BDCM) and TTHMs results for activated sludge of AQU P

Figure 5.11 describes the distribution of four individual THMs compounds increased by increasing incubation period. Generally chloroform is seen to dominate THM species. TTHMs consist of CF occupying 96% of TTHMs and BDCM occupying only 3.5%. It is obvious that TTHM concentrations increased over the incubation period. Species such as dibromochloromethane (DBCM) and bromoform (BF) aren't detected or below  $1\mu\text{g/L}$  due to low or no detection of bromide in source water. Wide variety of water quality and



treatment conditions can affect THMs formation such as: the applied chlorine dose for AS of AQU P is 200 mg/L with TOC 17.2 mg/L, initial pH 7.8 and 28 °C. High pH increases the rate of formation and concentration of THMs, at higher temperatures the rate of reaction increases. TOC is used as indicator for organics and DBP precursor, TDS, TN IC and Turbidity. All the mentioned conditions have strong relation to THMs formation; as TOC, chlorine dose, pH increase, THM formation increases.

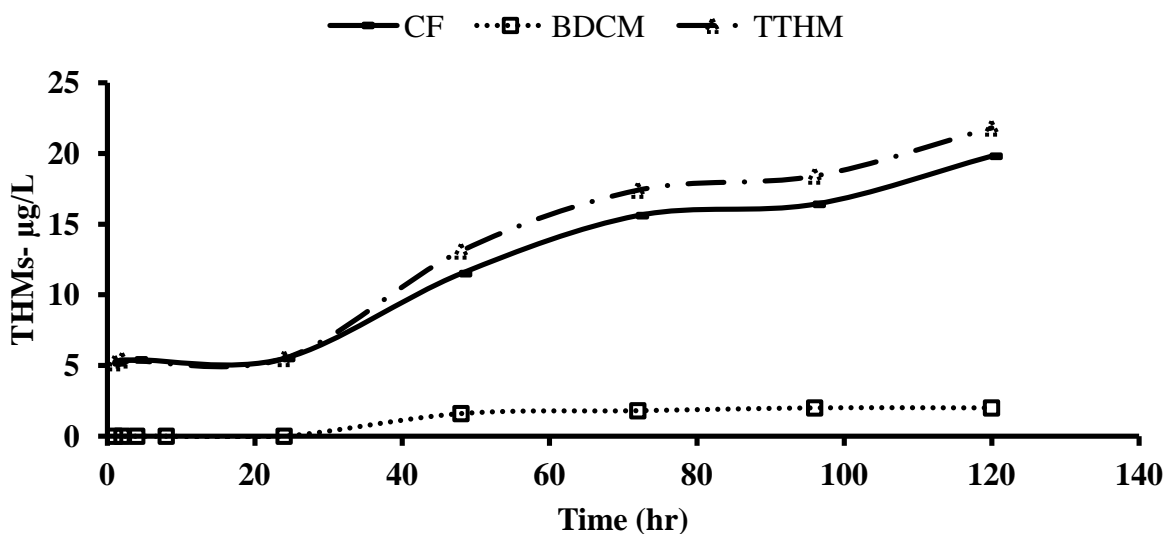


**Figure 5.12.** Chloroform (CF), bromodichloromethane (BDCM) and TTHMs for ultrafiltration of AQU P.

The major THMs species in UF of AQU P are CF and BDCM. Figure 5.12 shows the dominance of CF over BDCM in UF samples. TTHMs mainly consist of CF occupies 84% and BDCM occupies 15% however other species as DBCM and BF aren't detected or below 1µg/L due to low or no detection of bromide in source water.

