DISINFECTION BY-PRODUCTS FORMATION IN LOW - BROMIDE AND LOW - SUVA WATERS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

NURAY ATEŞ

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE DOCTOR OF PHILOSOPHY
IN
ENVIRONMENTAL ENGINEERING

MAY 2008

Approval of the thesis:

DISINFECTION BY-PRODUCTS FORMATION IN LOW - BROMIDE AND LOW - SUVA WATERS

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ABSTRACT

DISINFECTION BY-PRODUCTS FORMATION IN LOW - BROMIDE AND LOW - SUVA WATERS

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May 2008, 241 Pages

The main objective of this study was to conduct a systematic investigation of the disinfection by-products (DBPs) formation in low-bromide and low-specific ultraviolet absorbance (SUVA) waters and the control of DBP precursors by nanofiltration (NF) and ultrafiltration (UF) processes in such waters. To this end, firstly, the effect of bromide ion on the formation and speciation of DBPs was investigated. In fractionated Alibeyköy source water, increasing bromide concentrations in NOM fractions increased the concentrations of trihalomethanes (THMs), haloacetic acids (HAAs) and adsorbable organic halides (AOX) and resulted in a shift toward the formation of brominated species. Secondly, the impacts of SUVA and differential UV spectroscopy (ΔUV), which has been shown to correlate well with DBP formation has been elucidated in terms of DBP formation and speciation. Alibeyköy and Karacaören waters were fractionated employing various separation methods and it has been shown that SUVA did not correlate well with the formation and speciation of THMs and HAAs in tested low-SUVA waters. Similarly, no correlations were found among THMs/HAAs formations and ΔUV. Finally, the NOM rejection performances of NF and UF membranes were investigated. NF and UF membranes (<2000 dalton) was found to be suitable for the removal NOM from surface waters having low SUVA and low bromide contents. While higher molecular weight (HMW) fraction was successfully rejected (> 90%) by all membrane types, lower molecular weight (LMW) fraction could be removed with ranging efficiencies from 1.5 to 30%. NF membranes provided DOC, UV_{254} absorbance, THM, and HAA reductions up to 90%.

Keywords: Bromide, chlorination, disinfection by products, membrane filtration, SUVA.

ÖZ

DÜŞÜK - BROMÜR VE DÜŞÜK - SUVA SULARDA DEZENFEKSİYON YAN ÜRÜN OLUŞUMU

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Mayıs 2008, 241 Sayfa

Bu çalışmanın amacı, düşük-bromür ve düşük-spesifik ultraviyole absorbansı (SUVA) içeren sularda, dezenfeksiyon yan ürünlerin (DYÜ) oluşumunu ve bu tür sularda DYÜ'lerin ultrafiltrasyon (UF) ve nanofiltrasyon (NF) süreçler ile kontrolünü sistematik olarak incelemektir. Bu amaçla, ilk olarak, bromür iyonunun DYÜ oluşumu ve türleşmesi üzerindeki etkileri araştırılmıştır. Fraksiyonlamış Alibeyköy kaynağında, bromür konsantrasyonunun artması ile trihalometan (THM), haloasetik asit (HAA) ve adsorplanabilen organik halojen (AOX) konsantrasyonlarının arttığı ve bromlu türlere doğru kayma olduğu gözlenmiştir. İkinci olarak, DYÜ'ler ile aralarında güçlü korelasyonlar olduğu belirtilen SUVA'nın ve diferansiyel UV (ΔUV) spektroskopisinin DYÜ oluşumu ve türleşmesi üzerindeki etkileri ortaya konulmaktadır. Alibeyköy ve Karacaören suları çeşitli ayırma metotları kullanılarak fraksiyonlanmış ve incelenen düşük SUVA sularda SUVA'nın THM ve HAA oluşumları ve bunların türleri ile korele etmediği anlaşılmıştır. Benzer şekilde, ΔUV ile THM ve HAA oluşumları arasında da korelasyon gözlenmemiştir. Son olarak, UF ve NF membranlarının DOM giderimindeki performansları araştırılmıştır. NF ve UF (<2000 dalton) membranların düşük SUVA ve düşük bromür içeren sulardan DOM giderimi için uygun olduğu anlaşılmıştır. Tüm membranlarda yüksek moleküler ağırlıklı (YMA) organikler (>%90) başarılı şekilde uzaklaştırılırken, düşük moleküler ağırlıklı (DMA) organiklerin %1.5 ile 30'u giderilebilmiştir. DYÜ öncülllerinin giderimine bağlı olarak, NF süzüntü sularında THM ve HAA oluşumları %90 azaltılmıştır.

Anahtar Kelimeler: Bromür, klorlama, dezenfeksiyon yan ürünleri, membrane filtrasyon, SUVA.

To my parents…

ACKNOWLEDGEMENT

I would like to express my sincerest appreciation and thanks to my supervisor Prof.Dr. Ülkü Yetiş. Her skillful and scholarly guidance, patience, and gentle encouragement helped me persevere through the flow of research and made this dissertation possible. I would also like to express my deepest gratitude to my co-advisor Assoc.Prof.Dr. Mehmet Kitiş for supporting and encouraging me throughout this work. I will always appreciate their endless support, trust and friendship during my graduate tenure and I will forever be grateful.

I would also like to thank the Supervising Committee Members; Prof.Dr. Filiz B. Dilek and Prof.Dr. Işıl Balcıoğlu for their valuable advises and recommendation. I am also grateful to the Dissertation Committee Members, Prof.Dr. F.Dilek Sanin and Assist.Prof.Dr. Ayşegül Latifoğlu, for their valuable suggestions.

I would like to thank Environmental Engineering Department staff Mr. Kemal Demirtaş, Miss. Aynur Yıldırım and Mr. Ramazan Demir for their excellent assistance in the lab. I wish to thank to the State Hydraulics Institute for the technical and logistic support provided.

Financial support for this study was provided by the Turkish State Planning Organization (DPT) (Project No. DPT.2003K120920-01), the Scientific and Technical Research Council of Turkey (TUBITAK) (Project No. ICTAG –

C019) and the Scientific Research Foundation (METU) (Project No. BAP–2005-03-11-01).

It has been a pleasure and privilege to work with many outstanding colleagues, Tuba H. Ergüder, Mine Artuğ, Ayten Kaplan, Seda Çalışır, Başak Çelik, Okan T. Komesli, Güray Doğan, Ebru Acuner, Nimet Uzal, Burak Uzal, Eylem Doğan, Erkan Şahinkaya, Kadir Gedik and Recep Kaya, for endless their friendship and help throughout the my stay in Middle East Technical University.

In my dormitory years, I shared special times with Ayşe Seyhan, Levent Kaan, Gülderen Sağlam, Banu Soylu and Berna Hasçakır. I will never forget their priceless friendship and support that they have never left me alone whenever I need someone to have a heart-to-heart talk or a shoulder to cry. And also thanks to them for being with me for collecting data and samples at several late nights in the lab.

I want to express my special appreciation to Prof.Dr. Tanju Karanfil for giving me opportunity to study with him in Clemson University (SC). Our weekly meetings had been the most valuable time for me that I could have chance to make discussion. I will always remember the lovely times and talks with Meriç Selbes and Ş. Şule Kaplan and other friends in Clemson.

Last, but certainly not least, I am deeply grateful to my mother and father, Afife and Hüseyin Ateş, my sister Zehra Yüksel, my brothers Fevzi and Serkan Ateş, for their endless patience, encouragement, support and love for all the years in me and for making life easy all the time.

TABLE OF CONTENTS

APPENDICES

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

ABBREVIATIONS

AOX : Adsorbable Organic Halides
AROM : Aquagenic Refractory Organic Matter
CFV : Cross-flow Velocity
CHY : Chloral Hydrate
CMBR : Completely Mixed Batch Reactor
CNBr : Cyanogen Bromide
CNCl : Cyanogen Chloride
^{13}C-NMR : Carbon-13 Nuclear Magnetic Resonance
CP : Concentration Polarization
D/DBP : Disinfectant/Disinfection By-Products Rule
DBPs : Disinfection By-Products
DOC : Dissolved Organic Carbon
DOM : Dissolved Organic Matter
ΔUV : Differential Ultraviolet
EEC : European Economic Community
EPA : Environmental Protection Agency
FA : Fulvic Acid
GAC : Granular Activated Carbon
GC : Gas Chromatography
GPC : Gel Permeation Column
GC-MS : Gas Chromatography-Mass Spectrometry
HAAs : Haloacetic Acids
HANs : Haloacetonitriles

HA : Humic Acid
HAs : Haloamides
HKs : Haloketones
HMW : Higher Molecular Weight
HNMs : Halonitromethanes
HPSEC : High Performance Size Exclusion Chromatography
HS : Humic Substances
IA : Iodoacids
ICR : Information Collection Rule
LMW : Lower Molecular Weight
MCL : Maximum Contaminant Level
MF : Microfiltration
MIEX : Mignetized Ion Exchange Resin
MW : Molecular Weight
MWCO : Molecular Weight Cut-off
MWD : Molecular Weight Distribution
NF : Nanofiltration
NMR : Nuclear Magnetic Resonance
NOM : Natural Organic Matter
PAC : Powdered Activated Carbon
PACl : Poly-aluminum Chloride
POC : Particulate Organic Matter
PROM : Pedogenic Refractory Organic Matter
PSS : Polystyrene Sulfonate
RAC : Resin Adsorption Chromatography
RCWIHC : Regulation Concerning Water Intended for Human Consumption
RO : Reverse Osmosis
SDS : Simulated Distribution System
STTHMFP : Specific Total Trihalomethane Formation Potential

SUVA	: Specific Ultraviolet Absorbance
THMs	: Trihalomethanes
TMP	: Trans-membrane Pressure
TOC	: Total Organic Carbon
TOX	: Total Organic Halides
TTHM	: Total Trihalomethanes
THMFP	: Trihalomethane Formation Potential
TTHMFP	: Total Trihalomethane Formation Potential
UF	: Ultrafiltration
UFC	: Uniform Formation Condition
USEPA	: United States Environmental Protection Agency
USGS	: United States Geological Survey
UV	: Ultraviolet Absorbance
WHO	: World Health Organization

CHAPTER 1

INTRODUCTION

1.1. Introduction

Natural waters contain natural organic matter (NOM) ubiquitously as a result of the interactions between the hydrological cycle and the biosphere and geosphere. These interactions are responsible for the diverse nature of NOM as the organic content of a particular water body is dependent on the surrounding environments. NOM is a complex and heterogeneous mixture of organic materials and consist of humic materials, hydrophilic acids, proteins, lipids, hydrocarbons and amino acids (Aiken et al., 1985; Malcolm, 1985; Thurman, 1985a; Hayes et al., 1989; McKnight and Aiken, 1998; Chen et al., 2003; Murray and Parsons, 2004).

The presence of dissolved organic matter (DOM) in natural waters poses a broad range of problems in drinking water treatment and water distribution systems. These problems relate to the ability of DOM to serve as a precursor for formation of regulated disinfection by-products (DBPs), to act as substrate for biological re-growth in distribution systems, to bind regulated metals and hydrophobic organic chemicals and transport them through water treatment plants and distribution systems, to cause taste and odor in drinking water, to impair the effectiveness of treatment processes (e.g., fouling of activated carbons and membranes), and to exert increased coagulant and disinfectant/oxidant demands (Jacangelo et al., 1995a; Owen et al., 1995; Krasner et al., 1996b). However, one of the most pressing concerns from a public health point of view is the formation of suspected carcinogenic DBPs as a result of reactions between DOM and oxidants/disinfectants such as chlorine (Bellar et al., 1974; Rook, 1974; Bull, 1982; Bull and Kopfler, 1991; Owen et al., 1995; Oxenford, 1996).

The trihalomethanes (THMs) were the first halogenated DBPs identified in chlorinated drinking waters that were of health concern and regulated by the Turkish Ministry of Health and the US Environmental Protection Agency (USEPA). Four THMs often detected in chlorinated waters are chloroform, bromoform, bromodichloromethane, and dibromochloromethane. Other halogenated DBPs detected in chlorinated waters include haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), haloamides (HAs), chloral hydrate (CHY), halonitromethanes (HNMs), iodoacids (IA), cyanogen chloride (CNCl), cyanogen bromide (CNBr), and chlorophenols. Chlorinated and unchlorinated aliphatic mono- and di-basic acids, neutral and acidic carbonyl compounds, chlorinated oxo-acids, and unchlorinated aromatic acids have also been detected after chlorination (Christman et al., 1983; De Leer et al., 1985; Amy et al., 1987; Krasner et al., 1989; Becher et al., 1992; Singer et al., 1995; Richardson, 1998; Kronberg, 1999; Croue et al., 2000; Villanuevaa et al., 2003; Golfinopoulos and Nikolaou, 2005). It was reported that about 700 compounds were detected after chlorination of fulvic acid (Stevens et al., 1989). Of these, 500 were expected to relate to the chlorination process. Of the 500 compounds, 196 of them, either identifiable or not, were also found in samples of 10 drinking water utilities in US. Only about 40-60% of the total organic halides (TOX) can be assigned to identify individual DBPs (mostly THMs and HAAs) (Christman et al., 1983; Reckhow and Singer, 1984; Leer et al., 1985; Krasner et al., 1989; Singer and Chang, 1989; Singer, 1994; Richardson, 1998; Plewa et al., 2004; Richardson, 2005; Krasner et al., 2006).

DOM solutions can be characterized by non-specific and simple parameters such as organic carbon content (e.g, dissolved organic carbon (DOC) concentration) and ultraviolet light (UV) absorbance (Lawrence, 1980; MacCarthy and Rice, 1985; Chin et al., 1994; Peuravuori and Pihlaja, 1997a). Several researchers have reported strong correlations between aromatic carbon content and $UV_{254-280}$ absorbance of DOM isolates (Edzwald et al., 1985; Chin et al., 1994; Kitis, 2001). In order to compare the characteristics of different DOMs, UV absorbance at a particular wavelength must be normalized dividing by the DOC concentration. This normalized value is called absorptivity or specific UV absorbance (SUVA). SUVA provides a quantitative measure of unsaturated bonds and/or aromaticity within DOM (Edzwald and Van Benschoten, 1990; White et al., 1997; Kitis, 2001). The important practical advantages of SUVA are that it can be determined in a short period of time, using a small volume of sample, and does not require sophisticated sample pretreatment.

Since there is evidence that chlorine may attack DOM predominantly at electron-rich sites, i.e., activated aromatic sites or conjugated double bounds, which absorb UV light effectively at wavelengths of 254 to 280 nm, chlorination may decrease the UV absorbance of DOM at these wavelengths as a result of alteration and destruction of these sites (Korshin et al., 1997a,b; Li et al., 1998). Korshin and co-workers (1997a,b) quantified the difference in the UV absorbance before and after chlorination of natural waters and called it as differential UV (ΔUV_{λ}). The practical advantage of the use of differential UV spectroscopy is the ability to predict formation of DBPs in water treatment plants and distribution systems simply by measuring the UV absorbance before and after chlorination at a certain time and using the previously generated ΔUV_{λ}-DBP correlations.

It is evident that the simultaneous control of DBP formation and microbial quality is one of the greatest challenges currently faced by the water treatment industry. To comply with more stringent forthcoming regulations, drinking water utilities must develop strategies to minimize DBP formation.

1.2. Problem Statement and Motivation

Although the formation and speciation of DBPs from reactions between NOM and chlorine has been researched for many years, there is limited information in the literature regarding DBP formation and speciation in natural waters with low-DOC, low-SUVA and low-bromide levels. This mainly stems from the fact that many research studies tested waters mostly high in humic content (i.e., high SUVA and high DOC). There may be three major reasons for this trend: 1) many studies in the literature indicate that the main reactive sites in NOM components are high-SUVA aromatic moieties resulting in DBP formation; 2) many reactivity studies require that NOM be isolated from waters such as with resin adsorption chromatography method (RAC), which is more effective for isolating humic materials from high-SUVA and high-DOC waters; and, 3) there is not a well-defined and globally accepted method for isolation of NOM with mainly lower molecular weight (LMW) and hydrophilic in character (i.e., low-SUVA and low-DOC) for further reactivity studies.

Although it is expected that lower extent of DBP formation may be observed in waters with low-SUVA and low-DOC based on the literature findings from many studies on high-SUVA and high-DOC waters, there is a research need to investigate the formation and speciation behavior of DBPs in such waters in detail. The driving force for this research is related to the fact that DBP regulations are becoming more stringent and new regulations are planned for individual DBP species rather than DBP groups (e.g., THMs or HAAs). Therefore, even though these types of low-humic and low-organic containing waters may not be problematic for water utilities in meeting current regulations, it seems difficult to say so for future regulations and for new DBPs being identified as new and sophisticated analytical methods are being developed. Furthermore, it is generally suggested in the literature that there is a shift toward the formation of brominated DBPs over chlorinated ones with increasing bromide content in waters. This is especially important since recent toxicology studies indicate that individual THM and HAA species may have different health effects. For example, bromodichloromethane has been shown to pose a higher cancer risk than chloroform (USEPA, 1994; Krasner et al., 1996a; USEPA, 2006). Thus, there is also a need of systematic investigation of the impacts of low levels of bromide, DOC and SUVA all together on DBP formation and especially speciation.

In addition to studying the formation and speciation of DBPs, the effectiveness of selected DBP precursor removal technologies will also be evaluated in these waters with low levels of bromide, SUVA and DOC. Similar to DBP reactivity studies, there is also limited information in the literature in regard to DBP precursor control strategies for these waters. In this context, two processes, magnetic ion exchange resin (MIEX) and membrane filtration, were studied. MIEX, a new adsorptive commercial resin recently developed by Australian investigators, was tested for such low-SUVA, low-bromide and low-DOC waters. Ultrafiltration (UF) and nanofiltration (NF) are the mostly used membrane filtration processes for the removal of DOC, dissolved solids and bromide.

1.3. Objectives

Based on the above research needs determined through an extensive literature review, the main objectives of this doctoral work are summarized below:

1. Investigate formation and speciation of DBPs (THMs, HAAs and adsorbable organic halides (AOX)) in waters with low levels of bromide, DOC and SUVA. Evaluate the relationships between SUVA, bromide concentration and DBP formation and speciation.
2. Investigate the effect of bromide content on formation and speciation of DBP formation in low-SUVA waters, carrying out tests with bromide spike.
3. Determine the applicability of differential UV spectroscopy technique in estimating DBP formation in such waters.
4. Determine the relations between NOM fractions (obtained employing batch-mode adsorptive fractionation by XAD-8, XAD-4, granular activated carbon (GAC) and MIEX resins) and their DBP formation and speciation in such waters.
5. Determine the effectiveness of MIEX resins on DBP precursors (both DOM and bromide) removal in such waters.
6. Investigate the molecular weight distribution (MWD) of NOM in low-SUVA and low-DOC water and formation and speciation of DBPs (THMs and HAAs) in relation to precursors' MWs.

7. Evaluate the feasibility of treating low to medium DOC and SUVA surface water using UF and NF membranes in lab scale study.
8. Investigate the removal efficiency of NOM from water using UF and NF membranes and evaluate the relationship between the removed and the remaining NOM with their MWD.
9. Investigate the effect of trans-membrane pressure (TMP) and cross-flow velocity (CFV) on the effectiveness of NOM removal by UF and NF.
10. Investigate the fouling behavior of different UF and NF membranes in the removal of NOM from this type of waters.

1.4. Approach

This dissertation work was conducted in three main phases. The first phase involved the investigation of the impacts of bromide spike on DBP formation, speciation and their relations with SUVA and differential UV spectroscopy. The second phase contained the investigation of the DBP formation, speciation and their relations with SUVA and differential UV spectroscopy in fractionated samples. The third phase consisted of the investigation of the effectiveness of membrane filtration on removal of NOM and DBP formation and speciation in membrane-treated waters. To conduct these works, two different surface water sources, Alibeyköy and Karacaören, were chosen. DOC, bromide concentration and SUVA values of these waters were the basic criteria for choosing these sources. Indeed, Alibeyköy reservoir contains moderate-bromide and moderate-DOC levels which supply some portion of the City of Istanbul’s drinking water demand. Karacaören water is known to be one of the cleanest and prestigious drinking water sources in Turkey, with its very low-DOC and low-bromide content. In this perspective, the applications/experiments of each phase and corresponding fulfilled objectives are summarized in Table 1.1.

Table 1.1. Experimental Approach

Phase	Application	Objective No
Phase 1	➢ Batch XAD (XAD-8 and XAD-4) fractionation experiments ➢ Alibeyköy water ➢ 5-20,000 mg resin/L ➢ Differential UV spectroscopy ➢ Bromide spike ➢ THM, HAA and AOX analysis	Objective 1 Objective 2 Objective 3 Objective 4
Phase 2	➢ Batch XAD, GAC and MIEX fractionation experiments ➢ Alibeyköy and Karacaören waters ➢ 5-5,000 mg XAD/L, 50-4,000 mg GAC/L ➢ 2.5-30 mL MIEX/L ➢ Removal effectiveness ➢ Differential UV spectroscopy ➢ THM, HAA and AOX analysis	Objective 1 Objective 3 Objective 4 Objective 5
Phase 3	➢ Membrane Experiments ➢ Alibeyköy water ➢ GH-UF, PT-UF, DK-NF, DL-NF membranes ➢ Removal effectiveness ➢ Membrane fouling ➢ MWD ➢ THM, HAA and AOX analysis	Objective 6 Objective 7 Objective 8 Objective 9 Objective 10

1.5. Dissertation Overview

This thesis consists of eight chapters. Chapters 1, 2 and 3 include introduction, literature review, and materials and methods, respectively. Mainly, Chapters 4, 5 and 6 discuss significant findings and results of the study. Chapter 4 investigates the impacts of bromide spike on DBP formation, speciation, and their relations with SUVA and differential UV spectroscopy. Chapter 5 discusses the relations between the formation and speciation of DBPs and surrogate parameters, shown well correlated with DBPs, in low level SUVA and bromide content waters. Chapter 6 presents removal performances of UF and NF membranes on NOM and correspondingly the reduction in the formation of DBPs. Chapter 7 summarizes major conclusions and Chapter 8 proposes some further investigation following this study. Appendix A presents supplementary information for experimental procedure that includes calibration curves. Supporting figures and tables for discussion of results in Chapters 4, 5 and 6 are presented in Appendix B.

CHAPTER 2

LITERATURE REVIEW

2.1. Formation and Importance of DOM

NOM is widely distributed in soil, natural water and sediments, and consists of a mixture of the decomposition products of plant and animal residues, and of substances synthesized biologically and/or chemically from decomposed products or intermediate products (Chen et al., 2002). The nature of NOM within a water source is dependent on numerous factors including the type of vegetation and soil geochemistry in the watershed, and biological activity within the water source itself (Newcombe et al., 1997; Her et al., 2002). The size, chemical composition, structure, and functional groups, and polyelectrolytic characteristics of NOM may vary greatly, depending on the origin and age of the material (Harrington, 1997; Chen et al., 2002). It is this heterogeneity that has made the structural and functional characterization of NOM extremely challenging.

The transport mechanisms of NOM through soil into rivers and streams are important for catchment management strategies (Newcombe et al., 1997; Alberts and Takacs, 1999; Abbt-Braun and Frimmel, 1999). More specifically, a better understanding of the structural and functional properties of NOM may greatly improve our understanding of the underlying mechanisms responsible for the complexation, reduction, and mobilization or immobilization of heavy metals, radionuclides, pesticides, and other toxic chemicals with NOM (Chen et al., 2002; 2003).

The presence of NOM in water source causes a broad range of problems in drinking water treatment in terms of public health and water quality. The fraction of NOM that eludes removal by conventional drinking water treatment processes can react with disinfectants to form DBPs, which can compromise public health. NOM can also support bacterial regrowth within drinking water distribution systems (biofilms) (Owen et al., 1995; Afcharian et al., 1997). During coagulation and flocculation processes, NOM stabilizes dispersed and colloidal particles. They also compete with pollutants for adsorption sites on activated carbon. In the chlorination processes, NOM are precursors of potentially hazardous DBPs (Abbt-Braun and Frimmel, 1999).

Since NOM is also known as playing important roles on the fate and transport of many toxic organic or inorganic chemicals and in nutrient cycling throughout the environment, characterization of NOM is particularly useful for studying these reactions and processes (Rozenbaha et al., 2002; Chen et al., 2002, Chen et al., 2003). A proper understanding of NOM molecular composition is essential for advancing knowledge regarding its role in drinking water treatment and environmental processes (Frazier et al., 2003).

2.2. General Classification of DOM

NOM in dissolved, colloidal or particulate form presents ubiquitously in surface and ground waters. The dissolved and colloidal fractions (i.e., DOM, the components passing through a 0.45-µm filter) are the dominant form of NOM in natural waters (Malcolm, 1991; Gaffney et al., 1996). DOM in aquatic environments is derived from both external and internal sources of organic materials as results of various complex biotic and abiotic reactions (Croue et al., 1999). It is composed of a heterogeneous mixture of aquatic humic substances (HS), amino acids, sugars, aliphatic acids, aromatic acids, and a large number of other organic molecules (Thurman, 1985b; Harrington, 1997; Murray and Parsons, 2004).

Total organic carbon (TOC) is the most comprehensive measurement used to quantify the presence of organic matter in aquatic systems. The characterization of NOM can be based on the subdivision of TOC into operationally defined fractions such as DOC and particulate organic carbon (POC). POC and DOC may represent approximately 10-20% and 80-90% of TOC, respectively (Kitis, 2001; Leenheer and Croue, 2003). Various approaches have been proposed and employed for its classification. One approach is to divide DOC into humic and non-humic fractions (Singer and Harrington 1993; Barrett et al., 2000; Hwang et al., 2000; Lehtonen et al., 2000). HS are the major constituents of NOM, and HS account for approximately 50 percent of the DOC. About 30 percent of the DOC is comprised of hydrophilic acids. The remaining 20% of the DOC is carbohydrates (including polysaccharides), carboxylic acids, proteins, amino acids, LMW acids, lipids and peptides (Sohn, 2000; Fan et al., 2001; Kitis, 2001; Nikolaoua and Lekkas 2001).

HS are the most widely found naturally occurring organic substances in nature. The classical definition states that HS are “a general category of naturally occurring, heterogeneous organic substances that can generally be characterized as being yellow to black in color, of higher molecular weight (HMW) and refractory”, although recent studies demonstrate that their MW can be much lower than that suggested previously. HS are often divided into three fractions (Kitis, 2001; Nikolaoua and Lekkas 2001; Rozenbaha, et al., 2002; Wu et al., 2002):

(a) humin, the fraction of HS which are not soluble in water at any pH;
(b) humic acids (HA), the fraction which is not soluble in water under acidic conditions (below pH 2); and
(c) fulvic acids (FA), the fraction which is soluble under all pH conditions and are generally characterized by LMW but higher oxygen-containing organic components.

Aquatic humic materials are thought to have a moderate aromatic character (~25% of the total carbon) with a large numbers of carboxyl groups, some phenolic groups, alcohol OH groups, methoxyl groups, ketones and aldehydes (Hong and Elimelech, 1997; Wu, 1998; O'Melia et al., 1999). The structures of FA are somewhat more aliphatic and less aromatic than HA; and FA are richer in carboxylic acid, phenolic and ketonic groups (Wu, 1998).

Typically 90% of the dissolved HS in natural waters consist of FA and 10% of HA, a composition being in contrast to that of HS from soils, where HA are in very large excess over FA (Nikolaoua and Lekkas 2001). FA can be further fractionated on the basis of their adsorptive behavior on synthetic resins (Leenheer et al., 1995) or on a cross-linked polyvinyl pyrrolidone polymer (Chen et al., 2002). The HA fraction is highly reactive and readily removable by coagulation, while the FA fraction is less reactive (Singer and Harrington, 1993; USEPA, 2001; Freese et al., 2001).

It is also possible to subdivide HS into two groups depending on their origin:

- Pedogenic refractory organic matter (PROM) originates from soil and terrestrial vegetation and is a mixture of highly aromatic compounds (i.e., containing lignin). PROM may also be referred as allochthonous – entering the aquatic system from a terrestrial watershed (Croue et al., 1999; Leenheer and Croue, 2003).
- Aquagenic refractory organic matter (AROM) originates from water and contains mainly aliphatic organic substances. Algal and cynobacterial biomass and the intracellular components released after their decay, which are mostly aliphatic and low in phenolic and aromatic constituents (i.e., low lignin content), are the major sources of AROM. The algae – contributed part of AROM is called algogenic material. AROM may also be referred as autocthonous – being derived from biota growing in the water body (Kitis, 2001).

NOM in the aquatic environment can also be classified based on size. Indeed, the size of various HS samples has been related to DBP formation, coagulation efficiency, complexation of trace metals, adsorption of HS onto minerals and activated carbon and partitioning of organic pollutants (Cabaniss et al., 2000). Knowledge of NOM size distribution is of tremendous practical significance in the study of both natural and engineered aquatic and terrestrial systems. The design, evaluation and integration of water treatment processes such as coagulation, solid media and membrane filtration, disinfection and sorption on GAC are strongly influenced by NOM size distribution. In terrestrial and sedimentary environments, the fate and transport of synthetic organic chemicals, the complexation of metals and the fertility of soil have been shown to be intimately related to NOM size (Tadanier et al., 2000).

2.3. DOM Characterization and Reactivity

During drinking water treatment, DOM can be removed by coagulation, GAC adsorption, membrane filtration, or biological degradation, or it can be transformed by oxidants such as ozone or as part of an advanced oxidation process. Characterization of DOM is essential in understanding how to remove best DOM. In addition, an understanding of DOM's reactivity with disinfectants is critical in minimizing the formation of DBPs and in identifying which fraction of the DOM is most important to remove (Barrett et al., 2000; Frazier et al., 2003). Several attempts for characterization of DOM have been made using the following techniques (Nikolaoua and Lekkas 2001):

- fractionation, to separate hydrophilic/hydrophobic or HMW/LMW fractions of DOM,
- UV radiation spectroscopy, fluorescence and carbon-13 nuclear magnetic resonance (^{13}C-NMR), to determine degree of aromaticity of DOM,
- pyrolysis-gas chromatography-mass spectrometry (GC-MS), to identify individual compounds which compose DOM; and,
- statistical calculation of properties, based on elemental analysis of DOM.

2.3.1. DOM Isolation and Fractionation Methods

Fractionation of DOM offers advantages by selectively separating one group of organic compounds (or a subcomponent) from the others on the basis of their physical and chemical properties. Relatively well-defined DOM subcomponents or fractions are thus obtained, and their chemical and structural features can be better characterized. A common approach to determine fundamental chemical information on the biogenesis and environmental roles of DOM is to isolate and fractionate functionally distinct fractions of organic matters (Croue et al., 1999).

The most commonly used techniques to isolate the DOM fractions are fractionation on XAD-type macroporous resins (Leenheer, 1981; Thurman and Malcolm, 1981; Croue et al., 1999) by gel filtration (Bruchet et al., 1990; Shaw et al., 1994) and by ultrafiltration (Amy et al., 1988; Kainulainen et al., 1994). The characterization of the extracts collected is delicate and requires for complex techniques such as pyrolysis GC-MS (Bruchet et al., 1990) or ^{13}C-NMR spectra (Malcolm, 1992). Nevertheless, the great majority of the DOM content has not yet been elucidated clearly (Afcharian et al., 1997; Croue et al., 1999).

There is considerable debate regarding the advantages and disadvantages of working with isolated DOM versus DOM in its natural state. This also extends to the advantages and disadvantages associated with the different isolation methods. Example discussions include those by Aiken (1985), Leenheer (1985), Aiken (1988), Thurman et al. (1988), MacCarthy and Suffet (1989); Hayes et al. (1989); and Serkiz and Perdue (1990).

Advantages are:

- DOM is separated from the inorganic components in a water sample. This allows one to study the influence of DOM on treatment processes under more carefully controlled conditions; and,
- isolation of DOM also allows one to use characterization methods that cannot be used with the water sample itself. These characterization methods include elemental analysis, NMR, and vapor pressure osmometry.

Disadvantages are:

- the use of NOM fractions does not give a true picture of how the overall pool of NOM in a water supply will influence treatment processes; and,
- isolation is the potential for change in the physical and chemical characteristics of the DOM.

2.3.1.1. Resin Adsorption Chromatography

RAC methods have been used for isolating DOM from natural waters with a varying range of success employing a wide variety of sorbents (Mantoura and Riley, 1975; Aiken et al., 1979; Leenheer and Huffman, 1979; Leenheer, 1981; Thurman and Malcolm, 1981; Leenheer and Noyes, 1984; Aiken, 1985; Zhou and Banks, 1990; Peuravuori and Pihlaja, 1991; Aiken and Leenheer, 1993). The researchers at the U.S. Geological Survey (USGS) have developed and published detailed procedures for isolation and fractionation of DOM employing mainly XAD resins. Factors that greatly affect the procedure are (a) the chemistry of the binding sites on the resins and (b) the solution pH. The adsorption condition is acidic (pH 2) and elution is performed with NaOH (pH 12) (Nikolaou and Lekkas, 2001).

