2-1-2014

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School of Science and Engineering

Fate of Natural Organic Matter and Formation of Disinfection By-Products in a Conventional Water Treatment Plant

By

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A thesis submitted in partial fulfillment of the requirements of the degree of

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Fall 2013

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Fate of Natural Organic Matter and Formation of Disinfection By-Products in a Conventional Water Treatment Plant

A Thesis Submitted by Noha Hesham Abdel Rahim Sabry Abdel Halim

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Abstract

Elevated levels of disinfection by-products (DBPs), detected in Cairo residential water supply during the past decade, were the motivation to study the process of DBP formation at the water treatment plant (WTP) stage. It is hoped that an in-depth understanding of natural organic matter (NOM) characteristics and DBP formation/removal in an existing WTP will yield a baseline as well as insights for the development of optimum strategies for cost-effective reduction of potentially harmful drinking water compounds such as Trihalomethanes (THMs) and Haloacetic acid (HAAs). The objectives of this research were to: investigate the degree of removal of the various NOM fractions in conventional WTPs and identify the factors that may possibly enhance their removal; and investigate the levels of formed DBPs within conventional WTPs when pre-chlorination and post-chlorination are applied.

Water samples were collected from El-Fustat WTP in Cairo from 4 different points along the treatment process and covering the four different seasons of a year. NOM was quantified by classical surrogate parameters such as total organic carbon (TOC), dissolved organic carbon (DOC), and ultraviolet absorbance (UVA_{254}); and characterized more precisely according to its hydrophobic-hydrophilic properties using resin fractionation. THMs, HAAs and other water quality analyses were conducted for all collected samples.

Measurements of NOM fractions following each treatment unit indicate that the hydrophobic fraction is significantly removed by the coagulation/flocculation/sedimentation processes (56% to 13% in the various seasons) whereas the transphilic, and hydrophilic fractions were removed to much lower degree (51% to 10%) and (15% to 4%), respectively. The hydrophobic fraction had formed flocs with the added alum more than the other two fractions. No further removal of NOM takes place in rapid sand filtration or post-chlorination units.

Although the THMs values recorded for the entire study were complying with the Egyptian guidelines, it is not guaranteed that tap concentrations will comply to the guidelines limits. This is because THM/THMFP does not exceed 39%, leaving room for 61% to be reacted in pipe lines and storage tanks until it reaches the customers taps. In addition, HAAs concentrations at the plant effluent were much higher than the regulating limits, alarming the WTP to exert more effort to reduce THMs, and HAAs values.

On an attempt to identify the relative importance of NOM fractions in THMs formation, the measured values of the THMs were regressed to each NOM fraction and the coefficient of determination (R^2) was calculated. Results showed that unlike hydrophobic fraction and transphilic fractions ($R^2 = 0.01, 0.14$), respectively, hydrophilic NOM fractions are consistently most responsible for THM and HAAs production at the plant effluent ($R^2 = 0.77, 0.62$.

Although, hydrophilic fraction was the main contributor to THMs and HAAs formation in El-Fustat WTP; coagulation/flocculation and sedimentation could not successfully remove it during treatment. Accordingly, the processes of coagulation/flocculation/sedimentation/filtration are not guaranteed to be useful in decreasing the DBPs levels El-Fustat WTP does not technically implement "Enhanced Coagulation"; however, initial results from this study shows that the hydrophillic DOC fraction is less likely to be removed during Enhanced Coagulation but the major DOC contributor to DBPs formation. Future work should test this hypothesis through a bigger and wider sample size.

Free chlorine concentrations are responsible for the high THM levels at the plant effluent, which implies its responsibility on THMs formed in the plant and the formation potential in distribution pipelines. Therefore, reducing the chlorine doses as much as possible to reach zero free chlorine before post-chlorination and the minimum acceptable free chlorine residual for secondary disinfection is going to reduce the THMs and HAAs levels substantially.

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Acronyms

AWWA: American Water Works Association

BAC: Biological Activated Carbon

CDOM: Chromophoric Dissolved Organic Carbon

CHA: Hydrophilic Charged

CHCl$_3$: Chloroform

D/DBP: Disinfection/Disinfection by-Product

DBPs: Disinfection by-Products

DI: De-Ionized Water

DOC: Dissolved Organic Carbon

FA: Fulvic Acid

FTU: Formazin Turbidity Unit

GAC: Granular Activated Carbon

GC: Gas Chromatograph

HMW: High Molecular Weight

HPO: Hydrophobic

HA: Humic Acid

HAA5: Haloacetic Acid

H$_3$PO$_4$: Phosphoric Acid

KDa: Kilo Dalton

KMnO$_4$: Potassium Permanganate

LMW: Low Molecular Weight

NaOH: Sodium Hydroxide

NEU: Hydrophilic Neutral

NOM: Natural Organic Matter

OC: Organic Carbon

OFW: Organic Free Water

PAC: Powdered Activated Carbon

SUVA: Specific Ultra-Violet Absorbance

THMFP: Trihalomethane Formation Potential

THMs: Trihalomethanes

TOC: Total Organic Carbon

TRA: Transphilic

USEPA: United States Environmental Protection Agency

UVA: Ultra-Violet Absorbance

UV: Ultra Violet

WHO: World Health Organization

WTP: Water Treatment Plant

Chapter One

Introduction

1.1 Background

Delivering safe drinking water to consumers is the main target of water treatment plants, and is achieved by passing water through the treatment train suitable for its quality. Disinfection of biological contaminants is a vital process in the water treatment train as it is the primary method to prevent or inactivate microbial infections leading to common waterborne diseases such as typhoid, cholera, dysentery and diarrhea in consumers [Chang, 1982; Bhardwaj, 2006]. Compared to conventional filtration units, disinfection processes such as chlorination units are considered more feasible and efficient especially for large municipal water suppliers [Raucher, 1996].

The first disinfection attempt in modern municipal water supply was in 1908 in New Jersey City, U.S.A, in which chlorine was introduced to public waters to mitigate sewage discharge from river communities up-stream of the city's reservoir. As a result, causative agents of cholera and typhoid fever were efficiently removed, and the overall bacterial count was noticeably reduced. Since that time, chlorination has become widely accepted as a water disinfection technique [Raucher, 1996]. However, increasing pollution rates of rivers from agricultural drainage, industrial discharge, and domestic sewage has often prompted the need to increase chlorine doses. The attempt to alleviate the contamination danger has unfortunately produced another problem, namely, the formation of potentially harmful disinfection by-products (DBPs) at increasingly higher concentration [Bhardwaj, 2006]. Accordingly, water utilities must strike a risk-based balance between vital protection against pathogen contamination and DBP production in treated water.

In this context, using alternatives to chlorine is a viable idea in developed countries, but in populous developing countries like Egypt, chlorine disinfection is the most popular, economical, and efficient method for drinking water [Smith & Abdel Maksoud, 2009]. Moreover, chlorine can help to stop the algal growth in coagulation tanks and filters; i.e. pre-chlorination. This is due to the ability of chlorine to disrupt essential enzymatic processes, which sterilize living organisms and prevent them from growth. One of which is the

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enzymatic action by *triose phosphoric acid dehydrogenase,* which make aquatic biota lose their ability of oxidizing glucose, which in turn deactivate their growth [Smit, 1948]. Pre-chlorination is also used to lower the pH of the raw water. Such lowering can help to improve the efficiency of the alum coagulant to form flocs.

Using weaker disinfectants like chloramine can decrease DBP levels, but often will not provide the finished water with the necessary level of residual protection. In the same context, water treatment facilities usually use post chlorination injection point after sand filtration. This could ensure the deactivation of all pathogens and water borne diseases escaping the filters and provide the sufficient residual protection from further contamination through distribution networks. Therefore, replacing chlorine or moving chlorine injection locations to latter stages alone will usually not meet the full range of treatment objectives with respect to biological contaminants within the financial constraints facing most developing nations [WHO, 2008]. However, chlorination should be added with caution, due to the health risks of its excess doses.

1.2 DBP Health Risks and Regulations

In 1973, halogenated organic compounds were first identified in several drinking water suppliers in the U.S.A. [Raucher, 1996]. In response, extensive studies were conducted to identify the chemical and physical structure of these compounds and their risk to public health. The principle compound is chloroform ($CHCl_3$) produced from the reaction of chlorine with the naturally occurring organic matter (NOM) in water [Chang, 1982]. A number of other compounds were detected in tap water with the same chemical structure of chloroform, namely CHX_3 where X denotes the halogen atom. They are all categorized as trihalomethanes (THMs) [Florentin, 2011].

Additionally, there are more than 600 chlorinated DBPs detected in tap water, classified in three main groups; organohalogenics, non-halogenic organics and inorganics [Bhardwaj, 2006; Florentin, 2011].

Many toxicological studies have examined the health risks of ingesting $CHCl_3$ and found that it caused ailments such as *hepatocellular carcinoma* in laboratory mice due to oral application. However, large-scale epidemiological studies failed to find a direct relation between THM concentrations and stomach, hepatocellular, or rectum cancer mortalities in a

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defined human population [Chang, 1982]. At the very least, establishing a firm link between THMs and cancer in humans requires further focused studies [Florentin, 2011].

Despite the fact that proving a direct relation between THM concentrations and cancer is a very complicated issue that deals with various factors like drinking and eating habits, environmental exposure, and residence history; disinfection byproducts (DBPs) concentration is still an issue that attracts attention of public health professionals and engineers because of the great population exposed to it by digestion, inhalation or in swimming pools [Florentin, 2011].

Accordingly, the Unites States Environmental Protection Agency (USEPA) and other similar organizations sponsored numerous studies to specify the optimum concentrations of total THMs to be safely permitted to consumers [Chang, 1982]. The upper limit for total THMs in drinking water began with 100 ppb as a reasonable concentration to compromise between practicality and safety. This limit has since been reduced to 80 ppb [USEPA, 2012] as shown in Table 1.1.

Table 1.1 Guideline values for THMs and HAAs in tap water

Trihalomethanes (µg/l)	WHO[a]	US EPA[b]	Europe[c]	Canada[c]	Egypt
Chloroform	300				
Bromodichloromethane	60			16	
Dibromochloromethane	100				
Bromoform	100				
Total 4 THMs		80	100	100	100
Haloacetic Acid (HAA$_5$) (µg/l)		60		80[d]	80[e]

[a]Guidelines for drinking water quality, fourth edition 2011, Table 8.16[b] US EPA, 2012
[c] Florentin, 2011
[d]Canada Health (www.hc-sc.gc.ca)
[e]Egyptian Ministry of Health

1.3 Problem Statement

Many studies have attempted to characterize NOM in different drinking water sources, to draw either chemical or physical profiles for NOM as a step to study the treatability of each group. In the field of water treatment, NOM content is grouped into compounds of similar

operational behavior (size and solubility) into hydrophobic, transphilic, and hydrophilic fractions. The response of each fraction differs, depending on the treatment process used [Everett, 1972]. It is agreed that NOM profile differs from one location to another [Fabris *et al.*, 2008]. Roughly, fresh water NOM is a mixture of hydrophilic compounds originated in the water body itself due to the decomposition of plankton and aquatic bacteria. Or leached from the soil of the basin stream [Buffle *et al.*, 1990; Schmidt *et al.*, 2012], whose tends to be hydrophobic [Fabris, 2008]. Indeed, reactivity of each fraction to produce DBPs differ according to the source NOM derived from [Velten *et al.*, 2011].

A number of studies worldwide have tried to model the removal of NOM fractions during different stages of water treatment. These studies are commonly used locally as a baseline evaluation step preceding treatment optimization studies. Marhaba *et al.*[2000] reported that the treatment line that included ozonation led to a better overall removal of NOM. This effectiveness was attributed to the high degrading ability of ozone, which converts the large compounds to simpler and smaller compounds. Also, hydrophobic particles were efficiently removed by controlling coagulant dosage in conventional treatment for suspended solids removal. On the other hand, hydrophilic fraction is less likely removed by coagulation due to its negligible charge density. That is why it dominates in residual Dissolved Organic Carbon (DOC) versus hydrophobic components [Swietlik *et al.,* 2004].

In the same context, NOM removal during treatment is affected by a variety of factors, including its character in the source water, treatment processes arrangement and solute characteristics.

Chlorine dosage prior to coagulation and clarification (referred to as pre-chlorination) was found to initiate the DBPs formation process within the treatment plant itself. On the other hand residual chlorine resulting from post-post chlorination continues to form DBPs in the distribution network, if NOM is not totally removed within the treatment plant.

High trihalomethane concentrations violating the Egyptian standards and USEPA limits have been detected in the distribution systems in some of the residential communities fed by the effluent of El Fustat water treatment plant (WTP) [Smith & Ezzeldin, 2009]. A series of studies was conducted on the influent of El Fustat WTP focusing on characterizing classes of the influent natural organic matter (NOM) [Smith & Alqabany, 2009]. A follow-up study investigated the potential of enhanced coagulation in targeting the treatment of select NOM

fractions most responsible for DBP formation at the bench scale [Smith &Abdel Maksoud, 2009].

The above mentioned studies indicated that Nile water at Cairo vicinity consists of 48% hydrophilic fraction, 29% hydrophobic fraction, and 23% transphilic fraction of NOM on quantity bases. In a descending order, the reactivity of the transphilic fraction was higher than the hydrophobic and the hydrophilic fraction [Smith & Alqabany, 2009]. A laboratory study by Smith and Abdel Maksoud [Smith &Abdel Maksoud, 2009] indicated that using enhanced coagulation in treating the raw Nile water before adding chlorine achieved reduction in trihalomethane formation potential (THMFP) by as much as 65% under optimized conditions.

However, incorporating enhanced coagulation in the conventional treatment train first requires researches on tracking actual changes of NOM behavior through the existing (full scale) treatment line, as there is no available information on these variations. Previous literature suggests that these changes in NOM behavior are strongly correlated to the arrangement and type of processes in the treatment line [Chen *et al.*, 2008].

1.4 Thesis Objectives

The main objectives of this thesis are to:

- Investigate the degree of removal of the various NOM fractions in conventional water treatment plants and identify the factors that may possibly enhance the removal
- Investigate the levels of formed DBPs within the conventional water treatment plants when pre-chlorination and post-chlorination are applied

1.5 General Approach

A conventional water treatment plant was selected for monitoring of the NOM and its fractions and their variations along the treatment line, and the formation of DBPs along the treatment line and following each treatment unit. The sampling was carried on dates that attempt to incorporate the seasonal variations.

El-Fustat Water Treatment Plant (FWTP) was selected for the monitoring study. The FWTP is a large conventional water treatment plant treating Nile raw water and supplying several districts in Cairo (Maadi, Nasr City, New Cairo Fifth settlement, Heliopolis). The FWTP has

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three identical treatment streams. The treatment line consists of removing particulates greater than 5mm using bar screens, followed by pre-chlorination, coagulation-flocculation, sedimentation, and finally filtration and post chlorination steps.

Samples were collected on a seasonal basis over the four seasons of a year to represent the seasonal variations in Nile water NOM. Water quality parameters were measured; pH, alkalinity, Ultraviolet absorbance (UVA$_{254nm}$), and Total and Dissolved organic Carbon (TOC & DOC). Resin fractionation was also used to characterize NOM fractions on hydrophobic/hydrophilic bases, which are quantified as DOC in mg/l. THMs and HAAs were recorded for chlorinated water with the total and free chlorine levels and water temperature. As a result, an NOM removal profile could be drawn and the relation between individual NOM fractions and produced DBPs is abstracted. The drawn conclusion will shed light on other similar plants.

1.6 Thesis Organization

Chapter one introduces the problem, thesis objectives, and the adapted approach. In chapter two, a literature review on different approaches to characterize NOM, factors affecting DBPs formation versus NOM removal in treatment plants, and different treatment alternatives is presented. Chapter three discusses the detailed description of El-Fustat WTP with the experiment plan set and the laboratory tests performed. Chapter four discusses key results and findings and Chapter five presents the main thesis conclusions and the recommendations for future work.

Chapter Two

Literature Review

2.1 Overview

Natural Organic Matter (NOM) is found in all surface water sources. It consists of a heterogeneous mixture of various organic compounds. These compounds are produced due to aquatic plants decay, soil leaching, or uncontrolled wastewater discharge in water bodies [Matilainen *et al*., 2011]. It can also be secreted by aquatic biota if exposed to a high dose of an oxidant during the treatment process [Bouteleux *et al.,* 2004]. The amount and structure of NOM were found to be dependent on the water source; its geology, topography, and seasonal climatic changes [Fabris *et al.,* 2008; Wei *et al.,* 2008].