TOC is used as indicator for organics and DBP precursor removal effectiveness. After UF stage TOC reduced to become around 10 mg/L which reduced chlorine demand to 100 mg/L. Initial temperature and pH reduced to 27°C and 7.6 as a result of treatment and

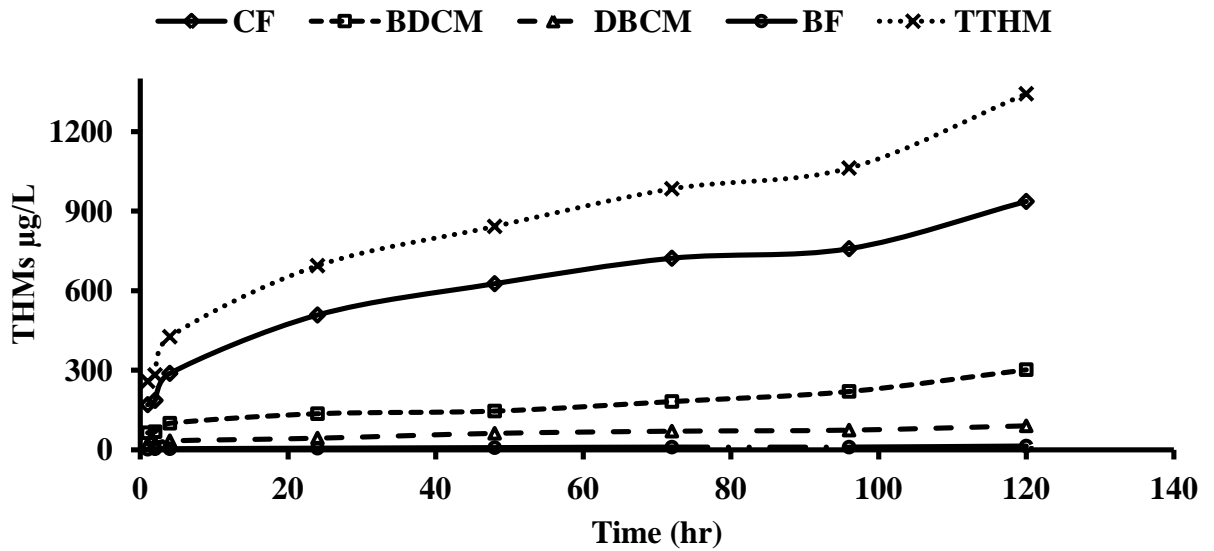
reduction in TOC, TDS, Turbidity, IC and TN which influence THM formation and formed less TTHM (372  $\mu\text{g/L}$ ) than AS (740  $\mu\text{g/L}$ ) stage after two successive UF stages.



**Figure 5.13.** Chloroform (CF), bromodichloromethane (BDCM) and TTHMs for reverse osmosis of AQU P

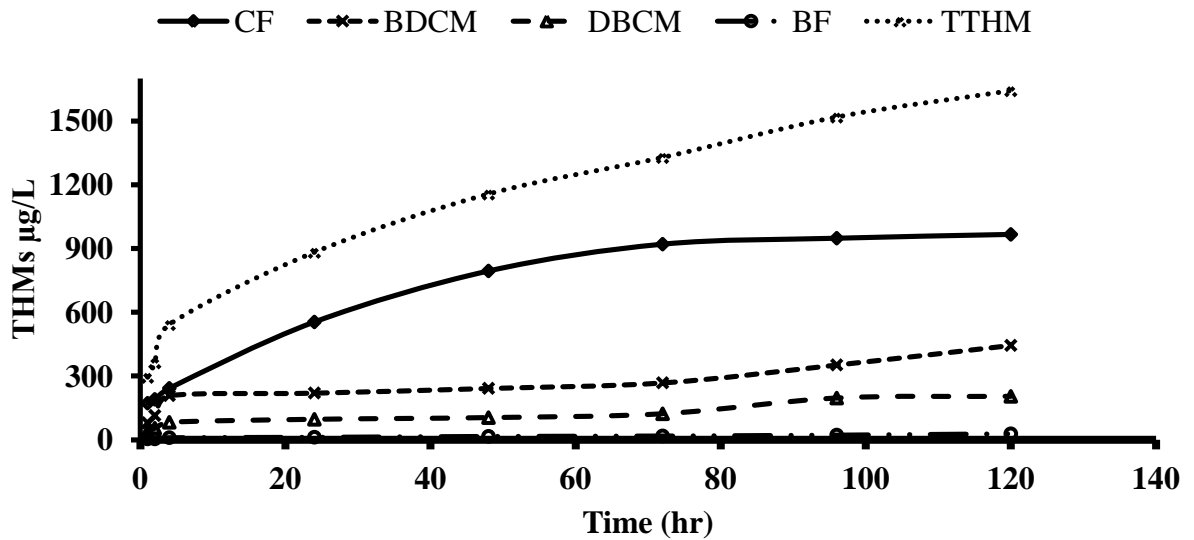
The major THMs species in RO of AQU P are CF and BDCM. Figure 5.13 shows the dominance of CF over BDCM in RO samples at the end of incubation period. CF occupies 90% of TTHMs. BDCM contains around 9.5% of TTHMs, DBCM and BF contain residues below 1  $\mu\text{g/L}$ .