XAD resins are nonionic, uncharged macroporous co-polymers with large surface areas. However, pore size, surface area, composition, cross-linkage, density and polarity of these resins vary between various types of XADs. XAD-4 is an aromatic polymer matrix of styrene-divinylbenzene, whereas XAD-8 is an aliphatic polymer matrix of methylacrylic acid (acrylic ester). The acrylic ester resins are non-aromatic, more hydrophilic and somewhat more polar than the more hydrophobic and essentially nonpolar styrene divinylbenzene resins, and have a measurable cation exchange capacity (on the order of 10-65 microequivalents per gram of resin). Sorption of DOM, especially HS, is controlled by the solute's aqueous solubility, resin specific surface area, resin pore size, chemical composition of the resin, and solution pH (Aiken et al., 1979; Leenheer, 1981; Aiken, 1985; Aiken et al., 1992; Malcolm, 1991).

The XAD-8 resin method proposed by the USGS research group for the isolation of the so-called HS (i.e., HA and FA) is now considered by a large part of the scientific community as the reference method. Using this approach, the hydrophobic fraction of NOM (also called the humic fraction) that is adsorbed at acidic pH onto the XAD-8 resin column is separated from the hydrophilic fraction. Hydrophilic fraction is traditionally referred to as the non-humic fraction, although more recent work has demonstrated that a large part is "humic-like" NOM. Typically, 40 to 60 percent of the NOM can be recovered from a sample using XAD-8 approach to isolate the hydrophobic acid fraction (Croue et al., 1999; Lehtonen et al., 2000).

Another approach to the fractionation of the organic matter in a water sample is to use two-column array of XAD-8 and XAD-4 resins. This two column setup is an extension of the method developed by Thurman and Malcolm (1981) that allows for the isolation and separation of both the hydrophobic acid fraction (containing aquatic HS) and a portion of the organic matter that is more hydrophilic. The fraction obtained from the XAD-4 resin will be referred to as *transphilic* because the compound in this fraction is also referred to as *hydrophilic acids*, *XAD-4 acids*, or *syn-fulvic acids* (Croue et al., 1999).

2.3.1.2. Reverse Osmosis

Only a few research studies have been devoted to the development of membrane processes for the isolation of aquatic NOM. Polyamide or polysulfone membranes have generally been preferred (Croue et al., 1999). RO is an efficient water concentration technique with a rejection coefficient for DOC above 90 percent. Several groups reported yields around 80-90% when applied to a variety of surface and ground waters. Maurice et al. (2002) reported over 90% recovery of DOC from a synthetic groundwater. The DOC recovery was with few cases near 70 percent (Serkiz and Perdue, 1990; Clair et al., 1991; Sun et al., 1995; Croue et al., 1996). Use of a portable RO system generally allows for rapid on-site isolation and concentration of many samples. Unlike the XAD sorption method(s), RO is not designed specifically to fractionate HS (Maurice et al., 2002). Some of the advantages of RO are (Croue et al., 1999; Kitis, 2001, Kitis, et al., 2001b):

- sample can be concentrated without removing the solutes from the aqueous matrix,
- very large recoveries of DOM (about 85-100% as DOC) with minimal fractionation are possible,
- large volumes can be processed in a relatively short period of time,
- sample is not exposed to harsh conditions such as extremes in pH, temperature or chemical additions; and,
- high concentration factors can be achieved.

The major drawbacks of RO are:

- inorganic ions can be concentrated along with DOM, which may need to be removed prior to subsequent characterization and reactivity studies,

- some DOM components may be lost due to sorption onto the membrane, leakage via permeate, or precipitation within the concentrate; and
- cost of membrane system is high compared to the other isolation techniques.

Because only a few studies have focused on DOM isolation using RO, and salts are concentrated along with the DOM due to analytical interferences, few data have been published regarding the nature of DOM isolated with RO membranes. The most important finding is that RO isolates are more hydrophilic in character than XAD resin isolates. Serkiz and Perdue (1990) concluded that polysaccharides and polypeptides were more abundant in the organic materials isolated using RO as compared to HS isolated from the same surface water (Suwannee River) using XAD-8 resin (Maurice et al., 2002). Croue et al. (1996) also found that the RO isolate obtained from the Blavet River (France) was enriched in proteins and amino-sugars as compared to the mixed XAD-8/XAD-4 isolate.

2.3.1.3. Bulk Water Fractionation

Another approach to study the reactivity of DOM is the use of bulk water fractionation techniques employing separation processes such as adsorption by GAC or synthetic resin (i.e., XAD resins), and coagulation/flocculation (i.e., using alum or iron salts as the coagulants). In these processes, DOM fractions are not isolated from waters; rather the DOM mixtures remaining in water after the treatment (e.g., after adsorption or coagulation) are referred to the *bulk water DOM fractions*. Since these processes may remove different components, several characteristically different DOM fractions can be obtained after treating the source waters with varying doses of GAC, XAD and alum (Kitis, 2001).

2.3.2. Aromaticity of NOM

2.3.2.1. UV Radiation Spectroscopy

Organic matters naturally present in surface waters absorbs light over a wide range of wavelengths (190 nm>λ>400 nm), while inorganic chemicals do not absorb light at λ> ~ 230 nm (MacCarthy and Rice, 1985; Bloom and Leenheer, 1989; Korshin et al., 1997a). Although a diversity of functional groups can contribute to the absorbance of a natural waters, the strong correlations were found between UV light absorbance and the aromatic carbon content of the sample (Traina et al., 1990; Novak et al., 1992). Therefore, the absorbance of light is a semi-quantitative indicator of the concentration of DOM in natural waters. Some researchers found that UV light absorbance at 254 nm was a useful parameter to monitor the concentration of DOM (Edzwald et al., 1985; Amy et al., 1987; Morrow and Minear, 1987). UV absorbance is caused by aromatic and unsaturated double bonds in the DOM. UV absorbance at 254 nm (or in some cases 285 nm) has been found to be a highly specific indicator of benzene carboxylic acids and phenols, which are constituents of DOM. When a molecule absorbs light, the functional groups containing the electrons are promoted and these functional groups are referred as chromophores. Chromophores responsible for the absorbance are likely to have conjugated double bonds and unbounded electrons like those associated with oxygen, sulfur, and halogen atoms. UV absorbance increases with pH, aromaticity, total C-content and MW and decreases with decreasing molecular size of DOM (Barrett et al., 2000; Leenheer, and Croue, 2003; Nikolaou and Lekkas, 2001).

2.3.2.2. Fluorescence

Fluorescence emission spectrometry has also been used to characterize NOM. The molecular structure affects intensity of fluorescence, which decreases with increasing molecular size. This may be caused by closed position of hydrophobic sub-units (aromatic moieties) inside the macromolecular structural skeleton masked by hydrophilic groups. The intensity of fluorescence decreases when electron-withdrawing groups (OH, NH_2) are present, whereas it increases at presence of electron-donating groups (COOH). Characteristic fluorescence wavelengths of NOM are 345 nm (used as excitation wavelength) and 415 nm (used as an emission wavelength) (Nikolaou and Lekkas, 2001).

2.3.2.3. ^{13}C-NMR Spectrometry

Solid-state ^{13}C-NMR has been used to characterize NOM compounds by determining the carbon functional groups (i.e., aliphatic or aromatic) in whole soils and humic extracts as well as UV spectrophotometry (Schnitzer and Preston, 1986; Reckhow et al., 1990; Hanna et al., 1991; Preston, 1996; Wong et al., 2002). The NMR spectra of the hydrophilic fractions are distinctly different from those of the hydrophobic fractions. Leenheer (1996) reported that the hydrophilic acid fraction had the largest carboxylic acid content, while the hydrophilic neutral fraction had the largest carbohydrate content. As the HA fraction was the most enriched in aromatic carbon and the least enriched in carboxyl carbon content. That the low aqueous solubility of HA fraction could be partially explained. On the other hand, FA had a greater amount of aromatic-carbon content and the higher C/O atomic ratio generally was observed for FA (Croue et al., 1999). While the NMR spectra of the hydrophobic fractions exhibited the general features of aliphatic, alkoxyl, unsaturated, and carbonyl carbons, the hydrophilic NOM samples had low organic carbon content and a high salt content in the study of Wong et al. (2002).

2.3.3. Pyrolysis-Gas Chromatography-Mass Spectrometry

Pyrolysis-GC-MS has shown the presence of carbohydrates, proteinaceous material, and N-acetylamino sugars in soil and aquatic HS (Bruchet et al., 1990). In HA and FA from lake water, the presence of volatile fatty acids, peptides, carbohydrates, sterols, phenols, lignin monomers and dimers as well as alkyl aromatics, naphthalene-, indene-, sulfur- and halogen-species has been shown (Schulten and Gleixner, 1999). N-heterocyclics such as pyrroles, pyrrolidines, pyridines, pyranes, and pyrazoles, have also been identified by analytical pyrolysis of aquatic HS (Schulten and Schnitzer, 1997). Chromatograms obtained with FA show the presence of aromatic-type structures, mainly phenol and cresol. Through these structures were lower at hydrophilic acids, hydrophilic acids are less aromatic than FA from the same origin. Hydrophilic acids have been found to contain a significant amount of sugars and amino sugars (Krasner et al., 1996b; Nikolaou and Lekkas, 2001).

2.3.4. Elemental Analysis

The elemental composition of aquatic HS has been evaluated in numerous studies (Malcolm, 1985; Stelink, 1985; Thurman, 1985b; Malcolm and MacCarthy, 1986; Aiken and Malcolm, 1987; Reckhow et al., 1990; Aiken et al., 1992; McKnight et al., 1992). These have been shown that the most abundant species are carbon, hydrogen and oxygen while other significant elements include nitrogen, sulfur, phosphorus and halogens. For aquatic HA which were evaluated in the works cited above, carbon content varied from 52 to 62 percent while oxygen content ranged from 23 to 40 percent. For aquatic FA, the carbon content varied from 52 to 63 percent while the oxygen content ranged from 29 to 39 percent. Aquatic HS isolated from groundwater sources had lower oxygen contents than those HS isolated from surface waters. In general, aquatic HS are highly oxidized organic materials and functional distribution of the oxygen has important implications with respect to water chemistry and drinking water treatment (Harrington, 1997).

The elemental composition of aquatic hydrophilic DOM fractions is relatively unknown. Aquatic hydrophilic bases are significantly different from other aquatic DOM fractions in their elemental composition, particularly with respect to nitrogen content. In addition, aquatic hydrophilic acids appear to have slightly greater oxygen content than aquatic hydrophobic acids (Aiken et al., 1992; Andrews et al., 1992; McKnight et al., 1992).

2.4. MW of DOM

MW and molecular size distributions are important properties for understanding the physical and chemical characteristics of NOM. Humic materials have a wide range of MWs, ranging from a few hundred to 100,000 daltons (Da), which is in the colloidal size range. Although HS have been regarded as macromolecular, current research on aqueous humic extracts from soil, lignite, and water revealed relatively small primary molecular structures (100–2000 Da) with macromolecular characteristics (Leenheer and Croue, 2003). Thurman et al. (1982) reported the molecular size obtained from several methods that aquatic FA had a MW of 500 to 2000 Da, while HA ranged from 2000 to 5000 Da.

Since HS are a very complex mixture of organic heterogeneous structures with a wide range of molecular sizes, it is not a simple task to determine MWs of aquatic HS. The most commonly used methodologies to determine MWD of aquatic organic matter are gel permeation chromatography (GPC) or the high-performance size exclusion chromatography (HPSEC) and UF (Thurman et al., 1982).

HPSEC has been applied to HS by several researchers since the invention of the high-pressure column in the last decade (Chin and Gschwend, 1991; Chin et al., 1994; Kilduff, 1995; Peuravuori and Pihlaja, 1997b; Zhou, 1999). In the studies, many advantages of HPSEC method were found compared to the other methods. The major advantage of HPSEC method that not only the molecular size distributions, but also number- (M_n) and weight-averaged (M_w) MWs with polydispersivity (ρ) of molecules can be obtained. Besides, no required any pretreatment prior to analysis is the other important advantage (Knuutinen et al., 1988; Chin and Gschwend, 1991).

A number of factors influence MW determinations of HS by HPSEC. First, calibration standards of the same molecular type as the sample (similar MW range, charge distribution, etc.) must be employed to obtain MW values precisely (Yau et al., 1979). Recent researchers (Chin and Gschwend, 1991; Chin et al., 1994; Kilduff, 1995; Peuravuori and Pihlaja, 1997b; Perminova et al, 1998; Zhou, 1999) have used polystyrene sulfonates (PSS), however LMW standards also need to be examined because of PSS having relatively HMW. Second, data processing of HPSEC chromatograms including baseline construction, baseline recovery, and MW cut-off (MWCO) affects the average values of MW (Mori et al., 1996,1997). Third, molecules of HS are subject to reactions with stationary phase of SEC column, including adsorption and electrostatic repulsion/attraction (Yau et al., 1979; Chin et al., 1994). The reactions can be minimized by optimizing the type of mobile phase (elute) with suitable ionic strength and pH (Chin et al., 1994). Fourth, the MW distribution curve (SEC chromatograms shape) and calculated MW averages of any given sample can vary with the detection method attached to the SEC system (Rause et al., 1991). The type of detector connected to HPSEC system also influences MW determinations of HS. Each type of detector has its limitations and advantages; UV/Vis is the most commonly used detection method for HPSEC HS research. Peuravuori and Pihlaja (1997b) stated the main function of the HPSEC method is that the obtained MW and molecular size distributions of the solutes respond as closely as possible to the real values.

2.5. Processes for the Removal of DOM

As previously mentioned, NOM defined as the complex matrix of organic material present in natural waters, affects significantly many aspects of water treatment, including the performance of unit processes. Aquatic NOM can be removed from raw water by various water treatment processes either directly or indirectly and varying degrees depending on its specific characteristics (e.g., MWD, carboxylic acidity, and HS content) and operational conditions (Collins et al., 1985). HMW NOM is more convenient to removal than LMW NOM, especially the fraction with MW less than 500 Da. Besides, NOM with the highest carboxylic acidity and so the highest charge density is generally difficult to remove by conventional treatment (Collins et al., 1986). While water source with HMW HA (5000–10000 Da) is a good candidate for chemical coagulation (Amy et al., 1992), the LMW species are more adsorbable presumably because more surface area is accessible to these substances (McCreary and Snoeyink, 1980).

2.5.1. Coagulation

In drinking water treatment systems, chemical coagulation is the major NOM removing process in many countries. This process is still dominant as one of the most economic method for larger treatment plants (Ratnaweera et al., 1999). The conventional treatment process for waters containing NOM is coagulation/flocculation using inorganic coagulants such as ferric chloride or aluminum sulfate.

Several mechanisms, precipitation, coagulation-flocculation, ion exchange, adsorption, enmeshment and co-precipitation, are of potential importance in the removal of organic compounds by coagulation. The affecting factors on which mechanisms may dominate are that pH, the type and dose of coagulant, the type and concentration of organic substances and other operational conditions (Randtke and Jepsen, 1981). Neutralization, entrapment, and adsorption are the most commonly referred mechanisms for NOM removal (USEPA, 2001). Charge neutralization is the mechanism used to explain the precipitation of NOM in operational regions where aluminum hydroxide precipitation is minimal. Colloidal NOM can act as nuclei for precipitate formation, or can become entrapped during floc aggregation (Owen et al., 1993; Singer and Harrington, 1993; Krasner and Amy, 1995).

Sinsabaugh et al. (1986) stated that the significant affecting factors for removing of DOC were molecular size, charge and solubility characteristics. Sinsabaugh and Hoehn (1984) showed that metal ion coagulants were efficient for removing HMW organic compounds. Similar findings were also reported by Knocke et al. (1986) that no significant residual organic matter above 10000 Da MW had been detected in the coagulated water sample. They were also determined that ferric sulfate and alum appeared to preferentially remove different organic compounds at pH of 5.5. Ferric sulfate was much better than alum to remove compounds in the 1000 to 10000 Da MW range. On the contrary, alum was slightly effective for removing organic compounds with a MW below 1000 Da, while ferric sulfate showed no significant removal of these extremely LMW species.

The effectiveness of coagulation is strongly dependent on pH and the dose of the coagulant. At higher coagulant doses, more metal for floc or complex formation is available. Typically, coagulation of NOM is most effective in the pH range of 5 to 6, as charge neutralization tends to be more effective at lower pH. In practice, optimum coagulant dosages are determined by TOC concentration for many and probably most surface water supplies. There is also a relationship between coagulants and TOC concentration in the water to be treated. This relationship depends on the types of organic substances to be treated, coagulant type and solution conditions (such as pH, hardness and temperature). Thus, TOC removal and DBP precursor removal can be enhanced by decreasing pH and/or by increasing coagulants doses (O'Melia et al., 1999; USEPA, 2001).

As well as traditional coagulants, based on aluminum and iron salts, there are now many commercial products that contain pre-hydrolyzed forms of the metals, mostly in the form of polynuclear species. In the case of aluminum, most materials are formed by the controlled neutralization of aluminum chloride solutions and are generally known as poly-aluminum chloride (PACl) (USEPA, 1999).

In literature, applying coagulation and flocculation processes in water treatment, expected DOC removal efficiencies were reported as 10-40% (Weber and Jodellah, 1985; Croue et al., 1993; Owen et al., 1993; Dennett et al., 1995; Edzwald, 1993; Crozes et al., 1995b; Volk et al., 2000), 40-60% (Dennett et al., 1995; Crozes et al., 1995b; Volk et al., 2000) and 20-40% (Volk et al., 2000) using alum, ferric chloride and poly-aluminum chloride (PACl) as coagulant, respectively. NOM with the highest carboxylic acidity and hence the highest charge density are generally difficult to remove by conventional treatment (Collins et al., 1986). Water source with HMW HA (e.g., 5000–10000 Da) is a good candidate for chemical coagulation. Besides, a water source with organics of medium MW (e.g., 1000-5000 Da) and size can be effectively treated by adsorption. On the other hand, the LMW and size FA are relatively hydrophilic and not amenable for removing by coagulation or adsorption (Amy et al., 1992; Chow et al., 1999; Matilainen et al., 2002).

2.5.2. GAC Adsorption

GAC is widely used for removal of synthetic organic chemicals from water supplies and municipal and industrial wastewaters. Background DOM has been found to significantly reduce the operational life and performance of GAC adsorbents in such applications (Smith et al., 1987; Summers et al., 1989; Carter et al., 1992; Carter and Weber, 1994).

The important affecting parameters are solute heterogeneity, pH, carbon dosage, types and concentrations of cations in solution and adsorbent particle size on both rates and capacities for adsorption of HS by activated carbon. McCreary and Snoeyink (1980) reported that the adsorption capacity varied extensively depending on the source of the adsorbate. Weber et al. (1983) showed that HS, as mixtures of compounds behaved differently with respect to adsorption than did single species. Lee et al. (1981) showed that the adsorption capacity and the uptake rate of HS increased while MW decreased. On the other hand, HS uptake rates were inversely correlated to the particle size of the carbon (Weber et al., 1978). HS could be more readily adsorbed on activated carbon as pH decreased (Weber et al., 1978; McCreary and Snoeyink, 1980; Lee, 1980; Weber et al., 1983). In addition, use of pretreatment (e.g., coagulation) precede GAC adsorption enhanced the adsorption capacity and the rate of uptake (Lee et al., 1981; Randtke and Jepsen, 1981). In addition to the adsorption of some trace synthetic organic micropollutants, NOM in most drinking water sources could be simultaneously adsorbed. This could negatively affect the adsorption capacity and adsorption kinetics of micropollutants (Pelekani and Snoeyink, 1999; Kilduff and Weber, 1994; Matsui et al., 1994; Yuasa, 1992; Sakoda et al., 1991; Najm et al., 1991; Wilmanski and Breemen, 1990; Smith and Weber, 1989). The capacity of activated carbon could be remarkably enhanced by certain cation species (Weber et al., 1983). The average size of DOM molecules had been reported to be approximately between 4 and 60 Å (Malcolm, 1985; Thurman, 1985a; Cornel et al., 1986; Hayes et al., 1989) whereas the bulk of GAC surface area was commonly located in pores with smaller widths than 20 Å (i.e., micropores) (Carter et al., 1992; Karanfil et al., 1996,1999).

The classical Freundlich isotherm equation has been used in many adsorption studies. However, as mentioned previously, NOM is composed of a heterogeneous mixture of aquatic HS, amino acids, sugars, aliphatic acids, aromatic acids, and a large number of other organic molecules. It has been well documented by many researchers that activated carbon preferentially adsorbs organic compounds. In case of preferential adsorption, the most adsorbable component in a mixture is removed from solution exclusively in lower adsorbent dose. The next most adsorbable component is removed only when adsorbent dose is increased sufficiently to completely remove the most adsorbable component (Kilduff et al., 1996). Therefore, a unique isotherm was developed to recognize the adsorption capacity of a given mixture composition. For this developed isotherm, the parameter is the amount of nonadsorbed solute per unit mass of adsorbent, computed by normalizing the equilibrium concentration by the adsorbent dose (Koopal, 1981; Summers and Robert, 1988). The normalized isotherm was expressed by a modified Freundlich isotherm model (Eq. 2.1) and has been used to model commercial, natural humic materials and DOM adsorption from natural waters (Summers and Roberts, 1988; Harrington and DiGiano, 1989; Kilduff et al., 1996):

$$q_e = K_F \left(\frac{C_e}{D_0} \right)^m \qquad \text{(Eq. 2.1)}$$

Where; q_e is the amount of adsorbed per unit mass of adsorbent (mg of TOC/g), C_e is the equilibrium liquid phase concentration (mg/L), D_0 is the adsorbent dose (mg/L), K_F is an empirical constant that represents the adsorption capacity at a value of C_e/D_o (dimensionless) and "m" is related to the magnitude of the adsorption driving force and to the distribution of the energy sites on adsorbent..

2.5.3. Membrane Filtration Process

Although it has been about 30 years since membrane filtration was introduced in drinking water treatment, the main applications were seawater and brackish water desalination in the first 20 years. Since the late eighties, the membrane process has been considered to be an effective means of removing turbidity, organics, microorganisms, and DBP precursors and to comply with the more strength regulatory controls (Thorsen, 1999). It offers many advantages, compared to conventional treatment, such as i) providing high quality water, ii) minimizing disinfectant demand, iii) being more compact, iv) easier control of operation and maintenance, and v) less production of sludge (Nakatsuka et al., 1996).

Membrane filtration can be broadly defined as a separation process that uses a semi-permeable membrane to divide the feed stream into two portions: a permeate that contains the material passing through the membranes and a retentate (concentrate) consisting of the species left behind (Mallevialle et al., 1996). The processes can be classified in many different ways according to the driving force (i.e., TMP, temperature, concentration and electrical potential), separation mechanism, membrane structure and its chemical composition or membrane construction geometry. Pressure-driven membrane separation processes have been recognized as the most promising membrane processes among them for water treatment (AWWA MTRC, 1992; Wiesner et al., 1994; Jacangelo et al., 1997; Macrorie et al., 2000).

Membrane processes for surface water treatment can further be divided into four groups, depending on pore size, separation mechanism and the target material to be removed. These are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and RO. MF will remove turbidity (particulates and bacteria), but no dissolved compounds, unless associated with colloids. UF remove NOM partially and viruses depending on the MWCO. NF process uses the membrane with the pore size between RO and UF. NF will remove NOM and hardness almost completely, however NF membranes are considered as uneconomic with respect to MF and UF membranes. RO process is mainly used to desalinize brackish water and seawater. Because of its small pore size, RO process has also been used to remove NOM, synthetic organic and other inorganic chemicals (Jacangelo et al., 1995a; Lee and Cho, 2004).

Various membrane materials have been proposed for water and wastewater treatment. Both organic polymers and inorganic materials with wider pH and temperature range have become available depending on the applications. One of the most important factors is to select proper membrane material for successful membrane process application. Ideally, the membrane to be used should have high permeate flux, good contaminant rejection, great durability, strong chemical resistant and low cost (Lee and Cho, 2004).

There are two ways to operate filtration equipment: the dead-end or cross-flow mode. In the dead-end filtration, the feed suspension flows perpendicularly through the membrane surface and all the suspended particles larger than the pore size of the medium are retained by the membrane. However, most UF and MF modules are operated in the cross-flow mode, in which the feed is pumped across or tangentially to the membrane surface. In this mode, there is one stream entering the module and two streams leaving the module: the retentate (concentrate) and the permeate (Cheryan, 1998).

The main advantage of the dead-end filtration mode is simplicity. The feed suspension is not recycled or passed across the membrane. However, intensive concentration polarization and fouling can occur under these conditions. In contrast, the cross-flow membrane filtration will continuously scour the rejected contaminants away from the membrane surface, thereby, minimizing the buildup of contaminants on the membrane surface and extent of membrane fouling. Although membrane cleaning is still periodically required, the self-cleaning nature of cross-flow filtration extends the filtration cycle prior to backwash. Thus, it has been widely used in nearly all commercial large-scale pressure-driven membrane plants (Hong, 2003).

2.5.3.1. Removal Performances in Membrane Filtration

MF is a filtration process that use porous membranes to separate particles in water with pore diameters between 0.1 and 10 µm. UF uses finer porous membranes, having average pore diameters between 0.05 µm to 1 nm, to separate micro solutes and water. The typical MWCO of NF membranes ranges from 200 to 1000 Da. While MF and UF membranes can achieve effective removal of particles and microorganisms, they are not as effective in removing color and dissolved constituents. Polymeric

NF and UF membranes have been widely examined for the removal of NOM from drinking water sources, to minimize the formation of chlorinated DBPs (Jacangelo et al., 1995a; Lee and Cho, 2004).

Wiesner et al. (1991) used ceramic MF membranes with and without coagulation as a pretreatment step for waters with moderate to high turbidities and TOC and THM formation potential (THMFP). They reported that the removal of turbidity, UV_{254} absorbance, TOC and THMFP are 99%, 60-87%, 48-59% and 40-65%, respectively. Significant removal of TOC could be achieved by MF alone.

Scanlan et al. (1997) studied the effectiveness of MF and UF of a low turbidity, moderate color and TOC water source. They found that UF was more effective on particle removal than MF, with or without chemical addition; however, the operation times of MF were much longer than those of UF. The concentrations of THMs and HAAs in treated water did not consistently meet the Stage 2 D/DBP requirements.

Jacangelo et al. (1995b) evaluated the efficiency of combined powdered activated carbon (PAC) and UF for removing DBP precursors. They found that UF alone could not remove DBP precursors effectively due to its high MWCO. Less than 15% of the TOC and less than 10% of the THM and HAA precursors were removed in their study. In other side, DBP precursor removal increased with increasing PAC dosages in the combined PAC-UF treatment.

Taylor et al. (1987) tested NF membrane with MWCO of 400 Da and observed a 96% removal efficiency of THMFP precursors. Amy et al. (1990) observed only a 65 to 70% reduction in THMFP by using NF membrane (MWCO<500 Da) for treating Colorado River water. The difference in the reductions of DBP in these studies may be caused by different characteristics of NOM.

Lozier and Carlson (1991) evaluated ultra-low pressure membrane processes (defined as typical TMP pressure requirements of 150 psi (~10 bar or less) to treat three surface waters in the eastern U.S. with TOC and THMFP concentrations ranging from 5 to over 50 mg/L and from 400 µg/L to greater than 2000 µg/L, respectively. They found that the NF (MWCO<300 Da) and the UF (MWCO=3000 Da) membranes were capable of reducing THMFP to less than 60 µg/L and TOC levels by more than 90 percent. Taylor et al. (1987) and Fu et al. (1994) showed that NOM could be effectively rejected by UF and NF membranes.

Siddiqui and collages (2000) evaluated NF, UF, and MF to determine the rejection of DBP precursors from low turbidity surface waters in Colorado. They found that the average rejections of DOC, THMFP, HAAFP and CHYFP of NF were all over 85%. MF was only moderately effective in particle removals, with virtually no DBP precursors removal provided. UF alone removed less than 30% of DOC. NF membranes with MWCO less than 300 Da removed an average of 90% DOC. Only 40% reduction of DOC was observed on permeates of NF with 500 Da of MWCO. Bromide rejections were among 40 and 80% in the study. Similar observations were reported by Allgeier and Summers (1995).

DiGiano and colleagues (1993) suggested that pretreatment of the raw water before NF would be necessary in order to remove THM precursors effectively if the concentrations of THMFP in the raw water were higher than 100 µg/L. Mulford et al. (1999) used incorporated MF or UF before NF to treat water containing 11 mg/L TOC, 336 µg/L simulated distribution system (SDS) THMFP, 227 µg/L SDS HAAFP, 24 mg/L chlorine demand.

High removal efficiencies were achieved and the average concentrations of TOC, SDS THMFP, SDS HAAFP and chlorine demand of finished water were 0.4 m g/L, 35 µg/L, 28 µg/L and 6.5 mg/L, respectively. Chellam et al. (1997) observed similar results and reported that surface water treated by dual membrane system (e.g., MF followed by NF) could meet current and anticipated THMs and HAAs regulations.

Laine et al. (1993) reported that NF membranes were effective for DBP precursor removal but ineffective for removing bromide, thereby resulting in increase in the bromide to TOC ratio and proportion of brominated to chlorinated THMs. Similar statement was also reported by Jacangelo et al. (1995b) using combined PAC and UF treatment that increasing of the bromide-to-TOC ratio was observed as TOC was removed by the PAC.

2.5.3.2. Membrane Fouling

Fouling phenomena caused by NOM in natural waters has raised interest in MF, UF, NF and RO processes. Fouling is essentially caused by the deposition of foulants on the membrane surface and led deterioration in the membrane performance through a decline in the flux and an increase in the resistance (Lee et al., 2002).

Membrane fouling occurs through one or more of the following mechanisms: (i) accumulation of solute and gradual irreversible changes to the polarized layer (such as cake formation), (ii) surface adsorption: deposition of solutes and (iii) adsorption: deposition of solute within the membrane. Generally, factors influencing NOM fouling can be classified as (a) characteristics of NOM and membranes, (b) hydrodynamic conditions, and (c) chemical composition of feed water (Kim et al., 1992; Hong and Elimelech, 1997; Jarusutthirak et al., 2002).

Chang and Benjamin (1996) suggested that, when the membrane rejected a portion of the NOM, it remained near the membrane surface, so its concentration was higher near the surface than in the bulk solution (this phenomenon is called concentration polarization (CP)). If the solubility of the NOM is exceeded in the CP layer, the NOM may form a new phase on the membrane surface, thereby increasing the hydraulic resistance across the membrane and limiting the permeate flux (the form and composition of the condensed phase is thought to be a gel). Thus, the association of NOM with the membrane matrix, membrane pore blockage and plugging, precipitation, deposition, and surface layer formation are the factors contributing to the fouling mechanisms and the resulting flux decline. These factors are confounded by one another and are difficult to separate.

Fouling tests revealed that the hydrophobic fraction of NOM was mostly responsible for permeate flux decline, whereas the hydrophilic fraction caused much less fouling. By this manner, general perception that only the large MW fraction of NOM contributed to the formation of a fouling layer (Crozes et al., 1993; Nilson and DiGiano, 1996; Hong and Elimelech, 1997). However, Amy and Cho (1999) reported that hydrophilic NOM (polysaccharides) were found to be a dominant foulant.

In general, the extent of irreversible fouling with proteins, polysaccharides and NOM has been found to be greater around the isoelectric point of the molecules, at high ionic strength, in solutions supersaturated with calcium, and on hydrophobic membranes (Laine et al., 1989). Crozes et al. (1993) showed that the adsorption of LMW molecules, smaller than the membrane pore size, could lead to significant irreversible fouling. The study also revealed that hydrophilic membranes were better suited for filtration of surface waters. Crozes et al. (1995a) also showed that the momentary accumulation of particulate or organic matter on the membrane surface did not necessarily lead to irreversible fouling of the membrane.

Adsorption kinetic studies showed that adsorption of HA was slower than that FA. This is mainly due to the diffusivity of molecule size and solubility of HA (HA have higher molecular size and is somewhat more hydrophobic than FA). In addition, HA molecules might have more attachment sites and therefore binding to the membrane surface could be enhanced. Adsorption decreased with increasing hydrophilicity and decreasing zeta potential. Moreover, upon adsorption of HS, the membrane becomes more hydrophilic and apparent pore charge becomes less negative (Tipping and Ohnstad, 1984; Cornel et al., 1986; Jucker and Clark, 1994; Maartens et al., 1998).

Schafer et al. (1998) stated that adsorption might only be an initial phenomenon, after which deposition would be due to precipitation or aggregation. Moreover, precipitation and aggregation effects in the membrane boundary layer were reported to be important phenomena in NF.

One of the important factors during adsorption process is pH that adsorption is greater at pH 7 because the charge on HS is less negative. (Maartens et al., 1998). Another factor on adsorption is inorganic ions that adsorption experiments showed an increase in adsorption with increasing calcium concentration. For HA, calcium was adsorbed in proportion to the amount of HA adsorbed. Calcium ion acted as a bridge between the membrane surface and the negatively charged HA molecules, and/or in between the negatively charged carboxyl groups which were not in contact with the membrane (Cohen-Stuart et al., 1991). Schafer et al. (1998) stated that there would be a competition between FA and calcium for the adsorption sites on the membrane surface. Amy and Cho (1999) investigated NOM interactions with UF and NF membranes operated under cross-flow conditions representative of spiral wound elements. While inorganic water quality appeared to have little effect on flux decline, high calcium or low pH enhanced NOM rejection. Electrostatic exclusion was determined to be an important NOM rejection mechanism, particularly for higher MWCO UF (versus MWCO lower NF) membranes.