This mixture has many negative effects on water quality. These include imparting unacceptable yellowish to brown color, taste and odor, and increased sludge quantities during treatment as a result of using increased coagulant doses. NOM is found to be responsible for increased levels of complexed heavy metals and adsorbed organic pollutants [Jacangelo *et al.,* 1995]. It may also adversely affect the performance of treatment processes; e.g, increase membrane-fouling rate, and block activated carbon pores, which in turn reduce the adsorption efficiency. If it remains during or after the treatment, it can produce hazardous DBPs after adding disinfectant [Fabris *et al.*, 2008]. Also, it can act as a substrate for microbial regrowth as *E-coli* in distribution lines [Bouteleux *et al.,* 2004; Jacangelo *et al.,* 1995]. All these effects hinder the delivery of safe drinking water to consumers. Nowadays, drinking water facilities are struggling to eliminate pathogens while minimizing DBP concentrations in finished water.

In order to achieve the desired NOM treatment, conventional water treatment processes should have a certain arrangement. In some cases the typical sequence of coagulation/flocculation followed by sedimentation/filtration is satisfactory [Jacangelo *et al.,* 1995; Matilainen *et al*., 2011]. Also, optimizing conventional treatment processes for example enhanced coagulation can reduce NOM and thus DBP production [Fabris *et al.,* 2008].

Lately, the issue of NOM is highlighted due to the global trend towards increasing levels in surface waters worldwide. This increase is believed to be due to unexpected climate change and its associated changes in aquatic ecosystem and soil pH [Fabris *et al.,* 2008].

2.2 NOM Characterization

There are many factors that could affect the presence and character of NOM in surface water, including the nature of aquatic system, small streams versus large rivers, population density, and human activity around the water source [Filella, 2009]. Fresh water NOM is a unique mixture of pedogenic and aquogenic organic matter. Pedogenic organic matter is produced due to the decomposition of higher plants by bacteria and fungi. It can be leached from the soil of the drainage basin itself after rainfall events. Therefore, the characteristics of these compounds are usually similar to soil fulvic acids [Buffle, 1990]. Aquogenic organic matter is considered to have originated in the water body itself due to the decomposition of plankton and aquatic bacteria [Schmidt *et al.*, 2012].

Due to the variability of NOM sources, they have appreciably different characteristics. From the existing NOM quantifying methods, there is not one of that can categorize NOM on purely elemental or even molecular bases. However, measuring the bulk parameters of the mixture can indicate the origin of NOM [Fiella, 2009]. From the widely used parameters are (C/N, C/O, C/H, C/S), particulate OC/TOC ratio, molecular size, isotopic ratios ($^{13}C/^{12}C$, $^{15}N/^{14}N$) and spectroscopic parameters related to NOM aromacity (UV-visible and fluorescence) [Tietjen *et al.,* 2005].

Mapping information of NOM in particular classes is the most common approach in its scientific analysis. Biochemical classification is a common approach in which NOM is sorted into four major classes; carbohydrates, proteins, lipids, and less degradable compounds class. The first three classes together account for approximately (20-40)% of the total organic matter in the source. Due to the structural variety of lipids, they can also be used as biomarkers [Filella, 2009].

NOM can also be operationally defined according to its colorimetric properties, which split organic materials into two broad species: transparent and yellow particles. The former are transparent on clear slides stained by Alcian Blue, the chemical structure of which, are polysaccharides [Passow and Alldredge, 1994; Grossart *et al.*, 1997]. The yellow particles are coomassie-stained proteins [Long and Azam, 1996; Carrias *et al.,* 2002].

In the field of water treatment, NOM content is analyzed by grouping it into compounds of similar operational behavior (size and solubility). Resulting fractions are of very complex chemical structure depending on the treatment process used [Everett, 1972]. Many studies

have attempted to characterize NOM in different drinking water sources. The specific objective of these studies was to draw either chemical or physical profiles for NOM as a step to study the treatability of each group [Fabris *et al*., 2008]. Previous literature had agreed on certain common properties for aquatic NOM according to their origin.

Matilainen *et al* [2011] have found that pedogenic or terrestrially derived organics consist of a complicated heterogeneous mixture of humic, yellowish to brown, non-polar solutes. This mixture is rich in aromatic carbon content, phenolic compounds, and low nitrogen content. Fabris *et al* [2008] added that these particles were found to be of high molecular weight (HMW) hydrophobic nature, and contribute more than half NOM quantity as dissolved organic carbon (DOC); which passes through 0.45 μm filter pores. Owing to its high specific colloidal charge, hydrophobic particles were efficiently removed by controlling coagulant dosage in conventional treatment for suspended solids removal.

Aquogenic algal derived hydrophilic NOM has different properties. It consists of higher nitrogenous compounds, aliphatic carbon content, and is typically of low molecular weight (LMW) compared to the hydrophobic fraction [Barrett *et al*., 2000]. Hydrophilic fraction can be described as amino acids, hydrocarbons, carbohydrates, fats, waxes, sugars and low molecular acids. This fraction was found to less likely removed by coagulation due to its negligible charge density. That is why it dominates in residual DOC as compared to hydrophobic components [Swietlik *et al*., 2004].

Indeed, reactivity of each fraction to produce DBPs is important to be studied. This can help when tracking the removal of the fraction of the highest contribution in DBP formation [Velten *et al*., 2011]. According to Chang *et al*. [2001], hydrophilic LMW fraction of particle size less than 1 kilo Dalton (KDa) are the most reactive particles. This result suggested that effective removal for the hydrophilic NOM could significantly reduce DBP concentrations in finished water. Effective removal could be obtained by enhancing conventional treatment processes according to source water NOM characteristics [White *et al*., 1997].

By contrast, a series of studies have been conducted in Egypt to characterize the chemical profile of NOM in Nile water using the resin fractionation technique. It was found that NOM in raw Nile water can be described as 48% hydrophilic, 29% hydrophobic, and 23% transphilic in which the transphilic fraction is the most reactive one followed by the hydrophobic fraction; *i.e*., each contributes 38% and 31% of the produced DBPs, respectively

[Smith &Alqabany, 2009]. Seasonal variations in the NOM profile in Nile water were also investigated in this study. Table 2.1shows the seasonal variations in NOM between Summer 05 and Summer 06.Differences in the NOM composition were detected over an entire year of sampling. Hydrophobic acids are the key ingredient in spring 06 and summer 06, while the hydrophilic neutral content flourishes in winter versus autumn, spring and summer. Mutual changes were detected between transphilic and hydrophilic charged fraction during the year. Also, sharp changes were found in the NOM composition between summer 05 and summer 06. These changes were clear in the hydrophobic fraction content, which increased by more than 100%. In contrast, the transphilic fraction decreased by more than 100%. The reactivity of NOM detected in this study was based on the 7-daytrihalomethane formation potential (THMFP) test. THMFP was highest for the transphilic fraction in autumn and summer 05. Hydrophobic acids were the most reactive during winter, spring, and summer 06 [Smith & Alqabany, 2009].

Table 2.1 Seasonal Variations of NOM fractions of Nile water[a]

Season	Date of Sampling	Composition	Reactivity
Summer	July 2005	HPA 21%, TRA 31%, CHA 12%, NEU 36%	HPA 20%, TRA 54%, CHA 8%, NEU 18%
Autumn	October 2005	HPA 25%, TRA 17%, CHA 17%, NEU 41%	HPA 19%, TRA 45%, CHA 14%, NEU 22%
Winter	January 2006	HPA 20%, TRA 23%, CHA 11%, NEU 46%	HPA 38%, TRA 24%, CHA 9%, NEU 29%
Spring	April 2006	HPA 36%, TRA 30%, CHA 5%, NEU 29%	HPA 38%, TRA 32%, CHA 14%, NEU 16%
Summer	July 2006	HPA 45%, TRA 14%, CHA 18%, NEU 23%	HPA 38%, TRA 36%, CHA 10%, NEU 16%

[a][Smith and Alqabany, 2009]

Smith and Abdel Maksoud [2009] conducted an optimization study on Nile water, a part of which was resin fractionation. Samples for fractionation were taken in two seasons only; summer 07 and winter 07. As shown in Table 2.2 the NOM character observed for Nile water in this study revealssharp differencesin the NOM character between the two seasons. Indeed, the seasonal trends and even actual percent distribution of the four fractions are comparable relative to the previous study of Smith & Alqabany [2009].

Table 2.2 NOM Characterization of Nile Water[a]

	Summer	Winter
Time of Sampling	July 07	December 07
NOM Profile (% of total NOM)	HP 56%, TRA 17%, CHA 15%, NEU 12%	HP 37%, TRA 11%, CHA 13%, NEU 39%

[a] [Smith & Abdel Maksoud, 2009]

Comparing the Nile NOM character with other water sources elsewhere seems difficult due to the tendency of researchers to give arbitary names to the resulting fractions [Filella, 2009]. Because the hydrophobic and hydrophilic neutral exexpression were commonly used, they can be compared easily.It was reported that the hydrophobic compounds represents between (0-68) % of the total DOC by weight while the hydrophilic neutral compounds were found to represent between (1-35) % [Aiken & Leenheer, 1993; Day *et al*., 1991; Korshin *et al*., 1997].

2.3 Factors affecting NOM removal and Disinfection By-Products formation

The complicated chemical process of DBPs formation involves interaction between various elements in a dynamic environment. Several factors affect this process: arrangement of water treatment processes, NOM quantity and quality, chlorine levels, and other reaction conditions like pH, water age, and incubation temperature. The effect of each will be explained in the following sections.

2.3.1. Arrangement of Conventional Water Treatment Processes

A number of studies have tried to model the removal of NOM fractions during different stages of water treatment. These studies are commonly used locally as a baseline evaluation step preceding treatment optimization studies. They also depend on the arrangement of processes in the treatment train. For this reason obtained results will often be site-specific even for the same source.

Roughly, DBP precursor removal efficiency increases proportionally with their molecular weight [Velten *et al*., 2011]. It also depends on the characteristics of the water source and the type and arrangement of treatment processes [Fabris *et al*., 2008]. Marhaba *et al*.[2000]conducted a full scale treatability study on two water treatment plants; Raritan/Millstone (R/M) and the Canal Road (CR) surface water treatment plants in U.S.A. The purpose of this study was to compare the effect of ozonated versus chlorinated treatment

lines on mass NOM removed using the same water source. Table 2.3 provides a summary for the characteristics of each plant. The researchers observed that the treatment line that included ozonation led to better overall removal of NOM. This effectiveness was attributed to the high degrading ability of ozone which converts the large compounds to simpler and smaller compounds. It was observed that the reported decrease of the hydrophobic bases compounds was concurrent to an increase in the hydrophilic base fraction. It is worth to mention that those studies did not consider the DBPs formation through the treatment line studied.

NOM removal during treatment is affected by a variety of factors, including its character in the source water, treatment processes arrangement and solute characteristics. Chlorine dosage was found to increase the final THMFP. Mutual hydrophobic to hydrophilic changes are reported due to chlorination. These hydrophilic compounds are of higher reactivity [Iriarte *et al*., 2007].

Labanowski and Feuillade [2011] confirmed these changes in the molecular and chemical structure of hydrophilic fraction as a result of chlorination with changes in their florescence. An example for NOM structural differences due to treatment processes is shown in Figure 2.1.

Table 2.3 Surface water Treatment Plants Details

Plant	Location	Source	Treatment line used
The Raritan/Millstone (R/M)	Central New jersey	Raritan and Millstone rivers enhanced by Spurce Run river	Pre-chlorination + Coagulation/Sedimentation+ Post chlorination + Sand filtration
		and Round Valley	
Canal Road (CR)		reservoirs and the Delaware and Raritan Canal	Pre-ozonation + Coagulation + Sedimentation + intermediate ozonation +multimedia filtration +post Chlorination

Chen *et al.* [2008] studied different conventional treatment processes versus advanced units, with their arrangement shown in Table 2.4. A pre-oxidation step using ozone was determined to be responsible for the high DBP concentrations. Also, pre-ozonation was found to biodegrade hydrophobic NOM to lower molecular weight compounds. By-products resulting from ozonation were found to contain hydroxyl $(OH)^-$ and carboxyl $(COOH)^-$ groups, confirming the biodegradability of ozone gas. This leads to the increase in the aliphatic

hydrophilic carbon content versus decreasing the aromatic carbon content. In contrast, coagulation and air floatation exhibited no selectivity on removal of hydrophobic and hydrophilic fractions. Sand filtration removed hydrophilic NOM successfully. Also, combining ozonation (O_3) with biological activated carbon (BAC) was effective in reducing the hydrophobic fraction.

Table 2.4 Water Treatment Processes Arrangement

Arrangement	Process Combination
1	Pre-O_3+Coagulation-air floatation+filtration+O_3-BAC
2	Coagulation-air floatation + filtration + GAC/O_3.BAC

2.3.2. Water temperature, pH, and chlorine levels

Previous research had found a direct link between rate of THM formation and the reaction temperature. The THM yield was also found to increase simultaneously with elevated NOM quantity, but not necessarily increase with high chlorine doses [Bond *et al*., 2013]. This was found to be in agreement with Liu and Reckhow [2013], who confirmed that chloroform increase simultaneously during summer with high chlorine doses and high water temperature. Bench scale studies, had manifested that high incubation temperature is responsible for high DBPs levels in chlorinated water samples of initial low water temperature. This was illustrated by their low reaction rate, yielding higher chlorine residuals, to produce elevated THMFP values compared to other samples at the same heating conditions [Liu and Reckhow, 2013].
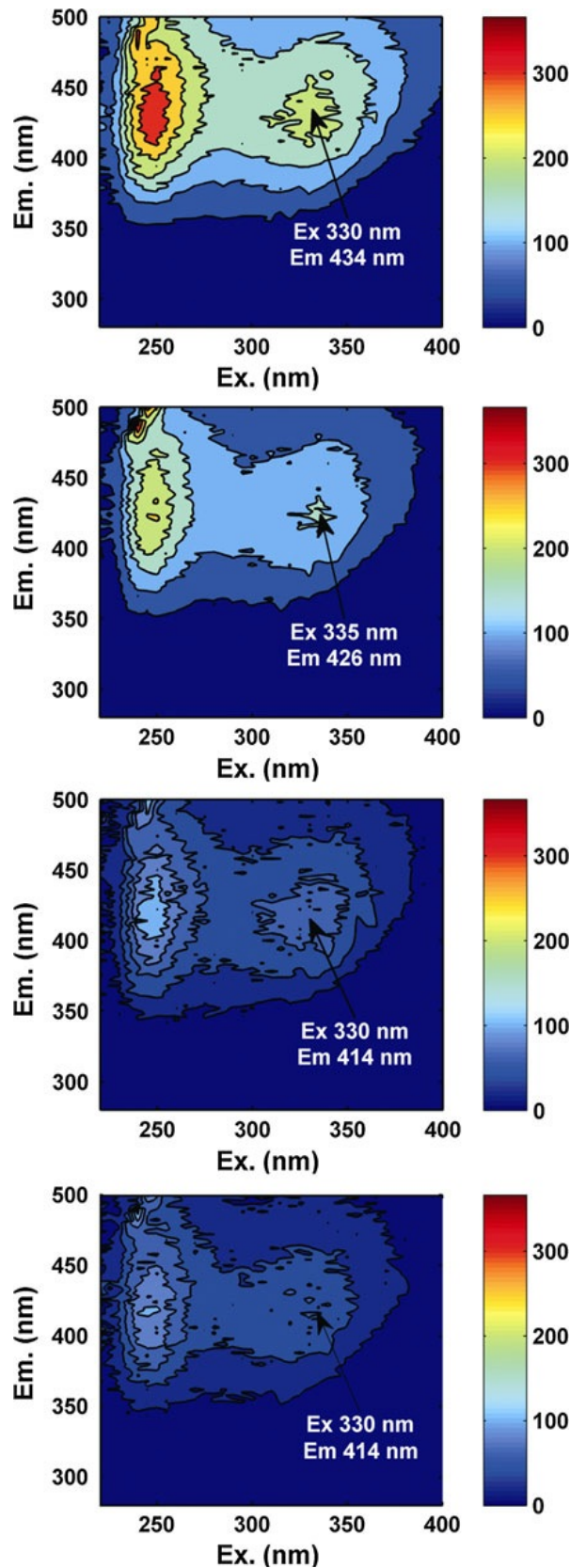
Figure 2.1 Florescence EEM of Raw, Post Clarification, Post GAC, and Final Water Courtesy of [Bridgeman *et al.,* 2011][1]

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Based on previous THM stoichiometry studies, THM formation process is a complex process, which depend mainly on the biological aquatic system; NOM content [Cox, 2003; Flegal and Schroeder, 1979]. Modeling studies had revealed that, THM formation best fits the first order time dependent model, as shown in equation 2.1. Using the actual THM levels in of variable water age samples from El-Fustat water treatment Plant developed this model. This predicting model, applies also to tape samples from the served areas.

$$THM_t = THM_0 \times e^{kt}$$ ………………….. (2.1)   [El Komos, 2008]

THM_t = THM concentration at time t, (µg/l)

THM_0 = initial THM concentration, (µg/l)

K = rate coefficient at 20 °C, (0.48 Day^{-1})

Based on previous studies on temperature dependent processes [Manivanan *et al*., 2013; Flegal and Schroeder, 1979], the validity of the correction technique was comfirmed. The correction was according to equation 2.2.

$$THM_T = THM_{@25°C} * \theta^{T-25}$$ ………… (2.2)

THM_T = THM concentration at any temperature, (µg/l)

$THM_{@25°C}$ = THM concentration at 25°C, (µg/l)

On the other hand, hot water was found to induce the reaction toward formation of THM_4 either with little or no chlorine residual, and the pH range 6:8. THM_4 especially chloroform was found to increase with high pH and reaction time. Additionally, heating of low aged samples *i.e.*, six hours, caused a substantial increase in THM_4 levels *i.e.*, 250%, 180%, and 100% at high pH levels 6, 7, and 8 respectively. However, at longer water age the rate of formation decrease in hot water *i.e.*, raised from 20 °C to 55 °C[2], 36%, 11%, 2% [Bond *et al*. 2013;Liu and Reckhow, 2013]. These findings could support the claim of production of a reservoir of halogenated intermediates right after chlorine addition to water. The rate of hydrolysis of these intermediates undergo, controls the amount of THM produced. In the same context, high pH levels facilitate the conversion of halogenated intermediates, resulting in high THMs levels [Bond *et al*. 2013;Liu and Reckhow, 2013].