RO is the most advanced technology in the study since it reduced the concentrations of all parameters such as initial temperature and pH, TN, IC, TDS, Turbidity and TOC to the least among all samples. Chlorine dose was 50 mg/L and TOC concentration reached to 2.2 mg/L after RO treatment which reflected in decreasing TTHM after chlorination of samples.



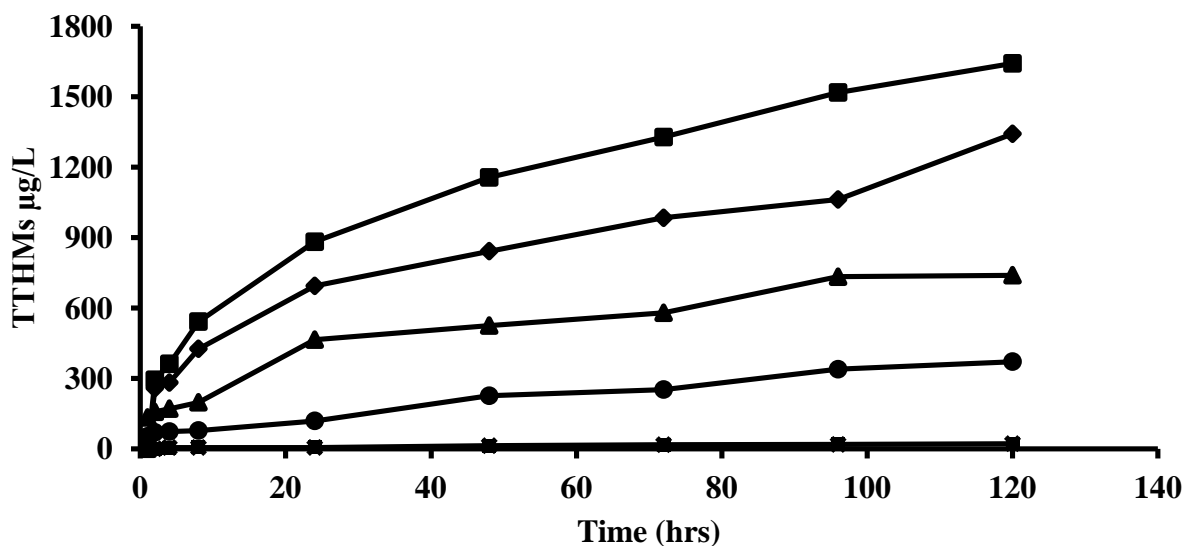
**Figure 5.14.** Chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (BF) and TTHM (totaltrihalomethanes) for Oasis P

The major THMs species in Oasis P are CF and BDCM. Figure 5.14 shows the dominance of CF over BDCM, DBCM and BF in Oasis samples. CF reach to 936 µg/L while BDCM ends up to 333 µg/L, thus TTHMs mainly consists from CF 69% and BDCM 22% however other species as DBCM and BF are detected but with lower concentrations 6% and 1% respectively. Bromide is present in source water in Jericho. If chlorine and bromine is present during chlorination, chlorine will act as oxidant while bromine becomes a halogenating agent because bromine atoms preferred substitution during formation of halogenated DBPs. Wide variety of water quality and water source can affect TTHMs formation such as TOC concentration in raw water which control the disinfection concentration; a lower Cl<sub>2</sub> residuals and higher TOC removal will result in lower TTHMs.