2.5.4. Ion Exchange Process

Potable waters containing large amounts of the LMW forms of HS can be difficult to treat by coagulation processes, especially if the waters are low in turbidity. The smaller molecules are less effectively removed by coagulation and are better taken out by adsorbents or by biological methods after oxidative degradation. Therefore, anion exchange processes have attracted increased attention in recent years as an efficient alternative technique for removing DOM. Since late of 1970s, the removal of NOM using of anion exchange resins with strong capacity have been demonstrated (Anderson and Maier, 1979; Snoeyink, 1979; Kunin and Suffet, 1980; Brattebo et al., 1987; Symons et al., 1995; Odegaard et al., 1999).

Fu and Symons (1990) indicated that anion exchange resins removed up to 80% of the DOC in natural waters and reported that removal efficiency was strongly related to the type of resin and the nature of the organic matter. They addressed the important factors for removing NOM by anion exchange resin as follow:

- the size of the pores and their size distribution within anion exchange resin were important as taking into account HMW,
- the hydrophilic character of the resin was significant when addressing intermediate fractions; and
- the exchange capacity was the main issue as LMW fractions were considered.

If a polar group was near the quaternary ammonium exchange sites, strong base resins were more efficient than weak base resins with reference to organic loading capacity (Brattebo et al., 1987; Bolto et al., 1999). Croue et al. (1999) reported similar results for isolated hydrophilic acid fractions, fractionated from the Suwannee River. Especially if the stock solutions were at acidic pH, the use of strong base resins achieved considerably higher DOC removals (70-77%) than weak base resins did (~42%). Besides the MW of the fraction had a major effect on the removal efficiencies that the higher MW of a compound the lower amount of DOC removed; hence hydrophilic neutral fractions were more readily removed than hydrophobic acid fractions.

The MIEX® DOC process was developed by Orica Watercare, South Australian Water Corporation and the CSIRO specifically for the removal of DOC from drinking water. The resin is a strong base anion exchange resin with a macroporous structure and type 1 quaternary ammonium active sites attached to a magnetic core. The MIEX® resin beads have a mean particle size of 150 µm. The MIEX® process was developed on a number of specifications as follows (Fearing, 2004): (a) resins with quaternary ammonia functional groups are more effective (Bolto et al., 2002; Singer and Bilyk, 2002), (b) resins with a polyacrylic skeleton are the best for NOM removal (Symons et al., 1995; Singer and Bilyk, 2002), (c) macroporous resins are more suited to continuous processes than gel resins (Singer and Bilyk, 2002), (d) resins need a high specific ion exchange capacity (Brattebo et al., 1987), and (e) smaller sized resin particles are more efficient (Meyers, 1995).

MIEX® is not limited to only DOC removal and will remove other negatively charged ions (anions) from water such as sulphate, sulphide, chromate, nitrate and arsenate. The extent of removal of these anions depends on the competition between other anions in the water source (Bourke, 2001, Chow et al., 2001, Hamm and Bourke, 2001).

The process involves adsorbing the DOC onto the MIEX® resin in a stirred contactor that disperses the resin beads to allow for maximum surface area. The magnetic part of the resin allows the resin to agglomerate into larger and faster settling particles, which allow for a recovery rate of greater than 99.9%. Any resin carried over is removed in downstream processes. A further treatment stage is then required as the MIEX® process does not remove suspended matter; therefore coagulation or microfiltration is usually used for this purpose (Smith et al., 2001; Drikas et al., 2003, Fearing, 2004).

It has been well known that the concentration of DOC tends to control the coagulant dosage required for effective turbidity (particle) removal for most natural waters. Hence, application of the MIEX® resin prior to coagulation is expected to remove a significant portion of DOC, thereby the coagulant demand for subsequent coagulation of particulate material was lowered (Singer and Bilyk, 2002; Chow et al., 2001).

Singer and Bilyk (2002) stated that MIEX® tended to show little preference for removal of UV-absorbing material or THM precursors relative to removal of TOC. Although there was no preferential removal of hydrophobic acids over hydrophilic acids, the removal performances of these fractions could be stated unequivocally. They expressed the fact that the resin gave greater removals for high SUVA waters.

2.6. Disinfection in Water Treatment Systems

2.6.1. DBPs

Disinfection is one of the most important processes in the water treatment systems. Chlorine and its compounds are the most commonly used disinfectants for water treatment. Chlorine has been much more popular than other disinfectants due to its lower cost, higher oxidizing potential, which provides a minimum level of chlorine residual throughout the distribution system and protects against microbial recontamination (Huang and Smith, 1984; Sadiq and Rodriguez, 2004). However, chlorine has been lost its popularity, since Rook (1974) discovered that the chlorination of drinking waters resulted in the production of chloroform and other THMs due to the reaction of chlorine with the organics in the water. In the literature, approximately 600-700 DBPs have been identified for the major disinfectants used (i.e., chlorine, ozone, chlorine dioxide, chloramines) as well as their combinations (Krasner et al., 1989; Stevens et al., 1990; Richardson, 1998; Krasner et al., 2006). After discovering of THMs, drinking water surveys have been focused on HAAs (Christman et al., 1983; Miller and Uden, 1983), HANs (Coleman et al., 1984; Reckhow and Singer, 1984; Smith et al., 1987; Singer et al., 1995), HKs (Tan and Amy, 1991; Koch et al., 1991), HNMs (Castro and Belser, 1981; Croue and

Reckhow, 1989; Wu et al., 2001; Krasner and Wright, 2005; Pearson et al., 2005; Chun et al., 2005; Lee et al., 2007), HAs (USEPA, 2002; Wagner et al., 2005; Krasner et al., 2006) short chain carboxylic acids, acetones, chlorinated phenols and phenolic acids (Kronberg, 1999), chlorinated quinones, benzoic acids and heterocyclic compounds (Blatchley et al., 2003). In recent studies, 28 new, previously unidentified, DBPs including brominated and iodinated haloacids, brominated ketone, and chlorinated and iodinated aldehydes were detected (Krasner et al., 2006).

Among the most commonly formed DBPs are the THMs (Nieminski et al., 1993; Kronberg, 1999; Blatchley et al., 2003). THMs being the first chlorination by-products to be identified and regulated, several improved methods were developed for their quantification. After the realization of adverse effect of THMs, removal methods of THMs along with their precursor from drinking water were also developed (Villanuevaa et al., 2003). Nieminski et al. (1993) stated that the concentrations of total HAAs are also high enough to be of health concern. These two classes contribute to about 75 percent of the total measured halogenated DBPs; however, the total halogenated DBPs measured only account for 25-50 percent of the total organic halide (Christman et al., 1983; Reckhow and Singer, 1984; Singer, 1994).

DBP formation and speciation is a complex phenomenon and depends on many factors such as NOM characteristics and concentration (as DOC), water quality parameters (e.g. pH and background inorganic matrix, especially the bromide concentration), chlorination conditions (e.g. temperature, chlorine dose and contact time), and ratios of bromide/DOC and bromide/chlorine concentrations (Symons et al., 1993,1996; Singer et al., 1995; Sketchell et al., 1995; Krasner et al., 1996a; Croue et al., 1999;

Chellam, 2000). NOM has been identified as the principal precursors in the formation of DBPs (Rook, 1976; Stevens et al., 1976, Reckhow et al., 1990).

Since 1980’s, DBPs have raised significant concern due to evidence of their adverse human health effects, in particular cancer and reproductive disorders (Cantor et al., 1988; Graves et al., 2002). Chlorinated drinking water contains a complex mixture of chlorinated by-products with different chemical and toxicological properties that may eventually enter the human body by ingestion, inhalation and dermal absorption (Villanuevaa et al., 2003). Kim and Walker (2001) stated that DBPs are potential carcinogens and are also linked to several health problems associated with the central nervous system. Consumption of chlorinated water has been linked with an increased risk of bladder cancer; and consumption of water containing DBPs associated with chlorination can increase the risk of bladder and rectal cancer in humans (Nissinen et al.; 2002; Blatchley et al., 2003). The research by reported Morris et al. (1992) supported a strong association between bladder cancer and exposure to DBPs in drinking water and also further indicated a fairly strong relationship between rectal cancer and chlorination by-products. Analytical epidemiologic studies have reported a moderate increase in the risk of bladder and colon cancer in population with a long duration to chlorinated drinking water (Craun, 1991; Simpson and Hayes, 1998).

USEPA promulgated D/DBP the Stage 1 Rule on December 18, 1998. This rule covers many areas including DBP monitoring and reporting, best available technologies for DBP control and coagulation provisions. In the USEPA guidelines, the maximum contaminant levels (MCL) specified in the DBP Stage 1 Rule were 80 µg/L for total THMs, 60 µg/L, for the sum of five HAAs, 10 µg/L for bromate and 1,000 µg/L for chlorite ion. Compliance with Stage 1 regulations for THMs and HAAs was based on the running annual averages, which represented averages of all samples collected in a utility's distribution system over a one-year period. The proposed Stage 1 DBP rule also included lower MCLs for total THMs (TTHM) (40 µg/L) and HAA5 (30 µg/L) as a "placeholder" to assure participants favoring further DBP controls that other members would return for Stage 2 DBP negotiations. For the Stage 2 DBP rule, the negotiators agreed that EPA would collect data on the parameters that influence DBP formation and occurrence of DBPs in drinking water through the Information Collection Rule (ICR). Based on this information and new data generated through research, EPA would reevaluate the Stage 2 DBP "placeholder" provisions and re-propose, as appropriate, depending on the criteria agreed on in a second regulatory negotiation (USEPA, 1998a). Stage 2 of the D/DBP (promulgated in January 2006) requires water utilities to comply with the same MCLs (for TTHMs 80 µg/L and HAA5 60 µg/L). However, these MCLs should not be exceeding at each individual monitoring location in a distribution system (i.e., locational running annual averages) in six years (USEPA, 2006).

Besides USEPA, the other governmental agencies of various countries have focused on DBPs and promulgated regulations. Drinking water guidelines for a few DBPs including THMs, HAAs, HANs, chlorite, CHY, formaldehyde and cyanogen chloride was published by the World Health Organization (WHO, 2004). In Canada, total THM was set to 100 µg/L as an interim maximum acceptable concentration as a guideline for Provincial regulations in 2001. No Canadian drinking water quality guideline exists for other DBPs for the time being. According to the Australia–New Zealand (Aus-NZ, 2000) and United Kingdom (UK, 2000) drinking water standards, TTHMs should be lower than 250 µg/L and 100 µg/L, respectively (Sadiq and Rodriguez, 2004). The European Community has regulated the TTHM concentration to 100 µg/L in the distribution system (EEC, 1998). Although there is yet no regulations on HAAs in Turkey, Turkish Ministry of Health has recently regulated TTHMs. TTHMs does not exceed 150 µg/L for municipal water supply up to December 31, 2012, then this limit will be decreased to 100 µg/L (RCWIHC, 2005). There is very limited research and information available on the occurrence and concentrations of various DBPs in Turkish drinking waters.

2.6.2. Chemistry of DBP Formation

While some DBPs symbolize halogen substitution by-products, the others are oxidation by-products. Additionally, secondary by-products can be formed by disinfectant combinations (e.g., from pre- and post disinfection). As previously stated, chlorine is a relatively inexpensive and widely used disinfectant in drinking water treatment processes around the world. Chlorine gas, sodium hypochlorite (NaOCl) or calcium hypochlorite ($Ca(OCl)_2$) may be used in disinfection practices to form a mixture of hypochlorite (OCl^-) and hypochlorous acid (HOCl) solution (Glaze and Pontius, 1990; White, 1992; Larson and Weber, 1994). When chlorine is added to water it hydrolyzes very rapidly to H^+, OCl^- and HOCl.

HOCl, a weak acid with a pKa of 7.5 at 25 ^{0}C, then dissociates very rapidly to form a OCl^- and a H^+. The relative abundance of OCl^- and HOCl in the solution depends on pH and HOCl becomes the dominant specie at pH values smaller than 7.5 at a given temperature. This pH dependency is important because HOCl has been shown to be a stronger disinfectant than OCl^- (Glaze and Pontius, 1990; White, 1992). The sum of the concentrations of HOCl and OCl^- represents the free residual chlorine in water. When HOCl oxidizes a substance, the Cl^+ in HOCl takes two electrons from the substance being oxidized, and becomes a chloride ion (Cl^-). Thus, the oxidizing capacity of HOCl is equal to two equivalents of atomic chlorine, or one mole of molecular chlorine. Both HOCl and OCl^- accept two electrons. The following compounds may have significant reactivities with chlorine: DOM, proteins, amino acids, and inorganic compounds such as bromide, nitrites, iron, manganese, hydrogen sulfide, and cyanides. Hence, they play important roles in the chlorine demand of drinking water sources.

In many research, chlorine consumption of several known organic solutes has been investigated. Chlorine consumption per mole of solute varies based on the structure of organic matter. Activated aromatic compounds generally consume more chlorine per mole of solute than aliphatic compounds, however some aliphatic compounds based on a carbon basis can be consume much more chlorine in amount. In studies of Reckhow et al. (1990) and Harrington (1997), a linear relationship between chlorine consumption and the activated aromatic carbon content of the various HA and FA was shown. The chlorine consumption and formation of each DBPs were relatively higher for the HA fraction, probably due to the greater aromatic carbon content of the fraction.

Chlorine consumption by aquatic FA varies from 1.0 to 1.7 mg Cl_2/mg C (Reckhow and Singer, 1985; Reckhow et al., 1990). For aquatic HS, chlorine consumption increases with increasing aromatic carbon content, particularly activated aromatic content. Chlorine consumption varies from 2.0 to 2.5 mg Cl/mg C for untreated aquatic HA (Reckhow et al., 1990). Chlorine consumption in natural waters varies from 1.1 to 4.5 mg Cl_2/mg C (Singer et al., 1981; Reckhow and Singer, 1990). On the other hand, some of this chlorine consumption may also arise from inorganic demand (Harrington, 1997).

2.6.3. The Effect of Bromide Ion on DBPs Formation

In the absence of bromide ion, chlorine reacts with NOM constituents to form chlorination by-products. The concentration of bromide in raw water is significant factor in the formation of chlorination by-products in finished water. When bromide is present, chlorine in the form of hypochlorous acid-hypochlorite ion ($HOCl-OCl^-$) oxidizes bromide ion to hypobromous acid-hypobromite ion ($HOBr-OBr^-$). Thereby, the presence of bromide in a water source is more critical than free chlorine when considering DBP speciation following disinfection. A mixture of HOCl and HOBr can lead to the formation of both chlorinated, brominated by-products and mixed chloro-bromo derivatives (Krasner et al., 1989; Tan and Amy, 1991, Peters et al, 1991; Heller-Grossman et al., 1993; Krasner et al., 1993; Pourmoghaddas et al., 1993; Pourmoghaddas and Stevens, 1995; Sketchell et al., 1995). Bromoform is only small part of the pool of identifiable brominated DBP compounds including bromoacetic acids, bromoacetones, and bromoacetonitriles, as well as ill-defined bromo-NOM (Siddiqui and Amy, 1993).

When HOCl and HOBr of equal concentrations are reacted together with water containing high levels of TOC, the brominated THM species are dominant, and chloroform formation is suppressed. It has been noted that the bromine substitution is favored over chlorine, even when chlorine is present in large excess compared with bromide concentration. These observations support the theory that bromine atom is more reactive than the chlorine atom during the halogenation of THM precursors. Presence of bromide ion has a change effect on the speciation of HAAs but not total of HAA, whereas speciation and formation of THMs is significantly affected in the case of higher bromide ion concentration (Pourmoghaddas et al., 1993). The distribution between chloro- and bromo- species depends on the Cl_2/Br^- ratio (Heller-Grossman et al., 1993). This is of concern since the MW of brominated species is higher than the chlorinated counterparts, leading to potential failure to comply with regulations. The regulations, specified as the mass per volume (in µg/L) of total THM and HAA be less than MCL, place more significant on brominated compounds (Marchand, 1996).

Cowman and Singer (1994) stated that significant concentrations of mixed bromo-chloro HAAs species were formed from the chlorination of bromide-containing water. Bromodichloroacetic acid was the most abundant among the bromo-chloro species formed (Cowman and Singer, 1994; Singer, 1994; Nikolaou et al., 1999). Increasing molar concentrations of nine HAA species (HAA9) have been measured with increases in the Br^- concentration for reaction times greater than 24 h (Chellam, 2000). Although the formation of HAAs increases with increasing bromide concentration, the distribution of the HAA species among mono-, di-, and trihalogenated forms is independent from the bromide ion concentration. On the other hand, Pourmoghaddas et al. (1993) stated that the presence bromide ion led a shift towards more brominated (dibromoacetic acid and tribromoacetic acid) and mixed halogenated (bromochloroacetic acid, dichlorobromoacetic acid and dibromochloroacetic acid) species in chlorinated HA solution. This study also revealed that for the HAAs, the brominated and mixed species would be dominant in the presence of a high Br^- concentration.

The concentration of both bromide ions and organic precursors affect the concentration and speciation of THM formed during water chlorination. Increasing the Br/DOC ratio increases the TTHMFP by increasing the amount of bromine or treatment techniques that decrease the DOC content of the water without affecting the bromine content. By that Br/DOC ratio will be increased and results in higher THM/DOC and an increase in proportion of brominated compounds. The presence of even low levels of bromide in raw water supplies affects the formation of THM species and their quantitative distribution in the finished water after chlorination. Therefore, changes in either Br^- or DOC by different mechanisms result in changes in the THM speciation (Siddiqui and Amy, 1993; Sketchell et al., 1995).

The bromine incorporation factor has been employed as a useful index to describe the distribution of DBP species in chlorinated natural waters. The following equation has been used for bromine incorporation factor (n) Gould et al., (1983):

$$n = \frac{\sum_{i=0 \text{ to } 3} i\left[CHCl_{(3-i)}Br_i\right]}{\sum_{i=0 \text{ to } 3}\left[CHCl_{(3-i)}Br_i\right]} \qquad \text{(Eq. 2.2)}$$

Where; n is bromine incorporation factor and i is the mole number of bromine. If n is equal to zero, there is only $CHCl_3$ formed and if n is equal to 3, only $CHBr_3$ is formed; n is computed by using molar THM concentrations. Gould *et al.* (1983) utilized n to illustrate that the speciation of THMs was sensitive to initial $HOCl/OCl^-$ and organic precursor concentrations.

2.6.4. Correlations of DBPs with Surrogate Parameters

In many studies, several researchers have tried to correlate water quality parameters to DBP formation in an effort to find a useful surrogate parameter to estimate DBP formation or to better understand the chemical nature of DBP formation processes. The most used surrogate parameters are DOM, UV absorbance and SUVA (UV absorbance divided by the DOC concentration). Although all surrogate parameters have limitations due to their substitution measurements and being non-specific, the important practical advantages of these surrogate parameters are to be determined in a short period of time, using a small volume of sample, and not require sophisticated sample pretreatment. The equipment needed to make DOC and UV measurements is available in most water treatment plants and is straightforward to operate by the treatment plant operators.

2.6.4.1. DOM – DBP Formations and Speciation

The amount and chemical structure of DOC play important role as a result of reacting with disinfectants in water treatment industry. Many researchers have shown that good correlations between organic compounds and DBPs formation potentials and stated that DOC can be used as a surrogate parameter to determine DBPs in chlorinated natural waters (McCarty and Aieta, 1984; Edzwald et al., 1985).

Singer and Chang (1989) showed that the TOC concentration of water was generally a good indicator to estimate the amount of THMs and other DBPs. In a study, the relationships DOC and DBPs formation potentials were investigated using water samples collected from three different locations in Arizona having DOC values in the widely range within almost 1 to 6 mg/L. Reasonable correlations were obtained between DOC and THMFP and between DOC and HAA5FP (total 5 species of HAA formation potential) with a R^2 as 0.79 and 0.82, respectively (Nguyen et al., 2002).

NOM molecules including OH, carbonyl, ester and carboxyl groups are thought to participate preferentially in reactions generating DBPs when water is chlorinated (Rook, 1974; Norwood and Christman, 1987; Reckhow et al., 1990). Since chlorine species are electrophiles, they tend to react with electron-rich sites in DOM. Some of electron-rich organic structures are activated aromatic rings, amino nitrogen, and aliphatic β-dicarbonyls (Reckhow et al., 1990; Hanna et al., 1991; Harrington et al., 1996). The cleavage of aromatic rings or oxidation of side-chains in humics followed by halogenation may result in the formation of chlorinated aliphatic compounds. Several ring-chlorinated aromatic compounds may also form after chlorination of DOM (Seeger et al., 1985; De Leer et al., 1985).

Rook (1976,1977) postulated that the *m*-dihydroxy structure of resorcinol was the principal chloroform precursor in aquatic humic materials. The bleaching effect of the chlorination process appeared to be caused by oxidation of double bonds in DOM without breakdown to smaller molecular size (Rook, 1976). Rook (1977) hypothesized that haloform reaction occurred with the resorcinol-type moiety of FA. The pathway is proposed as that carbon atoms, activated by ortho hydroxide substituents or phenoxide ions, are first involved in chlorination in an alkaline environment. The reaction initially yields the intermediate carbanion (carbon has an unshared pair of electrons and bears a negative charge), which is rapidly halogenated to the product shown in Figure 2.1. Following the aromatic structure has been halogenated and opened, cleavage at (*a)* will result in the formation of THMs (e.g., chloroform). Alternatively, oxidative and hydrolytic cleavages at (*b)* will yield an HAA (e.g., trichloroacetic acid or CHY). Besides, HK will be formed as a result of cleavage at (*c)*. In the presence of bromide, mixed bromochloro by-products will be produced (Krasner, 1999).

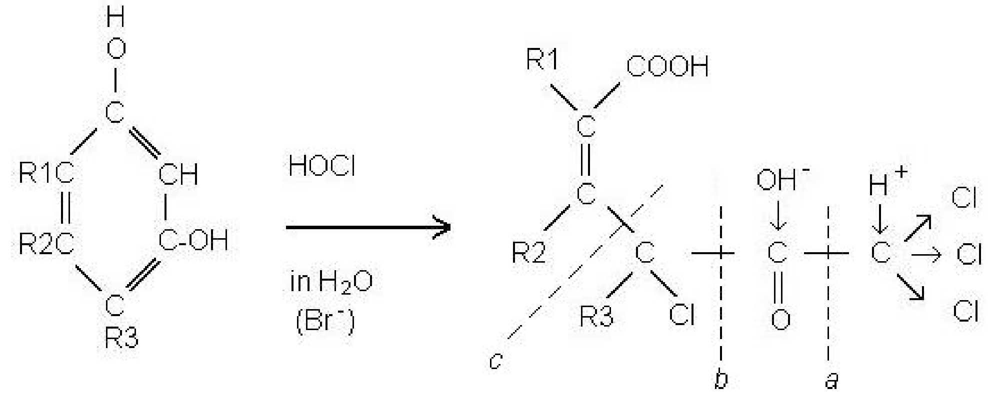

Figure 2.1. Haloform reaction with FA and resorcinol (Adapted from: Krasner, 1999).

Reckhow and Singer (1985) developed a simplified conceptual model for the formation of major organic halide products from FA. In this model, they used a β-diketone moiety (R′-CO-CH_2-CO-R) to represent the reactive site of DOM. The activated (middle) carbon atom will quickly become fully substituted with chlorine. Rapid hydrolysis of this moiety yields a monoketone group. If the remaining “R” group is hydroxyl group, the reaction will stop, yielding dichloro-AA. Otherwise, the structure will be further chlorinated to a trichloromethyl species. This intermediate specie is base-hydrolyzable to chloroform. At neutral pH, if the “R” group is an oxidizable functional group capable of readily donating an electron pair to the rest of the molecule, trichloro-AA is expected to form. NOM with higher values of SUVA probably has a higher amount of oxidizable functional groups, which will result in a higher formation of trichloro-AA (Reckhow and Singer, 1990; Krasner, 1999).

Hwang and his colleagues (2000) evaluated characteristic of tested water as low SUVA including a higher portion of β-diketone moieties with “R” groups that were hydroxly groups. They stated that these results suggested that DXAA and TXAA had different precursors and their low SUVA water contained a higher portion of dichloro-AA precursors. Croue et al. (2000) stated that hydrophilic NOM fractions enriched in nitrogeneous type structure were found to exert a strong chlorine demand associated with dichloro-AA production.

Liang and Singer (2003) stated no significant difference between hydrophobic and hydrophilic fractions in DXAA formation potentials for SUVA water; however, the hydrophobic fractions generally yielded higher formation potentials of DXAA, TXAA, TTHM, regardless of chlorination pH or origin and nature of the NOM. On the other hand, Sinha et al. (1997) proposed that the hydrophobic fraction was more reactive than the hydrophilic fraction for THM formation but that two fractions were equally reactive in terms of HAA formation.

Non-chlorinated by-products may also form from the oxidation of DOM by chlorine. Christman et al. (1980) and Johnson et al. (1982) observed non-chlorinated aromatic by-products after chlorination of HA. They stated that non-chlorinated aliphatic acids might also be formed from ring cleavage of humics.

2.6.4.2. UV Spectroscopy – DBP Formations and Speciation

Researchers have shown good correlations between THMFP and UV absorbance at 254 nm wavelength using raw and treated waters (Edzwald et al., 1985). Amy et al. (1987) showed that the multiplicative parameter UV absorbance and DOC was a good predictor of TTHMFP with short incubation time. In another study, it was found that UV absorbance was greater for the HA, reflecting their higher aromatic content and greater molecular size. Besides, HA led to the higher yields of TOX, THMs, HAAs, and HANs than the corresponding FA from the same source (Reckhow et al., 1990). Nguyen et al. (2002) investigated the relationships between UV absorbance and formation potential of DBPs. They showed that UV absorbance at 254 nm almost varied from 0.01 to 0.21 was better correlated with HAA5FP (R^2=0.91) than with THMFP (R^2=0.69).

2.6.4.3. SUVA – DBP Formations and Speciation

SUVA is regarded as an indicator of the DBP precursor removal (USEPA, 1998b). The high values of SUVA indicate double bound character (>C=C< or >C=O) and high SUVA waters are generally enriched in hydrophobic NOM such as HA and FA (Wong et al., 2002). ^{13}C-NMR measurements show a strong correlation between SUVA and the aromatic carbon contents of a large number of NOM fractions (Leenheer, and Croue, 2003; Croue et al., 1999). Therefore, the SUVA value of a water is considered to be a good surrogate for hydrophobic, aromatic, and HMW NOM fractions (Edzwald and Van Benschoten, 1990; White et al., 1997).

The possible reason of good correlations among UV absorbance or SUVA and DBP formations has been attributed to the likelihood that "activated" aromatic structures (aromatic sites substituted with oxygen- and nitrogen-containing functional groups, i.e., phenolics and aromatic amines) constitute the primary sites attacked by chlorine or other oxidants (Norwood et al., 1980; De Laat et al., 1982; Norwood and Christman, 1987; Reckhow et al., 1990; Harrington et al., 1996).

Singer (1999) showed that THM formation and TOX formation potential correlated well with SUVA for a variety of different materials. Because the hydrophilic components of NOM had a lower aromatic content and a correspondingly lower SUVA than the hydrophobic components, they tended to produce lower amounts of halogenated DBPs upon chlorination. Kitis et al. (2001a, 2002, 2004) observed strong correlations between DBP formations and SUVA values of NOM fractions obtained by various physicochemical separation processes. In their studies, such strong correlations were actually found for five source waters in the US. However, those waters had generally high $SUVA_{254}$ values, i.e., >3 L/mg org-C.m. In the study of Liang and Singer (2003) on five different source waters having values in the range of 3.1 and 4.7 L/mg org-C.m, well correlations were obtained between SUVA and DBPs. They reported that the waters with higher SUVA values tended to have higher levels of HAA and THM formation.

Croue et al. (1999) reported that better relationships between SUVA and TOXFP were obtained when each fraction was considered separately; similar results were also observed for THMFP. They stated that these findings might indicate that the nature of the aromatic precursor sites differ with the characteristics of the NOM fraction. Because NOM fractions isolated from various water sources did not exhibit the same chlorine reactivity (e.g., chlorine demand and DBPFP) even if they had similar SUVA values. Similarly, Fram et al. (1999) reported that a weak correlation was obtained between $SUVA_{254}$ and $STTHMFP_{7d}$ (specific total THMFP in 7 days) for whole water samples when data was compared with isolated systems. They also reported that SUVA could not be used for accurate prediction of THMFP in drinking water derived from a broad spectrum types of watershed. Because, DOC derived from different environments within the watershed had distinct composition and reactivity. Weishaar et al. (2003) compared isolated organic matter samples with filtered whole waters to evaluate the usability of SUVA as surrogate parameter for STTHMFP. They stated that $SUVA_{254}$ appeared to be a better indicator of reactivity of the compounds derived from aquatic HS than for the DOC present in whole water samples. Similar findings were observed for organic carbon from wetlands by Fleck et al. (2004) and Chow et al. (2006).

2.6.4.4. Differential UV Spectroscopy – DBP Formations and Speciation

Since there is evidence that chlorine may attack NOM predominantly at electron-rich sites, i.e. activated aromatic sites or conjugated double bonds, which absorb UV light effectively at wavelengths of 254 to 280 nm, chlorination may decrease the UV absorbance of NOM at these wavelengths as a result of alteration and destruction of these sites (Korshin et al., 1997a,b; Li et al., 1998). In the studies of Korshin and co-workers, the difference in the UV absorbance before and after chlorination of natural waters was quantified and called differential UV spectroscopy (ΔUV_λ).

Differential spectrum detects both chromophores that are destroyed by the reaction and any that are generated. In contrast, any non-reacting chromophores in the sample contribute the same absorbance to the original and chlorinated samples and therefore do not appear in the differential spectrum. Thus, by its nature, differential spectroscopy focuses strictly on the light absorbing sites that are involved in the reaction. This feature of differential spectroscopy is very attractive because it expands differential spectroscopy's applicability to water qualities in which the performance of conventional UV spectroscopy may be compromised by interfering species (Li et al., 1998).

Korshin et al. (1997a) plotted the concentration of chloroform formed during 2-72 h of incubation as a function of the decrease of UV absorbance at 254 nm and observed remarkably good correlation (R^2=0.90) considering the wide variation in source characteristics and reaction times. However, the linear best fit approximation for the correlation between ΔUV_{254} and chloroform concentration did not pass through the origin. Somewhat, at ΔUV_{254} <0.02, only small amounts of chloroform were produced, even though the change of absorbance was significant. They also stated that the correlations were between chloroform and difference in UV absorbance much better for individual sources. In another study of Korshin and his colleagues (1997b), the formation of chloroform was also correlated with ΔUV_{272}, however the correlation was strongly dependent on pH.

The magnitude of the decrease in the UV absorbance at 272 nm (ΔUV_{272}) was found to be an excellent indicator of TOX formation resulting from chlorination, independent of the ratio of chlorine to DOC, bromide concentration, pH from 5 to 11, reaction time, and DOM source (Korshin et al., 1997a,b,1999; Li et al., 1998,2000). Similarly, strong correlations between ΔUV_{280} and THMs or HAAs formations were observed in chlorinated NOM fractions of source waters with $SUVA_{280}$ values higher than 3 L/mg-m (Kitis et al., 2000).

CHAPTER 3

MATERIALS AND METHODS

In this chapter, materials used during experiments, sample collection and protection and experimental procedures are described. This chapter also includes the analytical procedures that were used in the experiments.

3.1. Experimental Materials

3.1.1. Source Waters

As mentioned in Chapter 1, this dissertation consists of three main phases. Source waters used in each phase are described below. The raw water characteristics are given in each corresponding chapter.

In the first phase, Alibeyköy reservoir containing moderate-bromide and moderate-DOC levels was selected and examined in order to study the impacts of different bromide levels. Alibeyköy reservoir supplies some portion of City of Istanbul's drinking water demand. A-30 L sample was collected in June 2004 in polyethylene bottles headspace free from the outlet part of the reservoir and shipped overnight to our laboratories in cooled containers. Sample was filtered using 0.45-μm polyether sulfone

(PES) filter papers and stored in the dark at +4^{0}C until analysis. Physicochemical characteristics of raw water were determined. Fractionated samples after filtration were analyzed for DOC, UV absorbance, SUVA, bromide, pH and total hardness. Fractionated samples were also chlorinated and measured for THMs, HAAs and AOX.

The tested surface waters in the second phase were Alibeyköy and Karacaören reservoirs, which are the major drinking water sources in the cities of Istanbul and Antalya, respectively. Alibeyköy and Karacaören samples were collected in December 2004 and June 2005, respectively. Similarly, a-30 L sample from each source was supplied in headspace free polyethylene bottles from the outlet part of the reservoir and shipped overnight to our laboratories in cooled containers. Sample was filtered using 0.45-µm polyether sulfone (PES, 0.45 µm pore size, Cat.No.15406-047N, Sartorious) filter papers and stored in the dark at +4^{0}C until analysis. Physicochemical characteristics of raw waters were determined. Fractionated samples after filtration were analyzed for DOC, UV absorbance, SUVA, pH, MW distribution (MWD) and total hardness. Fractionated samples were also chlorinated and measured for THMs, HAAs and AOX.