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[2] 55 °C is the optimum temperature recommended by WHO for scalding prevention and keeping pathogens environment

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HAAs had recorded a notable increase with high DOC levels and showed to be independent from chlorine doses at relatively low DOC concentrations [Bond *et al*. 2013;Liu and Reckhow, 2013]. In hot water, and pH range 6:8, HAA_5 production had showed less sensitivity to pH when compared to THM_4 dependence [Liu and Reckhow, 2013; Arora *et al.,* 1997].

2.4 Treatment process Modifications and Alternatives

2.4.1 Enhanced Coagulation

Enhanced coagulation refers to " The process of improving the removal of DBP precursors in a conventional WTP" [USEPA, 1999]. This could be obtained by modifying the conventional coagulation process to achieve higher NOM removal with minimal costs. Practically, this is achieved by using the optimum coagulant dose and at an adjusted pH, to create the optimum conditions for the maximum conventional coagulation efficiency. Potential risks of NOM presence in drinking water were the motivation for including enhanced coagulation requirements in the disinfection/disinfection by-product (D/DBPs) rule in the United States. The (D/DBP) rule established TOC removal guidelines based on source water characteristics as shown in Table 2.5. These guidelines are designed to help water treatment facilities to comply with enhanced coagulation requirements [White *et al.,*1997]. As shown in Table 2.4 below, the maximum proposed TOC removal percentage from enhanced coagulation is categorized according to alkalinity. This is because the role of alkalinity to indicate the ability of pH to be maintained stable in the water body. Accordingly, high alkalinity levels indicate the ability of the water body to neutralize acidic solutions and in turn, pH could fairly change. In the same context, there are many sources for alkalinity in water bodies namely; some plant activities, dissolved salts, and detergents and soap in industrial wastewater. Agricultural wastewater from lime added soils (to decrease its acidity) which run-off to fresh water bodies could increase water alkalinity [Gotovtsev *et al*., 2012].

Table 2.5 Percent Removal Requirements for Enhanced Coagulation

TOC (mg/l)	Source Water Alkalinity- mg/l as $CaCO_3$		
	0-60	>60-120	>120
>2.0-4.0	40	30	20
>4.0-8.0	45	35	25
>8.0	50	40	30

The American Water Works Association (AWWA) sponsored research to study enhanced coagulation as a control strategy for NOM. It was concluded that interpreting the results ofenhanced coagulation studies can be complicated by the impact of the source water characteristics; pH, alkalinity, initial TOC and DOC concentrations; and the hydrophobic/hydrophilic content of the NOM [White *et al.*, 1997]. Previous enhanced coagulation studies were conducted on Nile water at Cairo vicinity in El-Fustat WTP for this reason [Smith & Abdel Maksoud, 2009]. They   concluded that coagulation of Nile water is a challenge due to seasonal variations in alkalinity, and the corresponding reduction in NOM (DBP precursors) can also be difficult due to its relatively low specific ultra-violet absorbance (SUVA) values. Enhanced coagulation is effective for turbidity and NOM reduction during summer, but is not as effective during the remainder of the year due to higher alkalinity that necessitates high amounts of sulfuric acid to reach the optimum pH levels needed. Supplementing enhanced coagulation with powdered activated carbon (PAC) was found to increase the removal efficiency of DBPs precursorswhile maintaining alum and acid dosing at acceptable levels. PAC is also efficient to treat organic matter which is not easily removed by coagulation, but that is reasonably absorbable [Najm *et al.,* 1998].This was consistent with the conclusion of Smith and Abdel Maksoud [2009]. Considerable reduction in THMFP and turbidity was noticed due to supplementing enhanced coagulation with PAC, especially in winter, autumn, and spring when enhanced coagulation alone was less effective.

Although moving chlorination point to be after modified coagulation was believed to result in a substantial decrease in DBPs in finished water, it was not applicable with Nile water. This is because pre-chlorination helps in preventing algal growth in treatment tanks and decreasing water pH before alum injection [Smith & Abdel Maksoud, 2009].

2.4.2 Potassium Permanganate Pretreatment

The application of potassium permanganate ($KMnO_4$) to drinking water is due to its high oxidizing ability. The idea is to oxidize NOM, which in turn reduces the organic content in water before its contact with chlorine. However, using $KMnO_4$ could not replace pre-chlorination due to its questionable ability to prevent algal growth in treatment tanks [Chang, 1982].

Attention should be paid when using $KMnO_4$, especially with water characterized by high manganese levels as Nile water due to the exerted additional demand for the oxidant. Recent

monitoring studies held in Egypt found that manganese levels in Nile water are between 0.04 mg/l to 0.97 mg/l [Shehata and Badr, 2010], frequently above the recommended contaminant level of 0.05 mg/l in the U.S.A. [EPA, 2012]. Also, it is necessary to add a color treatment step to the treatment train due to the tendency of aqueous manganese compounds to tint water with a reddish color [Chang, 1982].

2.4.3. Granular Activated Carbon (GAC)

Problems with taste and odor due to the presence of natural and synthetic organic compounds led to intensified research on finding new and more effective water purification techniques such as the installation of activated carbon filters in drinking water facilities during the late 1980s [Suffet *et al.,* 1978; O'Connor, 2008]. Granular activated carbon (GAC) was reported by the USEPA [2012] to reduce disinfectant demand of water, which in turn increases the disinfectant efficiency.

The extent and rate of adsorption process are typically affected by type of adsorbent, adsorbate, and other solute properties. Due to variability in NOM structure, carbon, and water characteristics, the adsorption mechanism is not readily predictable [Velten *et al.*, 2011]. In general, one would expect hydrophobic organic compounds to readily adsorb unto activated carbon. Unlike coagulation, however, hydrophobic high molecular weight (HMW) compounds (>10,000 Da)are not easily adsorbed on GAC due to what is called 'the size exclusion effect' [Vuorio *et al.,* 1998; Matilainen *et al.,* 2006].It is also found that the transphilic NOM fraction of molecular weight in the size range 500 to 4000 Da has the highest affinity to be adsorbed through GAC mesopores[3] followed by the low molecular weight (LMW) hydrophilic fraction which is less adsorbable but is removed based on size considerations alone [Velten *et al.*, 2011].

In GAC applications as single- or dual-media in water treatment filters, GAC adsorption predictably increases the organic load in the filter media. This load can subsequently be utilized as substrate for microbial regrowth in the filter, which explains the presence of hydrophilic nitrogenous compounds in adsorbers effluents which represents the metabolic products of these organisms [Matilainen *et al.,* 2006]. Thus, activated carbon is then converted to biological activated carbon filter (BAC). It is used efficiently in highly polluted water such as Rhine River to reduce its organic content [Chang, 1982].

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[3]Defined as pores of diameter ranges between 2 to 50 nm

The regeneration process and interval of activated carbon filters is very important because carbon regeneration is an expensive process and impacts the efficiency of subsequent adsorption cycles. Regeneration intervals were found to be between a week and few months when used in municipal water supplies [Chang, 1982]. Electric regeneration was found to affect NOM adsorption efficiency on carbon caps, due to its negatively charged particles [Velten *et al.*, 2011].

To date, most of the available information about NOM adsorption by GAC is collected at bench scale, but records from a few pilot studies exist. For example, a recent pilot study by Velten *et al.* [2011] took place in Zurich, Switzerland in which a GAC cap of depth 22 cm was installed. These caps were set-up to treat lake Zurich water in a down flow, short contact time mode. Influent water characteristics are summarized in Table 2.6.The specific objective of this study was to determine the break through behavior of DOC and NOM fractions of interest; *i.e.* humic substances and LMW fraction. The results, summarized in the breakthrough curves of Figure 2.2, showed that NOM adsorb-ability is inversely proportional with its molecular weight (*i.e.* humics< LMW fraction).

Table 2.6 Influent Water Characteristics of lake Zurich[a]

Parameter	Unit	Value
DOC	mg/l	0.96±0.03
UVA$_{254nm}$	1/m	1.07±0.14
SUVA	l/mg.m	1.12±0.12
pH	--	8.1±0.3

[a][Velten *et al.*, 2011]

As shown in Figure 2.2, the overall DOC is found to decrease considerably in the early stages of the run due to NOM adsorption on the carbon cap. The removal decreases gradually during the first 40 days of operation after which it becomes almost constant. The carbon sites that adsorb humic substances are exhausted after 40 days as inlet and outlet concentrations are essentially the same. These relatively large molecules may also be responsible for the partial clogging of carbon pores, inhibiting the adsorption of other NOM fractions. Unlike humics, LMW organics that likely include even some hydrophilic components exhibit an ongoing

adsorption behavior and apparently control adsorption dynamics in the latter stage of the run, despite being present in much smaller quantity than the humic materials.
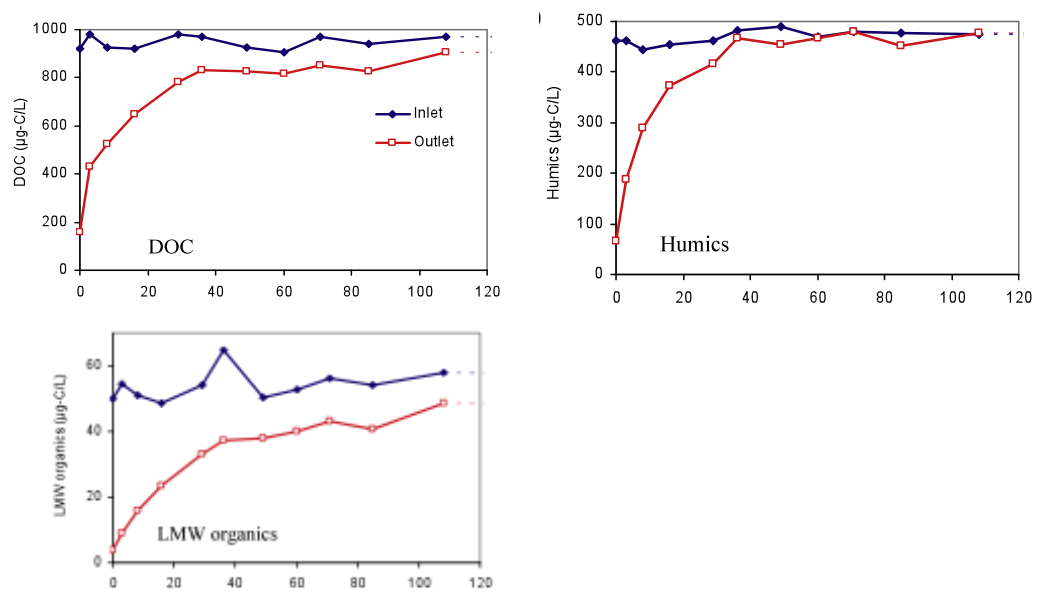

Figure 2.2 Influent (blue) and Effluent (red) DOC, Humics, and LMW Measured for GAC[4]

Chapter Three

Materials and Methods

The experimental portion of this work consisted of four major activities which were: 1) the experimental plan, 2) measurement of water quality parameters, and 3) NOM fractionation, 4) and DBPs analysis including; THMs and HAAs extraction from chlorinated samples and raw water THMFP. This chapter first describes El-Fustat WTP, in which all sampling has taken place, followed by the description of the four elements of the experimental program conducted in this study.

3.1 El-Fustat WTP description

This study is based on in-situ seasonal sampling from El-Fustat WTP. Five stages were highlighted for sample collection. This section will first lay-out the treatment techniques implemented by El-Fustat Water Treatment Plant enhanced with a detailed description for the plant; afterwards the sampling process will be illustrated. Figure 3.1 shows the flow line of treatment works at El-Fustat. Raw water is reach the plant from the Nile via an intake, and then pumped to the treatment plant by a 3 KM long transmission pipeline, 1600 mm diameter ductile cast iron pipe. Raw water samples were extracted from the in-plant raw pipe line, through the raw water tape designated by the plant engineers. El-Fustat has three extension phases; two working phases and one under construction. The diameter of each phase inlet pipe is 800 mm^2.

El-Fustat Water Treatment Plant is considered the second largest water treatment plant (WTP) in Egypt, serving Greater Cairo in which its total capacity reaches 1,081,037 m^3/day [Massoud, 2010]. It consists of two working streams and another one under construction. The average capacity of the sampling stream during the days of sampling for the entire study is $\approx$ 1700 m^3/hr based on El-Fustat records for those days. Chlorine is injected at two points; at the influent raw water named pre-chlorination point, and after the filtration process, referred to as post chlorination. The detailed flow line between the raw water intake and first chlorine injection point is shown in figure 3.1. The detailed cross-section for the sampling point 1 is presented in figure 3.2.

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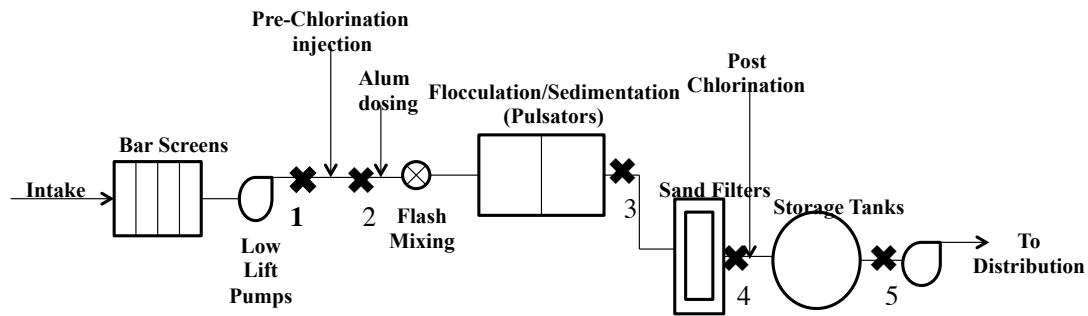
Figure 3.1 Sampling Sites in Water Treatment Flow line at El-Fustat WTP
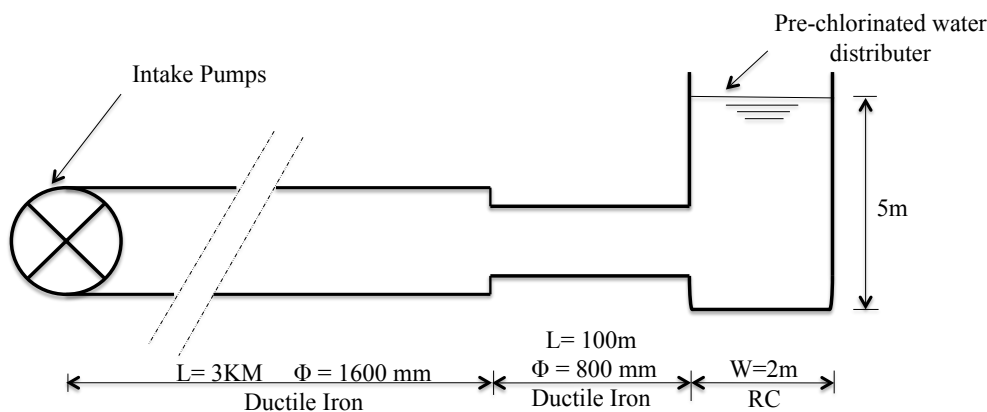
Figure 3.2 Detailing of the Second Sampling Point

Alum is added to the effluent immediately after the pre-chlorination stage. The recorded alum dose during the entire study was 30 mg/l. Flash mixing is done right after the alum feeding. Water is then distributed on six up-flow pulsators where, coagulation occurs, flocculated solids settle down, and clarified water goes up. Clarified water is then distributed to 16 filters. The dimensions of each pulsator and filter is (28x28x5) m, (14x11x3) m respectively. Rapid sand filtration is the used technique in the plant. Filtered water is then sent to the final storage and distribution after passing post chlorination injection.