**Figure 5.15.** Chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (BF) and TTHM (totaltrihalomethanes) for Auja P

The major THMs species in Auja P are CF and BDCM. Figure 5.15 shows the dominance of CF over BDCM, DBCM and BF in Auja samples. TTHMs mainly consist from 58% CF and 27% BDCM however other species as 12% DBCM and 1.7% BF are detected but with lower percentage. Brominated species are detected in Oasis and Auja P since the presence of bromide is involved in increase of TTHMs formation (Chowdhury et al., 2010). Bromide is present in Jericho as a result of Dead Sea intrusion to groundwater (Marie and Vengosh, 2001). TOC concentration was 9.2 mg/L and applied chlorine dose was 100 mg/L of Auja P which formed the highest concentration of TTHMs among all studied treatment plants.



**Figure 5.16.** Average TTHMs measured in five wastewater effluents in Palestine

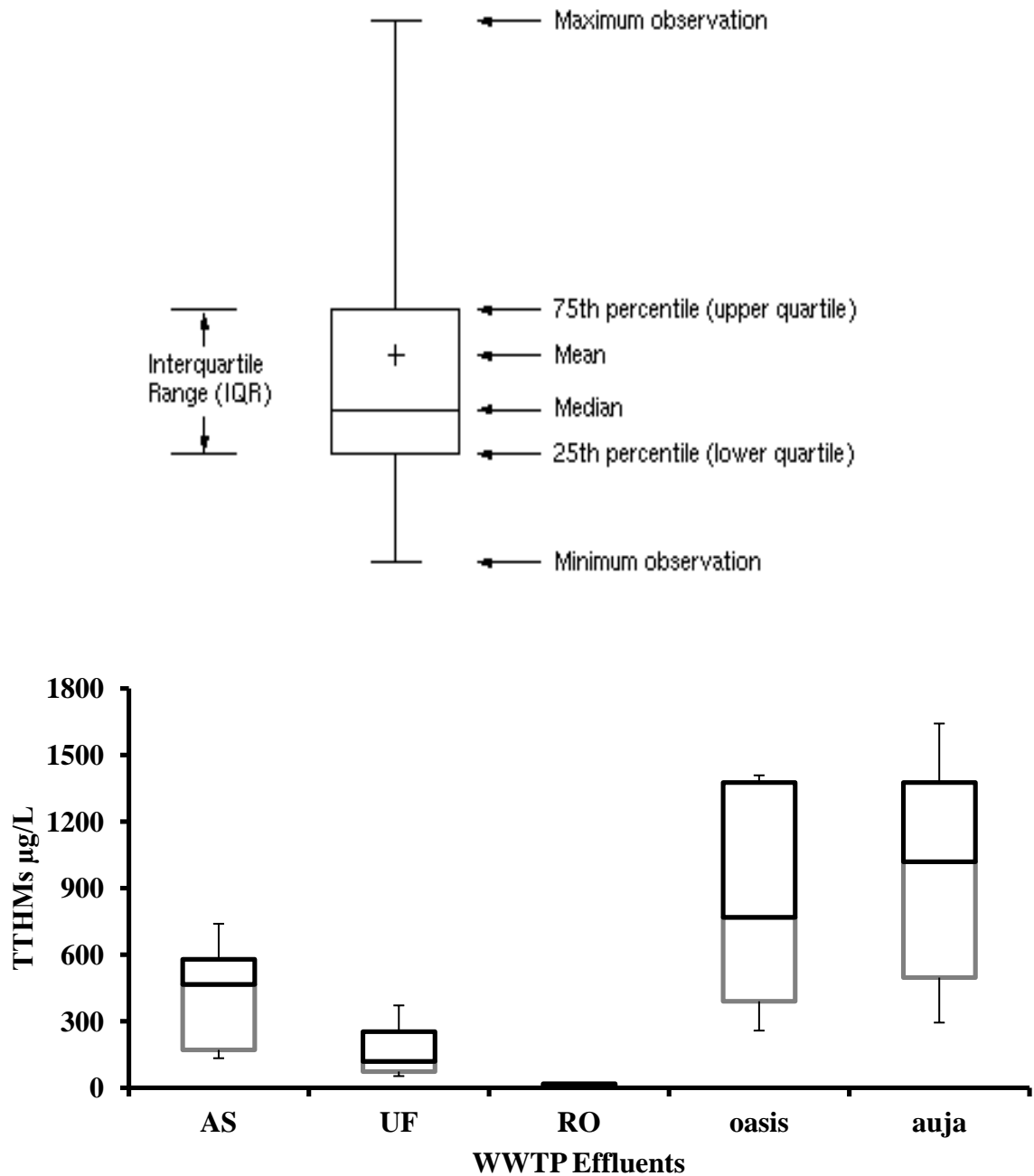
Figure 5.16 shows the average of TTHMs in five wastewater effluents that are chosen for this study. Auja P effluent indicates the highest concentration of TTHMs as a function of time although AS owns the potentiality to form greatest TTHMs according to high precursors (TOC,  $\text{Cl}_2$  dose, temperature, pH and other parameters). However, RO effluent of AQU P contains the poorest TTHMs formation. Generally, as precursor concentration increases, DBP production increases, but it will tend to plateau after the residual chlorine is exhausted (Pregeant, 1992).