In the last phase, the experiments were performed using raw water from Alibeyköy reservoir sampled in June 2006 in all experiments. A-550 L water sample was collected in headspace free polyethylene bottles from the outlet part of the reservoir. Sample was filtered using 1-µm (nominal size) glassfiber filter papers and stored in the dark at +4^{0}C until analysis and membrane filtration process. Physicochemical characteristics of raw waters were determined. Samples processed by membrane filter were analyzed for DOC, UV absorbance, pH, MWD, conductivity and total dissolved solids (TDS). Permeates were also chlorinated and measured for THMs, HAAs and AOX.

3.1.2. Resins and Adsorbents

In an effort to obtain many bulk water NOM fractions with a wide range of SUVA values, different types of adsorbents were used. XAD-8 (Supelite, Cat. No. 20278) and XAD-4 (Amberlite, Cat. No. 06444) resins, specified for the isolation and fraction of NOM from waters by the resin adsorption chromatography method, were obtained from Supelco and Fluka-Chemika, respectively. Since there may be some impurities in the received XAD resins, cleaning was performed employing the methodology described in Section 3.2.1.1. The cleaned and dried resins were put in beakers covered with parafilm and aluminum foil and stored in a desiccator to prevent the introduction of any moisture until use. Table 3.1 shows the characteristics of the XAD resins employed in this study. A coal-based GAC (AquaSorb® 1000, Jacobi Carbons) with a particle size range of 0.60-2.36 mm (8x30 USS mesh size) and a mean particle diameter of 1.4 mm was used. The GAC sample was pre-cleaned and used as-received without any further treatment. Table 3.2 shows the characteristics of the GAC employed in this study. The MIEX® DOC resin sample, developed specifically for the removal of NOM from waters, was obtained from Orica Advanced Water Technologies Pty. Ltd. Australia.

Table 3.1. Characteristics of XAD resins employed

XAD Resin	Type	Surface Area (m^2/g)	Pore Size (Å)	Cross-linkage	Density	Polarity
XAD-8	Acrylic Ester Polymer	160	225	low	1.23	Slight
XAD-4	Styrene-Divinylbenzene Polymer	750	50	high	1.09	None

Table 3.2. Characteristics of GAC employed

Adsorbent	Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Wettability (%)	Apparent Density (kg/m^3)	Particle Size (mm)
GAC (AquaSorb® 1000)	950	0.88	99.5	500	0.6-2.36

3.1.3. Membrane Filtration Unit

A lab-scale cross-flow flat-sheet configuration test unit (SEPA® CF II, Osmonics, GE Water & Process Technologies) was used for all membrane separation experiments, which simulates the flow dynamics of larger, commercially available spiral-wound membrane elements. Operating conditions and fluid dynamics can be varied over broad ranges. The membrane test unit accommodates any 19 cm x 14 cm (7.5 inch x 5.5 inch) flat-sheet membrane for a full 140 cm^2 (22 $inch^2$) of effective membrane area. The membrane cell body is made of 316 stainless steel. The membrane test system consisted of a high pressure pump (Hydra-Cell G13) equipped with digital variable frequency drive (ABB ACS-140) to adjust feed flowrates and its 1.1 kW motor, pressure relief valve, membrane cell, membrane cell holder, high pressure concentrate control valve, hydraulic hand pump, pressure indicators in the membrane cell, cell holder and high pressure pump outlet, feed tank (35-L max. solution volume, stainless steel), permeate collection tank, and connections/tubings made of either stainless steel or nylon-seal (Dayco-Imperial) plastic (Figure 3.1). The required pressure in the membrane cell and permeate and concentrate flowrates were adjusted by the concentrate control valve. Temperature of the feed tank was kept constant by circulating cool tap water through the jacket around the feed tank outer walls during the membrane tests. All experiments were performed at feed water temperatures of 20±2 °C. The membrane test system was operated in total recycle mode in which permeate and concentrate streams were returned back to the feed tank. The specifications of used membrane flat sheets are given in Table 3.3.

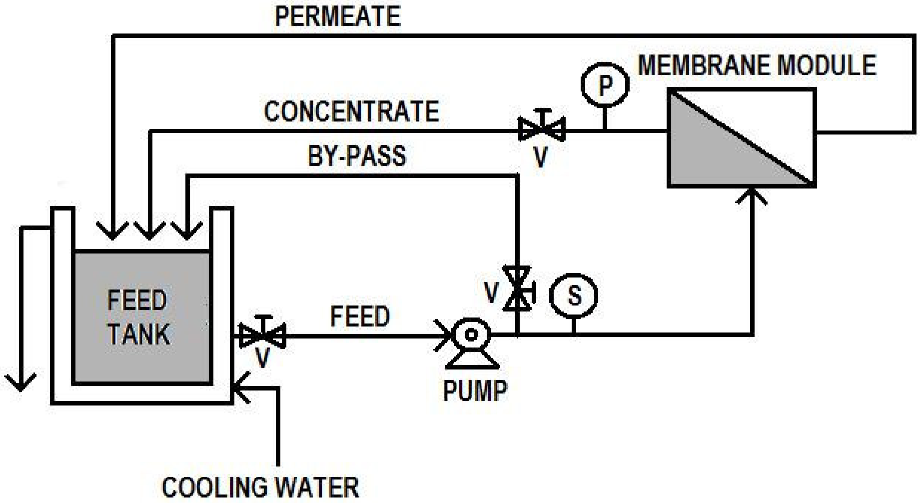

Figure 3.1. Schematic diagram of lab-scale membrane system
(P: pressure gauge, S: suction gauge, V: valve)

Table 3.3. Specification of Flat Sheet Membranes

Class	Polymer Structure	Designation	Rejection Size	pH Range @ 25 ^{0}C	Typical Flux / Pressure (L/m^2-h/bar)
UF	PES[a]	PT*	5K	-	153/3.5
UF	TF[b]	GH*	1K-PEG	2-11	34/10.4
NF	TF	DK*	98 $MgSO_4$	2-11	37/6.9
NF	TF	DL*	96 $MgSO_4$	2-11	53/6.9

[a] PES: Polyether sulfone
[b] TF: Thin film
*Commercial name of membrane filter.

3.2. Experimental Procedure

3.2.1. Bulk Water Fractionation of DOM

3.2.1.1. Cleaning and Preparation of XAD Resins

Since there are some impurities in the received XAD resins, further cleaning is required (Malcolm, 1991). Initially, resins were soaked in 0.1 N NaOH for a week, followed by a rinse with methanol, and then at least a 10 bed volume rinses with distilled and deionized water (DDW). After that, cleaning procedure was continued as that both resins were kept in acetone and methanol each for 24 hours, followed by a final rinse in methanol. The cleaned resins were then stored in methanol.

The resins were decanted off methanol and washed with approximately 100 bed volumes with DDW in the glass flow-through columns with glass microporous filters at the effluent. During this gravity-flow cleaning mode, periodic up-flow bed fluidizations using the pressurized DDW were performed to enhance washing off the resins from methanol. After 100 bed volumes of rinsing, the difference in DOC concentration of DDW between the influent and effluent of the column was found to be minimal, indicating an effective removal of methanol as a result of the washing process.

Resins were then put in large beakers filled with DDW and stored up to 4 days to determine if further DOC leaching was occurring. The amount of resins per DDW volume was approximately ten times larger than that of the typical XAD doses in the DOM fractionation experiments. Thus, if no DOC leaks even at very large XAD doses, then no leak would be expected in DOM fractionation experiments. However, control bottles dosed with different amounts of resin in DDW were included in fractionation experiments in order to assure that no leaching was occurring from the resins to the solution during mixing. The results showed that DOC concentrations of DDW in control bottles did not change after one day of mixing.

At the end of the washing process, water was decanted off the resins, which were then held in the hot room at a temperature of about 38-40 ^{o}C for 4 days in order to evaporate as much water as possible from the resin pores. The presence of any water in the resins would have caused an error in weighing for the isotherm bottles. To check whether all the moisture was removed from the resins, some sample resins were further exposed to higher temperatures such as 50 ^{o}C for 4 hours and then 60 ^{o}C for 18 hours. At the end, the dried resins were transferred to beakers covered with parafilm and aluminum foil and stored in desiccators to prevent the introduction of any moisture until use.

3.2.1.2. Batch Kinetic Tests with XAD Resins

Isotherms experiments were conducted in completely mixed batch reactors (CMBRs) using XAD-8 and XAD-4 resins separately for the bulk water fractionation of NOM. Since the main adsorption mechanism of DOM by these resin is hydrophobic interactions, the pH values of the water samples were reduced to 2.5±0.1 using different concentrations of HCl in order to protonate the DOM components (especially humics) and make them uncharged and relatively hydrophobic. Several 60-mL amber glass bottles sealed with PTFE screw-caps were filled with filtered and acidified source waters (50 mL sample volume) and dosed with either XAD-8 or XAD-4 resins 1,000 mg resin/L. The bottles were mixed on a shaker horizontally at room temperature of 20±2 ^{0}C for 2, 4, 8, 24, 48, 96, 168 and 336 hours. After each retention time, samples were taken and filtered (0.45 µm PES filter papers) to remove XAD resin particles and analyzed for DOC, UV_{254} absorbance and pH. Kinetic tests were performed to ensure sufficient time to reach equilibrium in following batch equilibrium tests.

3.2.1.3. Batch Equilibrium Tests with XAD Resins

For bulk water fractionation of DOM, variable-dose bottle-point isotherm experiments were conducted in CMBRs using cleaned and dried XAD-8 and XAD-4 resins separately. The dose of resins was chosen to yield a nearly continuous fractionation (based on SUVA) while assuring that changes in DOC and UV absorbance were sufficiently large for accurate quantification. Control bottles dosed with different amounts of resins in DDW were included in fractionation experiments in order to check for possible leaching of organic materials from the resin matrix after 4 days of mixing. The results showed that DOC leaching from resins in control bottles was close to the detection limit of TOC analyzer (about 0.1 mg/L) at the range of resin doses employed for fractionations.

The raw water pH was decreased to 2.5±0.1 for all resin fractionations to increase the uptake of NOM by the resin. CMBRs (125 or 275 mL amber glass bottles sealed with PTFE screw caps) with a solution volume of 100 or 250 mL were kept well-mixed on a shaker for a period of 4 days. Preliminary kinetic experiments showed that 4 days of mixing was sufficient to reach adsorption equilibrium. All isotherms were conducted at room temperature (20±2 ^{o}C). After equilibration, the DOM solution remaining in each bottle (i.e., the NOM fraction) was separated from the resin by filtration (0.45 µm PES filter papers) and analyzed for DOC concentration, UV_{254} absorbanceand pH. Filter papers were pre-washed with 900 mL of DDW, which was found to be adequate degree of washing to prevent leaching of organic material from the filter matrix.
DOC values of all fractions were adjusted to a constant pre-selected concentration via dilution using DDW having DOC less than 0.1 mg/L. The pH of each fraction was then adjusted to pH of the raw water (8.0) by NaOH solution.

3.2.1.4. Batch Kinetic Tests with GAC Resin

Batch kinetic tests were performed to find sufficient time to reach equilibrium of GAC adsorption. Several 60-mL amber glass bottles sealed with PTFE screw-caps were filled with filtered source waters in original pH (50 mL sample volume) and dosed with 500 mg GAC/L. The bottles were mixed on a shaker horizontally at room temperature of 20±2 ^{0}C for 1, 2, 4, 7, 10, 14, 21 and 30 days. After each retention time, the samples were filtered (0.45 µm PES filter papers) to remove GAC particles and analyzed for DOC, UV_{254} absorbance and pH.

3.2.1.5. Batch Equilibrium Tests with GAC Resin

Similar to XAD batch study, variable-dose bottle-point isotherm experiments were conducted in CMBRs using GAC for the bulk water fractionation of DOM. A-125 mL amber glass bottles were filled with filtered (0.45 µm PES filter papers) water samples (100 mL solution volume) and dosed with GAC in the range of 50-4,000 mg GAC/L. GAC doses were chosen to yield a nearly continuous fractionation (based on SUVA) while assuring that changes in DOC and UV absorbance were sufficiently large for accurate quantification.

The bottles were mixed on the shaker at original pH of the raw waters without any buffer addition, and at room temperature of 20 ± 2 ^{0}C for 21 days, which was shown to be quite sufficient of time to reach equilibrium obtained above kinetic studies. After equilibrium was attained, the bottles were opened and filtered (0.45 µm PES filter papers) to remove the GAC particles. Filter papers were pre-washed by filtering 900 mL DDW in order to prevent any possible leaching of organic material from the filter matrix. The water after adsorption at each CMBR was analyzed for DOC, UV_{254}, absorbance, SUVA and pH. DOC values of all fractions were adjusted to a constant pre-selected concentration via dilution so that a relatively constant Cl_2/DOC ratio can be applied for chlorination. UV_{254} absorbances were measured before and after chlorination to evaluate differential UV spectroscopy.

3.2.1.6. Batch Equilibrium Tests with MIEX® Resin

MIEX® resin was provided from producer in suspension in a plastic bottle. MIEX® resin in pilot and full scale treatment operations is applied as volume resin per volume raw water. Jar test apparatus was used in MIEX® resin batch study. A-500 mL homogeneously mixed unfiltered raw water in glass bakers was used for each batch test. The increasing dosages of MIEX® resin as 2.5, 5, 7.5, 10, 20, 30 mL resin/L were added to bakers filled with raw water. The resin was immediately added by pipettes and graduated cylinders, the residual resin was rinsed with water samples. The jar tester was set to 120 rpm during one hour and then allowed to settle of resin. After certain periods (5, 10 and 60 min), 100 mL of water samples were taken from each mixing bakers and immediately filtered with 0.45 µm pore size PES filter papers. Filtered samples were used to measure pH, conductivity, TDS, DOC, UV_{254} absorbance. Besides, pH, conductivity, TDS, temperature and turbidity were also determined in unfiltered samples which were settled for a few minutes after stopping of mixing.

3.2.2. Membrane Filtration Process

Alibeyköy water was used as source water in membrane filtration process. To remove suspended solids and to enhance the performance of UF and NF membranes, raw Alibeyköy water was microfiltered by vacuum filter apparatus using glass fiber filter in 1-µm nominal pore size (Cat. No. 13400-047 Q, Sartorius). Membrane filtration process was operated in total recycle mode that both retentate and permeate were returned to the feed tank, in order to obtain a constant feed composition. This is done to evaluate the performance of the membrane under stable conditions. Temperature of feed water was kept constant as 20±2 ^{0}C by cooling water.

Two UF (PT-UF and GH-UF) and two NF (DK-NF and DL-NF) flat-sheet membranes with different MWCOs or rejection sizes were tested in this study. The specifications of flat sheet membranes are given in Table 3.3. The membrane filtration tests were conducted in three phases. In first phase, all types of membranes were tested at pressures specified by the manufacturer (Table 3.3) and at constant CFV of 1.2 m/s. Based on the DOC and UV_{254} absorbance removal performances of tested membranes in this phase, DK-NF membrane was chosen for further testing in second phase, which included operations at variable pressures (6.9, 10.4 and 13.8 bar) and CFV (0.7 and 1.2 m/s). For the first and second phases, samples from permeate were collected and analyzed after equilibration of membranes was achieved (i.e., minimal change in DOC and UV_{254} absorbance rejections and flux). In these two phases, DBP measurements after chlorination were conducted on three consecutive permeate samples collected after equilibration. In third phase, membrane tests were carried out using PT-UF (3.5 bar pressure, 1.2 m/s CFV) and DK-NF (6.9 bar pressure, 1.2 m/s CFV) membranes for a 24 h operation period, and feed and permeate samples were taken at t: 0, 1, 2, 4, 6, 8, 10, 12, and 24 h during the operation for DBP (AOX, THMs, HAAs) formation, DOC, UV_{254} absorbance, MWD, conductivity, TDS, and pH analysis. Thus, the impact of NOM characteristics (as captured by DOC, UV absorbance, MWD measurements) in permeate samples on DBP formation after chlorination was investigated with respect to membrane operation time. DOC and UV absorbance removal efficiencies, MWD of organic compounds and DBPs formations in permeate water samples at which DOC, UV absorbance and flux did not change anymore (defined as steady state) were analyzed at first and second phase studies. At third phase, one UF and one NF membrane was selected to evaluate DBP formations in permeate water samples taken at certain period during filtration process (defined as unsteady state). Experimental matrix for membrane filtration is given in Table 3.4.

Table 3.4. Experimental Matrix for Membrane Filtration Study

	Membrane Type	Pressure (Bar)	Cross-flow Velocity (m/s)	Study Mode	Condition
Set 1	GH-UF	10.3	1.2	Total recyle	Steady State
Set 2	PT-UF	3.5	1.2	Total recyle	Steady State
Set 3	DK-NF	6.9	1.2	Total recyle	Steady State
Set 4	DL-NF	6.9	1.2	Total recyle	Steady State
Set 5	DK-NF	13.8	1.2	Total recyle	Steady State
Set 6	DK-NF	10.3	1.2	Total recyle	Steady State
Set 7	DK-NF	6.9	1.2	Total recyle	Steady State
Set 8	DK-NF	6.9	0.7	Total recyle	Steady State
Set 9	DK-NF	6.9	1.2	Total recyle	Unsteady State
Set 10	PT-UF	3.5	1.2	Total recyle	Unsteady State

The membrane filtration protocol contained 7 consecutive steps as summarized in Table 3.5. In order to minimize membrane compaction during the experiments, all membranes were compacted before under a pressure which is much higher than the operational pressure. Cleaning procedure was applied before and after feed water processing to remove deposits on or inside the membrane and to restore the membrane properties. To determine the membrane fouling degree and flux recovery rate, clean water fluxes were measured before and after membrane process in which test water was filtered.

Table 3.5. Membrane Filtration Protocol

Phase 1: Compaction		Phase 5: Clean Water Flux after Membrane Process	
Pressure	13.8 bar for GH-UF[a] 5.2 bar for PT-UF[a] 13.8 bar for DK-NF[a] 13.8 bar for DL-NF[a]	Pressure	10.3 bar for GH-UF[a] 3.5 bar for PT-UF[a] 6.9 bar for DK-NF[a] 6.9 bar for DL-NF[a]
CFV	0.7-1.2 m/s	CFV	0.7-1.2 m/s
Feed Water	DDW	Feed Water	DDW
Operation Duration	24 hours	Operation Duration	Up to steady state
Phase 2: Cleaning of Membrane before Membrane Process		Phase 6: Cleaning of Membrane after Membrane Process	
Pressure	3.5 bar	Pressure	3.5 bar
CFV	0.5 m/s	CFV	0.5 m/s
Feed Water	HNO_3 for 1 hour at pH 3 DDW for 1 hour NaOH for 1 hour at pH 9 DDW for 1 hour	Feed Water	HNO_3 for 1 hour at pH 3 DDW for 1 hour NaOH for 1 hour at pH 9 DDW for 1 hour
Phase 3: Clean Water Flux before Membrane Process		Phase 7: Clean Water Flux after Cleaning of Membrane	
Pressure	10.3 bar for GH-UF[a] 3.5 bar for PT-UF[a] 6.9 bar for DK-NF[a] 6.9 bar for DL-NF[a]	Pressure	10.3 bar for GH-UF[a] 3.5 bar for PT-UF[a] 6.9 bar for DK-NF[a] 6.9 bar for DL-NF[a]
CFV	0.7-1.2 m/s	CFV	0.7-1.2 m/s
Feed Water	DDW	Feed Water	DDW
Operation Duration	Up-to steady state	Operation Duration	Up-to steady state
Phase 4: Membrane Process			
Pressure	10.3 bar for GH-UF[a] 3.5 bar for PT-UF[a] 6.9 bar for DK-NF[a] 6.9 bar for DL-NF[a]		
CFV	0.7-1.2 m/s		
Feed Water	Microfiltered raw water		
Operation Duration	Up-to steady state		

[a] Tested membranes

CFV: Cross-flow velocity

DDW: Distilled and deionized water

3.2.3. Chlorination Protocol

Chlorination of the raw waters and fractionated samples was performed according to the uniform formation condition (UFC) protocol (Summers et al., 1996) with a minor change (i.e., phosphate instead of borate buffer was used). This protocol simulates the average chlorination conditions in drinking water distribution systems in the USA and requires a free chlorine residual of 1.0±0.4 mg/L be maintained after 24 hours of contact time. These doses were selected from previous chlorine demand analysis of water samples. Chlorination was accomplished head-space free in 60 mL amber vials with teflon-lined screw caps. Chlorine was spiked in each bottle using gas-tight glass syringes from a stock solution prepared from sodium hypochlorite solution (13% available free chlorine) (Cat. No. 71696; Fluka-Chemika). Chlorine stock solution was prepared in high concentration not to cause additional dilution of samples. Typical volumes of chlorine injections were 250-500 μL. Solutions were buffered with NaOH (ranging from 0.1 to 1 N) as pH was 8.0±0.1. The chlorinated samples were incubated at 20±2 ^{o}C, in the dark, for a 24 h reaction period. Residual free chlorine was measured according to SM 4500 Cl G (APHA, AWWA, WEF, 1998) and was immediately quenched with sodium sulfite prior to analysis for UV_{254} absorbance and DBPs. This was necessary because DBP formation, which is time dependent, was targeted to be quantified after 24 hours. Depending on the measured residual chlorine concentration of the sample, sodium sulfite in slight excess of the stoichiometric requirement (theoretically, 2 mg sodium sulfite quenches 1 mg chlorine) was added from stock solutions. It was found in the preliminary experiments that a mass ratio of 2.25-2.5 sodium sulfite/chlorine was more conservative in completely quenching residual chlorine. Residual sodium sulfite after quenching did not interfere with UV absorbance measurements. The quenched chlorinated samples were transferred quickly to vials using glass pipettes for further DBP extraction and UV absorbance measurements.

3.2.4. Differential UV Spectroscopy

UV_{254} absorbance in each chlorinated fraction was measured to determine the difference in the UV_{254} absorbance before and after chlorination and correlate the reduction in UV_{254} absorbance with DBP formation. Such approach, called the differential UV spectroscopy (ΔUV_{λ}), was proposed by Korshin et al. (1997a,b).

3.3. Analytical Methods

3.3.1. DBP Analysis

3.3.1.1. THMs Analysis

THMs (chloroform, bromodichloroform, dibromochloroform, and bromoform) were measured according to SM 6232 B (APHA, AWWA, WEF, 1998) employing liquid-liquid extraction (with pentane) and gas chromatography (GC) measurement. Calibration standards were prepared using the standard mixture purchased from Supelco (Cat.No. 47904, Sigma-Aldrich Co., USA). Calibration curves had at least 8 points, and calibration standards were also extracted with the same protocol as samples in order to compensate for the extraction efficiency effects. Calibration standards for THM measurements were prepared using the test mix produced by Supelco at concentrations ranging from 2.5 to 250 µg/L (r^2 = 0.99). Each individual calibration curves for THMs were drawn area counts versus concentration. THMs concentrations of samples were calculated using THMs calibration curves. A representative chromatogram of a 250 µg/L standard of THMs is seen at Figure A.1. The calibration curves for each individual species were given at Appendix Figure A.2-5. A Varian CP3380 model GC with an electron capture detector was used for THM measurements. The capillary column used for measurements have the following characteristics: CP-Sil8 column, length: 24 m, ID: 0.32 mm, film thickness: 0.25 µm (Varian MD-21-10-1). Ultra high purity helium (1.8 mL/min) and nitrogen (25 mL/min) were used as the carrier and make-up gas, respectively. The detection limits for THM species were about 0.5-1.5 µg/L. The percent relative standard deviations were less than 10% (0-7%). GC operating conditions for THM measurements were as following: injector temperature: 280 ^{0}C, detector temperature: 290 ^{0}C, injection volume: 1 µL, temperature program: 40 ^{0}C for 2 min, 4 ^{0}C/min ramp to 80 ^{0}C, 20 ^{0}C/min ramp to 110 ^{0}C, total run time: 13.5 min.

3.3.1.2. HAAs Analysis

Nine haloacetic acids (monochloro-, dichloro-, trichloro-, monobromo-, dibromo-, tribromo-, bromochloro-, bromodichloro-, dibromochloro acetic acid) were analyzed employing liquid-liquid extraction and further derivatization with acidic methanol according to USEPA 552.3 method (USEPA, 2003). Calibration standards were prepared using the standard mixture purchased from Supelco (Cat.No. 47787, Sigma-Aldrich Co., USA). Calibration curves had at least 8 points, and calibration standards were also extracted with the same protocol as samples in order to compensate for the extraction efficiency effects. Calibration standards for HAA measurements were prepared using the test mix produced by Supelco at concentrations ranging from 0.1 to 600 µg/L (r^2=0.98-0.99).

Each individual calibration curves for HAAs were drawn area counts versus concentration. HAAs concentrations of samples were calculated by using HAAs calibration curves. A representative chromatogram of a 600 µg/L standard of HAAs is seen at Figure A.6. The calibration curves for each individual species were given in Appendix Figure A.7-15. Samples (25 mL) after chlorination were quenched with sulfite, and then 2 mL of concentrated sulfuric acid and 11 g sodium sulfate (to facilitate extraction of acids) were added. Then, samples were extracted with 4 mL of Methyle tert-butyl ether (MTBE) for 3 minutes at 200 rpm with a mechanical shaker at room temperature (20±2 ^{o}C). For the acidic methanol derivatization, 3 mL of extract was transferred into a-15 mL vial containing 3 mL of 10% acidic methanol (methanol and concentrated sulfuric acid). The vials were capped with PTFE faced septa and screw caps and kept in a 50°C-water bath for 2 hours. After adding 7 mL of 10% sodium sulfate solution, the vials were recapped and shaken for 10 seconds by hand. The lower (acidic aqueous methanol) phase was discarded from each tube with a long pasteur pipettes as leaving no more than 0.3 mL of aqueous phase to ensure complete neutralization in the following step. Then, 1 mL of saturated sodium bicarbonate solution was added and shaken tubes for 5 seconds as five times to complete the neutralization reaction. After first shaking of tubes, the tube caps were loosen to release the evolved CO_2 and left settling and phase separation for 2 minutes. A-1 mL of MTBE extract was transferred to a-2 mL autosampler vial. The vials were kept at 4 ^{0}C until GC analysis. A Varian CP3380 model gas chromatograph with an electron capture detector was used for HAA measurements. The capillary column used for both measurements have the following characteristics: CP-Sil8 column, length: 24 m, ID: 0.32 mm, film thickness: 0.25 µm (Varian MD-21-10-1). Ultra high purity helium (1.8 mL/min) and nitrogen (25 mL/min) were used as the carrier and make-up gas, respectively. The detection limits for HAA species were about 0.5-1.5 µg/L.

The percent relative standard deviations were less than 10% (3-7%). GC operating conditions for HAA measurements were as following: injector temperature: 200 ^{0}C, detector temperature: 290 ^{0}C, injection volume: 1 µL, temperature program: 40 ^{0}C for 20 min, 5 ^{0}C/min ramp to 120 ^{0}C, 3-min hold, 10 ^{0}C/min ramp to 150 ^{0}C, total run time: 42 min.

3.3.1.3. AOX Analysis

In addition to THMs and HAA analysis, AOX measurements were employed for all samples. AOX measurements were performed according to ISO 9562 method (ISO, 1989) using a Euroglass AOX Analyzer. Chlorinated samples were diluted with DDW water (1/10) and added 5 mL AOX solution (17 g $NaNO_3$ and 1.4 mL HNO_3 in 1 L). pH of samples was reduced to 2-3 with nitric acid. Then, approximately 1 g. of activated carbon was added and the samples were placed in a horizontal shaker for 1 hour. Samples were filtered to separate activated carbon on filter papers with 0.22 µm pore size and then activated carbon on filter papers was introduced to AOX analyzer. Operating conditions for AOX measurements were as following: drying at 200 ^{0}C for 1 min, combustion at 1000 ^{0}C for 4 min and cooling for 5 min.

3.3.2. MWDs

The average MW of a mixture of molecules can be represented in several ways. For a set of n molecules, the number-average MW, M_n, can be calculated by summing the total mass and dividing by n; M_n is thus the weight of the “average” molecule. Alternatively, it may be supposed the molecules are divided into n fractions according to MW, the ith fraction having a characteristic MW, MW_i, and a characteristic frequency, f_i. If the number of fractions is large enough (and the MW spread in each fraction is small enough) then the number-averaged MW, M_n, is determined by the equation:

$$M_n = \frac{\sum_{i=1}^{n} f_i MW_i}{\sum_{i=1}^{n} f_i} \quad \text{(Eq. 3.1)}$$

The weight average MW, M_w, is the weight of the molecule to which the "average" atom belongs and is given by:

$$M_w = \frac{\sum_{i=1}^{n} f_i MW_i^2}{\sum_{i=1}^{n} f_i MW_i} \quad \text{(Eq. 3.2)}$$

A pure substance will have M_w=M_n. However, for a mixture of molecules M_w>M_n it is referred to such a system as polydisperse, with polydispersity, ρ. Sample polydispersity is determined from the ratio of the weight- to number-averaged MWs ($\rho=M_w/M_n$). A third "average" MW, M_z, is calculated from the third moment of the distribution:

$$M_z = \frac{\sum_{i=1}^{n} f_i MW_i^3}{\sum_{i=1}^{n} f_i MW_i^2} \quad \text{(Eq. 3.3)}$$

MWDs were measured by HPSEC method that high-pressure liquid chromatography (HPLC) was equipped with gel permeation column (GPC)

(Shimadzu Corp., Kyoto, Japan). The system consisted of a mobile phase pump, a variable wavelength UV absorbance detector, a rotary injector valve equipped with a 20 µL sample loop, and NUCLEOGEL AQUA-OH 40 column (Cat. No. 719440, Macherey-Nagel). NUCLEOGEL® aqua-OH columns for the GPC of water soluble samples are packed with a rigid, macro porous polymer with hydrophilic surface (8 µm particle size). The different available pore sizes allow separations of substances up to very high MWs. The column had a general MWCO between 500-100,000 g/mole and 300 Ǻ pore size. The mobile phase consists of 0.1 M NaCl, 0.002 M KH_2PO_4 and 0.002 M Na_2HPO_4 solutions buffered to pH 6.8. The flowrate was 0.75 mL/min and the oven temperature was 45 ^{0}C. All samples were filtered through a 0.45 µm PES membrane filter washed with 900 mL DDW before filtration. The HPLC-GPC system was calibrated using different MW sodium salt of PSS (PSS, 32, 18, 13, 8, 4.6 KDa) from Fluka-Aldrich. All PSS standards and samples were detected at 224 nm wavelength. Although a PSS 1.8 K was available, it could not be used as a standard because it displayed wide multiple peaks in the HPSEC chromatogram. The calibration curve for MWDs is given in Appendix A, Figure A.16.

3.3.3. DOC Analysis

DOC analysis was performed by the high temperature combustion method according to SM 5310 B (APHA, AWWA, WEF, 1998) using a TOC-5000A TOC analyzer (Shimadzu Corp., Kyoto, Japan), which utilizes high purity oxygen as the carrier gas and for sample sparging. This equipment uses infrared detection to measure the CO_2 created from the combustion of the sample in the presence of a platinum catalyst within the combustion tube. Reagent grade potassium hydrogen phthalate (KHP) (Cat. No. 43,142-7, 99.99+%, Aldrich) were used to prepare external standards, which were then used to develop a calibration curve. Standard concentrations ranged between 0.0 and 4.0 mgC/L, which was an optimum range for the use of a high-sensitivity catalyst. A representative calibration curve for DOC measurement was given in Appendix A, Figure A.17. The pH of all samples and standards were adjusted to 2.5-3 by different solutions of HCl (0.05 N) to facilitate the stripping of inorganic carbon from the sample through dry air sparging. Samples were sparged for 10 minutes. This was important because the inorganic carbon concentration in many natural waters is significantly larger than the organic carbon concentration, which can decrease the accuracy of DOC measurements. The minimum detection level of the TOC analyzer was approximately 0.1 mg/L. Precision of the samples was generally about 0.05-0.15 mg C/L. Each sample was injected minimum 3, maximum 5 times regarding to standard deviations of measurements. Blank checks were periodically performed in the equipment.

3.3.4. UV Spectroscopy Analysis

UV absorbance was measured using a Varian 100 Spectrophotometer connected a PC with 1-cm quartz cells. The measurements were conducted at a wavelength of 254 nm in order to minimize the interferences from compounds such as nitrate, nitrite, ferrous iron and bromide (APHA, AWWA, WEF, 1998). The spectrophotometer was calibrated by DDW. The sample cells were washed to prevent accumulation of residues on the cell walls every each measurement by DDW.

3.3.5. Free Residual Chlorine Analysis

The free available residual chlorine concentration was measured according to the SM 4500 Cl$^-$ G DPD Colorimetric Method (APHA, AWWA, WEF, 1998) using Hach Dr 2000 Model Spectorophotometer at 530 nm wavelength. After a-24 hour incubation period for chlorination, the required volume of sample (25 mL) was transferred quickly to cell and add free chlorine DPD reagent. Then, DPD added samples were shaked a-20 seconds and placed in spectorophotometer.

3.3.6. Bromide Analysis

Bromide measurements carried out during the initial stages of the study (results presented in Chapter 4) were analyzed by TUBITAK-MAM according to SM 4110 B ion chromatography method (APHA, AWWA, WEF, 1998). Later, bromide ion concentrations were measured using Hach Dr 2000 Model Spectrophotometer at 530 nm wavelength. A-25 mL sample was transferred quickly to the spectrophotometer cell and total DPD reagent was added as required. After shaking the mixture for 20 sec, a reaction time of 3 min was provided. Then the cell was placed in the spectorophotometer for the measurement of bromide concentration.