3.2 The Experimental Plan

As mentioned before, the baseline study at the El-Fustat WTP, five samples were collected for each event: 1) Nile raw water, 2) after pre-chlorination prior to alum addition, 3) clarifier effluent, 4) filter effluent, and 5) final plant effluent. Four seasonal samples were collected for the study between autumn 2011 and summer 2012, following the timetable shown in Table 3.1. This timetable shown is constructed based on previous studies, representing seasonal variations in the Nile water quality [Smith & Alqabany, 2009].

Table 3.1 Sampling timetable

Season	Duration
Autumn	September: November 2011
Spring	March: May 2012
Summer	June: August 2012
Winter	December 2011: February 2012

Each sample consisted of 3 liters at each of the five sampling points. All samples were collected using pre-cleaned 1000, 250, 60, and 40 milliliter (mL) amber glass bottles. Each bottle size is reserved for an assigned analysis due to different preservation conditions of each analysis. Collected samples were preserved below 4°C in an ice chest until transferred to the laboratory. Table 3.2 illustrates the sampling schedule for each of the sampled seasons; (Autunm 2011(November 16th), winter 2012 (February 29th), Spring 2012 (May 5th), and summer 2012 (May 30th). This schedule was repeated during the other three seasons. In all the sampling seasons, two samples were collected from each sampling site as shown in figure 3.1, following each unit operation (treatment unit).

Table 3.2 Field Sample Collection Plan

Season	Autumn (November 16th, 2011)				
Sample designation	Raw Water	Pre-Chlorinated	After Settling	Post Filtration	Effluent
	Raw Water transmission line inside the plant	Pre-chlorination tank. After the addition of chlorine dose, prior to alum addition	Sedimentation tank	Filter bed number 9	Final storage tank at the exit
No of Replicates Collected for each analysis	2	2	2	2	2

The raw water sample was collected from a raw water tap point at the pipe entrance to the plant designated by the plant engineers. Pre-chlorinated samples were taken from the pre-chlorination tank after adding the assigned chlorine dose. Sufficient reaction time for chlorine in water could not be guaranteed at the time of sampling. Samples were taken from approximately mid-depth of the treatment tank by dipping the sampling bottles inside the

treatment tanks, away from the tank walls and at approximately half depth as possible. Total chlorine, free chlorine, and water temperature were measured on site at the time of sampling.

The main water quality parameters of the collected samples of were analyzed in the environmental laboratory of the American University in Cairo. A total of five characteristics were experimentally determined at room temperature; namely, pH, alkalinity, TOC/DOC, UVA_{254}, turbidity, THMs, and HAAs.

3.3 Measurement of Water Quality Parameters

Water quality parameters related to turbidity and DBP formation were evaluated for the source Nile water and treated water samples. This was done in order to track any reduction of NOM and production of DBPs during the treatment cycle and to correlate the produced DBPs with key water quality characteristics. For each water sample, the tests are summarized in Table 3.3 were carried out at room temperature.

3.3.1 General Parameters

Temperature was measured in situ using mercury thermometer. The thermometer was dipped in the treatment tank for two or three minutes until readings are stabilized then recorded. pH was measured for all the raw and treated water samples at room temperature. Pre-calibration for the pH meter is done using two buffered solutions of pH 4 and 7.

Total alkalinity was measured using titration method of sample to the electrochemically-determined endpoint at pH 4.5 using sulfuric acid and methyl orange indicator. Alkalinity was determined by using the following equation

$$\text{Alkalinity} \left(\frac{mg}{l} \text{ as CaCO3} \right) = (A \times N \times 50000) \div \text{ml of sample} \ldots \ldots \ldots (3.1)$$

Where:

A = ml of acid used

N = Normality of acid used

Water turbidity was determined using the multi-function spectrophotometer with a 25 ml unscratched glass cell. Results were obtained in Formazin Turbidity Units(FTU). The spectrophotometer was calibrated before being used by zero turbidity de-ionized (DI) water sample. Samples were agitated before testing to ensure that the sample is representative to the

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actual turbidity of the sample. Four replicates were taken for each sample and the mean value was recorded.

Table 3.3 Preservation and storage of samples[a]

Test	Maximum storage period	Notes
Total and Free Chlorine	On site test	Treated water
Turbidity	Refrigerate in dark for 24 hrs.	Raw and treated water
PH	Kept at 4°C for 0.25 hr.	Raw and treated water
Alkalinity	Kept at 4°C for 24 hrs.	Raw and treated water
TOC/DOC	Kept acidified at 4°C for 7 days	Raw and treated water
UVA$_{254nm}$	Kept at 4°C for 48 hrs.	Raw and treated water
THM	Kept at 4°C for 14 days	Chlorinated water
THMFP	Kept at 4°C for 14 days	Raw Samples only
HAAs	Kept at 4°C for 14 days	Treated water

[a]APHA *et al.*, 1998

3.3.2 Total and Free Chlorine

Total and free chlorine were measured on site using the portable *HachSpectrophotometer* with color DPD reagents. Free and total chlorine levels were measured for all treated water samples. Readings were taken in duplicates for free and total chlorine and the mean value was recorded. Calibration was performed by using a DI water sample prior to the real sample.

3.3.3 Total and Dissolved Organic Carbon

Total organic carbon (TOC) includes particulate and dissolved organic carbon existing in natural waters,and was determined for unfractionated water samples. Dissolved organic carbon (DOC) is defined here,as the organic content after passing water by 0.45 μm filter. It was carried out on fractionated and unfractionated samples to quantify each NOM fraction separately. Although dissolved organic carbon (DOC) is the most commonly used test to quantify NOM, it gives no idea about its chemical and physical structure [Matilainen *et al.*, 2011].

Phoenix 8000 UV- persulfate TOC analyzer was used in this study.Analysis was performed according to the Persulfate-Ultraviolet Oxidation Standard Method 5310C [APHA *et al.*, 1998].In this method, DOC is completely oxidized to CO_2 by a process known as *wet catalytic oxidation* using persulfate salt at high temperature $\cong 600°C$ [Sharp, 2002].Instrument calibration was carried out before running each sample using four standard concentrations of

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2, 3, 4, and 5 ppm of sodium persulfate stock solution.Eight readings were taken for each DOC sample in which the standard deviation was automatically calculated by the operating software. Allowable standard deviation referenced by the manufacturer is ±20%.

3.3.4   Ultra-violet Absorbance

UVA is considered as one of the acceptable spectroscopic techniques usually used in NOM characterization studies and is an indication of the chromophoric dissolved organic matter or (CDOM)[Tietjen *et al.,* 2005]. Itis used as a surrogate measure for the aromacity of NOM, by using the wavelength spectra between 200 nm to 280 nm. This wide spectrum is due to the variety of NOM chemical and physical structure. The wavelength 254 nm used in this study is accepted according to the literature to be the most appropriate to describe the aromatic groups in DOC [Matilainen *et al.*, 2011]. Results obtained by using this visual detection method are not only affected by the concentration of NOM in the sample, but also by NOM aromacity. Consequently, this approach could not be representative to the actual quantity of NOM in the sample [Weishaar *et al.,* 2003].

UVA254nmwas carried out on all the treated and raw water samples; before and after sample fractionation. SUVA value was also useful to be calculated. It can give an indication about the tendency of NOM to be removed by coagulation as it quantifies the ratio of aromatic carbon content in the sample which is more amenable to be removed by coagulation to the total DOC content which constitutes more than half the aquatic NOM [Matelainen et al., 2011].

Shimadzu UV-1650 PC, UV-vis spectrophotometer was used in this study. Calibration was done by measuring the absorbance of an organic free water (OFW) sample using a 5 mm quartz cell. To ensure the precision of readings, twelve replicates are taken for each sample.

3.3.5 Trihalomethane Formation Potential, Trihalomethanes, and Haloacetic Acids

THMFP is a seven-day standard test, which is used to determine the tendency of raw water to react with chlorine to produce trihalomethanes. The experimental procedures followed the standard method 5710B [APHA, 1998].This test was carried out on the raw water samples; *i.e.,* before chlorine addition at the plant.

This was obtained by injecting the buffered 250 ml of sample with 5ml of 5000 mg/l of chlorine dosing solution and then storing it in a temperature-controlled environment. After the seven days period, the incubated sample was extracted for THMs using pentane after which concentrations of chloroform, dichlorobromomethane, chlorodibromomethane and

bromoform were detected using the **Gas Chromatograph**(GC) following Standard Method 6232 B. In this method the extract is injected into a GC equipped with a linearized electron capture detector, used for analysis. Injection and analysis time of the GC for a 2ml extract vial was10 minutes.

Actual THM levels and halo-acetic acid (HAA) levels were detected for partially treated and treated samples, *i.e.* after the addition of chlorine. Extraction is done for THMs and HAAs species using pentane and methyl-butyl ether, respectively. THMs liquid- liquid extraction followed the standard method 6232A while, HAAs were extracted following method number(552.2)set by the EPA [1995].

For all THMFP, THMs, and HAAs analyses, samples were extracted in duplicates with less than 10% variation and the mean values were reported.

3.4 NOM Fractionation

A resin fractionation technique was employed in this study using **synthetic Amberlite resins**; XAD7, XAD4, and IRA958. This is considered the most common NOM fractionation technique used since it was first introduced by the International Humic Substances Society [Chow, 2005]. This technique is able to classify NOM to fulvic acids (FA) of the hydrophilic nature and humic acids (HA) of the hydrophobic nature [Matilainen *et al.*, 2011].

The experiment was carried out on the raw and treated water sample with the detailed plan of action shown in Figure 3.3, in which each fraction is quantified as:

Hydrophobic fraction (HP): XAD7 (influent) – XAD7 (effluent) ……………(3.2)
Transphilic fraction (TRA): XAD7 (effluent) – XAD4 (effluent) …………….(3.3)
Hydrophilic charged fraction (CHA): XAD4 (effluent) – IRA958 (effluent) …(3.4)
Hydrophilic neutral fraction (NEU): IRA958 (effluent) ……………………….(3.5)

3.4.1   Resins Preparation and Handling

There are some pre-packing cleaning steps for the XAD7 and XAD4 resins. They were kept in methanol for 24 hours, followed by diethyl ether for another 24 hours. Resins were then kept in acetonitrile for the last 24 hours. After that resins were kept in methanol until further use [Alqabany, 2006; Abdel Maksoud, 2008].

For the actual fractionation experiments, resins were packed in **Luer-lock liquid chromatography glass columns** of 2 cm diameter, 30 cm length, and 53 mlvolume.

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After packing, resins were prepared for running the sample by:

- Rinsing with 1000 ml DI to remove methanol traces.
- Rinsing with 500 ml (0.1N) NaOH solution to remove any DOC contamination that could reach the sample.
- Rinsing with 500 ml DI water.
- The last two steps were repeated to ensure the removal of any impurities.
- Rinsing with 300 ml (0.1N) H_3PO_4 solution as a final step [Alqabany, 2006; Abdel Maksoud, 2008]

Resins were used twice for which they were cleaned as follows:

- Rinsing with 750 ml (0.1N) NaOH solution followed by 500 ml DI and stored in DI overnight.
- Resins were packed, rinsed with 750 ml (0.1) NaOH solution, 500 ml DI water and then with 300 ml of (0.1N) H_3PO_4 solution [Alqabany, 2006].
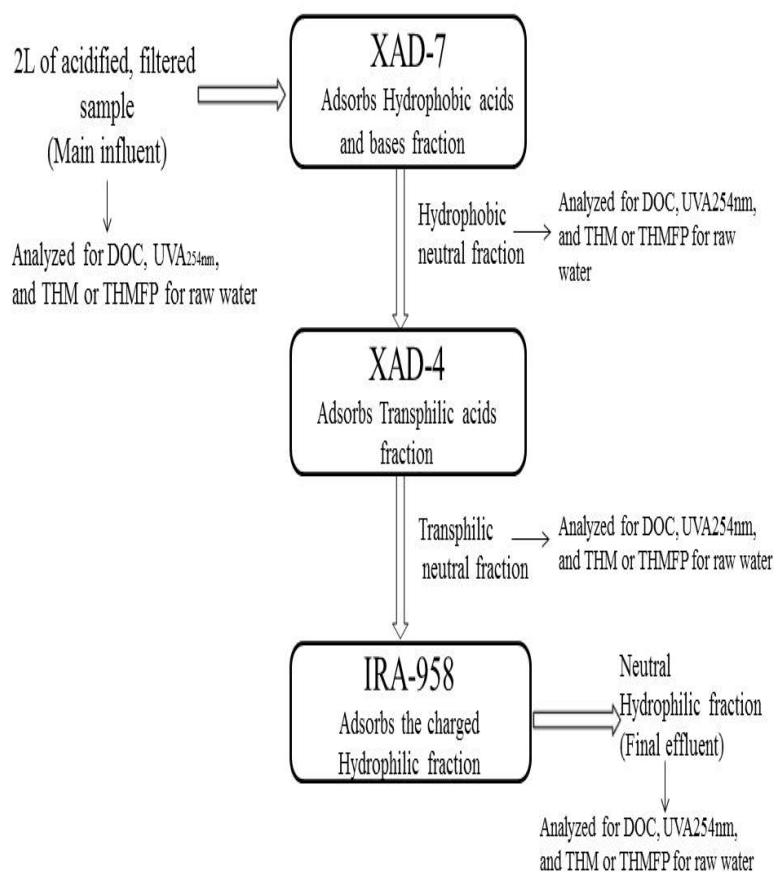
Figure 3.3 Schematic diagram for the fractionation action plan

3.4.2 Sample Preparation and Running

Two liters samples were filtered using 0.45μm cellulose nitrate filter paper [Chow *et al.*, 2005]. H_3PO_4 was used to acidify all water samples to reach the pH 2 for which pH papers were used as a check. Figure 3.4 shows the full setup of the experiment. Adjusting the pumping flow rate is very crucial when using the resin fractionation technique as reasonable time of analysis is required while maintaining a sufficient contact time between samples and the resins. Previous study by Chow [2005] focused on finding the optimum pumping flow rate while decreasing the experiment running time. In this context, two pumping rates were evaluated in which experiment running time was decreased form 12 hours to 6 hours. It was found [Smith & Abdel Maksoud, 2009] that using a flow rate of 11 ml/min in NOM fractionation experiment produced consistency of results. In their study, 10 ml/min was the flow rate used. It was adjusted by carrying out a simple steady state check for all pumps before connecting them to columns.

Figure 3.4 Resin fractionation setup

Chapter 4

Results and Discussion

4.1 Water Quality Analysis

Water quality parameters namely; pH, alkalinity, UVA_{254nm}, TOC and DOC are as important and effective in DBPs production process. The effect o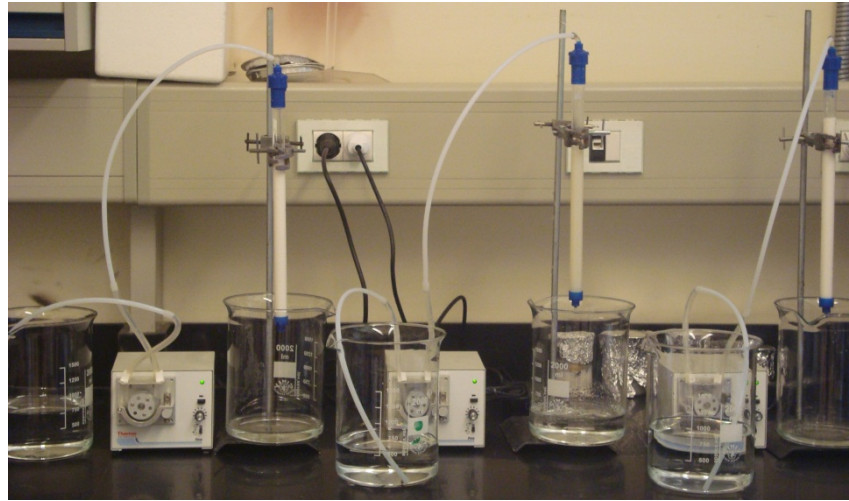f each parameter will be discussed in details later. Table 4.1 illustrates the characteristics of the raw and treated water for the four seasons; namely, Autumn 2011, Winter 2012, Spring 2012 and Summer 2012. The seasonal effect on these characteristics is highlighted in this section. TOC, DOC, and turbidity appear to be the most sensitive parameters in terms of seasonal variations. The monitored least values for TOC, DOC, and turbidity were also in winter. This was accompanied by decreased UVA_{254nm} values, which can explain the decreasing hydrophobic content quantified as DOC. During autumn, summer and spring, TOC, DOC, and turbidity were also relatively of higher levels than in winter. All actual THMs and HAAs concentrations with all the raw data from resin fractionation, UVA_{254nm}, and Gas Chromatography output samples are presented in Appendix I.