Activated sludge of AQU P was expected to have the most abundant TTHMs concentration because it has the highest TOC and applied chlorine dose among all wastewater samples. However GC-MS analysis shows highest THMs concentration for Auja P then Oasis P comes in the second place.

Bromide is present in Auja and Oasis water source from salt water intrusion, bromide serves as inorganic precursor for THMs and it adds up extra formula weight on TTHMs. The conventional treatment processes in Auja and Oasis (biological) was able to remove TOC but not bromide ion which resulted in increase of bromide ion to TOC ratio. TOC is

an indicator of mass organic substance and doesn't differentiate between the chemical compounds that form precursors compound thus the variety of chemical compounds and functional groups of organics is a significant factor in explaining why different water sources with similar TOC concentrations will form different DBPs concentration under identical disinfection conditions (Kimbrough and Suffet). Moreover, longer chlorine contact time will result in higher DBP formation. As time increases chlorine contact and reaction with NOM increase and allow intermediate molecules more time to react until completion (Hua et al., 2015). The chlorine dose has a similar effect on DBP formation as the dose rise the DBP concentration rise and reaching a plateau (Pregeant, 1992). The chlorine dose can also affect the speciation of DBP as the dose increases the ratio of THM to total halogenated DBP ratio also increases (Doederer et al., 2014; Cho et al., 2003). In general the lack of linear correlation between average annual TOC and DBPs doesn't mean the samples collected at individual water system lack any kind of relationship

WHO regulated 200 µg/L for chloroform. USEPA assigned 80 µg/L for TTHMs. The European Union (EU) determined 100µg/L for TTHMs (WHO, 2005). Unfortunately, specific standards are not available for treated wastewater used for agriculture irrigation, except for the maximum permissible chloroform concentration in soils receiving untreated municipal wastewater which approximately 0.47 mg/kg (WHO, 2006). Concentration of TTHMs After incubation period in AS samples exceeded drinking water standards of 80 µg/L and 100 µg/L after one hour of incubation to reach to 714 at the end of incubation period. However UF samples exceeded the limits after 20 hour of incubation. RO samples maintain lower concentrations of TTHMs under the drinking water standards for the whole period of incubation. Oasis and Auja samples exceeded the limits after one hour of incubation to reach very high concentrations after 120 of incubation.



**Figure 5.17.** Box-and-whisker plot of TTHMs for WWTP effluents

Figure 5.17 displays the comparison of distribution of THMs from five different wastewater treatment effluents showing extreme values, median and 25<sup>th</sup> and 75<sup>th</sup> percentiles. In general UF and RO produced the least TTHMs concentrations according to least TOC precursors. The two highest median resulted in Oasis P and Auja P, the highest median, maximum and minimum are respectively 1019, 1642 and 294µg/L are in Auja P

which resulted from high NOM from surrounding environment and low treatment efficiency.