3.3.7. Turbidity Analysis

Turbidity analysis was performed using Hach 2100 N model turbidimeter. Before sample analysis, turbidimeter was calibrated with standard formazin solution.

3.3.8. Conductivity and TDS Analysis

Conductivity and TDS analysis were measured directly using Hach Sension 378 pH/Conductivity/DO meter.

3.3.9. pH Analysis

pH was determined according to Standard Method 4500-H^+ (APHA, AWWA, WEF, 1998) using an OAKTON pH 110 meter with pH probes. Calibration standards of pH 4, 7, and 10 were used to calibrate the pH meters at room temperature. The accuracy of the meters as reported by the manufactures was about ±0.01 pH units.

CHAPTER 4

THE EFFECTS OF BROMIDE ION AND NATURAL ORGANIC MATTER FRACTIONS ON THE FORMATION AND SPECIATION OF CHLORINATION BY-PRODUCTS

4.1. Introduction

Bromide ion has a very important role especially in the speciation of DBPs. A mixture of HOCl/HOBr leads to the formation of various brominated and chlorinated DBP species (Symons et al., 1987,1996). Brominated THMs were first reported by Rook (1974) and Bellar et al. (1974) in drinking water disinfection processes using chlorine. As the amount of bromide ion increases in waters, a shift toward brominated DBP species over chlorinated ones may occur, with all other factors held constant (Heller-Grossman et al., 1993; Pourmoghaddas et al., 1993; Krasner et al., 1994; Symons et al., 1996; Ichihashi et al., 1999). The extent of bromine substitution into THMs and HAAs can exceed 50% of the bromide ion concentration initially present in water (Symons et al., 1996).

DBP regulations are globally becoming more stringent (Golfinopoulos and Nikolaou, 2005; Lin et al., 2006; Zhao et al., 2006) and the World Health Organization already established new guidelines for individual DBP species rather than DBP groups (e.g., THMs or HAAs) (WHO, 2004). This is especially important since recent toxicology studies indicate that individual THM or HAA species may have different health effects. For example, bromodichloromethane has been shown to pose a higher cancer risk than chloroform (USEPA, 2006). Therefore, the water treatment industry will need to pay more attention to bromide levels in raw waters and to the control of brominated by-products after disinfection processes if new regulations are issued for individual THM or HAA species.

The main objective of this part of the study was to determine the impacts of both different bromide levels and NOM characteristics together on the formation and speciation of DBPs in chlorinated NOM fractions. Aqueous NOM fractions were obtained in a single raw water employing bulk water XAD-8 or XAD-4 resin fractionation. For bulk water fractionation, variable-dose bottle-point isotherms were conducted in CMBRs using each resin under oxic conditions. Since a total of 20 fractions from a single water were obtained with a wide range of NOM characteristics as measured by SUVA it was possible to determine the impacts of both NOM characteristics and different bromide levels (by spiking bromide) together on the formation and speciation of DBPs.

4.2. Materials and Methods

4.2.1. Source Water and Resins

In order to study the impacts of different bromide levels, a raw water (Alibeyköy) containing moderate-bromide and moderate-DOC levels was selected. Alibeyköy reservoir supplies some portion of the City of Istanbul’s drinking water demand. Table 4.1 presents the physicochemical characteristics of this surface water.

Table 4.1. Physicochemical characteristics of Alibeyköy water

Parameters	Alibeyköy water[a]
DOC (mg/L)	3.5 ± 0.2
UV_{254} Absorbance	0.111 ± 0.002
$SUVA_{254}$ (L/mg org-C.m)	3.17 ± 0.04
Bromide (µg/L)	110 ± 0.007
pH	7.6 ± 0.05
TDS (mg/L)	263 ± 2
Conductivity (µS/cm)	530 ± 2
Total hardness (mg $CaCO_3$/L)	100 ± 8
Alkalinity (mg $CaCO_3$/L)	125 ± 5
Total Fe (mg/L)	0.13 ± 0.002

[a] Raw water sample was filtered (0.45 µm) before measurements. Values reported are the average of triplicate measurements.

In an effort to obtain many bulk water DOM fractions with a wide range of SUVA values, two different types of resins were used. XAD-8 and XAD-4 resins, specified for the isolation and fraction of NOM from waters by the RAC method. Kinetic experiments in CMBRs were performed, as described in detail in Section 3.2.1.2.

4.2.2. Experimental Procedures

Variable-dose bottle-point isotherm tests were conducted in CMBRs using XAD-8 and XAD-4 resins separately for the bulk water fractionation of NOM in Alibeyköy water, as described in detail in Section 3.2.1.3. The dose range employed for both resins was 5-20,000 mg/L, which was chosen to yield a nearly continuous fractionation (based on SUVA) while assuring that changes in DOC and UV absorbance were sufficiently large for accurate quantification. After mixing period, DOC values of all fractions were adjusted to a constant pre-selected concentration (2 mg/L) via dilution using DDW having DOC less than 0.1 mg/L. Out of 20 fractions, only 3 XAD-8 fractions (after doses of 1,000, 5,000 and 20,000 mg/L) had DOC concentrations less than 2 mg/L (between 1.8 and 2.0 mg/L). Therefore, these fractions were not diluted. The pH of each fraction was then adjusted to pH of the raw water (7.6) by phosphate buffer.

In order to investigate the impact of bromide levels on the formation and speciation of DBPs, three different bromide levels were selected: original water bromide level (60-110 µg/L), 250 and 500 µg/L. These selected concentrations capture the range typically observed in source waters, for example, the bromide levels in the source waters of 100 water utilities in the United States were reported to range from 2 to 429 µg/L (Amy et al., 1994). For bromide levels of 250 and 500 µg/L, each NOM fraction obtained from XAD-8 or XAD-4 was spiked with bromide using potassium bromide. Bromide was not spiked in the first set of experiments conducted for original water bromide level. Since dilutions were employed to achieve constant DOC level in each fraction, bromide concentrations ranged between 60 and 110 µg/L in fractions of the first set experiments. Therefore, bromide levels studied in this work are presented as 60-110, 250 and 500 µg/L throughout this chapter. After adjusting DOC and pH for constant level and bromide spikes if necessary, UV_{254} absorbance was measured again in each fraction prior to chlorination. This was done because dilutions reduced the UV absorbance of NOM fractions.

All fractions were chlorinated according to the UFC protocol (Summers et al., 1996) as described in detail in Chapter 3.2.3. According to the preliminary chlorination experiments Cl/DOC ratio was found to be 1.5, which is consistent with those (i.e., 1.2-1.8) reported for UFC conditions by

Summers et al. (1996). All fractions in all sets of bromide-level experiments were chlorinated with a constant Cl_2/DOC ratio of 1.5. Therefore, for each set of bromide-level experiments, chlorine dose, pH, DOC and bromide concentrations were also constant; only the characteristics of NOM as measured by SUVA varied among fractions.

4.2.3. Analytical Methods

Analyses of all parameters were performed according to the methods described in Section 3.3.

4.3. Results and Discussion

4.3.1. Adsorption of NOM by XAD Resins

In this work, the modified Freundlich isotherm approach was used for adsorption isotherm modeling. As stated in Section 2.5.2, the traditional Freundlich isotherm equation could not be used in NOM adsorption studies due to heterogeneous character of NOM.

In Table 4.2, modified Freundlich isotherm parameters and confidence intervals (95%) based on both dose and surface area are given for adsorption of NOM by XAD-8 and XAD-4 resins. The results of adsorption isotherms normalized by dose and surface area are also presented in Figure 4.1 and 4.2, respectively. As seen from the figures and table, XAD-8 exhibited a higher degree of NOM uptake with respect to dose basis adsorption capacity (K_F) than XAD-4 did. The normalized isotherms based on surface area were also necessary to compare the degree of NOM uptake by resins that have different surface area and pore size distribution.No significant difference was observed between XAD-8 and XAD-4 resin with respect to equilibrium solution concentration based on normalized surface area (K_F). The affinity values of resins were more or less the same and had similar confidence intervals. Given the resins characteristics in Table 3.1 (Section 3.1.2), the surface area of XAD-4 resin (750 m^2/g) was much higher than that of XAD-8 (160 m^2/g). While XAD-4 exhibited smaller adsorption capacity than XAD-8 on mass basis, on surface area basis, the uptake capacity of XAD-4 was much higher than that of XAD-8. The reason of this finding was related with the pore sizes and in turn total pore area of these resins. Although surface area of XAD-4 was five times greater than that of XAD-8, smaller pore size of XAD-4 led to lower degree of NOM uptake. While nearly 50% of NOM was adsorbed by XAD-8 resin, adsorption of NOM was only 30% by XAD-4 resin at equilibrium. On the other side, a smaller n value of XAD-8 corresponded to the creation of a more energetically heterogeneous surface for NOM uptake.

Table 4.2. Dose and Surface Area Modified Freundlich Isotherm Coefficients for Isolated DOMs on XAD Resins

Resin Type	Modified Freundlich Isotherm Constants		
	K_F[b]	K_F[c]	m[d]
XAD-8	0.702 (0.557-0.885)[a]	0.266 (0.210-0.336)[a]	0.809 (0.746-0.872)[a]
XAD-4	0.318 (0.266-0.381)[a]	0.322 (0.249-0.415)[a]	1.002 (0.950-1.053)[a]

[a] Values in the parantheses for K_F and m are the 95% confidence intervals.
[b] Mass-normalized Freundlich affinity parameter (mg DOC/g resin)$^{1-m}$,
[c] Surface area-normalized Freundlich affinity parameter (mg DOC/m^2 resin)$^{1-m}$,
[d] Dimensionless.

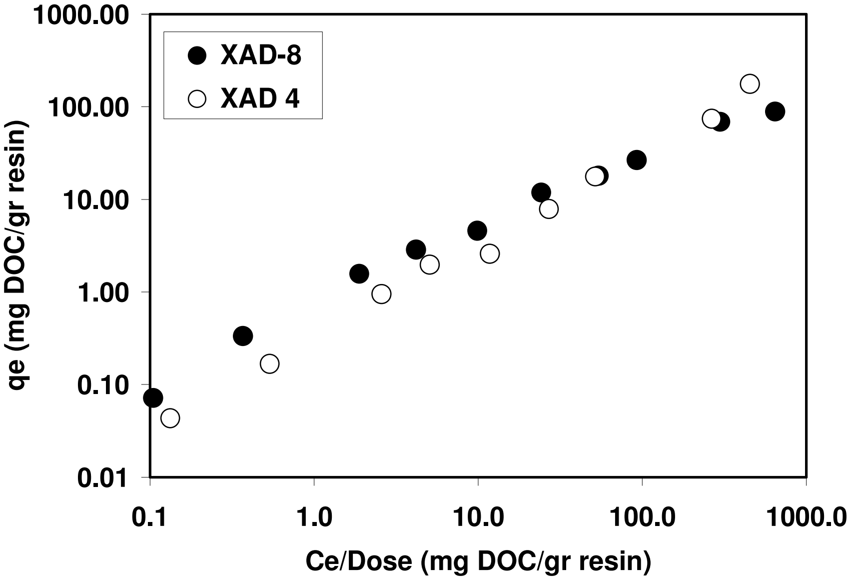

Figure 4.1. Adsorption of Alibeyköy NOM by XAD resins (dose-normalized Modified Freundlich isotherms).

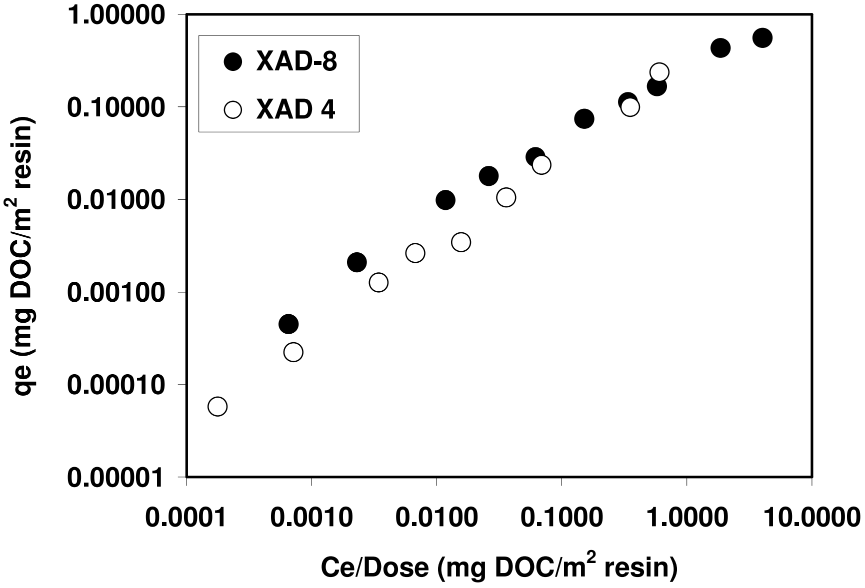

Figure 4.2. Adsorption of Alibeyköy NOM by XAD resins (surface area normalized modified Freundlich isotherms).

4.3.2. NOM Fractionation

Batch adsorption experiments were conducted to fractionate NOM in Alibeyköy water using XAD-8 and XAD-4 resins separately. A total of 20 bulk water fractions with a wide range of $SUVA_{254}$ values were obtained (Figure 4.3). Measurements of UV_{254} absorbance and DOC in remaining solutions (i.e., fractions) after contacting different resin doses demonstrated that XAD-8 or XAD-4 adsorption fractionates NOM solutions with regard to SUVA, consistent with the findings of Kitis et al. (2001, 2004). It was found that an increase in XAD-8 dose decreases the SUVA value of fractions, indicating that high SUVA components of NOM are preferentially removed from solution. In other words, the UV_{254} absorbing components of NOM were removed to a greater extent than DOC as the dose was increased. It is generally accepted that the UV_{254} absorbance of natural waters is caused primarily by NOM moieties containing unsaturated double bonds and/or π-π electron interactions (i.e., aromatic structures and chromophores); the changes in SUVA as a result of adsorption can be interpreted as changes in the aromatic content of the DOM fraction. These observations are consistent with the fact that XAD-8 resin is specified in the RAC method for the separation of HS (known to be rich in aromatic moieties, hydrophobic and HMW NOM) (Malcolm 1991). As mentioned in Section 2.3.1.1, in RAC method, DOM is isolated and fractionated into operationally-defined fractions based on their adsorption and back-elution affinities with different synthetic resins (Amberlite XAD-8, MSC-1 or Bio-Rad AG-MP-50 cation exchange and Duolite A-7 anion exchange resins). XAD-4 resin is specified in the RAC method for the isolation of LMW hydrophilic acid fractions. Although XAD-4 resin fractionated NOM based on SUVA, the data was somewhat scattered and an increasing SUVA trend was observed at lower resin doses (raw water $SUVA_{254}$=3.15) (Figure 4.3). Apparently, low-UV_{254} absorbing NOM components (i.e., LMW hydrophilic acids) that can better compete for adsorption sites were preferentially adsorbed over all NOM components in lower doses. However, higher XAD-4 doses resulted in decreasing SUVA values, which may be explained by the presence of excessive resin surface available to high-UV_{254} absorbing components as well. Each resin type provided different end points of fractionation; i.e., lowest $SUVA_{254}$ value obtained by XAD-8 and XAD-4 resin was 0.70 and 2.37, respectively. Nevertheless, by bulk water fractionation using XAD resins, it was possible to obtain a continuous fractionation based on $SUVA_{254}$ values from 3.91 to as low as 0.70.

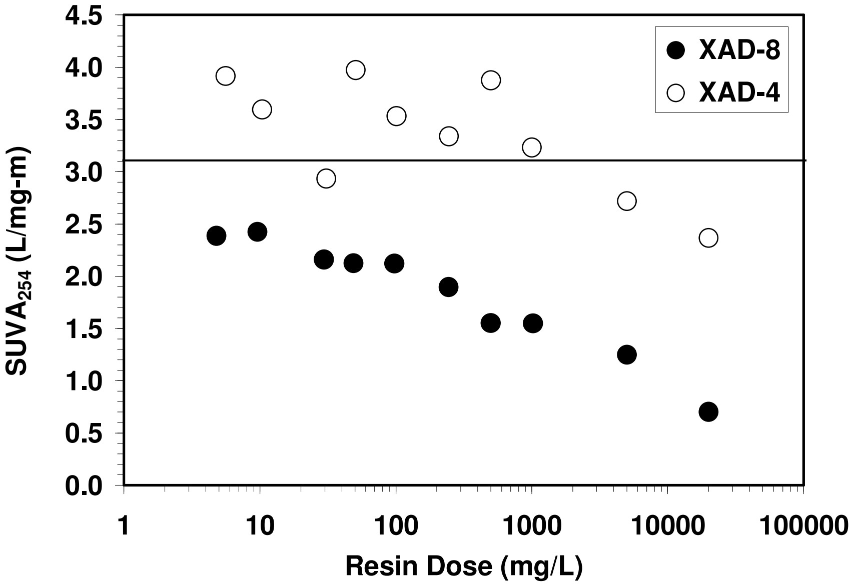

Figure 4.3. Bulk water fractionation of NOM in Alibeyköy water by XAD-8 and XAD-4 resin batch-adsorption.

4.3.3. Impact of SUVA on DBP Formation and Speciation

Among all the different parameters for characterizing NOM composition of waters, it is stated in the literature that UV absorbance and SUVA at wavelengths around 254-280 nm may correlate well with DBP formation. Figure 4.4 shows the correlations between the SUVA values and HAA formations of all fractions at three different bromide levels. It should be noted that each NOM fraction had constant DOC, pH, Cl_2/DOC ratio, and bromide concentration (at a given bromide level); the only factor affecting DBP formation was NOM characteristics as measured by SUVA. However, although a wide range of $SUVA_{254}$ was investigated, no correlation between SUVA and HAA formation was found for each bromide level. Similarly, no correlations were observed for SUVA-THMs (Figure 4.5) and SUVA-AOX (Figure 4.6). This contradicts with previous studies (Kitis et al., 2001, 2004; Reckhow et al., 1990; Croue et al., 2000; Liang and Singer; 2003; Archer and Singer, 2006) in which strong correlations between DBP formations and SUVA values were observed for many NOM fractions obtained by various physicochemical separation processes in a single water source. These different results suggest that the effectiveness of SUVA in correlating with DBP formation is water specific. In other words, SUVA as a bulk parameter may not capture the reactive sites on NOM moieties responsible for DBP formation in all source waters, given the high degree of NOM heterogeneity among waters. Furthermore, in addition to the finding that no correlations exist between SUVA and DBP formation in the tested water, any consistent impact of bromide levels on SUVA-DBP relations was also not found. This finding was consistent with our previous study in which rather poor correlations were found between SUVA and THM and HAA concentrations in 29 unfractionated chlorinated surface waters (Ates et al., 2007). This had been attributed to the presence of NOM with LMW, less hydrophobicity and aromaticity in the tested waters.

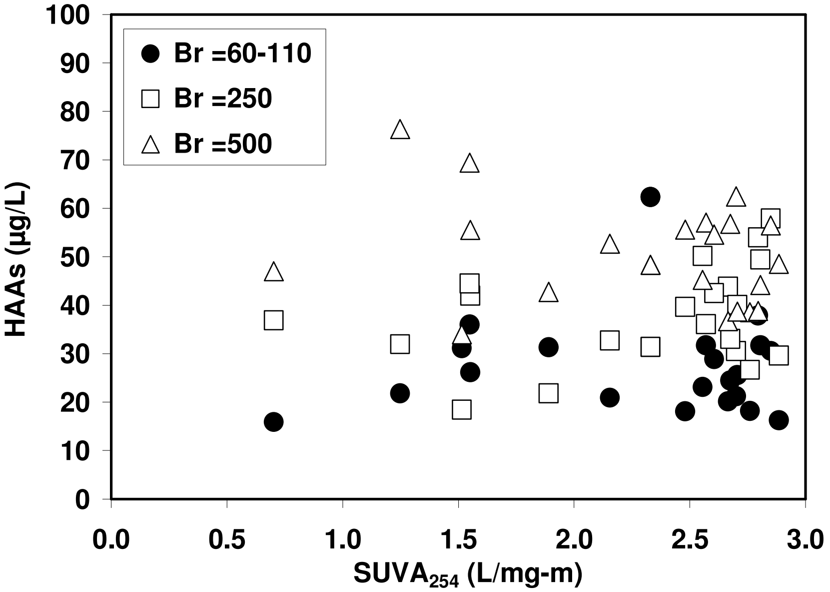

Figure 4.4. The impact of SUVA on HAAs formation at different bromide levels of all NOM fractions. Bromide concentrations are in µg/L.

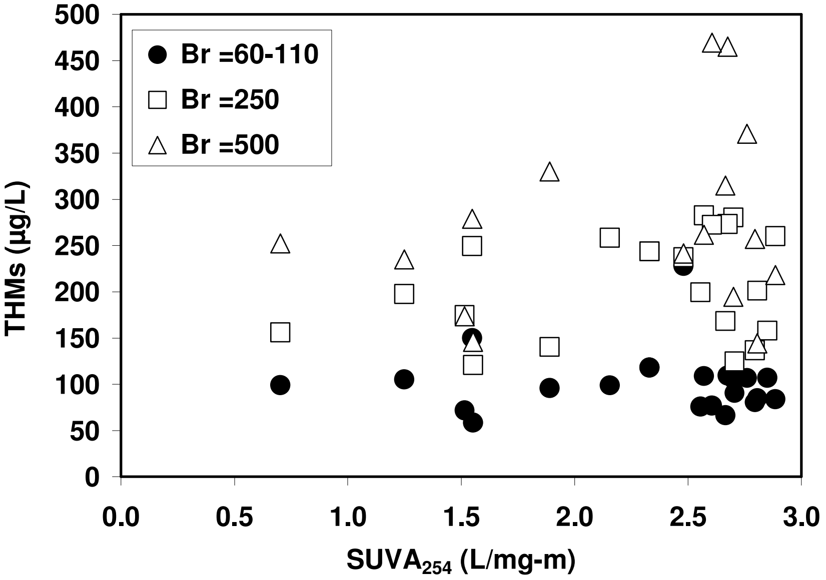

Figure 4.5. The impact of SUVA on THMs formation at different bromide levels of all NOM fractions. Bromide concentrations are in µg/L.

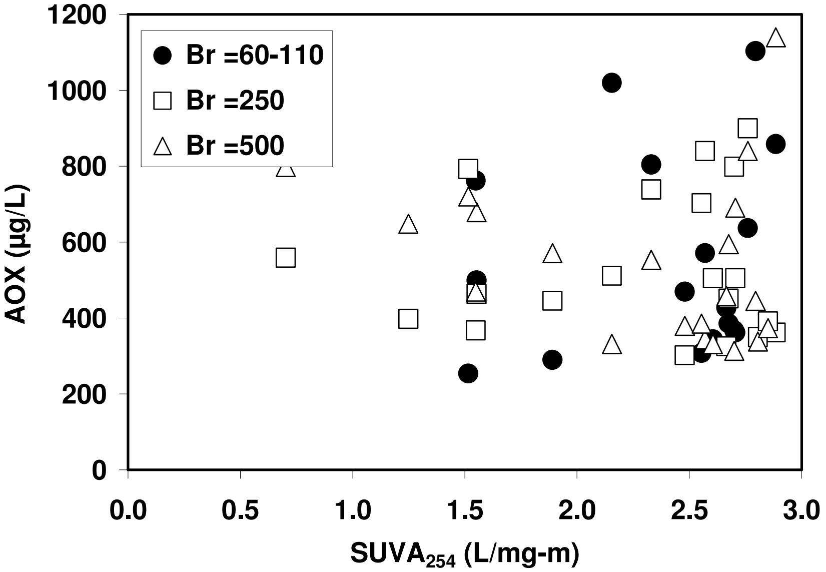

Figure 4.6. The impact of SUVA on AOX formation at different bromide levels of all NOM fractions. Bromide concentrations are in µg/L.

Figure 4.7 and Figure 4.8 show the impact of SUVA on THM and HAA speciation, which is discussed in terms of bromine incorporation factor (n). This factor expresses the extent of brominated DBPs and is calculated by the total moles of bromine incorporated divided by total moles of species formed in a given DBP class. The value of n for THM species may vary between 0 (e.g., for chloroform) and 3 (e.g., for bromoform) (Symons et al., 1996). For bromide levels of 60-110 µg/L, bromine incorporation factors both for THMs and HAAs did not vary significantly over the range of SUVA values studied. It appears that the extent of bromine incorporation into NOM components at constant DOC, pH, Cl_2/DOC ratio, and bromide concentration is constant and independent of SUVA in the source water tested. This finding contradicts with a previous work of Kitis et al., 2002, in which bromine was found to be more effectively incorporated into low UV-absorbing (i.e., low SUVA) NOM components in other waters. On the other hand, for the higher bromide level (500 µg/L), variations between SUVA and bromine incorporation factors were more pronounced. Similar observation was also found for 250 µg/L bromide level. Overall, SUVA was not a good predictor of THM and HAA speciation in the tested source water. Similar to results found for SUVA-DBP formations, SUVA appears to not be able to define the specific NOM structures to which chlorine or bromine attacks, especially when bromide ion is present in higher concentrations. Bromine incorporation factors both for THMs and HAAs were higher at bromide concentration of 500 µg/L compared to those at 60-110 µg/L, as expected (Figure 4.7 and Figure 4.8). In addition, for all 20 NOM fractions, THM bromine incorporation factors were higher than those of HAAs at each bromide level. THM bromine incorporation factors as high as 2.5 were calculated at 500 µg/L bromide. These results indicate that NOM in Alibeyköy water is more susceptible to the formation of brominated THM species as opposed to brominated HAAs. This finding was also confirmed on the mass or concentration basis of formed species.

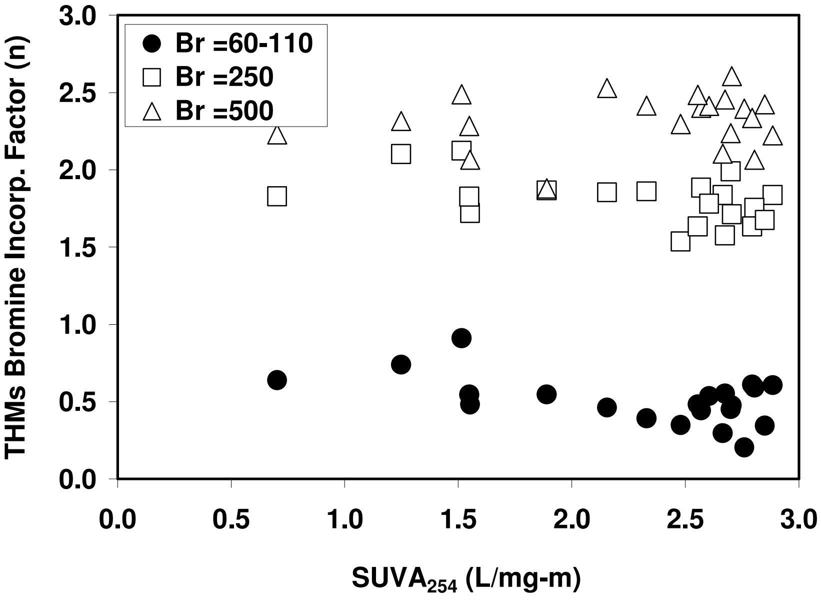

Figure 4.7. The impact of SUVA on THM speciation at different bromide levels of all NOM fractions.

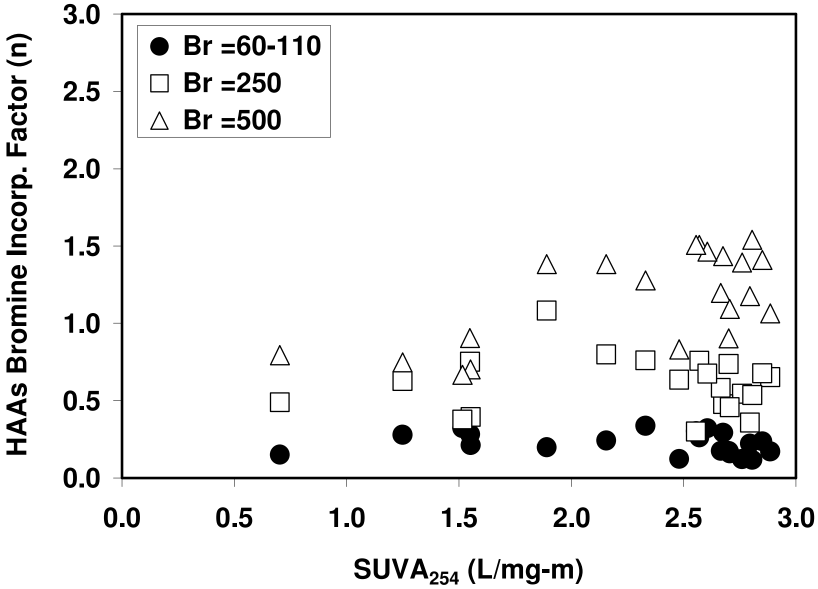

Figure 4.8. The impact of SUVA on HAA speciation at different bromide levels of all NOM fractions.

4.3.4. Differential UV Spectroscopy

Differential UV spectroscopy, the difference in the UV absorbance before and after chlorination of natural waters, was found to be an excellent indicator of TOX formation in many researches. The magnitude of the decrease in the UV absorbance at 272 nm (ΔUV_{272}) was well correlated with TOX formation resulting from chlorination, independent of the ratio of chlorine to DOC, bromide concentration, pH from 5 to 11, reaction time, and NOM source (Korshin et al., 1997a,b; Li et al., 1998). Similarly, strong correlations between ΔUV_{280} and THMs or HAAs formations were previously observed in chlorinated NOM fractions of source waters with $SUVA_{280}$ values higher than 3 (Kitis et al., 2000). The practical advantage of the use of differential UV spectroscopy is the ability to predict the formation of DBPs in water treatment plants and distribution systems simply by measuring the UV absorbance before and after chlorination at a certain time and using the previously generated ΔUV_λ-DBP correlations.

In this study, no correlations were found between ΔUV_{254}-THMs (Figure 4.9) and ΔUV_{254}-HAAs (Figure 4.10) formations in chlorinated NOM fractions of Alibeyköy water at any bromide level. Similar result was also found for AOX (in Appendix B, Figure B.1). In other words, the destruction in the UV_{254} absorbance from chlorination did not correlate with DBP formation. This finding suggests that DBP precursors in Alibeyköy water can not be identified by simple UV absorbance measurements, which is further supported with the findings for SUVA as discussed in the previous section. Apparently, NOM moieties which do not absorb UV light at 254 nm significantly contribute to DBP formation in Alibeyköy water. A similar result was found in our previous study in which differential UV spectroscopy correlated weakly with DBP formation in low-$SUVA_{254}$ (<2.3) waters (Edzwald and Van Benschoten, 1990; White et al., 1997; Edzwald and Tobiason, 1999). These results suggest that the robustness of differential UV spectroscopy in correlating with DBP formation depends on specific NOM characteristics in a source water. The bromide levels also did not have any discernible impact on ΔUV_{254}-DBP relations (Figure 4.9 and Figure 4.10). In terms of relations between ΔUV_{254} and bromine incorporation factors of both THMs and HAAs, it was found that as ΔUV_{254} increased bromine incorporation factors for each bromide level did not vary and stayed at constant values (Figure 4.11 and Figure 4.12). These results overall indicate that in addition to DBP formation, DBP speciation is also not linked to the destruction of UV_{254} absorbing NOM moieties in Alibeyköy water after chlorination.

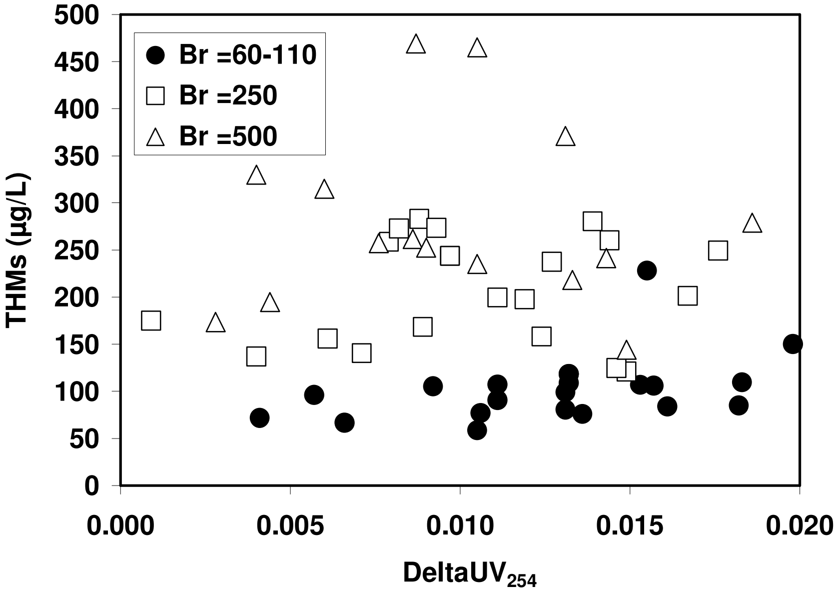

Figure 4.9. Relations between THMs formation and ΔUV (differential UV spectroscopy) of all NOM fractions at different bromide levels.