4.2 Fate of NOM in EL-Fustat Conventional Water Treatment Plant

The Fustat plant can be classified as a conventional water treatment plant except for its clarifiers, which are of the up-flow pulsator type, which might affect the removal of the various NOM fractions. As noted before, El-Fustat has been pre-chlorinating the raw water in all the measurement events, and has been using a constant alum dose of 30 mg/l. Chlorine doses added ranges from 8.5 mg/l to 5.3 mg/l for pre-chlorination and 0.5 mg/l to 1.3 mg/l for post-chlorination. The removal efficiency of each NOM fractions will be explored individually. This aims to provide a practical insight about persistent fractions, plant operation, and the effectiveness of conventional and advanced treatment processes to remove each fraction, towards allocating the most efficient treatment processes. Tables 4.2, 4.3, and 4.4 show the removal % of each NOM fraction individually.

Table 4.1 Water Quality Parameters for Nile Water in the Entire Study

	Fall				Winter			
	Pre-chlorinated	Settled water	After filtration	Final effluent	Pre-chlorinated	Settled water	After filtration	Final effluent
Total Chlorine (mg/l)	8.6±0.0	1.8±0.1	2.5±0.1	1.6±0.1	7.5±0.0	5±0.0	4.5±0.0	2.8±0.0
Free Chlorine (mg/l)	5.5±0.1	1.7±0.0	2.3±0.0	1.5±0.0	6.4±0.0	3.8±0.0	3.5±0.0	2.4±0.0
Temperature (°C)		25				20		
pH	7.70±	7.00±0.1	7.03±0.0	7.20±0.1	7.63±0.0	7.01±0.0	7.07±0.0	7.39±0.0
Alkalinity (mg/l as $CaCO_3$)	130±1	110±1	112±2	120±1	110±0	100±0	104±0	107±0
TOC (mg/l)	4.62±0.2	3.72±0.1	3.47±0	3.82±0	4.07±0	3.82±0	2.73±0	2.52±0
DOC (mg/l)	4.21±0.1	3.27±0.2	3.24±0.0	3.65±0.1	1.65±0	1±0	1.8±0	1.16±0
UVA$_{254nm}$	0.118±0.00	0.052±0.00	0.046±0.00	0.075±0.00	0.06±0	0.038±0	0.04±0	0.03±0
Turbidity (FTU)	18±1	3±1	1±0	1±0	7±0	1±0	0±0	0±0

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	Spring				Summer			
	Pre-chlorinated	Settled water	After filters	Final effluent	Pre-chlorinated	Settled water	After filtration	Final effluent
Total Chlorine (mg/l)	6.5±0.0	2.6±0.1	2.6±0	3.1±0.1	5.3±0.0	2.7±0.0	1.9±0.0	3.2±0.0
Free Chlorine (mg/l)	6.1±0.2	2.3±0.1	1.8±0	2.4±0.2	4.6±0.1	2.3±0.0	1.8±0.1	2.5±0.0
Temperature (°C)		30				37		
pH	7.73±0.1	7.0±0.0	7.12±0.1	7.88±0.1	6.33±0.2	6.88±0.1	6.87±0.0	6.82±0.0
Alkalinity (mg/l as $CaCO_3$)	116±1	106±2	100±1	100±2	126±1	114±1	104±0	104±0
TOC (mg/l)	4.53±0.1	3.15±0.0	3.14±0.0	2.88±0.1	4.47±0.0	3.70±0.0	3.76±0.0	3.24±0.0
DOC (mg/l)	4.2±0.2	1.74±0.0	1.33±0.0	1.28±0.1	1.54±0.0	1.12±0.0	1.50±0.0	1.39±0.0
UVA$_{254nm}$	0.21±0.03	0.12±0.04	0.12±0.02	0.09±0	0.075±0.002	0.04±0.002	0.028±0.001	0.025±0.001
Turbidity (FTU)	13±1	2±0	2±0	1±0	8±1	3±1	2±0	2±0

As shown in Table 4.1, different removal efficiencies had been recorded for DOC in various seasons; 13%, 30%, 70%, 15%, for autumn, winter, spring and summer, respectively. As mentioned above, spring possessed the highest DOC removal efficiency, while autumn had recorded the least DOC removal. On the other hand, the three NOM fractions namely; hydrophobic, transphilic, and hydrophilic, may be removed by various degrees due to the main treatment units (unit processes) at El-Fustat treatment plant; pre-chlorination, clarification, filtration, and post chlorination). This approach is better than assessing the gross removal efficiency of the NOM (quantified as total DOC or TOC), due to the likely different effect each unit process may have on each individual fraction.

4.2.1 Removal of Hydrophobic (HPO) Fraction

Figure 4.1 shows the concentration of the Hydrophobic (HPO) fraction quantified as DOC (mg/l), immediately following the four main unit treatments (pre-chlorination, clarification, filtration and post chlorination) for the four seasonal measurement program (Autumn, Winter, Spring, and Summer). During spring, the HPO concentration is much higher (nearly 1 mg/l) at the inlet to the treatment stream than in the other three seasons (0.5-0.6 mg/l). The HPO fraction generally decreased, in nearly the four seasons, due to coagulation and clarification; although not with the same degree of removal.

Table 4.2 presents the percent removal of the HPO fraction as a result of each treatment unit. The clarifiers removed 56% of the HPO fraction in winter, and 39 % in autumn, and to a much less degree in summer (15 %) and spring (13 %). The large removal ratios observed in the autumn and winter seasons seem to be due to the colloidal structure of the HPO fraction [Sharp, 2002; Bose and Reckhow, 2007] and the high capacity of alum to form flocs of Hydrophobic NOM because of its high charge density as noted by Qualls *et al*. [2002]. A possible explanation for the low removal ratio for spring may be attributed to the use of a constant dose of Alum in the four seasons although the HP concentration is much higher in the spring and the alkalinity may vary. Smith and Abdel Maksoud [2009] had noted that Nile water is characterized by its high alkalinity (121±10) mg/l as $CaCO_3$, which may hinder its ability to be coagulated using the baseline dose (30 mg/l Alum), please refer to section 4.1.1.

Table 4.2 shows that filtration decreased the HPO fraction concentration in two seasons (spring and autumn), but nearly had no effect in the other two (summer and winter). It appears that sand filtration may have variable effect on removing the HPO fraction depending on the amount of flocs escaping the clarifier, and the actual pore size between the sand grains. The

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pore sizes can change following the backwash and prior to the next backwash. It is worth noting that, floating flocs were observed inside the clarifier and in clarified water samples from the same clarifier, which could explain the additional removal of the hydrophobic content by sand filtration in spring and summer.

Figure 4.1 and Table 4.2 show that post chlorination and final storage generally do not reduce the HP fraction concentration. The total DOC of finished water consisted of 65% of hydrophobic compounds, of the total NOM level in the finished water. The total HP removal in finished water, ranges from 34% in summer to 66% in autumn.
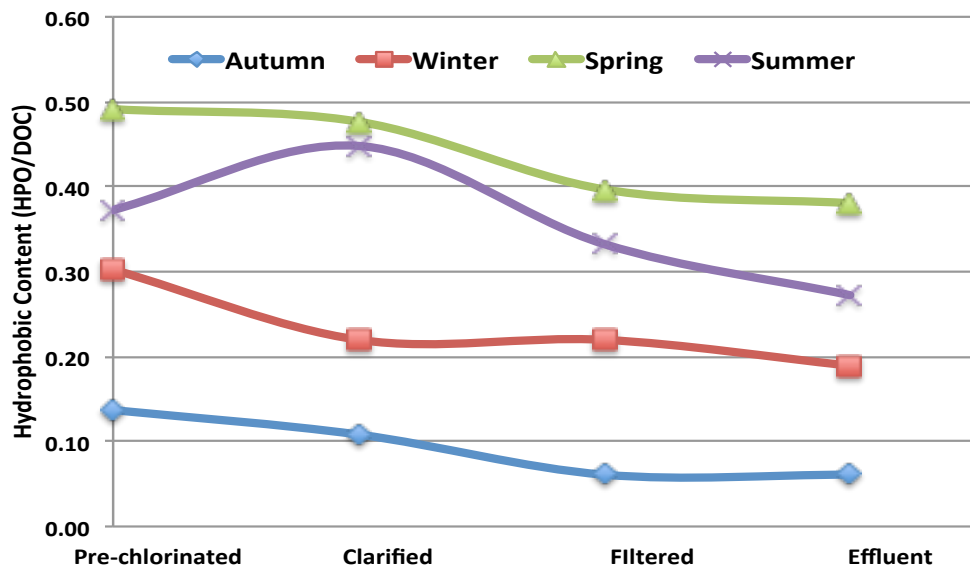
Figure 4.1 Removal Scheme of Hydrophobic Compounds

Table 4.2 Percent removal of Hydrophobic fraction (%)[*]

	Hydrophobic			
	After Clarification	Post Filtration	After post-chlorination	Overall HPO removal
Autumn	39	44	0	66
Winter	56	0	0	56
Spring	15	37	7	50
Summer	13	0	24	34

* % calculated based on the previous unit process

4.2.2 Removal of the Transphilic (TRA) Fraction

Figure 4.2 shows the concentration of the transphilic fraction, quantified as DOC (mg/l) immediately following the four main unit treatments (pre-chorination, clarification, filtration and post chlorination) for the four seasonal measurement plan (Autumn, Winter, Spring, and summer).

The transphilic fraction concentration is relatively high in the raw water in spring and autumn (0.5 mg/l) than the winter (0.37 mg/l), and summer (0.25 mg/l). Figure 4.2 shows that the concentration of the transphilic fraction deceases only due to coagulation and clarification. Filtration and post chlorination/storage do not nearly have a noticeable effect on its concentration. Table 4.3 shows the removal percentages (%) of the transphilic fraction as a result of each treatment unit. The removal percentages reached 51% in the summer, and 32 % in winter. Less removal percentages were observed in both autumn 31% and spring 10%.

Similar to the hydrophobic fraction, the transphilic NOM can form flocs in the presence of alum (Qualls *et al.*, 2002) and be partially removed in the clarifiers.

In spring, coagulation/sedimentation process reduced the transphilic fraction by 10%. Filtration further removed the transphilic fraction slightly by $\cong 1.2\%$. This observed trends of transphilic reduction is likely due to the continuing oxidation effect of chlorine from pre-chlorination step [Marahba *et al.*, 2008]. Similar reduction 2 % seems to have taken place in the summer.
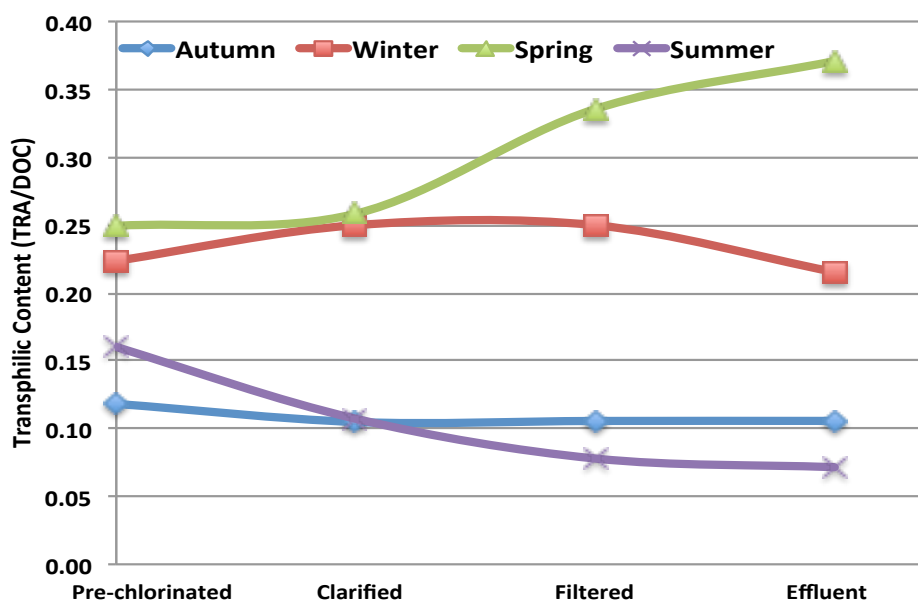

Figure 4.2 Removal Scheme of Transphilic Compounds

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Table 4.3 Percent removal of Transphilic fraction (%)

	Transphilic			
	After Clarification	Post Filtration	After post-chlorination	Overall TRA removal
Autumn	31	0	0	31
Winter	32	0	0	32
Spring	10	1.2	0	5
Summer	51	2	15	59

* % calculated based on the previous unit process

4.2.3 Removal of Hydrophilic Fraction

Figure 4.3 shows the concentration of the hydrophilic fraction quantified as DOC (mg/l), immediately following the four main unit treatments (pre-chlorination, clarification, filtration and post chlorination) for the four seasonal measurement programs (Autumn, Winter, Spring, and summer). The hydrophilic fraction concentration is much higher in the raw water in autumn (3 mg/l) as compared to summer (0.8 mg/l), and winter (0.6 mg/l). Conversely to the hydrophobic fraction, spring had the lowest Hydrophilic fraction of 0.4 mg/l. This reflects the variation of NOM fractions in the Nile among the various seasons.

As seen from Figure 4.3, the degree of removal of the Hydrophilic fraction is rather limited due to any of the plant treatment units. This is the general trend for all the seasons, except for the autumn and summer where clarification decreased the hydrophilic concentration modestly.

In the autumn and summer, the coagulation and clarification process decreased the hydrophilic fraction by 12 to 15 % based on the pre-chlorinated DOC concentrations. The removal efficiency of hydrophilic fraction is quite less than both hydrophobic and transphilic fractions. This is believed to be due to the negligible charge density of hydrophilic fraction, which affect its ability to form large and settle-able flocs during coagulation and sedimentation [Swietlik *et al*., 2004].
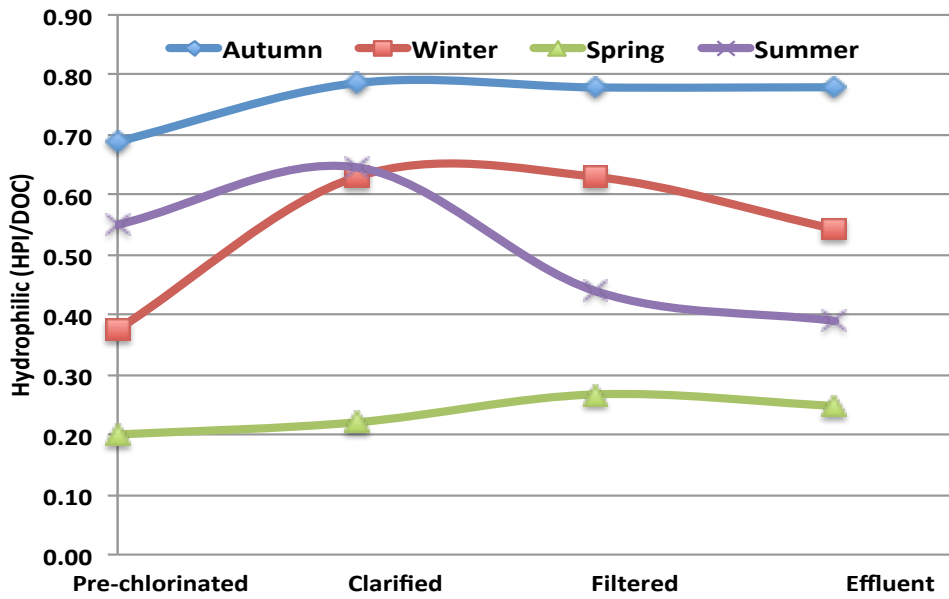
Figure 4.3 Removal Scheme of Hydrophilic Compounds

Table 4.4 Percent removal of Hydrophilic Fraction (%)

	Hydrophilic			
	After Clarification	Post Filtration	After post-chlorination	Overall HPI Removal
Autumn	12	2	0	13
Winter	0	0	0	0
Spring	4	8	10	21
Summer	15	8	18	36

* % Calculated based on the previous unit process

Table 4.4 shows that filtration generally has a limited removal efficiency of the hydrophilic fraction ranging from 0 in winter, 2 % in autumn, 8 % in both spring and summer. The observed limited decrease in the hydrophilic fraction concentration was also likely due to the continuing oxidation effect of chlorine [Marahba *et al.,* 2008]. However, the relatively high decrease in hydrophilic fraction in summer might be attributed to the high chlorination dose added to the treatment line, compared to other seasons.