The results of TTHMs indicate that the level of TTHM increases with the residence time in the laboratory incubation conditions. At AQU P effluents, TTHMs concentrations are highest in TTHMs per unit of TOC at AS stage of AQU P 793.5  $\mu\text{g/L}$  due to the high TOC content 17.2 mg/L; after that wastewater passes through UF units (hollow fiber and spiral wound) which reduce TOC to 10.75 mg/L and TTHMs concentration 371.5  $\mu\text{g/L}$ . While the RO unit of AQU P yields TOC content of 2.2 mg/L which resulted in 21.8 $\mu\text{g/L}$  TTHMs.

Among five effluents of WWTPs, Auja P is the richest source of TTHMs of 1642  $\mu\text{g/L}$ . RO examined the lowest TTHMs. Oasis P and Auja P contain all four trihalomethanes species CF, BDCM, DBCM and BF. Lowest concentrations of THMs were found in wastewater from UF/RO with minimum average respectively. In AQU P UF and RO removes a large proportion of THMs precursors as turbidity, TDS, TOC.

Some municipal wastewater treatment plants in New Jersey established limits for trihalomethanes after wastewater chlorination; for chloroform 221, BDCM 3.3, DBCMB 2.4 and bromoform 26  $\mu\text{g/L}$  (Patoczka et al., 2011). During this study only RO effluents didn't exceed the limits of CF and BDCM, however all other samples AS, UF, Oasis and Auja achieved higher values

In the finished wastewater effluent from all plants chloroform was the predominant THM compound. In Oasis P and Auja P the predominant brominated THM was BDCM; which after BF is the second most important THM species from toxicological analysis (Ding et al., 2013) however the levels of this compound is low.



## Chapter Six

### Conclusions, Recommendations and References

#### 6.1 Conclusions

- Measured free chlorine residuals will differ in wastewater samples collected from different WWTP sources, as shown by the variation in free chlorine residual measured during dosage testing in three WWTPs.
- Wastewater sources that contains less content of organic matter as indicated by COD and BOD and inorganic mainly ammonia will have lower chlorine demand, resulted in higher free chlorine residuals.
- The addition of insufficient doses of chlorine to wastewater from different sources may result in not satisfying the demand. Thus one dosing scheme is not appropriate for all wastewater treatment plants of AQU P, Oasis P and Auja P, depend on their different characteristics.
- For the investigated wastewater treatment plants AQU P, Oasis P, Auja P,  $\text{CHCl}_3$  was the most dominant THM species observed after the chlorination of wastewater samples.
- The levels of THMs formed upon chlorination of wastewater depended on several operational conditions, but chlorine dose, TOC and contact time, are the major factors in this study.
- The distribution of each species of THM will vary according to wastewater source, the treatment processes and conditions operated at the wastewater treatment works. As occurs in Oasis and Auja that contain bromide resulted in formation of brominated by-products.
- To compare data from different systems there is no universal relationship that can predict DBPs based on TOC values.

## 6.2 Recommendations

- The variation in raw water quality has a strong influence on the formation of THM upon contact with chlorine. However, before introducing chlorine to wastewater, significant adjustment and treatment can be made to reduce the quantity of potential precursor material. These changes are governed by wastewater effective treatment.
- The levels of THMs formed upon chlorination of wastewater depended on several operational conditions, but chlorine dose, TOC and contact time, are the major factors in this study. Thus, further study of disinfection methods to reduce DBP formation is needed.
- Find bromide concentration is necessary for future studies to correlate bromide concentration to brominated DBPs resulted.
- Auja P has simple treatment which wasn't efficient in removing THMs precursors thus further advanced treatment is recommended to increase the efficiency of treatment.
- Oasis P should increase the applied dose to properly disinfect wastewater.
- The actual occurrence of THMs in wastewater treatment plants are required to investigate the correlation of chlorine applied in each treatment plant to THMs formation.
- A standards and specifications to THMs concentrations in water should be maintained in water and wastewater by Palestinian water authority and other local water institutes because of potential carcinogenic and mutagenic risks associated with THMs.