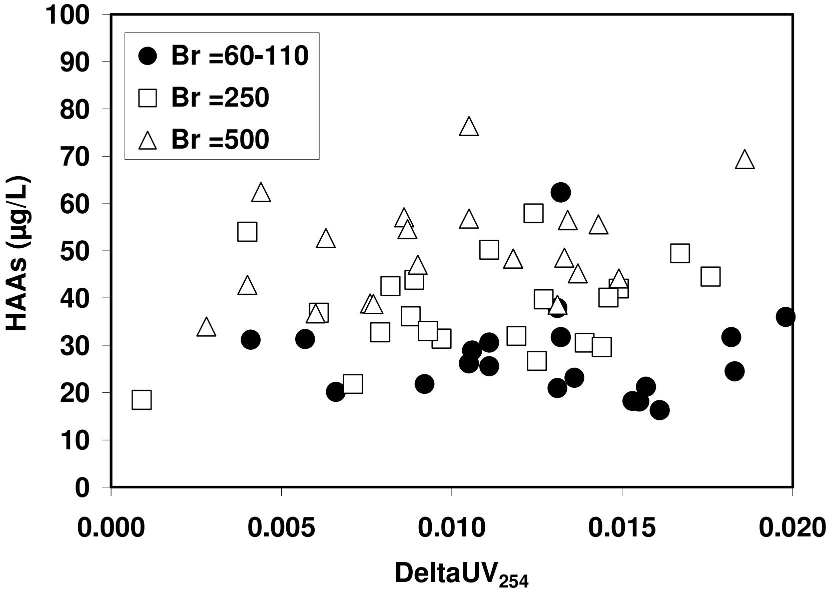

Figure 4.10. Relations between HAAs formation and ΔUV (differential UV spectroscopy) of all NOM fractions at different bromide levels.

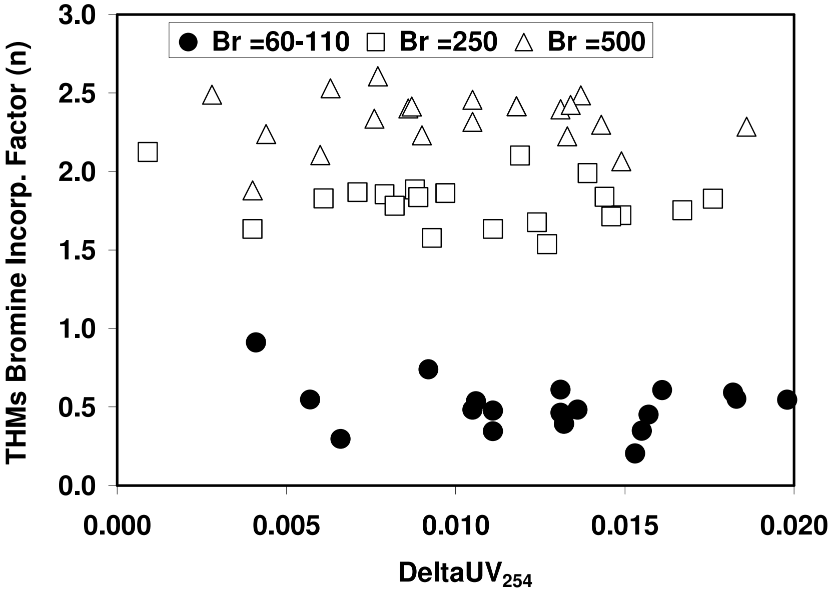

Figure 4.11. Relations between THM speciation and ΔUV (differential UV spectroscopy) of all NOM fractions at different bromide levels.

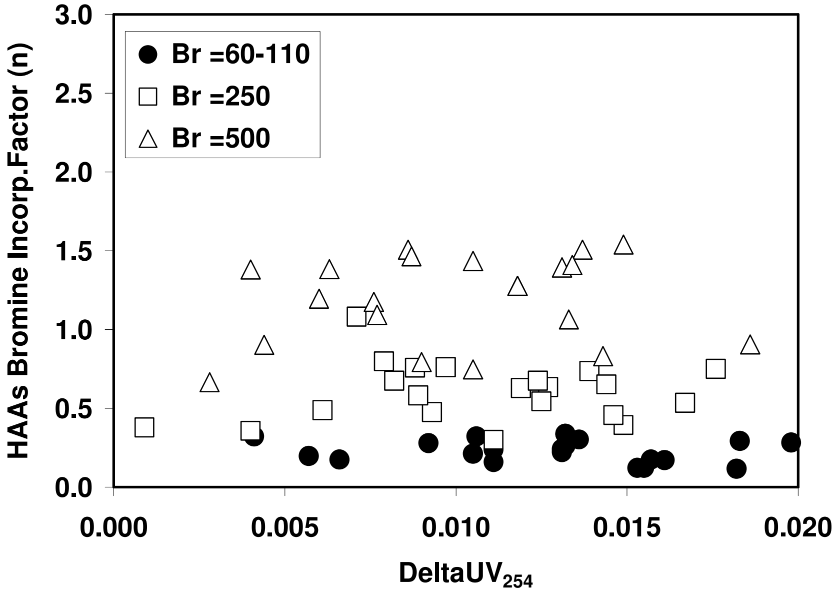

Figure 4.12. Relations between HAA speciation and ΔUV (differential UV spectroscopy) of all NOM fractions at different bromide levels.

4.3.5. Impact of Bromide Concentration on DBP Formation and Speciation

Figure 4.13 and 4.14 show the impact of bromide concentrations on HAAs and THMs formations of NOM fractions in Alibeyköy water. It was found that almost for all NOM fractions as the bromide concentrations increased from 60-110 to 500 µg/L THMs and HAAs formations increased at constant DOC, chlorine dose and pH. Similar trend was also observed for AOX (in Appendix B, Figure B.2). While THMs formation was between 59 and 228 µg/L at bromide level of 60-110 µg/L, it was between 144 and 371 µg/L at 500 µg/L bromide concentration. On the other hand, HAAs formation was between 16 and 36 µg/L at bromide level of 60-110 µg/L, it was between 39 and 76 µg/L at 500 µg/L bromide concentration. It was reported in some studies that the presence of bromide ion during free chlorination did not appreciably change the amount of TOX (Symons et al., 1987), THMs, HAAs, and HANs (Wu, 1998) produced; however, the speciation shifted towards more brominated DBPs. On the contrary, other studies reported that bromide addition markedly increased the yields of brominated THMs and total THMs (Oliver, 1980; Symons et al., 1993). It was found that bromination had a higher efficiency than chlorination in reaction with aliphatic precursors (Heller-Grossman et al., 1993). These results overall indicate that the impact of bromide levels on the amount of DBP formations varies by source water and its NOM characteristics.

It is often stated in the literature that bromine substitution is favored over chlorine, even when chlorine is present in large excess compared with bromide concentration. The presence of low levels of bromide in raw water supplies has been shown to influence the THM species formed and their quantitative distribution in the finished water after chlorination (Sketchell et al., 1995). Stevens et al. (1990) analyzed finished waters in 10 water utilities for DBPs including THMs, HANs, HAAs, haloaldehydes, HKs, chlorophenols, chloropicrin and cyanogens chloride. They found that 28 of 196 organic chlorination by-products were formed only in the presence of bromide. Cowman and Singer (1994) stated that significant concentrations of mixed bromo-chloro HAAs species were formed from the chlorination of bromide-containing water. Furthermore, a shift toward the formation of brominated DBP species occurs with increasing bromide concentrations in chlorinated waters (Pourmoghaddas et al., 1993; Krasner et al., 1994; Symons et al., 1996). Consistent with this general observation, increasing bromide levels at constant DOC, chlorine dose and pH resulted in a significant shift toward the formation of brominated THM and HAA species as indicated by bromine incorporation factors (Figure 4.13 and Figure 4.14). At Br^-/DOC ratio of 250 µg/mg (bromide concentration: 500 µg/L), the calculated THM bromine incorporation factors were in the range of 2.1-2.5. It should be noted that an n value of 3.0 indicates that only bromoform is formed among four THM species. For all bromide levels, THM bromine incorporation factors were higher than those of HAAs. Furthermore, a larger impact of increasing bromide levels on the formation of brominated species was observed for THMs compared to HAAs (Figure 4.15 and Figure 4.16).

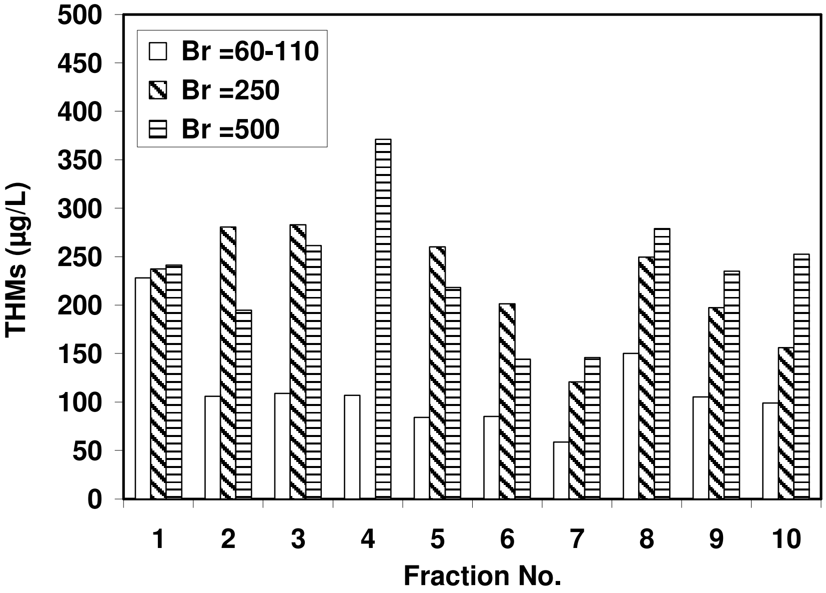

Figure 4.13. The impact of bromide concentrations on THMs formation of NOM fractions in Alibeyköy water (XAD-8 fractions).

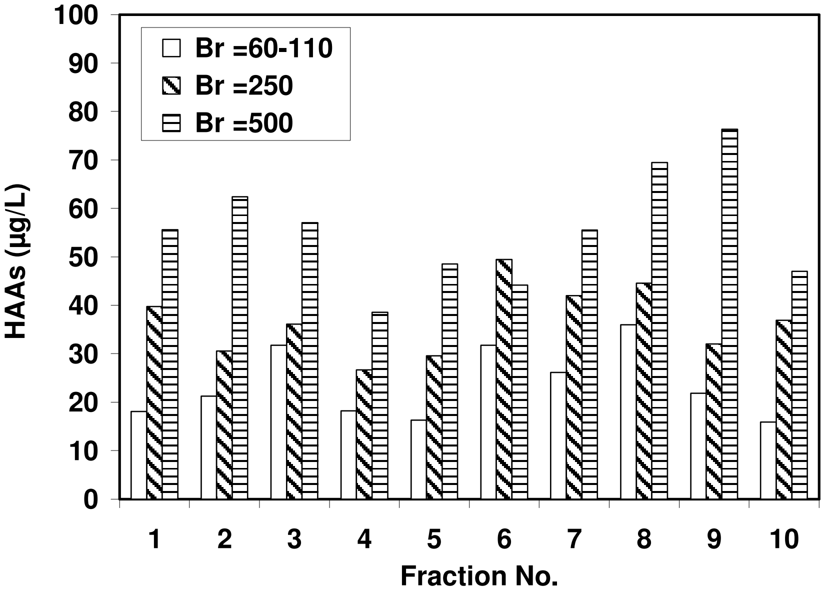

Figure 4.14. The impact of bromide concentrations on HAAs formation of NOM fractions in Alibeyköy water (XAD-8 fractions).

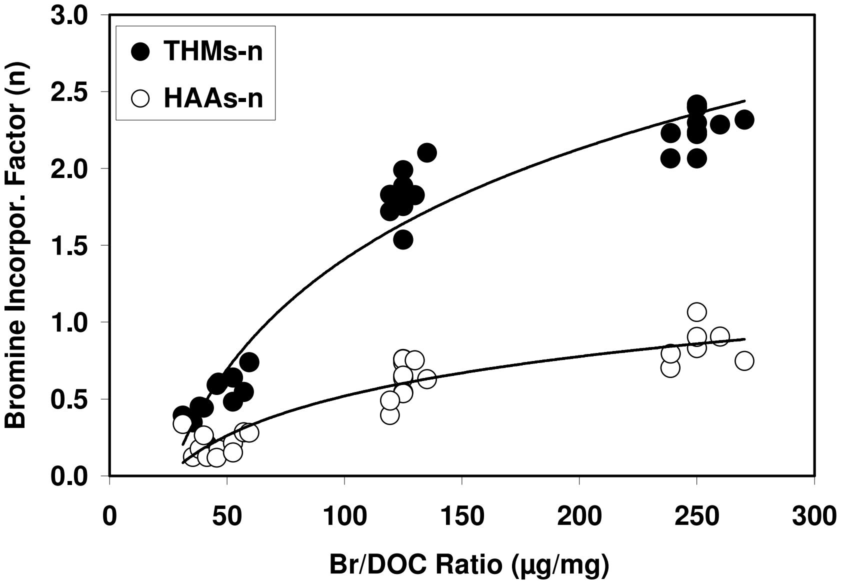

Figure 4.15. The impact of bromide concentrations on THM and HAA speciation in NOM fractions (XAD-8) of Alibeyköy water.

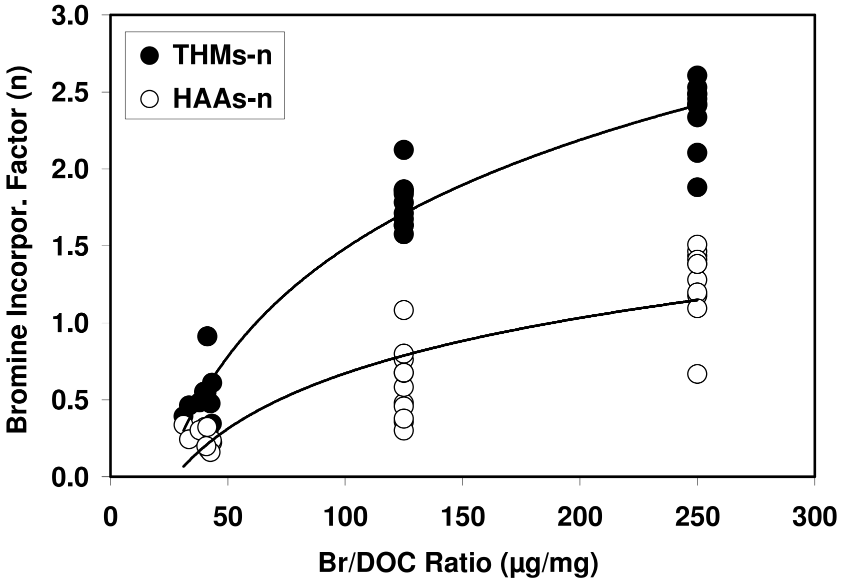

Figure 4.16. The impact of bromide concentrations on THM and HAA speciation in NOM fractions (XAD-4) of Alibeyköy water.

While all four THM species were present in all fractions and bromide levels, the dominant THM species were chloroform and bromoform at bromide concentrations of 60-110 and 500 µg/L, respectively. Significantly high bromoform concentrations were measured (70-174 µg/L) at 500 µg/L bromide level. For HAAs, only monochloro-, dichloro-, trichloro-, and bromochloro acetic acids were detected at 60-110 µg/L bromide; dichloro acetic acid having the highest concentrations. On the other hand, all of the nine HAA species were detected at higher bromide concentrations (250 and 500 µg/L) in all fractions. At the bromide level of 250 µg/L, the concentrations of HAA species measured in all fractions were as following on an average basis: dichloro> monochloro> trichloro> chlorodibromo> bromochloro> dibromo> tribromo> bromodichloro> monobromo acetic acid. However, at the bromide level of 500 µg/L, the order changed significantly to the dominance of di- and tri-brominated species: dibromo> tribromo> monochloro> chlorodibromo> dichloro> bromochloro> trichloro> monobromo> bromodichloro. Similarly, Pourmoghaddas et al. (1993) stated that bromide in chlorinated HA solution shifted the distribution of HAAs to more brominated (dibromo- and tribromo acetic acid) and mixed halogenated (bromochloro-, bromodichloro- and chlorodibromo acetic acid) species. It was interesting to note that di-halogenated species (dichloro acetic acid for 60-110 and 250 µg/L bromide and dibromo acetic acid for 500 µg/L bromide) were always detected at highest concentrations in Alibeyköy water. Consistent with the results in this study, it is stated that bromoform and dibromo acetic acid may be the major species in waters with very high bromide concentrations (Singer, 1994). This is of concern since the MW of brominated species is higher than the chlorinated counterparts, leading to potential failure to comply with regulations.

It is indicated in the literature that about 30-60% of TOX can be assigned to identified individual DBPs, mostly THMs and HAAs (Christman et al., 1983; Reckhow and Singer, 1984; Singer, 1994). A significant part of the organic-bound chlorine may also be associated with non-volatile organic compounds. The unidentified DBPs may be too large (non-volatile) or too small (polar) in MW to be detected by available analytical methods. Figure 4.17 shows the total contribution of halogens (chlorine and bromine) in THM and HAA species to AOX on a percent mass basis at each bromide level. Halogens in THMs and HAAs only accounted for 10-46% of AOX at bromide concentration of 60-110 µg/L in NOM fractions. However, at higher bromide concentrations, the contribution of halogens in THMs and HAAs to AOX was significantly higher, i.e., values as high as 84% were found at 500 µg/L bromide. These results indicate that significant amounts of halogenated by-products other than THMs and HAAs are formed in Alibeyköy water NOM fractions at low bromide levels. On the other hand, the relative occurrence of such other halogenated by-products decreases with increasing bromide levels, due to the formation of THM and HAA species in higher concentrations. Apparently, for this water source, higher bromide levels provide a competitive advantage to THM and HAA precursors in NOM moieties over precursors of other DBPs, which may include HANs, HKs, CHY, chloropicrin, cyanogen chloride, chlorophenols, chlorinated quinones, chlorinated aliphatic mono- and di-basic acids, and possibly other known or unknown halogenated by-products. However, it should be noted that only one source water was tested in this study and the results may not be applicable to other waters with varying NOM characteristics.

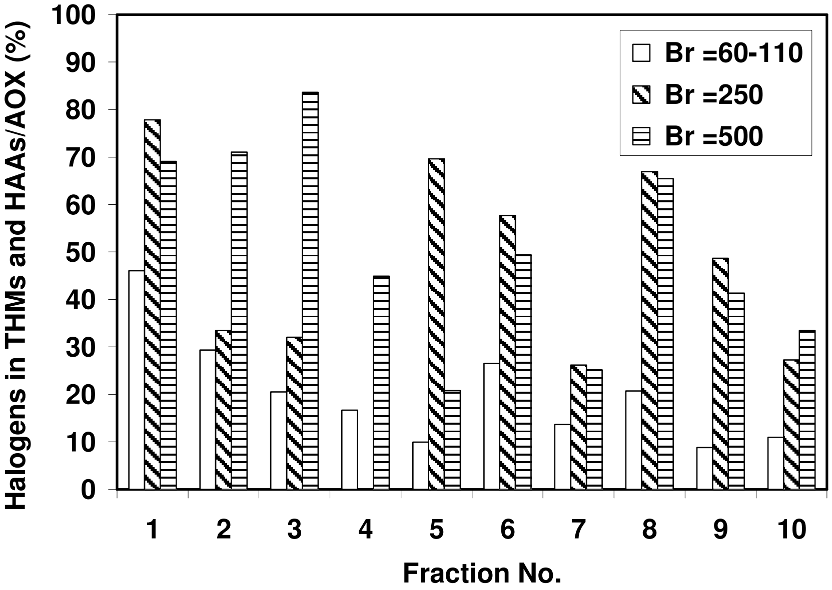

Figure 4.17. The total contribution of halogens (chlorine and bromine) in THM and HAA species to AOX on a percent mass basis at each bromide level of Alibeyköy NOM fractions.

4.4. Conclusions

A total of 20 bulk water NOM fractions with a wide range of $SUVA_{254}$ values were obtained from Alibeyköy raw water after batch XAD-8 or XAD-4 resin adsorption. While XAD-8 preferentially removed high SUVA NOM components from water at all resin doses, XAD-4 removed low SUVA components at lower resin doses. No correlations between SUVA and DBP (THMs, HAAs and AOX) formations of NOM fractions were found at constant DOC, pH, Cl_2/DOC ratio, and bromide concentration. Similarly, SUVA was not a good predictor of THM and HAA speciation as measured by bromine incorporation factor. For bromide level of 60-110 µg/L, the extent of bromine incorporation into NOM fractions at constant DOC, pH, Cl_2/DOC ratio was constant and independent of SUVA. It appears for this source water that SUVA as a bulk parameter does not capture the reactive sites on NOM moieties responsible for DBP formation and speciation. Bromine incorporation factors both for THMs and HAAs were higher at bromide concentration of 500 µg/L compared to those at 60-110 µg/L. THM bromine incorporation factors were always higher than those of HAAs at each bromide level, suggesting that NOM in Alibeyköy water is more susceptible to the formation of brominated THM species as opposed to brominated HAAs.

The destruction in the UV_{254} absorbance from chlorination (ΔUV_{254}, differential UV absorbance spectroscopy) did not correlate with DBP formation in NOM fractions of Alibeyköy water at any bromide level, further proving that DBP precursors in this water can not be identified by simple UV absorbance measurements. NOM moieties which do not absorb UV light at 254 nm significantly contributed to DBP formation in Alibeyköy water.

Di-halogenated HAA species (dichloroacetic acid for 60-110 and 250 µg/L bromide and dibromoacetic acid for 500 µg/L bromide) were always detected at highest concentrations in Alibeyköy water. The dominant THM species were chloroform and bromoform at bromide concentrations of 60-110 and 500 µg/L, respectively. Mass balance calculations on halogens using THMs, HAAs and AOX data indicated that significant amounts of either identifiable or unidentifiable halogenated by-products (>54% of AOX) other than THMs and HAAs are formed in Alibeyköy water NOM fractions at 60-110 µg/L bromide. The relative occurrence of such other halogenated by-products decreased with increasing bromide concentrations. Increasing bromide concentrations in NOM fractions of this water at constant DOC, chlorine dose and pH; 1) increased the total concentrations of measured DBPs including THMs, HAAs and AOX, 2) resulted in a shift toward the formation of brominated species, 3) increased the spectrum of detected species, i.e., occurrence of all nine HAAs, and 4) provided a competitive advantage to THM and HAA precursors in NOM moieties over precursors of other DBPs.

CHAPTER 5

FORMATION OF CHLORINATION BY-PRODUCTS IN WATERS WITH LOW-SUVA- CORRELATIONS WITH SUVA AND DIFFERENTIAL UV SPECTROSCOPY

5.1. Introduction

In many studies, several researchers have tried to correlate water quality parameters to DBP formation in an effort to find a useful surrogate parameter to estimate DBP formation or to better understand the chemical nature of DBP formation processes. The most used surrogate parameters are UV absorbance, SUVA and DOC. Researchers have shown good correlations between THMFP and UV absorbance at 254 nm wavelength using raw and treated waters (Edzwald et al., 1985). Singer and Chang (1989) showed that the TOC concentration of water was generally a good indicator to determine the amount of THMs and other DBP precursors present. In another study, it was found that UV absorbance was greater for the HA, reflecting their higher aromatic content and greater molecular size. Besides, HA led to the higher yields of TOX, THMs, HAAs, and HANs than the corresponding FA from the same source (Reckhow et al., 1990). The SUVA value of a water has been found to be a good surrogate for hydrophobic, aromatic, and HMW NOM fractions, such as HA and FA (Edzwald and Van Benschoten, 1990; White et al., 1997). The possible reason of good correlations among UV absorbance or SUVA and DBP formations has been attributed to the likelihood that “activated” aromatic structures (aromatic sites substituted with oxygen- and nitrogen-containing functional groups, i.e., phenolics and aromatic amines) constitute the primary sites attacked by chlorine or other oxidants (Norwood et al., 1980; De Laat et al., 1982; Norwood and Christman, 1987; Reckhow et al., 1990; Harrington et al., 1996).

Some researchers have proved that simple and reliable relationships exist between change in UV absorbance of NOM after chlorination and the formation of chlorinated byproducts (Korshin et al., 1997a, 1999, Li et al., 1998, 2000; Karanfil et al., 2000; Kitis, 2001). Since there is evidence that chlorine may attack NOM predominantly at electron-rich sites, i.e. activated aromatic sites or conjugated double bonds, which absorb UV light effectively at wavelengths of 254 to 280 nm, chlorination may decrease the UVA of NOM at these wavelengths as a result of alteration and destruction of these sites (Korshin et al., 1997a, 1999; Li et al., 1998, 2000). The magnitude of the decrease in the UV absorbance at 272 nm (ΔUV_{272}) was found to be an excellent indicator of TOX formation resulting from chlorination, independent of the ratio of chlorine to DOC, bromide concentration, pH from 5 to 11, reaction time, and NOM source (Korshin et al., 1997a,b,1999; Li et al., 1998,2000).

The important practical advantages of SUVA and differential UV are that these parameters can be determined in a short period of time, using a small volume of sample, and does not require sophisticated sample pretreatment and analytical equipment. The equipment needed to make DOC and UV measurements is available in most water treatment plants and is straightforward to operate by the treatment plant operators.

Although UV absorbance and SUVA were generally shown to correlate well with DBP formation, especially in waters with relatively high DOC concentration (>3 mg/L) and high $SUVA_{254}$ values (>2-3 L/mg C.m), there is limited information in the literature on the correlations of such parameters with DBP formation for waters having low DOC and low SUVA values. These waters may be characterized by having NOM of hydrophilic character and less aromaticity. Therefore, the main objective of this work was to investigate the effectiveness of SUVA in predicting DBP formation in waters with low SUVA and low DOC levels. Two different raw waters were studied for this purpose, and the NOM in each water was fractionated using XAD-8, XAD-4, MIEX® resins, and GAC adsorption applying variable-dose batch experiments. The obtained bulk water NOM fractions (i.e., the filtered solutions after contact with the adsorbent or resin at various doses), with a wide range of SUVA values, were chlorinated at constant DOC and bromide concentration (after adjustment), pH, and Cl_2/DOC ratio. Thus, the only different variable among fractions was SUVA, i.e., the character of NOM, enabling the evaluation of the impact of SUVA alone on DBP formation. Finally, THMs and HAAs were measured in each chlorinated fraction. Different types of resins or adsorbents were selected and used in bulk water fractionation to remove different type and quantity of NOM from raw waters and to obtain many fractions with a wide range of SUVA values, based on the successful previous experience (Karanfil et al., 2000; Kitis et al., 2001, 2004). These resins or adsorbents remove NOM from solutions by physical separation; thus, the NOM in solution is not subject to harsh chemical conditions.

5.2. Materials and Methods

5.2.1. Source Waters and Materials

The tested surface waters in this work were Alibeyköy and Karacaören reservoirs, which are the major drinking water sources in the Cities of Istanbul and Antalya, respectively. Alibeyköy and Karacaören waters were sampled in December 2004 and in June 2005, respectively. Table 5.1 presents the physico-chemical characteristics of these waters.

Table 5.1. Physico-chemical characteristics of the tested raw waters

Parameters	**Alibeyköy**[a]	**Karacaören**[a]
DOC (mg/L)	3.7 ± 0.2	1.2 ± 0.2
UV_{254} Absorbance	0.076 ± 0.003	0.023 ± 0.004
$SUVA_{254}$ (L/mg org-C.m)	2.03 ± 0.08	1.93 ± 0.06
Bromide (µg/L)	40 ± 5	20 ± 0
pH	8.1 ± 0.04	8.1 ± 0.05
TDS (mg/L)	288 ± 0.03	169 ± 0.02
Conductivity (µS/cm)	577 ±0.03	336 ± 0.02
Total hardness (mg $CaCO_3$/L)	120 ± 12	70 ± 9
Alkalinity (mg $CaCO_3$/L)	225 ± 15	268 ± 13

[a] Raw water sample was filtered (0.45 µm) before measurements.
Values reported are the average of triplicate measurements.

Both of the raw waters had $SUVA_{254}$ values ≤2 L/mg org-C.m; thus, both waters may be regarded as low-SUVA waters. Karacaören water is known to be one of the cleanest and prestigious drinking water sources in Turkey, with its very low DOC, bromide and TDS content. DOC concentrations of Alibeyköy and Karacaören waters were 3.7 and 1.2 mg/L, respectively.

Although having somewhat higher DOC level, Alibeyköy water had a $SUVA_{254}$ value of 2 L/mg org-C.m.

In an effort to obtain many bulk water NOM fractions with a wide range of SUVA values, different types of resins and adsorbents were used. XAD-8 and XAD-4 resins, a coal-based GAC and MIEX$^{®}$ DOC resin were employed for bulk water fractionation.

5.2.2. Experimental Procedures

Kinetic experiments in CMBRs were performed using XAD resins and GAC adsorbent, as described in detail in Section 3.2.1.2 and 3.2.1.4, respectively. While all four adsorbents (XAD-8, XAD-4, MIEX$^{®}$ resins and GAC) were used for Alibeyköy water, XAD-8, XAD-4 and GAC were tested for Karacaören water. For Alibeyköy water, the range of dosages employed for XAD resins, GAC and MIEX$^{®}$ were 5-5,000 mg/L, 50-4,000 mg/L and 2.5-30 mL/L, respectively. For Karacaören water, such ranges were 5-1,000 mg/L and 10-4,000 mg/L for XAD resins and GAC, respectively. These dosages were chosen to generate fractions with a wide range of SUVA values, while assuring that changes in DOC and UV absorbance were sufficiently large for accurate quantification. For fractionation by the MIEX$^{®}$ resin, batch tests were conducted using 4 doses of MIEX$^{®}$ (2.5, 5, 10, 30 mL resin/L). Fractions obtained from XAD-8, XAD-4, GAC and MIEX$^{®}$ resin were adjusted for constant DOC and pH levels.

All fractions were chlorinated according to the UFC protocol (Summers et al., 1996) as described in detail in Section 3.2.3. According to preliminary chlorination experiments, the required Cl_2/DOC ratios were found to be 2 and 1.5 for Alibeyköy and Karacaören waters, respectively, which are consistent with those (i.e., 1.2-1.8) reported for UFC conditions by Summers et al. (1996). Each of the source water and its fractions were chlorinated at these constant Cl_2/DOC ratios.

5.2.3. Analytical Methods

Analyses of all parameters were performed according to the methods described in Section 3.3.

5.3. Results and Discussion

5.3.1. Adsorption of NOM by XAD Resins/GAC Adsorbent

The adsorption isotherms on mass and surface area bases were given in Figure 5.1 and 5.2 for Alibeyköy and in Figure 5.3 and 5.4 for Karacaören, respectively. As seen from the Table 5.2, the highest NOM uptake (K_F) was obtained by GAC adsorbent followed by XAD-8 and XAD-4 resins on mass base for Alibeyköy water. On the other hand, the similar uptake rates (K_F) based on surface area were obtained by XAD-8 resin and GAC adsorbent, which of XAD-4 was lower for Alibeyköy water. On the other hand, for Karacaören water, GAC adsorbent yielded the highest NOM uptake on mass base, then following higher result was obtained by XAD-4 resin (Table 5.2). Considering to surface area base, the preferential adsorption of NOM was more favored by XAD-4 resin than XAD-8 resin and GAC adsorbent for Karacaören water. These findings were probably occurred related with the characteristics of resin or adsorbent (i.e., chemical structure, surface area and pore size distribution) and characteristics of organic compounds (i.e., molecular size distribution, moiety, hydrophobicity/hydrophilicity) in water resource. It is known that XAD-8 and XAD-4 resins adsorb organic compounds preferentially that the XAD-8 resin favors the isolation of the HMW NOM fraction (the most hydrophobic) which is the most aromatic in nature (Croue, 2004).

Table 5.2. Dose and Surface Area Modified Freundlich Isotherm Coefficients for Isolated DOMs on XAD Resins/GAC Adsorbent

Water Source	Resin/Adsorbent Type	Modified Freundlich Isotherm Constants		
		K_F[b]	K_F[c]	m[d]
Alibeyköy	XAD-8	0.312 (0.243-0.395)[a]	0.150 (0.127-0.177)[a]	0.856 (0.795-0.916)[a]
	XAD-4	0.144 (0.105-0.196)[a]	0.131 (0.090-0.191)[a]	0.986 (0.903-1.069)[a]
	GAC	2.011 (1.621-2.495)[a]	0.150 (0.127-0.177)[a]	0.492 (0.391-0.594)[a]
Karacaören	XAD-8	0.818 (0.319-2.101)[a]	0.403 (0.141-1.149)[a]	0.856 (0.795-0.916)[a]
	XAD-4	0.931 (0.592-1.464)[a]	0.986 (0.903-1.069)[a]	0.283 (0.583-0.137)[a]
	GAC	2.011 (1.621-2.495)[a]	0.062 (0.034-0.112)[a]	0.492 (0.391-0.594)[a]

[a] Values in the parantheses for K_F and n are the 95% confidence intervals.