4.3 Contribution of NOM fractions to THMs formation

In Figure 4.4, the THMs levels at El-Fustat final effluent compared with the Egyptian and USEPA limits are presented. As shown, results of THMs concentrations recorded for the entire study, showed to be complying to the Egyptian standards but not all of them comply to

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the USEPA guidelines. However, treatment facilities should still work on decreasing THMs as possible to guarantee safe drinking water to reach the consumers.
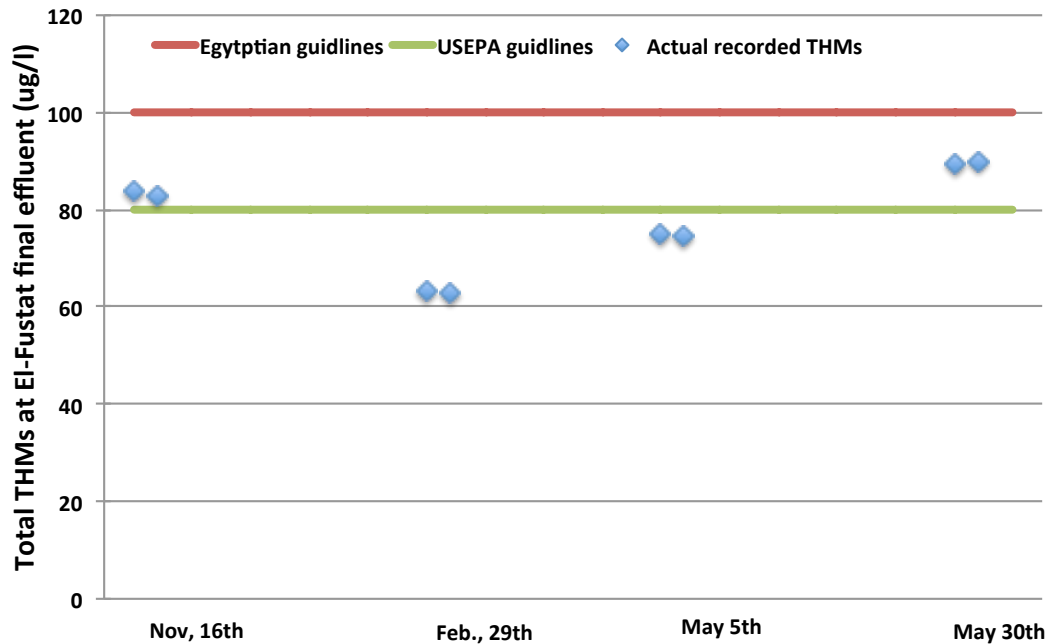
Figure 4.4 Actual total THMs w.r.t. USEPA and Egyptian guidelines

Towards finding the most reactive form of NOM to produce THMs, Figure 4.5 shows the relation between TOC & DOC with the produced THMs (before temperature correction). As shown, and unlike TOC, DOC has a strong relation with the produced THM.

Figure 4.5 Relation between DOC, TOC and produced THM

In the same context, finding a relationship between each individual NOM fraction quantified, as DOC is now important. Previous literature on THMs stoichiometry by [Flegal and Schroeder, 1979], elaborated on THM formation reaction. They had proven the link between

THM yield and other factors; organic precursors, residual chlorine concentrations, water temperature, and reaction time. Analyzing the meas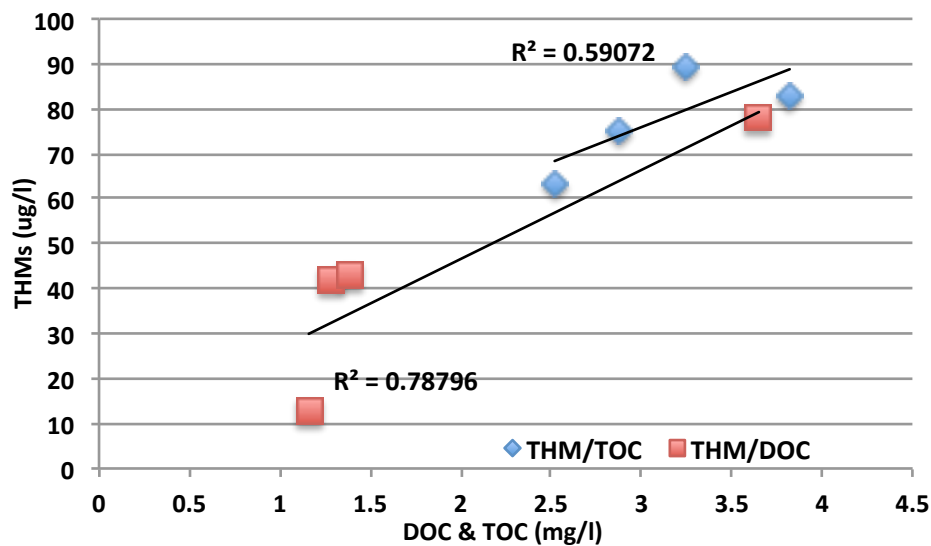ured data for the entire study; THMs, and HAAs concentrations, it was evident that temperature, DOC and chlorine are the main drivers of THMs formation. Figure 4.6 shows the importance of temperature on the THMs formation. Since the THMs samples were collected and analyzed on seasonal basis, in which water temperature varies in a wide range, THMs values were corrected for the effect of temperature on the reaction. Therefore, blocking the impact of temperature when studying the impact of DOC on THMs formation is possible.
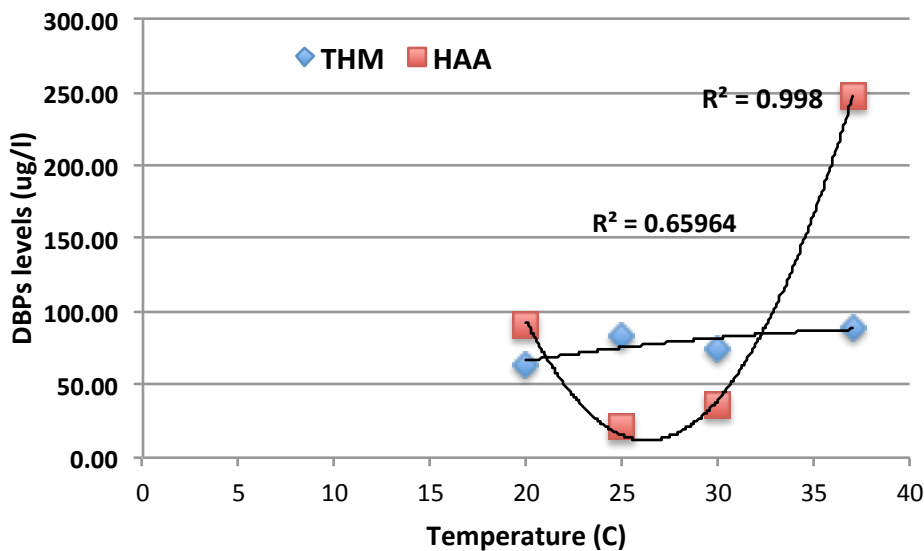
Figure**4.6** Influence of Temperature on formation of DBPs

Temperature correction process was conducted according to Arhaneous relationship for temperature correction, which suggests changes to happen for the rate of reaction according to variation of temperature. As shown, equation 4.1 explains the change in rate of reaction coefficient value based on a reference temperature 25°C. It is worth to mention that the validity of Arhaneous relationship extends to the majority of biological environmental processes namely; Biochemical Oxygen demand (BOD), Dissolved Oxygen modeling (DO), etc. [Cox, 2003; Flegal and Schroeder, 1979]. Based on previous studies on temperature dependent processes, the validity of the correction technique was validated. The correction was according to Equation 4.2 [Manivanan *et al.,* 2013; Cox, 2003; Flegal and Schroeder, 1979].

$$THM_T = THM_{@25°C} * \theta^{T-25} \ldots\ldots\ldots (4.1)$$

Accordingly, the results of the sampling program were used to relate the raw NOM with its nominated fractions to the actual temperature adjusted THMs formed in the final effluent of the plant. Figures 4.7a, 4.7b, and 4.7c, show the relation between each NOM fraction; hydrophobic, transphilic, and hydrophilic, and produced THMs at the end of the treatment stream.

Statistically, box and whisker graphical representation is useful summarizing NOM data in for the four seasonal values; 25th percentile, 75th percentile, median value, maximum and minimum values of a sample. Accordingly, box plot can indicate which of the observations is considered as an outlier. Grubbs [1969] defined outliers as the distant observation from the rest of data. As shown in figure 4.7, NOM fractions are represented as three explicit numerical data sets. The entire hydrophobic fraction population falls between the upper and lower quarters except only one value; spring pre-chlorinated effluent. Also, one value of the transphilic population is considered an outlier i.e., fall filtered sample. Outliers may occur by chance in any sample distribution however, they occur likely due to measurement errors.
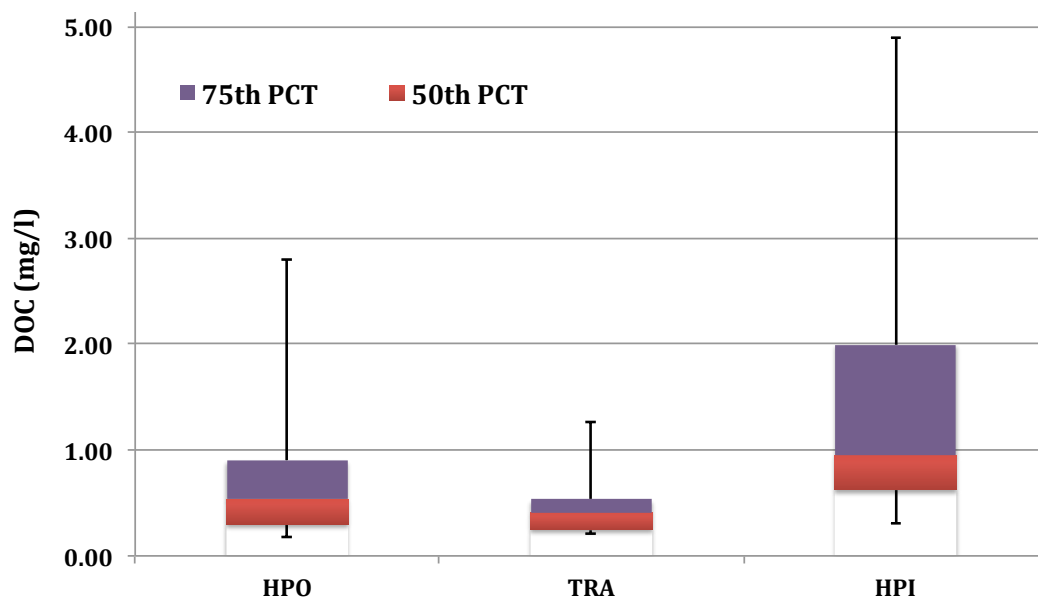
Figure 4.7 Box and Whisker Plot for NOM Values

Figure 4.8a, shows the relatively low correlation (R^2=0.01) between hydrophobic content and the produced THMs at the plant effluent. Previous bench scale studies had indicated that the transphilic, hydrophobic, and hydrophilic are the major contributors for the formation of THMs by 38%, 31% and 31%, respectively [Smith and Alqabany, 2009; Smith and Abdel Maksoud, 2009]. The low correlation observed for the Fustat water treatment plant may be due to the early removal of the hydrophobic fraction in the clarifier.

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Figures 4.8c and 4.8b show that transphilic and hydrophilic fractions have a stronger correlation between their concentration in the plant influent and the formed THMs formed in the plant final effluent. This is found to be in agreement with the previously referred to bench studies. The observation regarding the hydrophobic fraction and its relation with effluent THMs concentrations supports the suggestion of enhancing coagulation to reduce the formation of THMs. However, the earlier sections; 4.2.1, 4.2.2, and 4.2.3, has indicated the limited removal of both the hydrophilic and transphilic fractions under the baseline coagulation conditions which is the same behavior of these fraction at the enhanced coagulation conditions.
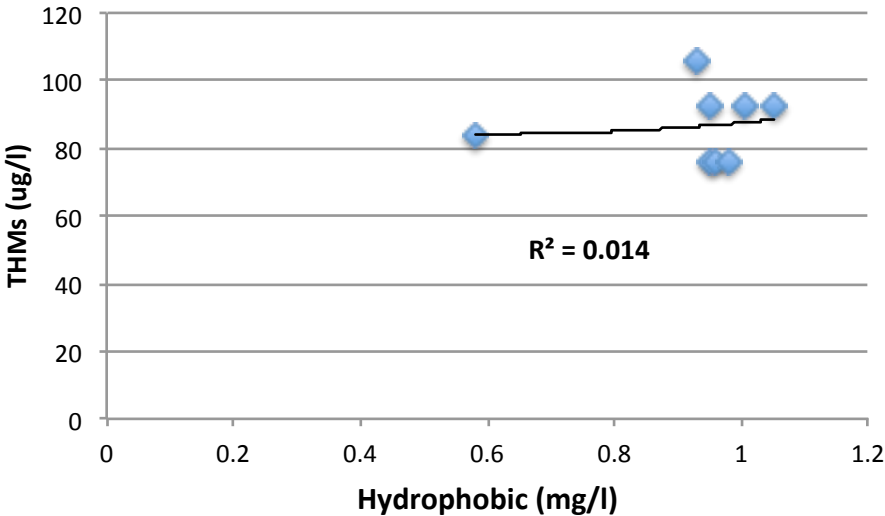

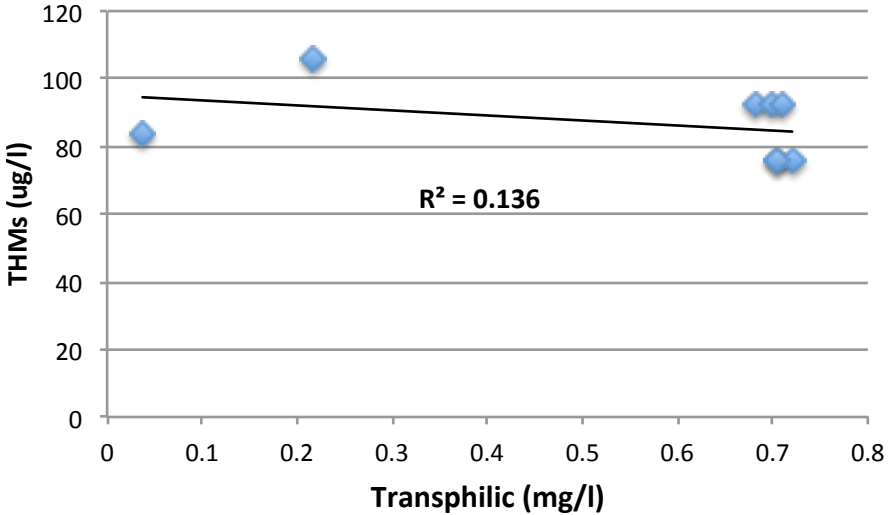**Figure 4.8a** Concentration of the hydrophobic fraction vs THM formed

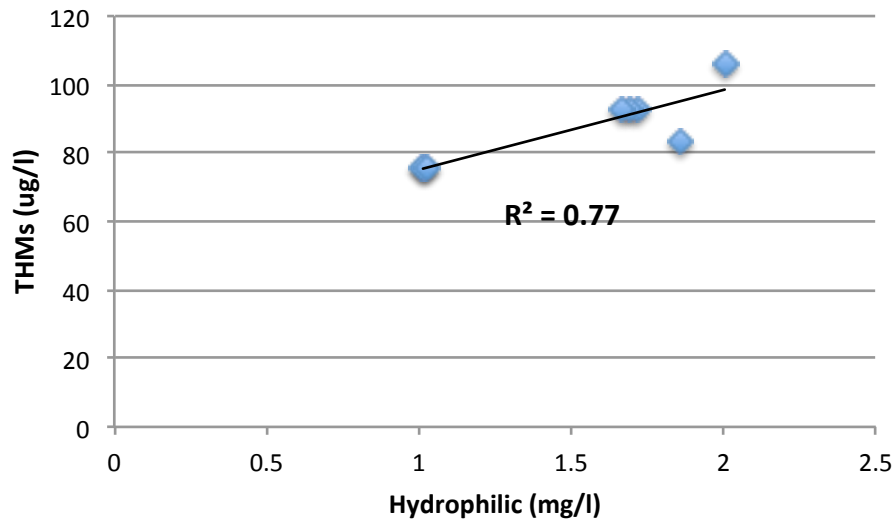**Figure 4.**8b Transphilic fraction concentration vs. THMs

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Figure 4.8C Transphilic fraction concentration vs. THMs

4.4 Contribution of Chlorination to THMs formation in a conventional Treatment line

Not only precursors are the main contributors to form THMs, but chlorination is one of the key parameters to produce high DBPs levels in a plant final effluent. So, reconsidering chlorine doses added to water through the treatment line should be helpful in decreasing the risky DBP levels. This is found to be in acceptance with Hua and Reckhow [2008] who proved that different DBP classes show distinct responses to changes in reaction time, pH, oxidant dose, and changes in temperature.