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## مجموع الترايهالوميثانات المتكونة في محطات معالجة المياه العادمة في فلسطين

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### ملخص

يستخدم الكلور في تعقيم مياه الشرب وتعقيم المياه العادمة قبل الاستعمال البشري أو طرحها في البيئة حتى لا تسبب مخاطر أو عدوى للإنسان أو للبيئة المحيطة به.

بعد عملية الكلورة يتم إنتاج مواد ثانوية غير مرغوب بها تؤثر على صحة الإنسان وتكون ممرضة ومسرطنة. تعد مجموعة المركبات ثلاثية الهيدروجينات (الهالوميثانات) من أبرز المواد الجانبية الضارة التي تنتج عن عملية كلورة مياه الشرب أو المياه العادمة. أكثر الهالوميثانات تكونا هي الكلوروفورم و بروميد ثنائي كلورو الميثان و ثنائي بروميد كلورو الميثان والبروموفورم.

كلورة المياه في فلسطين هي أكثر عملية تعقيم شائعة إلا أن هذه المواد لم يتم قياسها في المياه العادمة من قبل ولم يتم وضع معايير تحدد وجود هذه النواتج الكيميائية.

اتجهت الأنظار مؤخرا الى أهمية معالجة المياه العادمة وإعادة استعمالها بسبب نقص المياه في فلسطين تبعا لتغير المناخ وتحكم السلطات الاسرائيلية بمصادر المياه و بكميات المياه التي يستهلكها الفلسطينيون.

لقد تم اختيار ثلاث محطات معالجة للقيام بهذا البحث وتختلف كل محطة عن نظيراتها باختلاف الطرق المتبعة في المعالجة والتي تنتج خصائص مختلفة لعينات المياه بعد انتهاء كل مراحل المعالجة وقد تم تقييم بعض المكونات والخصائص لكل نتاج المحطات وقياس كمية الأمونيا والكمية اللازمة التي تحتاجها المياه للكلورة والتعقيم.

المحطات المختارة هي محطة جامعة القدس ومحطة فندق الواحة (أوازييس) في اريحا ومحطة معالجة المياه الرمادية في مركز العوجا البيئي في قرية العوجا.

الهدف الأهم لهذا البحث هو ايجاد كمية الترايهالوميثانات الناتجة بعد عملية كلورة المياه العادمة ومقارنتها بالمعايير العالمية المسموح بها.

تحتوي محطة جامعة القدس على كميات عالية من الترايهالوميثانات حوالي 740 ميكروغرام/لتر و 372 و 96 ميكروغرام/لتر بعد المرحلة الاولى والثانية والثالثة على التوالي.

تحتوي المرحلة الثانية والثالثة على تقنية الفلاتر الدقيقة الحجم والفلاتر التي تعتمد على عكس الخاصية الاسموزية في نفاذية الماء دون السماح بمرور أدق الجزيئات كالنترات والأمونيا.

يتكون الكلوروفورم بأعلى النسب من مجموع الهالوميثانات فعلى سبيل المثال تحتوي محطة الواحة ومحطة العوجا على نسب من الكلوروفورم بمقدار 69% و 58% من مجموع الترايهالوميثانات الكلي بالإضافة لوجود نسب أعلى من البروموهالوميثانات التي لم تتكون بنسب تذكر في عينات محطة جامعة القدس.

محطة العوجا احتوت على أعلى نسبة من الهالوميثانات بمقدار 1600 ملغم/لتر بينما اقل نسبة من الهالوميثانات تشكلت بعد كلورة الناتج الأخير من محطة القدس الذي هو عبارة عن غشاء يعمل بمبدأ الخاصية الاسموزية العكسية.

عند مقارنة جميع التراكيز بالنسب العالمية وجد ان التراكيز الناتجة أعلى من التراكيز المسوح بها عالميا لمياه الشرب و أعلى من النسب المتكونة في الدراسات السابقة حيث لم تتجاوز المحطات الاخرى 200 ميكروغرام/لتر ولكن التراكيز الفلسطينية في البحث بدأت من 200 ميكروغرام/لتر ووصلت حتى 1600 ميكروغرام/لتر.