[b] Mass-normalized Freundlich affinity parameter (mg DOC/g resin or adsorbent)$^{1-m}$,

[c] Surface area-normalized Freundlich affinity parameter (mg DOC/m^2 resin or adsorbent)$^{1-m}$,

[d] Dimensionless.

However, GAC adsorbent does not show any preference in adsorbing NOM. Although the pore size of XAD-8 resin was five times greater than than that of XAD-4 resin, surface areas of these resins varied reversely (Table 3.1). The organic compounds in Alibeyköy and Karacaören waters were analyzed by HPSEC method; and it was found that the distributions of organic compounds in those waters varied in different ratio (detailed in

Section 5.3.2). The ratio of LMW to HMW organic fraction was relatively higher and additionally initial NOM concentration was much lower in Karacaören water than in Alibeyköy water. Therefore, higher NOM uptake for Karacaören water was observed in XAD-4 fractions than in XAD-8 fractions on both mass and surface area bases because of favored preferential adsorption of hydrophilic fraction. On the other hand, GAC adsorbent showed preferential adsorption based on mass (detailed in Section 5.3.2).

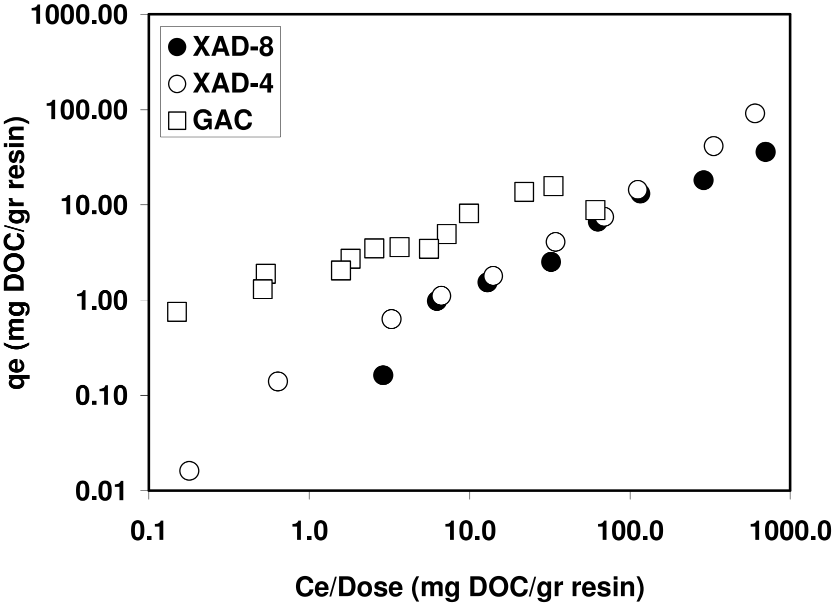

Figure 5.1. Adsorption of Alibeyköy NOM by XAD resins/GAC adsorbent (dose-normalized Modified Freundlich isotherms).

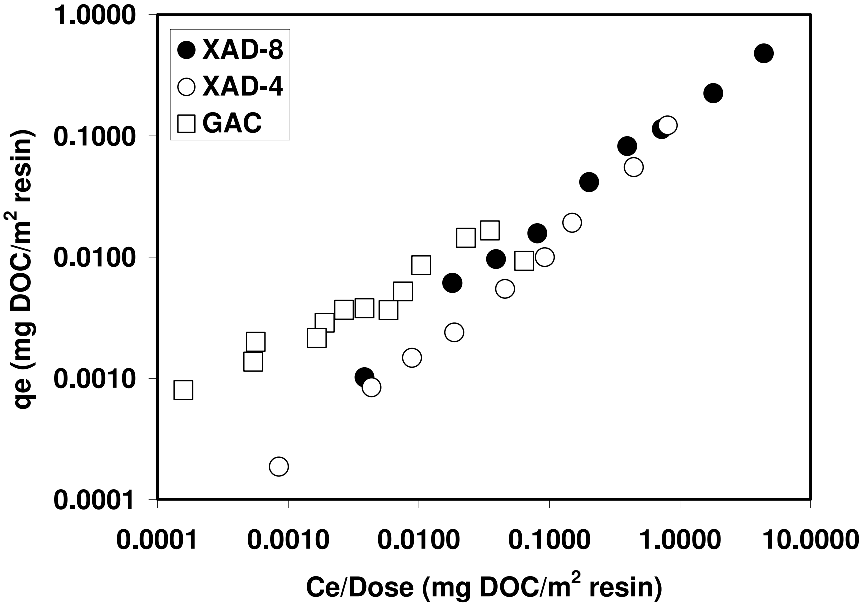

Figure 5.2. Adsorption of Alibeyköy NOM by XAD resins/GAC adsorbent (surface area-normalized Modified Freundlich isotherms).

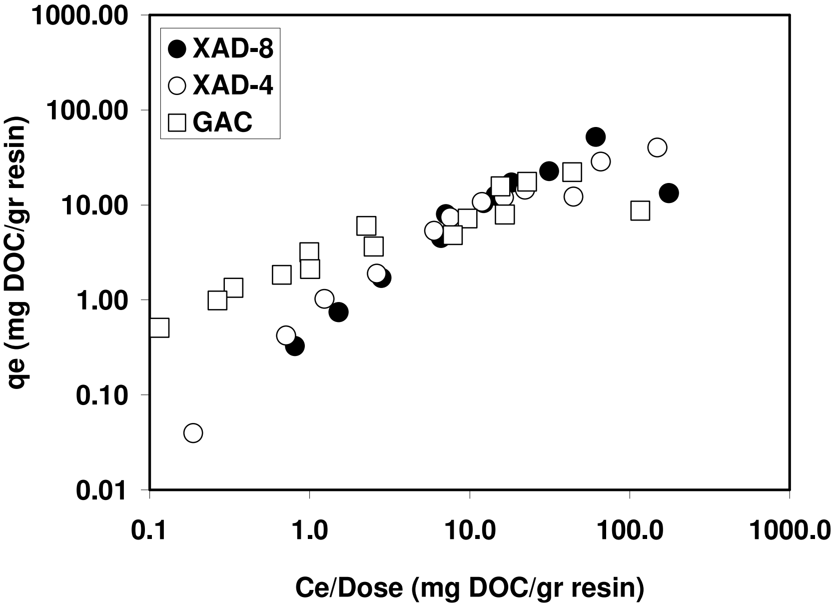

Figure 5.3. Adsorption of Karacaören NOM by XAD resins/GAC adsorbent (Mass base Modified Freundlich isotherms).

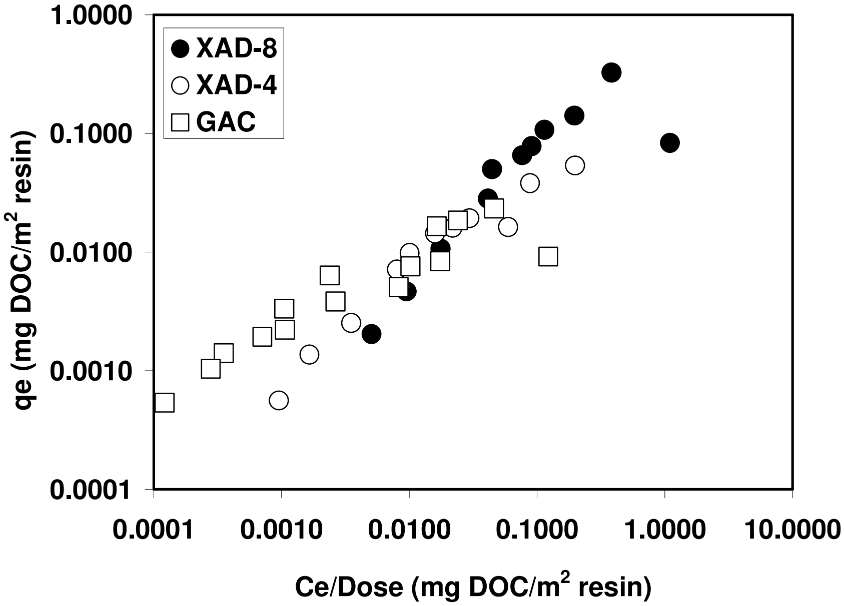

Figure 5.4. Adsorption of Karacaören NOM by XAD resins/GAC adsorbent (Surface area base Modified Freundlich isotherms).

5.3.2. Fractionation of NOM

Figure 5.5 illustrates the MWD of organic compounds in filtered Alibeyköy (a) and Karacaören (b) raw waters obtained by HPSEC measurements. MWD analysis showed that two main different types of organic fractions were present in Alibeyköy and Karacaören waters. According to HPSEC analysis, average MW of these organics were 11,089 Da (MW_z) (M_n=7,982; M_w=9,562; ρ=1.21) and 1,865 Da (MW_z) (M_n=1,745; M_w=1,806; ρ=1.03) in Alibeyköy water and 10,410 Da (MW_z) (M_n=7,489; M_w=9,028; ρ=1.21) and 1,777 Da (MW_z) (M_n=1,672; M_w=1,726; ρ=1.03) in Karacaören water. Since different organic components in their nature give different responses with respect to calibration standards (PSS), the actual amounts of subjected organic fractions in water samples could not be determined. The proportions of organic fractions could only be estimated.

The responses of these two types of organic fractions demonstrated that 45% and 55% of NOM in Alibeyköy water were of HMW and LMW, respectively. On the other hand, the distributions of HMW and LMW NOM in Karacaören water were 23% and 77%, respectively.

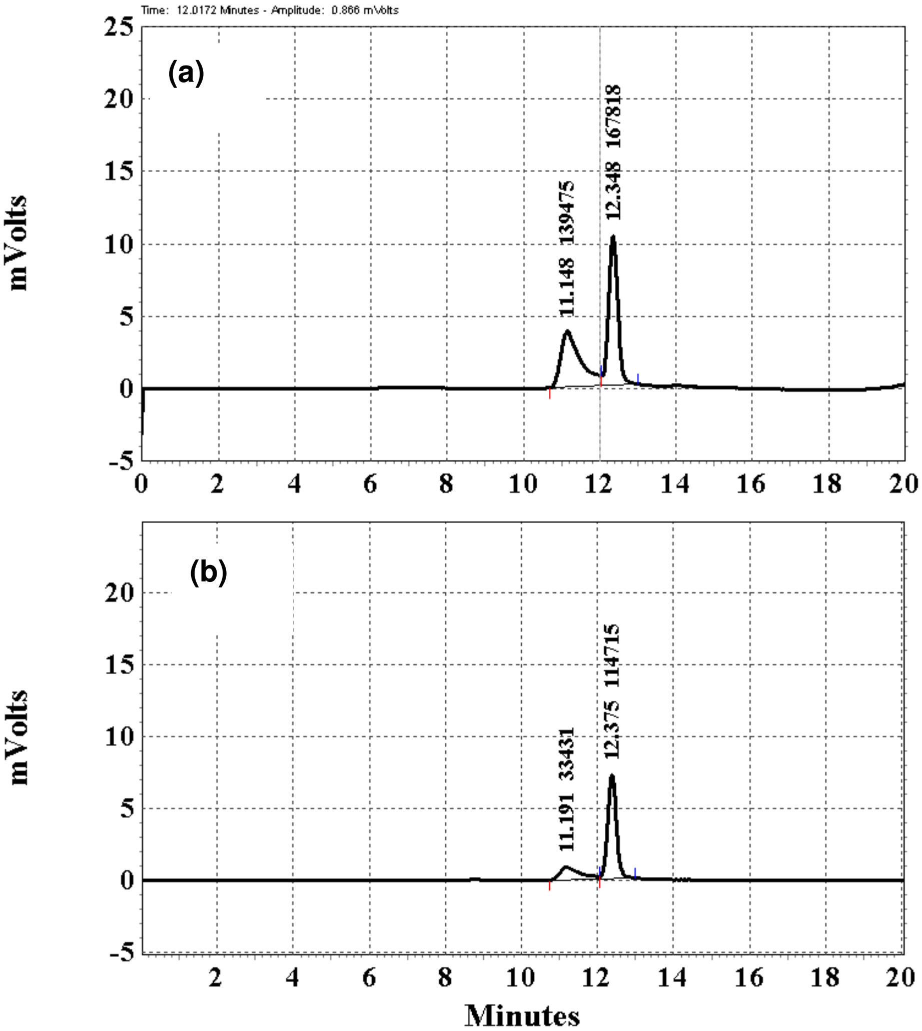

Figure 5.5. MWDs of organic compounds, (a) Alibeyköy, (b) Karacaören (filtered raw waters). Sampling dates for Alibeyköy and Karacaören waters are December 2004 and June 2005, respectively.

The $SUVA_{254}$ values of Alibeyköy and Karacaören waters were 2.03 and 1.93 L/mg org-C.m, respectively (Table 5.1). It is generally indicated in the literature that natural waters with high $SUVA_{254}$ values, e.g., ≥4 L/mg org-C.m, have relatively high content of hydrophobic, aromatic, and HMW NOM fractions, while waters with $SUVA_{254}$ at ≤2-3 L/mg org-C.m contain mostly hydrophilic, non-humic and LMW fractions (Edzwald and Van Benschoten, 1990; White et al., 1997; Edzwald and Tobiason, 1999). Thus, NOM in the tested waters contain dominantly LMW fractions and low aromaticity with respect to the SUVA and HPSEC measurements,

From the batch adsorption tests, a total of 44 and 39 bulk water fractions for Alibeyköy and Karacaören raw waters with wide range of $SUVA_{254}$ values were obtained, respectively (Figure 5.6 and 5.7). The $SUVA_{254}$ values of all fractions varied from 0.41 to 2.41 and from 0.78 to 2.69 L/mg org-C.m for Alibeyköy and Karacaören waters, respectively (Table 5.3).

As can be seen from Table 5.3, $SUVA_{254}$ values were generally decreased in all NOM fractions by increasing XAD resin doses that $SUVA_{254}$ values ranged from 1.22 to 1.87 L/mg org-C-m and from 1.61 to 1.90 L/mg org-C-m in XAD-8 and XAD-4 resin fractions, respectively (Table 5.3). In Chapter 4, the study on the impact of bromide on DBPs formations was investigated using Alibeyköy water sampled in June, 2004. In that part of the study, much higher $SUVA_{254}$ values in NOM fractions were obtained using these resins. $SUVA_{254}$ values varied between 0.70-2.39 L/mg org-C.m in XAD-8 resin and 2.37-3.91 L/mg org-C.m in XAD-4 resin (Figure 4.3). Besides, $SUVA_{254}$ value of Alibeyköy raw water was 3.15 L/mg org-C.m. At the maximum resins doses, the removal efficiencies in $SUVA_{254}$ were 60 and 25% in Chapter 4, whereas they were only 37 and 17% in this part of the study by XAD-8 and XAD-4, respectively. The possible reason of much narrow SUVA range in this part of the study was due to sampling time that the nature of NOM was more hydrophilic and less aromatic in Alibeyköy water sampled in December than in June. As stated in the literature, this result is consistent with the fact that XAD-8 resins have been used specifically in the RAC method for the separation of HA and FA, which are thought to be rich in aromatic moieties. Although DOC and UV_{254} absorbance were reduced gradually up to 1000 mg GAC/L dose, in higher dosages, there was not observed considerable change in UV_{254} absorbance, but DOC contents were decreased fairly in Alibeyköy fractions. On the contrary to UV_{254} absorbance, DOC removal in higher GAC dosages revealed that hydrophobic and hydrophilic fractions of NOM were preferentially removed based on GAC dose. At the maximum GAC dosage, the removal of DOC, UV_{254} absorbance and $SUVA_{254}$ were 83, 94 and 72%, respectively. The SUVA values ranged from 0.5 to 2.5 L/mg org-C.m in Alibeyköy GAC fractions (Figure 5.6b). Higher removal efficiencies were observed in DOC and UV_{254} absorbance even in low MIEX® resin dose using Alibeyköy water. DOC, UV_{254} absorbance and $SUVA_{254}$ could be reduced to 54, 75 and 44% by MIEX® resin, respectively. The $SUVA_{254}$ values were distributed in the range of 1.15 to 1.52 L/mg org-C.m in MIEX® resin fractions (Figure 5.6c). In respect of DOC removal by MIEX® resin, the negatively charged DOC is removed from water by exchanging with chloride ion on active sites on the resin surface (Bourke, 2001). Consistent results with the literature were observed that as removing DOC from the samples, a small increase in TDS and conductivity was recorded.

Table 5.3. The SUVA and DOC values of all fractions. DOC removals (%) are with respect to the raw water

XAD-8			XAD-4			GAC			MIEX		
SUVA$_{254}$ (L/mg org-C.m)*	**DOC (mg/L)**	**Removed DOC (%)**	**SUVA$_{254}$ (L/mg org-C.m)***	**DOC (mg/L)**	**Removed DOC (%)**	**SUVA$_{254}$ (L/mg org-C.m)***	**DOC (mg/L)**	**Removed DOC (%)**	**SUVA$_{254}$ (L/mg org-C.m)***	**DOC (mg/L)**	**Removed DOC (%)**
					Alibeyköy Water						
1.86	3.5	10	1.90	3.4	13	2.28	3.2	13	1.52	2.8	22
1.82	3.5	11	1.86	3.5	11	2.41	2.5	32	1.58	2.3	36
1.87	3.4	14	1.84	3.5	11	2.35	2.2	39	1.36	2.2	40
1.85	3.2	17	1.79	3.5	10	1.84	2.0	45	1.50	2.1	42
1.78	3.2	17	1.89	3.5	11	1.65	2.2	41	1.42	1.8	49
1.63	3.3	16	1.90	3.5	11	1.19	2.2	38	1.23	1.8	50
1.59	3.1	20	1.93	3.3	14	0.91	1.8	50	1.16	1.7	52
1.52	2.9	25	1.90	3.3	16	0.82	1.5	58	1.18	1.5	57
1.22	3.1	21	1.61	3.2	18	0.67	1.5	60	1.02	1.7	53
						0.41	1.6	56	1.11	1.6	55
						0.56	0.8	78	1.07	1.7	54
						0.52	1.0	72	1.15	1.6	55
						0.75	0.6	83			
					Karacaören Water						
1.65	1.1	7	1.97	0.9	21	1.59	1.2	7			
2.69	0.6	46	2.11	0.8	30	2.07	0.8	34			
2.42	0.7	42	1.85	0.9	22	2.26	0.7	44			
2.34	0.6	48	2.42	0.7	40	2.28	0.6	50			
2.35	0.6	46	2.49	0.7	42	1.72	0.9	32			
2.21	0.6	46	2.60	0.6	48	1.89	0.7	43			
2.47	0.5	53	2.61	0.6	49	1.75	0.8	38			
2.03	0.7	41	2.47	0.6	47	1.35	0.3	73			
1.91	0.7	38	2.50	0.7	42	1.21	0.5	59			
1.57	0.8	33	2.50	0.6	45	1.07	0.3	76			
1.36	0.8	29	1.99	0.7	37	1.06	0.4	68			
						1.52	0.3	73			
						1.83	0.3	80			
						1.95	0.3	79			
						1.82	0.2	82			
						0.78	0.2	85			

* SUVA values of fractions were measured before dilution of fractions.

In DOC and UV_{254} absorbance removal, different trends were observed by fractionation of XAD resins using Karacaören water. Higher DOC removals were obtained in fractions of XAD-4 resin than those of XAD-8 resin with 37 and 29%, respectively (Table 5.3). On the other hand, related with the structure of XAD-8 and XAD-4 resins, the removal of UV_{254} absorbance was higher in XAD-8 (50%) than in XAD-4 fractions (35%). The $SUVA_{254}$ values ranged between 1.36 and 2.69 L/mg org-C.m and between 1.85 and 2.61 L/mg org-C.m in XAD-8 and XAD-4 fractions, respectively (Figure 5.7a). It could be stated that Karacaören water was mostly hydrophilic in character with low SUVA corresponding to both XAD fractions and the HPSEC analysis. DOC and UV_{254} absorbance were gradually removed by increasing GAC dosages using Karacaören water. In GAC fractions, 85 and 94% removal efficiencies were observed in DOC and UV_{254} absorbance, respectively. However, the removal of $SUVA_{254}$ was not as much high as that of DOC and UV_{254} absorbance. At the end point of fractionation; lowest $SUVA_{254}$ value obtained by GAC was 0.78 L/mg org-C.m. Apparently, both UV-absorbing and non-UV absorbing NOM components were removed at lower GAC doses. However mostly UV-absorbing NOM components were adsorbed on GAC at higher doses over all NOM components. The $SUVA_{254}$ values ranged from 0.78 to 2.28 L/mg-m in all Karacaören fractions (Figure 5.7b).

It was found for both waters that an increase in XAD-8 dose generally decreased the SUVA value of fractions, indicating that higher-SUVA components of NOM were preferentially removed from solution. This is consistent with the RAC method, in which DOM is isolated and fractionated into operationally-defined fractions based on their adsorption and back-elution affinities with different synthetic resins (Amberlite XAD-8, MSC-1 or Bio-Rad AG-MP-50 cation exchange and Duolite A-7 anion exchange resins). While no significant change in SUVA was observed for

Alibeyköy water with increasing XAD-4 dosages up to 1,000 mg/L, SUVA values gradually decreased at higher doses. For the Karacaören water, SUVA values somewhat increased with increasing XAD-4 dosage although the data was scattered. However, for both waters, increasing XAD-4 dosages increased DOC removals. Thus, the results indicated that the removal of UV absorbing fractions was proportional to non-UV absorbing fractions by this resin in Alibeyköy water for resin dosages up to 1,000 mg/L. In addition, for Karacaören water, XAD-4 resin preferentially removed non- or lower UV absorbing fractions, resulting in higher SUVA values with increasing dosage. This may be expected since XAD-4 resin is used to isolate transphilic organic fractions (i.e., non-humics or lower UV absorbing fractions) from waters in the RAC method.

Different trends were observed among waters for GAC fractionation (Figure 5.6 and 5.7). UV absorbing fractions were preferentially removed by GAC in Alibeyköy water. However, for Karacaören water having a DOC concentration of only 1.2 mg/L, no consistent trend was observed with respect to fractionation based on SUVA, although increasing GAC dose consistently removed more DOC. Adsorption of NOM by GACs is a complex phenomenon which is mainly related to size, charge density, hydrophobicity/hydrophilicity of NOM fractions and GAC characteristics including pore size distribution (i.e., size exclusion effects), surface energy and chemistry, and raw material type. It is generally indicated that GACs preferentially remove hydrophobic and UV absorbing NOM fractions, especially in waters with high SUVA values. However, in this study, this trend was valid for Alibeyköy water but not for Karacaören water, both of which were low-SUVA waters. This result may suggest that the preferential removal of UV absorbing NOM fractions by GAC is water specific, especially for low-SUVA waters.

Similar to XAD-8 and GAC adsorption, MIEX® resin also preferentially removed higher UV-absorbing fractions in Alibeyköy water although the extent of fractionation based on SUVA was not as large as obtained by the GAC. The DOC removal with MIEX® resin was about 55% at a dose and contact time of 10 mL/L and 10 min, respectively. On the other hand, Singer and Bilyk (2002) stated that MIEX® resin tended to show little preference for removal of UV-absorbing material relative to removal of TOC. While resin appeared to remove both hydrophobic and hydrophilic acids, there was no preferential removal of hydrophobic acids over hydrophilic acids. Furthermore, the resin provided greater removals for high SUVA waters (Singer and Bilyk, 2002).

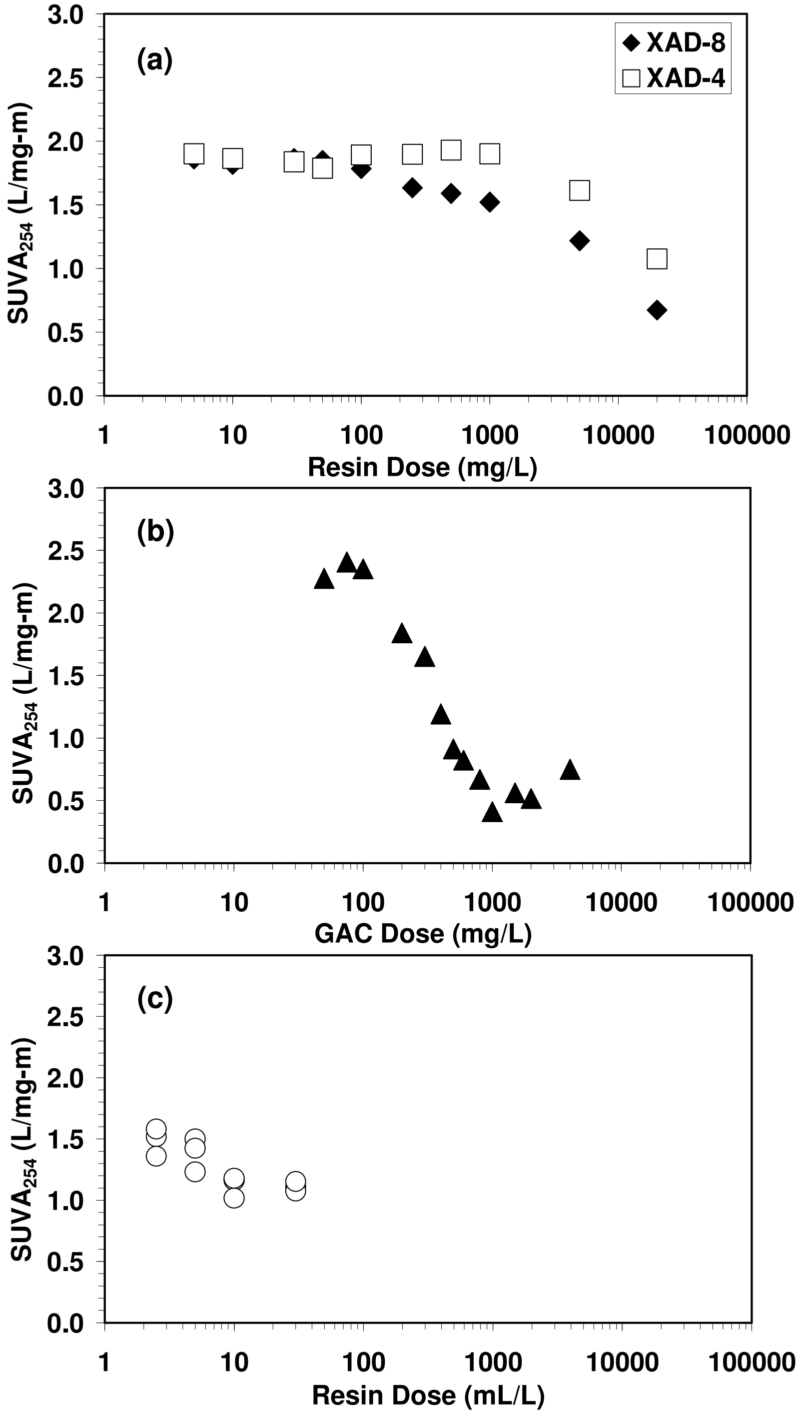

Figure 5.6. Bulk water fractionation of NOM in Alibeyköy water by batch adsorption, (a) XAD-8 and XAD-4, (b) GAC, (c) MIEX® resin.

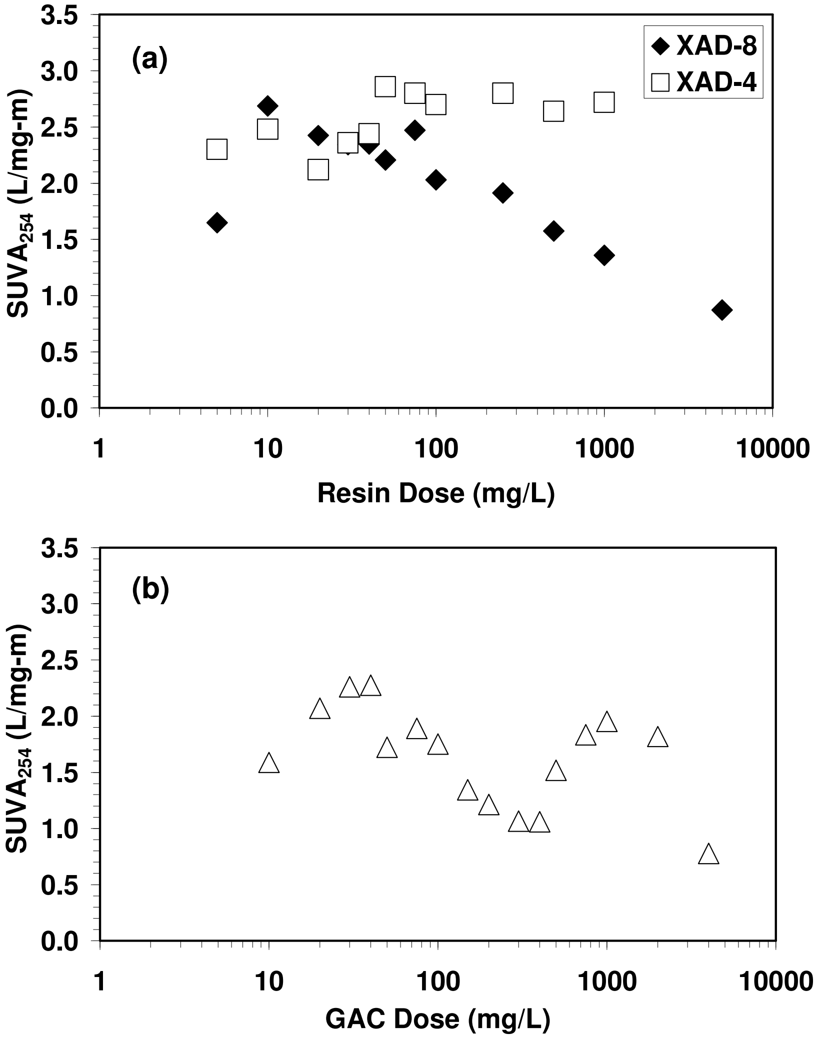

Figure 5.7. Bulk water fractionation of NOM in Karacaören water by batch adsorption, (a) XAD-8 and XAD-4, (b) GAC.

5.3.3. Formation of DBPs in NOM Fractions

A total of 83 bulk water NOM fractions were obtained from the fractionation of both waters after adsorption with XAD-8, XAD-4, MIEX® resins and GAC. All fractions of each water source were adjusted to constant DOC (via dilution) and bromide concentrations, pH and Cl_2/DOC ratio. Thus, the only different variable among fractions was SUVA, enabling the evaluation of the impact of SUVA alone on DBP formation after chlorination. While average THM and HAA concentrations of Alibeyköy fractions (including raw water) were 45 µg/L and 27 µg/L, respectively (Table 5.4); such average concentrations were 16 µg/L and 7 µg/L in Karacaoren fractions (Table 5.5). It should be noted that the constant DOC levels set for Alibeyköy and Karacaoren fractions were 1.0 and 0.5 mg/L, respectively. As a general trend, NOM fractions of both waters led to higher THM concentrations than those of HAAs. SUVA values, formations of THM, HAA and AOX in all fractions from Alibeyköy and Karacaören waters are given in Table B.1 and B.2 (in Appendix B), respectively.

Table 5.4. DBPs formations in all Alibeyköy fractions*

Resin/Adsorbent Type	$SUVA_{254}$ (L/mg C-m)	THMs (µg/L)	HAAs (µg/L)	AOX (µg/L)
XAD-8	1.76-2.31	31-72	22-37	77-180
XAD-4	1.61-2.17	52-75	18-23	70-151
GAC	0.34-2.11	7-53	10-37	26-279
MIEX	1.05-1.32	34-52	31-38	62-353

* SUVA values, formations of THM, HAA and AOX in all fractions were given in Table B.1.

Table 5.5. DBPs formations in all Karacaören fractions*

Resin/Adsorbent Type	$SUVA_{254}$ (L/mg C-m)	THMs (µg/L)	HAAs (µg/L)	AOX (µg/L)
XAD-8	2.00-2.80	14-22	7-11	19-136
XAD-4	2.12-2.86	15-22	7-10	15-143
GAC	0.78-2.66	7-17	3-6	15-81

* SUVA values, formations of THM, HAA and AOX in all fractions were given in Table B.2.

In literature, responsible organic fractions on formation THMs or HAAs were reported in few studies. Croue et al. (1999) suggested that hydrophilic fractions of NOM were more significant precursors of THMs than HAAs in finished drinking water. In their study, hydrophilic fractions being dominant in NOM led to larger relative yields of THMs to HAAs than from chlorinated hydrophobic HS. Besides, Liang and Singer (2003) reported that higher ratio of HAA9 to THM4 in the hydrophobic fraction than in the hydrophilic faction at pH 8. Similar to these studies, Alibeyköy and Karacaören waters tested in this study were mostly hydrophilic in character with respect to their SUVA values and HPSEC analyses, THM formations were higher than HAA formations in all fractions. On the contrary, Hwang et al. (2000) found that in four low humic waters, more HAAs especially dihaloacetic acids were produced from the hydrophilic (polar) fractions than THMs. On the other hand, Sinha et al. (1997) suggested that the hydrophobic fraction is more reactive than the hydrophilic fraction for THM formation but that the two fractions are equally reactive in terms of HAA formation. The higher proportion of aliphatic structures in the hydrophilic carbon makes the HAA9/THM4 ratio lower in the hydrophilic fractions than in the hydrophobic fractions (Reckhow et al., 1990).