Many studies tried to compare the chlorine consumption and DBPs formation with model natural organic matter (NOM) in the pH range 7-9 [Bougeard *et al.*, 2010; Chen *et al.*, 2008; Lee *et al.*, 2007; swietlik *et al.*, 2004]. They had found that, the NOM fraction mainly affects the rate of chlorine consumption reaction Vs. THMs formation, and they could be classified from fast to slowly reacting organic matters [Galard and Gunten, 2002]. This is consistent with Hong et al [2009] who found that the formation of THMs and HAAs significantly increased with long reaction time, **high chlorine doses** and the increased pH levels.

Figure 4.9 and figure 4.10 represent the relation between chlorine doses added during the treatment line and the final THM formed at the end of treatment. Chlorine reaction rates werecalculated by plotting the average chlorine doses vs. time, and fitting the data with a first-order reaction plot. The slope of the curve depicts the reaction rate. The rate of reactions were

calculated for the four seasons and plotted vs. average chlorine doses and actual THMs concentrations in figures 4.9 and 4.10, respectively.

Reaction rates are calculated for the present analysis by plotting the variation in total chlorine concentration with time. Then plotting the resulting rates with the total chlorine doses added through the treatment line to result in figure 4.9 the correlation coefficient between the total chlorine dose and the rate of chlorine hydrolysis ($R^2=0.76$) shows the strong relation between pre-chlorination dosages added to water and the rate of hydrolysis. This could prove the high potential of THMs formation with high chlorine doses added.

The chart shows data points with the fitted equation:

$$y = 0.0017e^{0.2014x}$$
$$R^2 = 0.76585$$

X-axis: **Average chlorine dose (mg/l)**
Y-axis: **Rate of reaction**
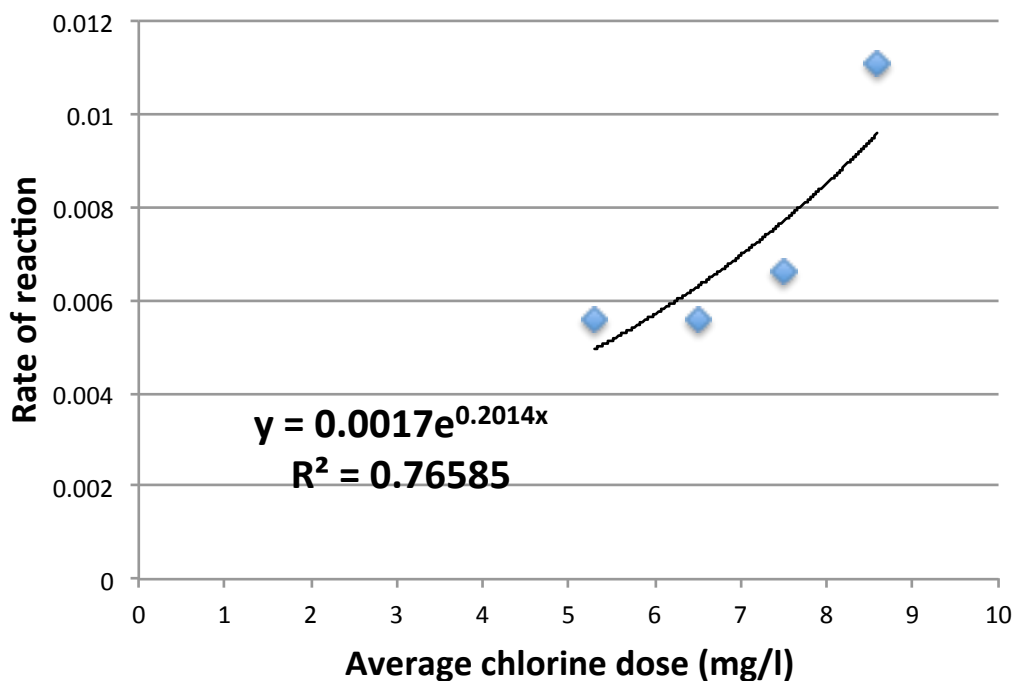
Figure 4.9 Rate of Chlorine Reaction with Average dose

In the same context, figure 4.10 represents the relation between the rate of chlorine reaction and THM concentrations formed through the whole treatment line. The plot shows the strong relation between the chlorine doses added and the produced THM levels at the end of treatment ($R^2 = 0.61$). Accordingly, water treatment facilities should take care of the chlorine dose added to water prior to removing a considerable amount of DBP precursors.
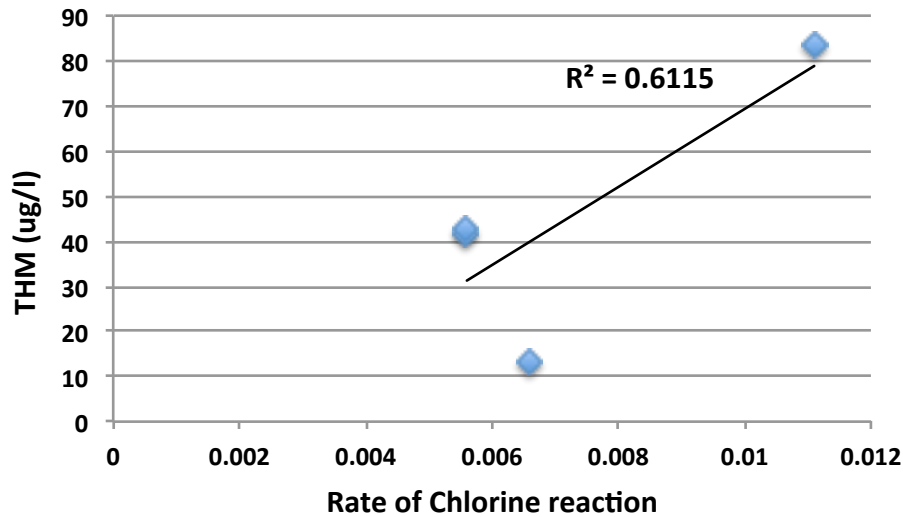
Figure 4.10 THM concentrations with rate of chlorine reaction

Typically, the main concern of water treatment facilities is to achieve a safe drinking water to consumers with the most feasible treatment techniques. Due to the fact that THMs formation in drinking water is one of the major challenges facing treatment facilities, facilities should target the most effective factor, which is responsible for the high THM levels towards optimizing the water treatment process. Table 4.5 shows the effect of some nominated factors on the THM formation process namely; total and free chlorine levels, total DOC, and individual NOM fractions. THM/THMFP ratios are calculated using THMs values adjusted to a temperature of 25 °C, in order to provide similar comparison base between THMs and THMFP values extracted at 25 °C (for more details on THMFP experimental procedure, please refer to section 3.3.5). The correlation coefficients presented below, are calculated when plotting the THM/THMFP ratios with the factors mentioned above. Total and free chlorine values used are the recorded values during the sampling process. The seasonal effect on THM/THMFP ratios is reflected here in the total and free chlorine concentrations used, and the share of every NOM fraction; HPO, TRA, and HPI in the total DOC.

Table 4.5 Correlation between NOM fractions and Chlorine doses with THM/THMFP (as R^2)

	Total Cl_2 (mg/l)	Free Cl_2 (mg/l)	Total DOC (mg/l)	HPO (mg/l)	TRA (mg/l)	HPI (mg/l)
THM/THMFP	0.39	0.49	0.14	0.02	0.03	0.14

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As shown in the table above, all the nominated factors share a responsibility for the high THM/THMFP ratio. However, the most significant correlation is found to be between the free chlorine concentration and THM/THMFP ratio ($R^2 = 0.49$). Also, the equivalence between R^2 of total DOC and HPI content, emphasizes the importance of HPI when forming THMs, which is consistent with previous findings in Section 4.2.3., and 4.3. On the other hand, these results suggest the relatively high influence of free chlorine on the formation of THMs in the distribution pipelines, and increase the possibility of the formation of extra THMs to reach tapes at un-safe limits. Based on the THMFP values in various seasons; 335 µg/l,165.6 µg/l 216 µg/l, and 358 µg/l for autumn, winter, spring and summer, respectively.

4.5 Contribution of NOM fractions to HAAs formation

In Figure 4.12, the HAAs levels at the effluent from El-Fustat as compared to the Egyptian and USEPA limits are presented. It is now obvious that the majority of concentrations from HAAs samples, were violating the both the Egyptian and USEPA standards. This is considered an alarm to pay the attention of treatment facilities on finding ways to reduce these levels.
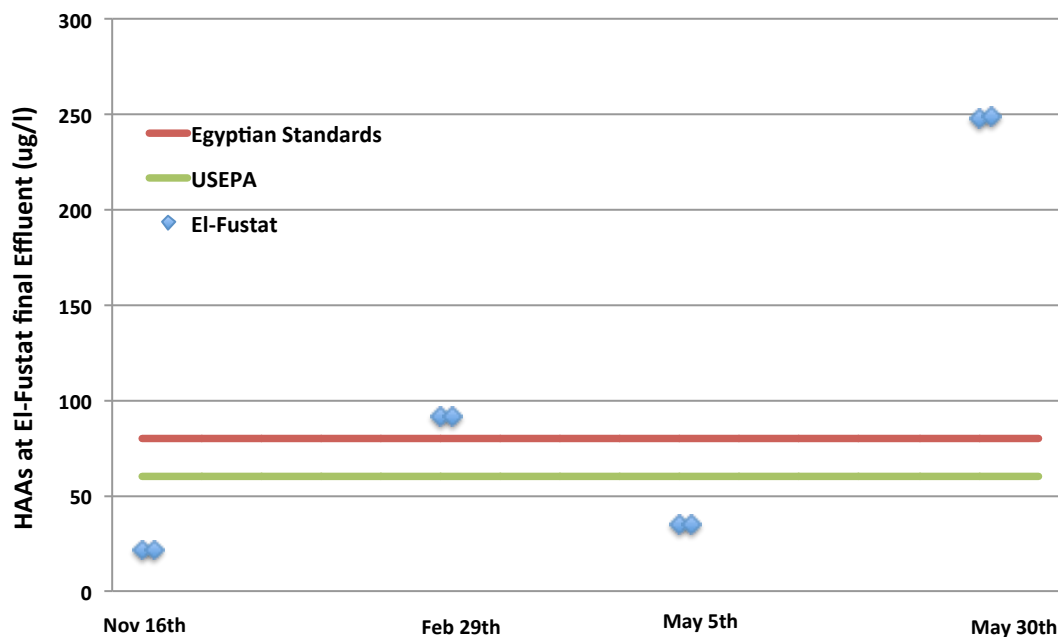
Figure 4.12 Actual HAAs w.r.t. USEPA and Egyptian guidelines

As from the regulated DBPs by the USEPA are the HAA_5. They consist of five individual compounds, namely; monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), and dibromoacetic acid (DBAA). The allowable maximum contaminant level (MCL) for HAAs in drinking water accepted by the latest Egyptian ministry of health guidelines is 80 µg/l. HAAs happen when

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naturally occurring aquatic organic matter react with the disinfectant added; chlorine. Samples collected from El-Fustat water treatment plant verified high HAAs levels getting out of the treatment plant due to pre-chlorination and post chlorination step. Figures 4.13a, 4.13b, 4.13c represent the contribution of each individual NOM fraction in the total HAAs produced during the treatment train. These results were obtained by processing the R^2 values displayed on each plot.

As shown, the transphilic and hydrophilic content respectively occupy the major share of HAAs produced due to chlorine addition in the treatment train at El-Fustat, while the hydrophobic fraction occupies the least share. This could be attributed to the high potential of hydrophilic and transphilic fraction to form HAAs than the hydrophobic one. Referring to the findings illustrated in section 4.4, the transphilic and hydrophilic compounds are now the most dominant fraction with the highest potential to form HAAs. Accordingly, targeting these compounds in treatment facilities will decrease the concentrations of both HAAs and THMs.

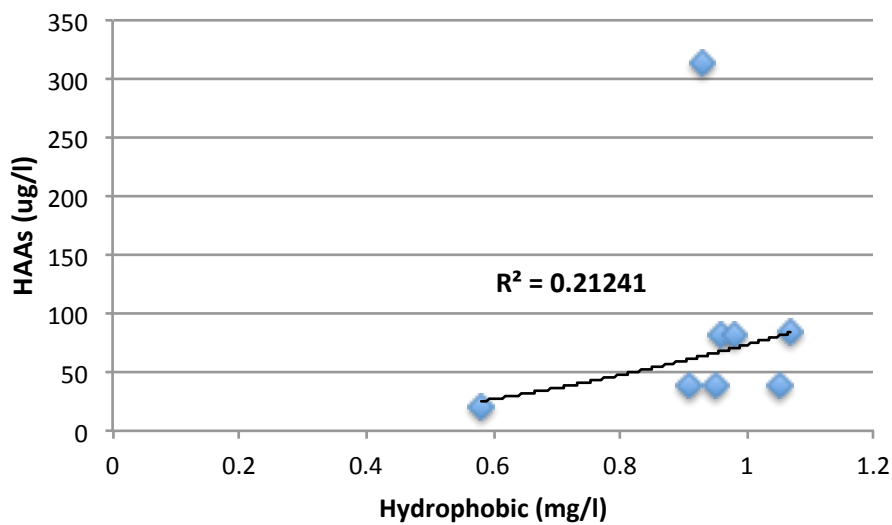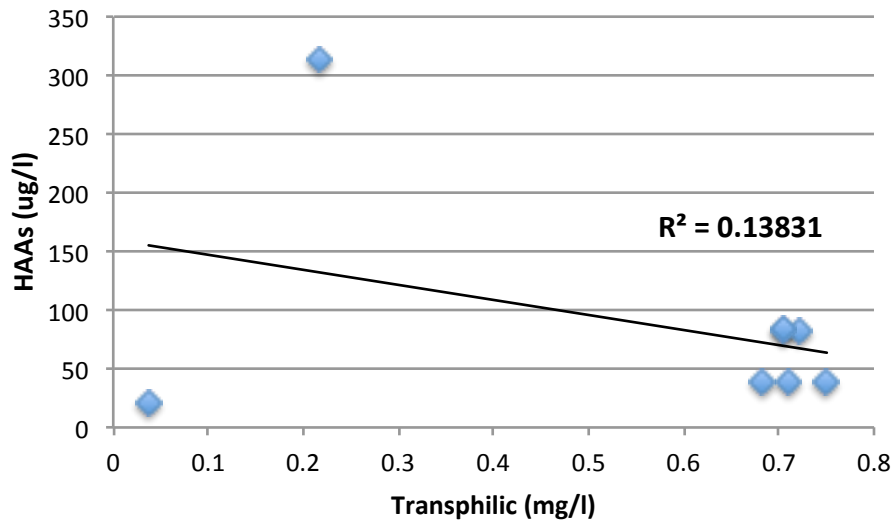**Figure 4.13a** The contribution of HPO fractions to form HAAs

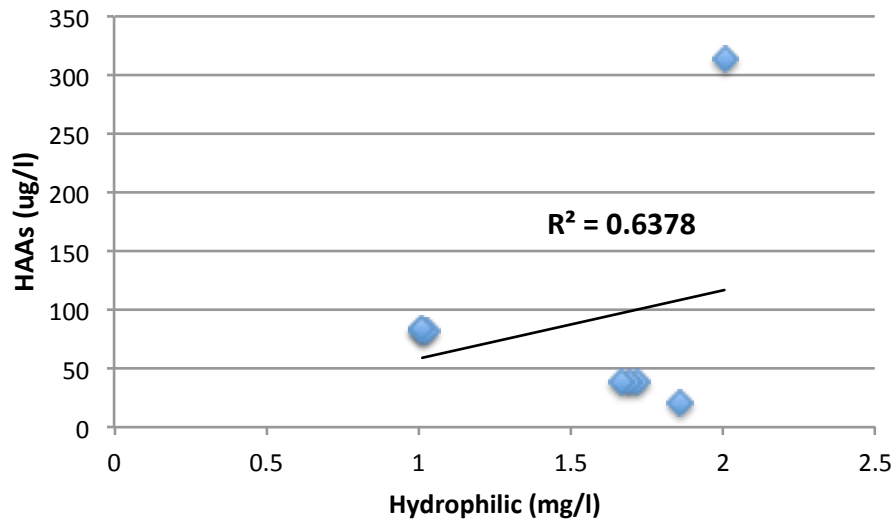**Figure 4.13b** The contribution of TRA fractions to form HAAs

Figure 4.13C The contribution of HPI fractions to form HAAs

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Chapter Five

Conclusions and Recommendations

Recorded high levels of DBPs in Cairo residential water supply during the past decade were the motivation to study the process of DBP formation/DBPs precursors removal at the treatment plant stage. An in-depth understanding for NOM removal and DBP formation in an existing conventional water treatment facility will provide a baseline for the development of optimum strategies for cost-effective reduction of potentially harmful drinking water compounds; namely THMs, and HAAs. The study was conducted at the El-Fustat WTP in Cairo over the duration of one year to observe seasonal variations in NOM as DBPs precursors. NOM was quantified by classical surrogate parameters such as TOC, DOC, and UVA_{254}; and characterized more precisely according to its hydrophobic/hydrophilic properties using rapid resin fractionation technique. Raw water samples were tested for THM formation potential. Removal profiles of individual NOM fractionswere drawn, and simple regression analyses was calculated to discuss the contribution of NOM in DBPs formation.

The small field data set collected from one WTP (El-Fustat WTP) limit the validity of the results to the case study. Based on the limited data set obtained, the following conclusions can be made:

5.1 Conclusions

- The amount and character of NOM varies seasonally in the Nile water. Also, each individual fraction sustained seasonal fluctuations in their removal efficiency. The Hydrophobic fraction had possessed variable removal percentages in which winter had possessed the highest removal; (56%) and the least was during summer; (34%). Transphilic fraction was efficiently removed during summer and less removed during spring. Hydrophilic fraction has experienced the least percentage removal (36% in Summer and 13% in Autumn).

- The coagulation/flocculation and sedimentation processes were the most efficient to decrease hydrophobic, transphilic and hydrophilic fractions by maximum of 56%, 51%, and 15%, respectively, followed by sand filtration which was found to decrease the same individual fractions by 44%, 2%, and 8%, respectively based on the maximum removal values obtained. Pre-chlorination and post chlorination had no significant role on removing NOM fractions.

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- The THMs values recorded for the entire study were complying with the Egyptian guidelines, it is not guaranteed that tap concentrations will comply to the guidelines limits. This is because THM/THMFP does not exceed 39%, leaving room for 61% to be reacted in pipe lines and storage tanks until it reaches the customers taps.
- HAAs concentrations at the plant effluent were much higher than the regulating limits, which is considered as an alarm to treatment facilities to reduce HAAs values.
- Hydrophobic and transphilic organic content did not show a significant contribution in the THMs and HAAs produced at the final plant effluent.
- The hydrophilic fraction was the main contributor to THMs and HAAs formed at El-Fustat WTP.
- Although, hydrophilic fraction is the main contributor to THMs and HAAs formation in El-Fustat WTP; coagulation/flocculation and sedimentation could not successfully remove it during treatment. Accordingly, the processes of coagulation/flocculation/sedimentation/filtration are not guaranteed to be useful in decreasing the DBPs levels.
- The aeration taking place by outlet weirs is likely responsible for escaping the volatile THMs, resulting in decreasing their levels post filtration.
- Average chlorine doses added in the treatment line is a driving factor affecting the amount of DBPs; THMs and HAAs produced due to pre-chlorination and post chlorination. This could be described by the faster chlorine hydrolysis rates that increases by increasing chlorine doses, leading to the formation of high THMs concentration.
- This study showed that the transphilic fraction is the highest reactive with chlorine $R^2 = 0.95$, while the hydrophilic fraction was less reactive ($R^2 = 0.57$). The hydrophobic content proved to be the least reactive one ($R^2 = 0.18$).
- Free chlorine concentrations are responsible for the high THM levels at the plant effluent, which implies its responsibility on THMs formed in the plant and the formation potential in distribution pipelines. Therefore, reducing the chlorine doses as much as possible to reach zero free chlorine before post-chlorination and the minimum acceptable free chlorine residual for secondary disinfection is going to reduce the THMs and HAAs levels substantially.

5.2 Recommendations

- A larger sample size needs to be investigated by sampling from a number of conventional WTPs in order to able to generalize this study outcomes.

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- El-Fustat WTP does not technically implement "Enhanced Coagulation" as the treatment process does not target NOM removal in the operating alum doses or optimize pH and other important variables for NOM removal. However, initial results from this study shows that the hydrophillic DOC fraction is less likely to be removed during Enhanced Coagulation but the major DOC contributor to DBPs formation. Future work should test this hypothesis through a bigger and wider sample size.

- Research should be directed to target the removal of the most problematic DOC fraction, namely; the hydrophilic fraction.

- Reconsidering possible hydraulic design modifications to allow an efficient aeration process to water, or the use of air diffusors at the end of treatment line will allow volatile DBPs to escape before water is transmitted through distribution networks.

- Using unplanned, high pre-chlorination doses for the whole year at El-Fustat WTP is considered a poor practice, which needs to be reconsidered. The pre-chlorination dose should be tailored to the pre-chlorination goal that should change seasonally.

- Most water treatment plants use pre-chlorination to prevent algal growth in treatment tanks, but not for deactivating bacteria, viruses and protozoa. Therefore, other algal control alternatives should be considered. Approaches like microscreening or ultra-sonic waves, which have no recorded contribution on DBPs formation, should be considered.

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Appendix I

The Actual DBPs and NOM Concentration

First Sampling Trip

Date of Sampling: November, 2011

Season: Autumn 2011

Water Temperature: 25 °C

Total Discharge: 17583 m^3/hr

Raw Water

PH: 7.84

Alkalinity: 140 mg/l as $CaCO_3$

Turbidity: 18 FTU

TOC: 3.51 mg/l

DOC: 2.91 mg/l

THMFP (based on TOC): 379.56 µg/l

THMFP (based on DOC): 334.88 µg/l

Pre-Chlorinated Water:

Total Chlorine Level: 8.6 mg/l

Free Chlorine Level: 5.5 mg/l

PH: 7.7

Alkalinity: 130 mg/l as $CaCO_3$

Turbidity: 18 FTU

TOC: 4.62 mg/l

DOC: 4.21 mg/l

THMs: 21.6 µg/l

HAAs: 10.4 µg/l

Settled Water (Post Sedimentation):

Total Chlorine Level: 1.8 mg/l

Free Chlorine Level: 1.7 mg/l

PH: 7

Alkalinity: 110 mg/l as $CaCO_3$

Turbidity: 3 FTU

TOC: 3.72 mg/l

DOC: 3.27 mg/l

THMs: 71.92 µg/l

HAAs: 1.8 µg/l

Filtered Water (After Filtration):

Total Chlorine Level: 2.5 mg/l

Free Chlorine Level: 2.3 mg/l

PH: 7.03

Alkalinity: 112 mg/l as $CaCO_3$

Turbidity: 1 FTU

TOC: 3.47 mg/l

DOC: 3.24 mg/l

THMs: 97 μg/l

HAAs: μg/l

Final Plant Effluent:

Total Chlorine Level: 1.6 mg/l

Free Chlorine Level: 1.5 mg/l

PH: 7.2

Alkalinity: 120 mg/l as $CaCO_3$

Turbidity: 1 FTU

TOC: 3.82 mg/l

DOC: 3.65 mg/l

THMs: 83 μg/l

THMs at temperature 25C:

HAAs: 91 μg/l

Fractionation Results

	DOC	HPO	TRA	HPI
Raw Water	2.9067	1.0103	0.0372	1.8592
After Prechlorination	4.2116	0.5795	0.7303	2.9018
After Sedimentation	3.265	0.3544	0.343	2.5676
After Filtration	3.2412	0.1988	0.517	2.5254
Effluent	3.65	0.2734	0.5897	2.7869

UVA$_{254nm}$ for Total DOC values and NOM Fractions

	Before Columns	XAD7 effluent	XAD4 effluent	IRA958 effluent
Raw Water	0.057	0.053	0.033	0.031
After Prechlorination	0.111	0.968	0.821	0.110
After Sedimentation	0.0123	0.0121	0.0120	0.0121
After Filteration	0.031	0.031	0.032	0.068*
Effluent	0.0180	0.0170	0.0100	0.0177

Second Sampling Trip

Date of Sampling: February, 2012

Season: Winter

Water Temperature: 20 °C

Total Discharge: 14490 m^3/hr

Raw Water

PH: 7.93

Alkalinity: 140 mg/l as CaCO$_3$

Turbidity: 7 FTU

TOC: 2.861 mg/l

DOC: 2.78 mg/l

THMFP (based on TOC): 308.16 µg/l

THMFP (based on DOC): 165.641 µg/l

Pre-Chlorinated Water:

Total Chlorine Level: 7.5 mg/l

Free Chlorine Level: 6.4 mg/l

PH: 7.63

Alkalinity: 110 mg/l as $CaCO_3$

Turbidity: 7 FTU

TOC: 4.06 mg/l

DOC: 1.65 mg/l

THMs: 15.37 µg/l

HAAs: 0.4 µg/l

Settled Water (Post Sedimentation):

Total Chlorine Level: 5 mg/l

Free Chlorine Level: 3.8 mg/l

PH: 7

Alkalinity: 100 mg/l as $CaCO_3$

Turbidity: 1 FTU

TOC: 3.82 mg/l

DOC: 1 mg/l

THMs: 60.75 µg/l

HAAs: 427.3 µg/l

Filtered Water (After Filtration):

Total Chlorine Level: 4.5 mg/l

Free Chlorine Level: 3.5 mg/l

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PH: 7.07

Alkalinity: 104 mg/l as $CaCO_3$

Turbidity: 0 FTU

TOC: 2.73 mg/l

DOC: 1.8 mg/l

THMs: 62.1 µg/l

HAAs: 930.8 µg/l

Final Plant Effluent:

Total Chlorine Level: 2.8 mg/l

Free Chlorine Level: 2.4 mg/l

PH: 7.39

Alkalinity: 107 mg/l as $CaCO_3$

Turbidity: 0 FTU

TOC: 2.52 mg/l

DOC: 1.16 mg/l

THMs: 63.32 µg/l

HAAs: 228 µg/l

Fractionation Results

	DOC	HPO	TRA	HPI
Raw Water	2.78	1.06	0.708	1.012
After Prechlorination	1.65	0.66	0.37	0.62
After Sedimentation	1	0.12	0.25	0.63
After Filtration	1.8	0.22	0.48	1.1
Effluent	1.16	0.28	0.54	0.88

UVA_{254nm} for Total DOC values and NOM Fractions

	Before Columns	XAD7 effluent	XAD4 effluent	IRA958 effluent
Raw Water	0.05	0.017	0.007	0.001
After Prechlorination	0.035	0.016	0.014	0.01
After Sedimentation	0.027	0.013	0.01	0.026
After Filteration	0.026	0.019	0.008	0.014
Effluent	0.026	0.018	0.014	0.023

Third Sampling Trip

Date of Sampling: April, 2012

Season: Spring

Water Temperature: 30 °C

Total Discharge: 16754 m^3/hr

Raw Water

PH: 8.36

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Alkalinity: 120 mg/l as $CaCO_3$

Turbidity: 11 FTU

UVA_{254nm}: abs

TOC: 3.95 mg/l

DOC: 3.38 mg/l

THMFP (based on TOC): 225.6 μg/l

THMFP (based on DOC): 216.2 μg/l

Pre-Chlorinated Water:

Total Chlorine Level: 6.5 mg/l

Free Chlorine Level: 6.1 mg/l

PH: 7.73

Alkalinity: 116 mg/l as $CaCO_3$

Turbidity: 13 FTU

TOC: 4.53 mg/l

DOC: 4.2 mg/l

THMs: 18.11 μg/l

HAAs: 25.8 μg/l

Settled Water (Post Sedimentation):

Total Chlorine Level: 2.6 mg/l

Free Chlorine Level: 2.3 mg/l

PH: 7

Alkalinity: 106 mg/l as $CaCO_3$

Turbidity: 2 FTU

TOC: 3.15 mg/l

DOC: 1.74 mg/l

THMs: 96.08 µg/l

HAAs: 235.5 µg/l

Filtered Water (After Filtration):

Total Chlorine Level: 2.6 mg/l

Free Chlorine Level: 1.8 mg/l

PH: 7.14

Alkalinity: 100 mg/l as $CaCO_3$

Turbidity: 2 FTU

TOC: 3.14 mg/l

DOC: 1.32 mg/l

THMs: 77.5 µg/l

HAAs: 116.9 µg/l

Final Plant Effluent:

Total Chlorine Level: 3.1 mg/l

Free Chlorine Level: 2.4 mg/l

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PH: 7.12

Alkalinity: 100 mg/l as $CaCO_3$

Turbidity: 1 FTU

TOC: 2.88 mg/l

DOC: 1.27 mg/l

THMs: 74.9 μg/l

HAAs: 672.9 μg/l

Fractionation Results

	DOC	HPO	TRA	HPI
Raw Water	3.382275	0.980675	0.7101	1.6915
After Prechlorination	4.2047	1.889	0.351	1.96455
After Sedimentation	1.741567	0.830067	0.5266	0.3849
After Filtration	1.3255	0.52622	0.444605	0.354675
Effluent	1.279775	0.487342	0.474558	0.317875

UVA_{254nm} for Total DOC values and NOM Fractions

	Before Columns	XAD7 effluent	XAD4 effluent	IRA958 effluent
Raw Water	0.146	0.100	0.095	0.088
After Prechlorination	0.118	0.097	0.084	0.085
After Sedimentation	0.089	0.076	0.067	0.074
After Filteration	0.100	0.070	0.069	0.080
Effluent	0.113	0.039	0.027	0.033

Fourth Sampling Trip

Date of Sampling: June, 2012

Season: Summer

Water Temperature: 37 °C

Total Discharge: 17165 m^3/hr

Raw Water

PH: 7.88

Alkalinity: 130 mg/l as CaCO$_3$

Turbidity: 14 FTU

TOC: 3.54 mg/l

DOC: 3.15 mg/l

THMFP (based on TOC): 372 µg/l

THMFP (based on DOC): 357.9 µg/l

Pre-Chlorinated Water:

Total Chlorine Level: 5.3 mg/l

Free Chlorine Level: 4.6 mg/l

PH: 7.33

Alkalinity: 126 mg/l as CaCO$_3$

Turbidity: 8 FTU

TOC: 4.47 mg/l

70

DOC: 1.54 mg/l

THMs: 18.61 µg/l

HAAs: 56.7 µg/l

Settled Water (Post Sedimentation):

Total Chlorine Level: 2.7 mg/l

Free Chlorine Level: 2.3 mg/l

PH: 6.88

Alkalinity: 114 mg/l as $CaCO_3$

Turbidity: 3 FTU

TOC: 3.70 mg/l

DOC: 1.12 mg/l

THMs: 72.41 µg/l

HAAs: 66.1 µg/l

Filtered Water (After Filtration):

Total Chlorine Level: 1.9 mg/l

Free Chlorine Level: 1.8 mg/l

PH: 6.87

Alkalinity: 104 mg/l as $CaCO_3$

Turbidity: 2 FTU

TOC: 3.76 mg/l

DOC: 1.5 mg/l

THMs: 60.74 µg/l

HAAs: 207 µg/l

Final Plant Effluent:

Total Chlorine Level: 3.2 mg/l

Free Chlorine Level: 2.5 mg/l

PH: 6.82

Alkalinity: 104 mg/l as $CaCO_3$

Turbidity: 2 FTU

TOC: 3.24 mg/l

DOC: 1.39 mg/l

THMs: 89.64 µg/l

HAAs: 400.5 µg/l

Fractionation Results

	DOC	HPO	TRA	HPI
Raw Water	3.1489	0.92914	0.21576	2.004
After Prechlorination	1.5435	0.5757	0.2465	0.7213
After Sedimentation	1.1166	0.5004	0.0728	0.5434
After Filtration	1.5032	0.5449	0.1175	0.8408
Effluent	1.3932	0.3798	0.3525	0.6609

UVA$_{254nm}$ for Total DOC values and NOM Fractions

	Before Columns	XAD7 effluent	XAD4 effluent	IRA958 effluent
Raw Water	0.056	0.014	0.003	0.001
After Prechlorination	0.052	0.019	0.09	0.037
After Sedimentation	0.012	0.008	0.004	0.010
After Filteration	0.026	0.011	0.010	0.011
Effluent	0.036	0.011	0.000	0.004

d HAAs corrected concentrations (ug/lTHMs an

Season	THMs	HAAs
Autumn	83.66	21.10
Winter	75.77	19.11
Spring	92.37	23.30
Summer	106.11	26.76