Chlorinated species dominated over brominated ones in both waters, a consistent trend found for both THMs and HAAs. This is expected since the bromide concentrations in Alibeyköy and Karacaoren fractions were only <40 and <20 µg/L, respectively. Chloroform was found to be the major THM species (44%), followed by bromodichloromethane (26%), dibromochloromethane (21%), and bromoform (9%), on average concentration basis in Alibeyköy fractions (Table 5.6). The major HAA species formed in the fractions of Alibeyköy water were dichloroacetic acid (34%) and bromochloroacetic acid (21%), on average concentration basis

(Table 5.7). These HAA species were followed by monochloroacetic acid (13%), dibromoacetic acid (9%), trichloroacetic acid (7%), dibromochloroacetic acid (7%), tribromoacetic acid (4%), bromodichloroacetic acid (4%) and monobromoacetic acid (1%) (Table 5.7). For all fractions of Alibeyköy water, concentrations of monobromo-, bromodichloro-, dibromochloro-, and tribromoacetic acid were near minimum quantification limits. The formations of THM and HAA species were also given in Alibeyköy fractions in Appendix B, Table B.3 and B.4.

The most abundant species among THMs was chloroform (67%) in chlorinated Karacaoren fractions, on average concentration basis. Following species were bromodichloromethane (20%) and dibromochloromethane (13%) (Table 5.8). Bromoform concentrations were near minimum quantification limits. The most abundant species among HAAs was dichloroacetic acid (54%) in chlorinated Karacaoren fractions (Table 5.9). Trichloroacetic acid (10%), monochloroacetic acid (10%), bromochloroacetic acid (9%), dibromoacetic acid (7%), bromodichloroacetic acid (5%), tribromoacetic acid (3%) and dibromochloroacetic acid (2%) followed dichloroacetic acid; monobromoacetic acid was near minimum quantification limits. It was interesting to find that the relative concentration of trichloroacetic acid, usually found to be major HAA species especially in high-SUVA waters (Liang and Singer, 2003), was very low in both of the studied low-SUVA waters. The formations of THM and HAA species were also given in Karacaören fractions in Appendix B, Table B.5 and B.6, respectively.

Table 5.6. Percentages of THM species (%) in all Alibeyköy fractions*

	TCM	BDCM	DBCM	TBM
XAD-8	52	23	20	5
	56	24	17	4
	50	25	20	5
	50	24	21	5
	54	23	19	4
	55	23	17	4
	52	24	19	5
	49	23	21	7
	47	26	20	6
	64	19	13	4
XAD-4	54	24	18	4
	58	22	16	4
	51	26	18	4
	59	23	15	3
	60	21	15	4
	55	25	16	4
	55	25	16	4
	54	26	16	4
	53	28	20	5
	49	33	14	4
GAC	50	25	21	4
	40	27	27	7
	37	27	28	7
	24	28	36	12
	24	33	33	11
	18	33	35	14
	17	44	20	19
	10	30	40	19
	22	37	20	21
	18	28	35	19
	26	3	7	65
	12	2	59	28
	35	4	9	51
MIEX	46	31	19	4
	39	32	23	6
	32	30	28	10
	40	32	21	7
	34	38	22	7
	65	23	10	2
	32	35	24	9
	42	35	18	5
	40	34	20	7
	45	31	19	6
	63	25	10	2
	67	23	10	0
Average	44	26	21	9

*THM species: chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM).

Table 5.7. Percentages of HAA species (%) in all Alibeyköy fractions*

	CAA	BAA	DCAA	TCAA	BCAA	DBAA	BDCAA	DBCAA	TBAA
XAD-8	3	1	39	3	37	8	4	4	1
	5	1	43	4	29	7	4	4	1
	6	1	40	4	32	7	5	5	1
	4	1	39	4	33	7	5	5	1
	17	1	33	4	29	7	5	5	1
	16	1	34	3	30	7	4	4	1
	12	1	36	4	29	7	5	5	1
	6	1	35	4	34	9	4	5	2
	14	0	36	5	27	6	5	5	2
	21	1	36	7	22	4	4	4	1
XAD-4	10	1	37	4	29	6	5	5	1
	10	0	39	8	29	6	3	3	1
	4	0	43	4	32	7	4	4	1
	6	0	47	7	27	6	4	3	1
	2	0	41	4	34	8	5	4	1
	4	0	39	3	35	8	5	4	1
	6	0	41	4	31	7	5	5	1
	10	0	38	3	30	7	6	5	1
	5	1	37	3	33	8	5	6	1
	7	1	47	3	27	8	0	4	1
GAC	6	1	31	3	32	7	4	10	4
	4	1	30	3	31	9	5	12	6
	5	1	26	3	30	8	6	16	5
	10	1	23	2	26	9	5	18	6
	17	1	20	2	23	8	5	17	6
	8	1	31	2	21	9	4	17	7
	10	1	27	2	21	9	4	18	9
	12	1	28	1	18	10	3	18	8
	32	1	20	1	23	12	1	6	3
	25	1	25	3	19	8	3	11	6
	26	1	24	1	19	8	2	10	10
	25	1	27	2	14	5	1	16	9
	26	9	17	2	20	6	2	12	8
MIEX	16	2	29	18	5	14	4	3	7
	16	3	27	15	5	17	4	3	8
	20	4	22	12	5	20	4	4	10
	18	3	30	15	5	15	4	3	8
	23	3	35	10	4	14	3	3	5
	19	3	27	12	4	16	4	3	11
	18	2	35	14	4	11	4	3	9
	21	2	33	13	4	12	4	3	8
	17	3	29	19	3	10	3	2	13
	14	1	46	19	3	5	3	2	7
	11	2	47	21	3	5	3	2	6
	2	2	44	26	3	6	3	2	11
Av.	13	1	34	7	21	9	4	7	4

*HAA species: monochloro-AA (MCAA), monobromo-AA (MBAA), dichloro-AA (DCAA), trichloro-AA (TCAA), bromochloro-AA (BCAA), dibromo-AA (DBAA), bromodichloro-AA (BDCAA), dibromochloro-AA (DBCAA), tribromo-AA (TBAA).

Table 5.8. Percentages of THM species (%) in all Karacaören fractions*

	TCM	BDCM	DBCM	TBM
XAD-8	65	24	10	0
	62	25	13	0
	63	24	12	0
	62	25	13	0
	63	25	12	0
	62	26	12	0
	60	27	13	0
	63	26	11	0
	65	24	11	0
	66	24	11	0
	67	22	10	0
XAD-4	58	28	14	0
	65	24	11	0
	69	22	9	0
	65	24	11	0
	59	27	15	0
	66	23	11	0
	63	25	12	0
	64	25	12	0
	66	23	11	0
	68	21	11	0
	67	22	10	0
GAC	79	12	9	0
	79	12	9	0
	75	12	12	1
	77	12	11	0
	73	14	13	0
	71	14	14	1
	67	14	17	2
	60	14	23	3
	61	18	20	1
	62	14	21	3
	57	18	23	2
	72	9	16	3
	74	9	15	2
	71	11	16	2
	79	9	11	2
	66	17	15	2
Average	67	20	13	1

*THM species: chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM).

Table 5.9. Percentages of HAA species (%) in all Karacaören fractions*

	CAA	BAA	DCAA	TCAA	BCAA	DBAA	BDCAA	DBCAA	TBAA
XAD-8	13	0	63	8	7	4	5	0	0
	11	0	61	9	8	5	6	0	0
	9	0	66	8	4	7	6	0	0
	8	0	68	9	4	6	5	0	0
	9	0	68	7	6	5	5	0	0
	11	0	63	10	6	4	6	0	0
	11	0	64	10	3	5	6	0	0
	10	0	65	8	6	4	7	0	0
	11	0	64	6	7	5	6	0	0
	10	0	63	8	5	6	7	0	0
	12	0	62	9	6	6	5	0	0
XAD-4	11	0	60	8	8	6	6	0	0
	10	0	65	10	3	5	6	0	0
	11	0	64	12	5	3	6	0	0
	11	0	64	9	6	5	5	0	0
	12	0	61	7	7	7	6	0	0
	8	0	63	8	9	7	5	0	0
	10	0	59	9	10	7	6	0	0
	11	0	60	8	9	6	6	0	0
	9	0	63	9	7	6	6	0	0
	4	0	64	7	14	7	5	0	0
	8	0	67	3	11	6	5	0	0
GAC	9	0	51	14	11	3	4	2	6
	7	0	49	16	13	4	4	3	5
	17	0	40	10	15	7	3	3	5
	17	0	50	10	9	2	2	2	8
	9	0	45	13	14	6	4	3	6
	8	0	45	12	16	6	4	3	6
	9	0	41	12	16	8	4	4	7
	8	0	43	7	14	12	4	5	7
	6	0	44	11	15	10	5	4	6
	14	0	28	11	13	16	5	6	8
	9	0	36	12	13	13	5	5	7
	17	0	23	8	13	13	5	7	14
	16	0	24	11	12	11	5	6	14
	20	0	25	8	10	10	4	7	16
	9	0	50	20	7	5	4	3	3
	7	0	51	21	8	5	4	2	2
Av.	10	0	54	10	9	7	5	2	3

* HAA species: monochloro-AA (MCAA), monobromo-AA (MBAA), dichloro-AA (DCAA), trichloro-AA (TCAA), bromochloro-AA (BCAA), dibromo-AA (DBAA), bromodichloro-AA (BDCAA), dibromochloro-AA (DBCAA), tribromo-AA (TBAA).

It was interesting to find that the relative concentration of trichloroacetic acid, usually found to be major HAA species especially in high-SUVA waters (Liang and Singer, 2003), was very low in both of the studied low-

SUVA waters. Several reaction mechanisms had been proposed that the most comprehensive model was developed by Reckhow and Singer (1985) for THM and HAA formation from FA during chlorination. Based on this model, they used a β-diketone moiety, (i.e., R'-CO-CH_2-CO-R) to represent the reactive site of DOM. This moiety would quickly be fully substituted with chlorine, forming R'-CO-CCl_2-CO-R. Rapid hydrolysis of this moiety yielded a monoketone group, $CHCl_2$-CO-R, which either formed DCAA (if R is a hydroxyl group) or is further chlorinated to a trichloromethyl species (CCl_3-CO-R), the precursor for TXAA and THM. On the other side, NOM with higher values of SUVA probably had a higher amount of oxidizable functional groups, which would result in a higher formation of trichloro-AA (Reckhow and Singer, 1990). Hwang et al. (2000) evaluated their water characteristic as low SUVA including a higher portion of β-diketone moieties with "R" groups that were hydroxly groups. They stated that these results suggested that DXAA and TXAA had different precursors and their low SUVA water contained a higher portion of dichloro-AA precursors. In this study, higher DCAA formation over TCAA in both Alibeyköy and Karacaören fractions showed these source waters might be dominantly the hydrophilic in character including a higher portion of β-diketone moieties with "R" groups that were hydroxyl groups with respect to previous researches. Furthermore, these results also supported by the SUVA distribution and MWD in both source waters.

5.3.4. Impact of SUVA on DBPs Formation and Speciation

Figure 5.8 and 5.9 show the correlations between the SUVA values and DBP formations (THMs and HAAs) in all fractions of Alibeyköy and Karacaören waters, respectively. Although a wide range of $SUVA_{254}$ values was investigated, no strong correlations between SUVA and THM formations and SUVA and HAA formations were found in both waters. The linear correlation coefficients (R^2) obtained for THMs and HAAs were 0.35 and 0.002, respectively, in Alibeyköy water. On the other hand, the correlation coefficients were higher for the Karacaören water; 0.69 and 0.44 for THMs and HAAs, respectively. Although a relatively high correlation coefficient was obtained for SUVA-THM relation in Karacaören fractions, highly variable THM concentrations existed at a constant SUVA level. For example, the THM concentrations varied between 13 and 35 µg/L at a $SUVA_{254}$ value of 1.8 L/mg org-C.m. Similarly, no correlations were obtained between SUVA and AOX concentrations (Figure 5.8c and 5.9c). Furthermore, similar to total THMs and HAAs formations, SUVA also did not correlate with the formations of any THM or HAA species in either water source. Representative figures for THM species for Alibeyköy and Karacaören waters were given in Figure 5.10 and 5.11, respectively. The impact of SUVA on HAA species in all NOM fractions were given in Appendix B, Figure B.3-5 and B.6-8 for Alibeyköy and Karacaören waters, respectively. When the SUVA and DBP data was examined separately for the fractions of each sorbent in each water, no strong correlations were found, consistent with the results obtained for all fractions together.

These results contradict with some previous studies (Kitis et al., 2001, 2002, 2004), in which strong correlations were observed between DBP formations and SUVA values of many NOM fractions obtained by various physicochemical separation processes. In those studies, such strong correlations were actually found for a total of five source waters in the US. However, those waters had generally high $SUVA_{254}$ values, i.e., >3 L/mg org-C.m. These different trends basically suggest that the effectiveness of SUVA in correlating with DBP formation is water specific. In other words, SUVA as a bulk parameter may not capture the reactive sites on NOM moieties responsible for DBP formation in all source waters, given the high degree of NOM heterogeneity among waters. Apparently, the DBP formation prediction capability of SUVA is weak in waters with low SUVA values and containing LMW NOM fractions. The majority of NOM in the tested Karacaören and Alibeyköy waters had average MW less than 2000 Da as PSS.

Similarly, Fram et al. (1999) reported that a weak correlation between $SUVA_{254}$ and $STTHMFP_{7d}$ (specific total THM formation potential in 7 days) was obtained for whole water samples. They reported that SUVA could not be used for accurate prediction of THMFP in drinking water derived from a broad spectrum of watershed types. Weishaar et al. (2003) compared isolated organic matter samples and filtered whole waters to evaluate the usability of SUVA as surrogate parameter for STTHMFP. They stated that $SUVA_{254}$ appeared to be a better indicator of reactivity of the compounds that comprise aquatic HS than for the DOC present in whole water samples. Similar findings for organic carbon from wetlands were observed by Fleck et al. (2004) and Chow et al. (2006).

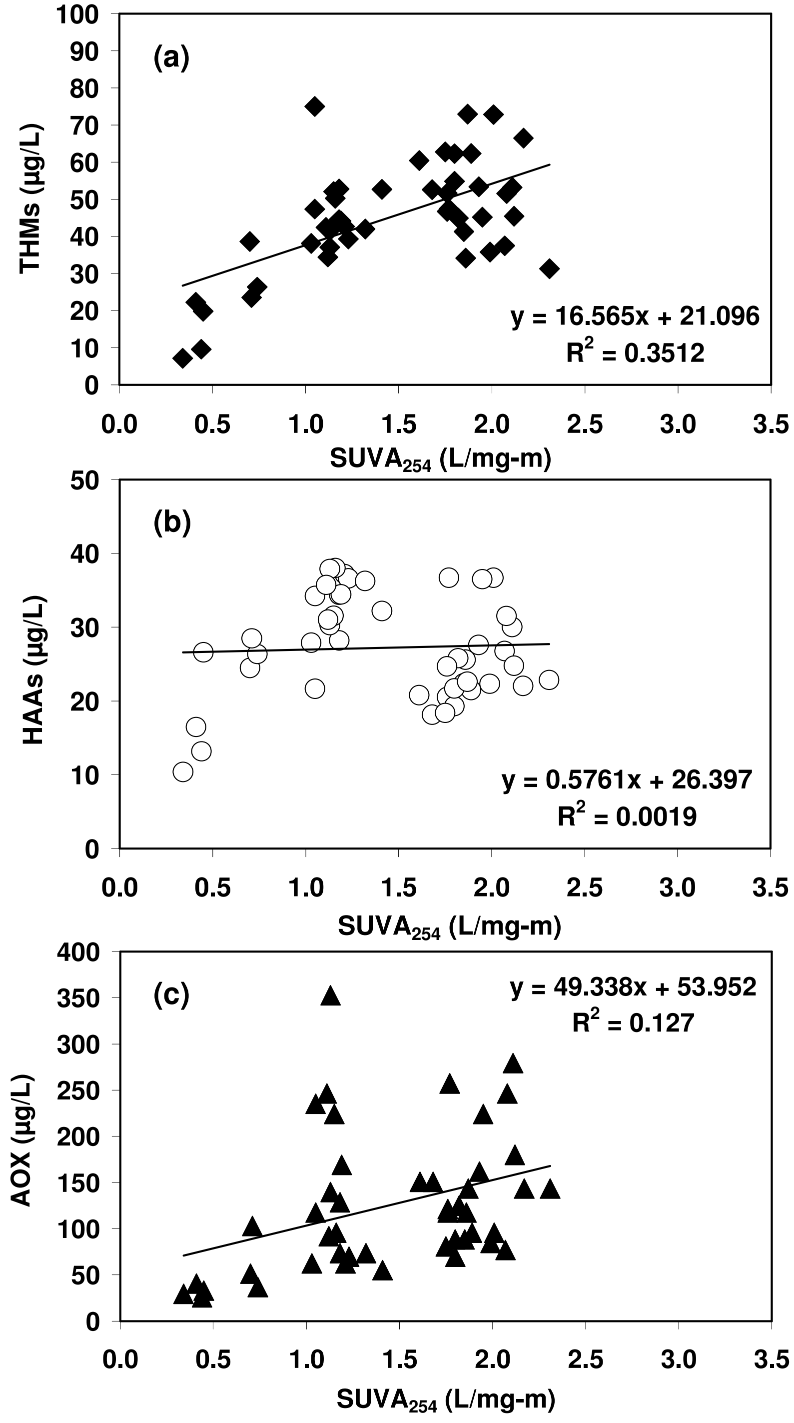

Figure 5.8. The impact of SUVA on THMs (a), HAAs (b) and AOX (c) formation in all NOM fractions of Alibeyköy water.

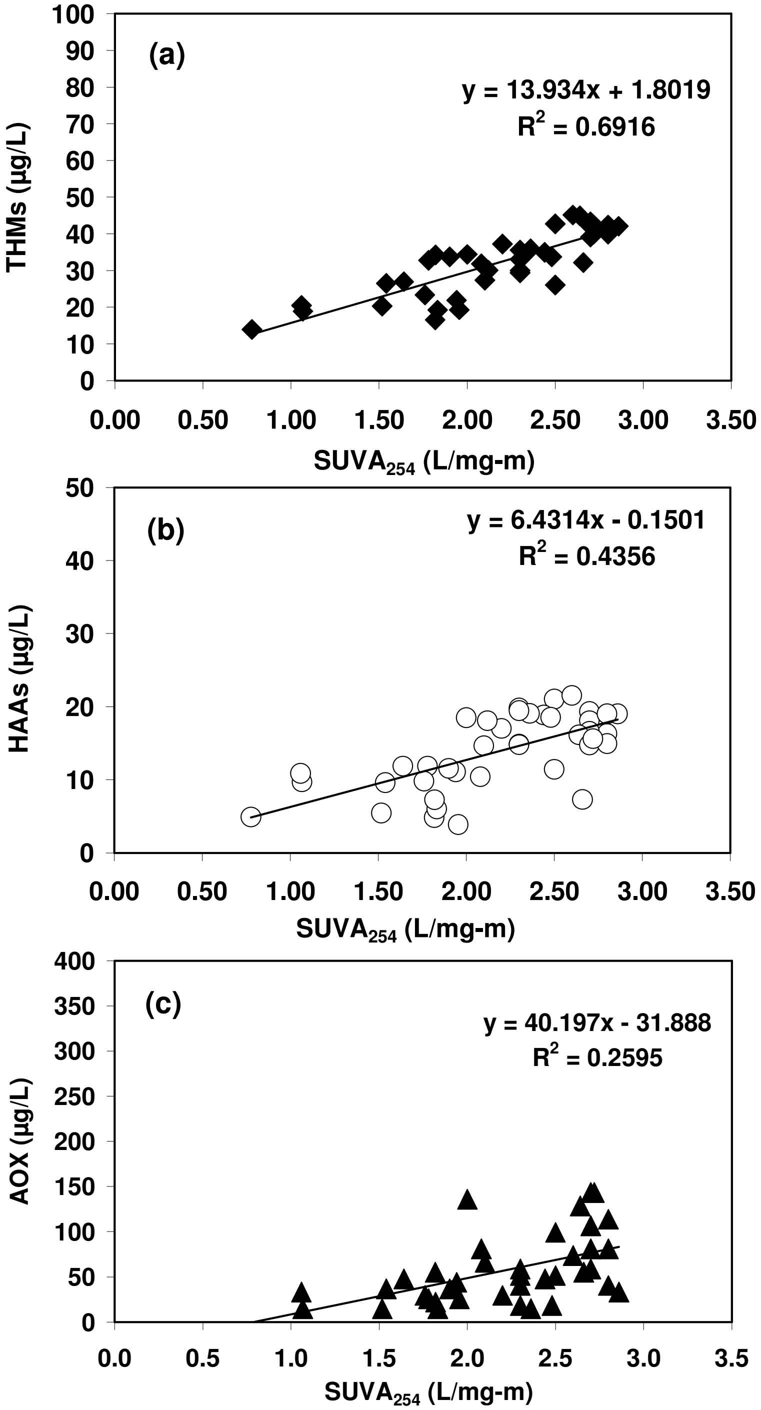

Figure 5.9. The impact of SUVA on THMs (a), HAAs (b) and AOX (c) formation in all NOM fractions of Karacaören water.

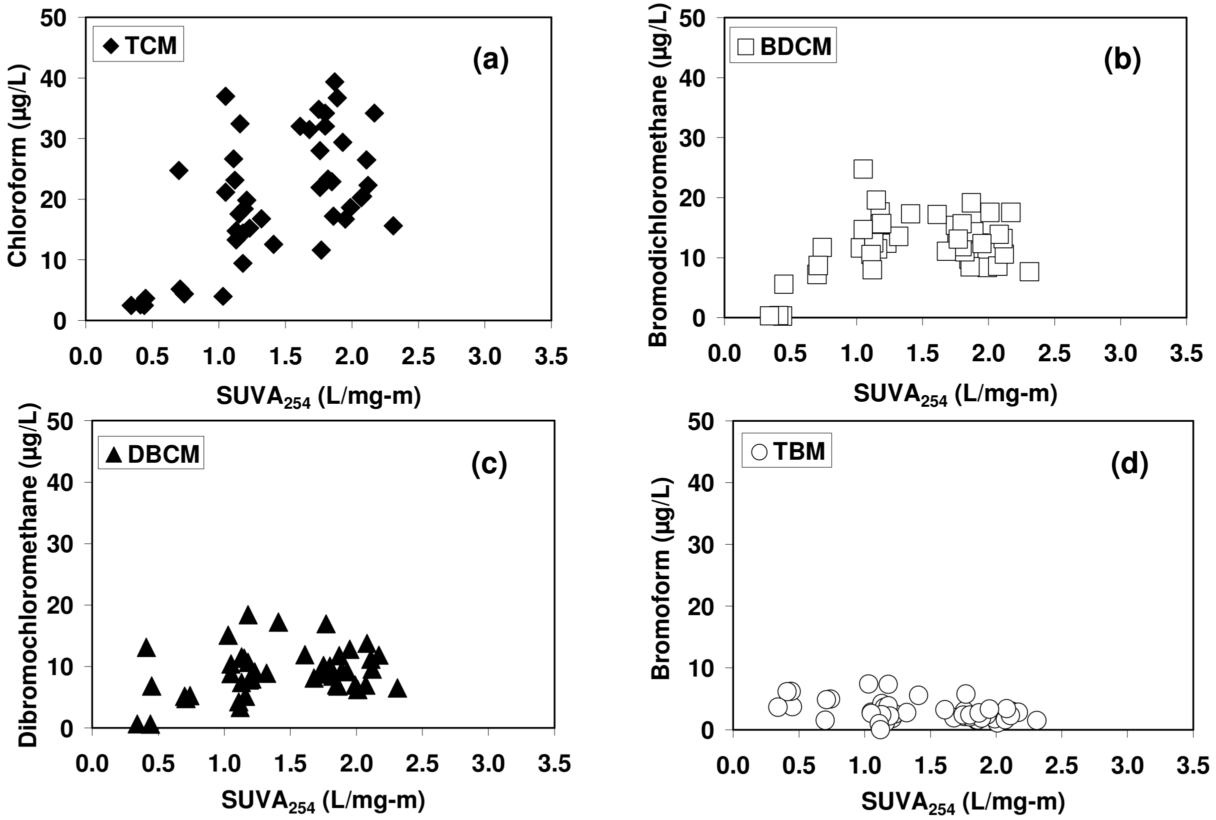

Figure 5.10. The impact of SUVA on THM species in all NOM fractions of Alibeyköy water.

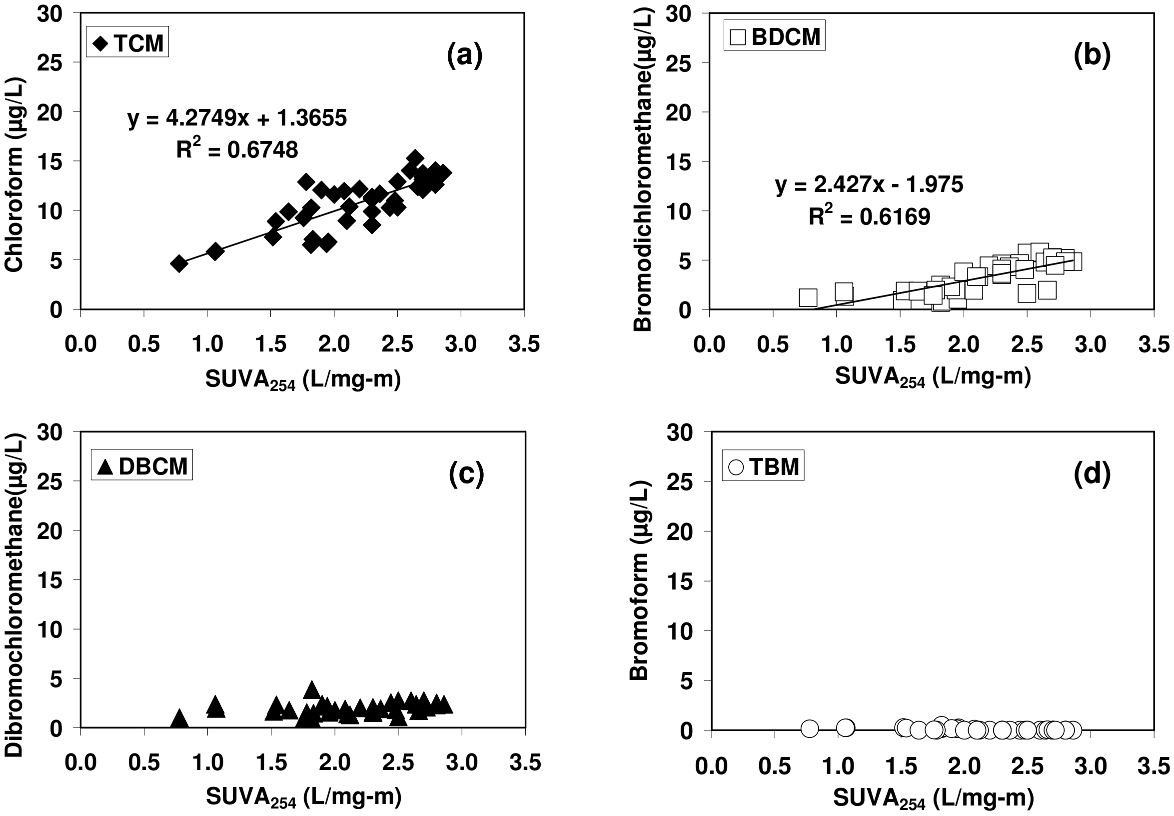

Figure 5.11. The impact of SUVA on THM species in all NOM fractions of Karacaören water.

5.3.5. Impact of ΔUV on DBP Formation and Speciation

The destruction in UV_{254} absorbance after chlorination (i.e., differential UV spectroscopy) did not correlate with THMs or HAAs formations in both of the tested waters (Figure 5.12 and 5.13). Same trend was also observed for single THM and HAA species. This result indicates that the formation of THMs and HAAs are not directly dependent on the destruction in UV_{254}-absorbing sites after chlorination. It seems that other NOM moieties not absorbing UV light also play important roles in DBP formations in waters with low-SUVA values, i.e., waters hydrophilic in character. Furthermore, although chlorine may destroy the UV-absorbing sites on NOM, such reactions do not directly link with DBP formation. Furthermore, similar to total THMs and HAAs formations, destruction in UV_{254} absorbance also did not correlate with the formations of any THM or HAA species in either water source. Representative figures for THM species for Alibeyköy and Karacaören waters were given in Figure 5.14 and 5.15, respectively. The impact of ΔUV_{254} on HAA species in all NOM fractions were given in Appendix B, Figure B.9-11 and B.12-14 for Alibeyköy and Karacaören waters, respectively. When the ΔUV_{254} and DBP data was examined separately for the fractions of each sorbent in each water, no strong correlations were found, consistent with the results obtained for all fractions together.

Consistent with the findings for SUVA, it is apparent that formation of DBPs in low-SUVA waters may not be estimated by simple UV absorbance measurements. However, it should also be noted that since the tested raw waters had already low UV_{254} absorbance, ΔUV_{254} values were also low. Therefore, this provided a narrow range of differential UV spectroscopy to study (0-0.015 and 0-0.005 cm^{-1} for Alibeyköy and Karacaören, respectively). Standard deviations in UV_{254} absorbance measurements were typically ±0.001 cm^{-1}. Thus, especially for the Karacaören water, some degree of analytical error (including those from DBP measurements) is associated with ΔUV_{254}-DBP relations. However, the lack of any relation among ΔUV_{254} and DBP formations is clear for both waters. These results overall may suggest that the robustness of differential UV spectroscopy in correlating with DBP formation depends on NOM characteristics in a specific source water.

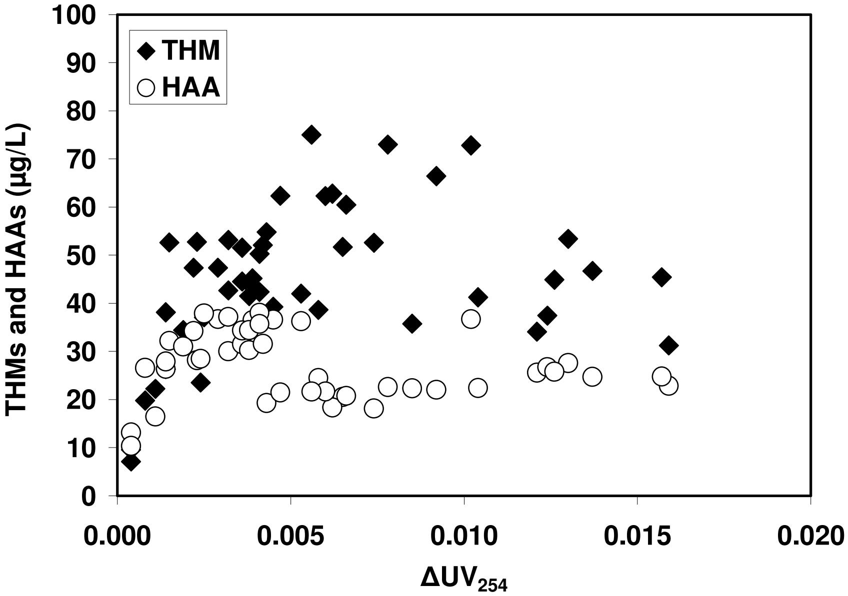

Figure 5.12. The impact of ΔUV on THMs and HAAs formation in all NOM fractions of Alibeyköy water.

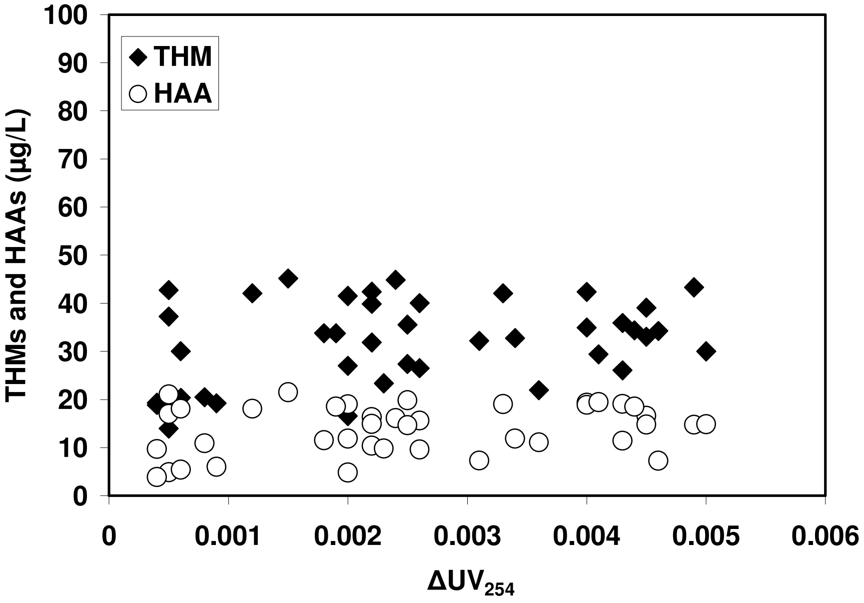

Figure 5.13. The impact of ΔUV on THMs and HAAs formation in all NOM fractions of Karacaören water.

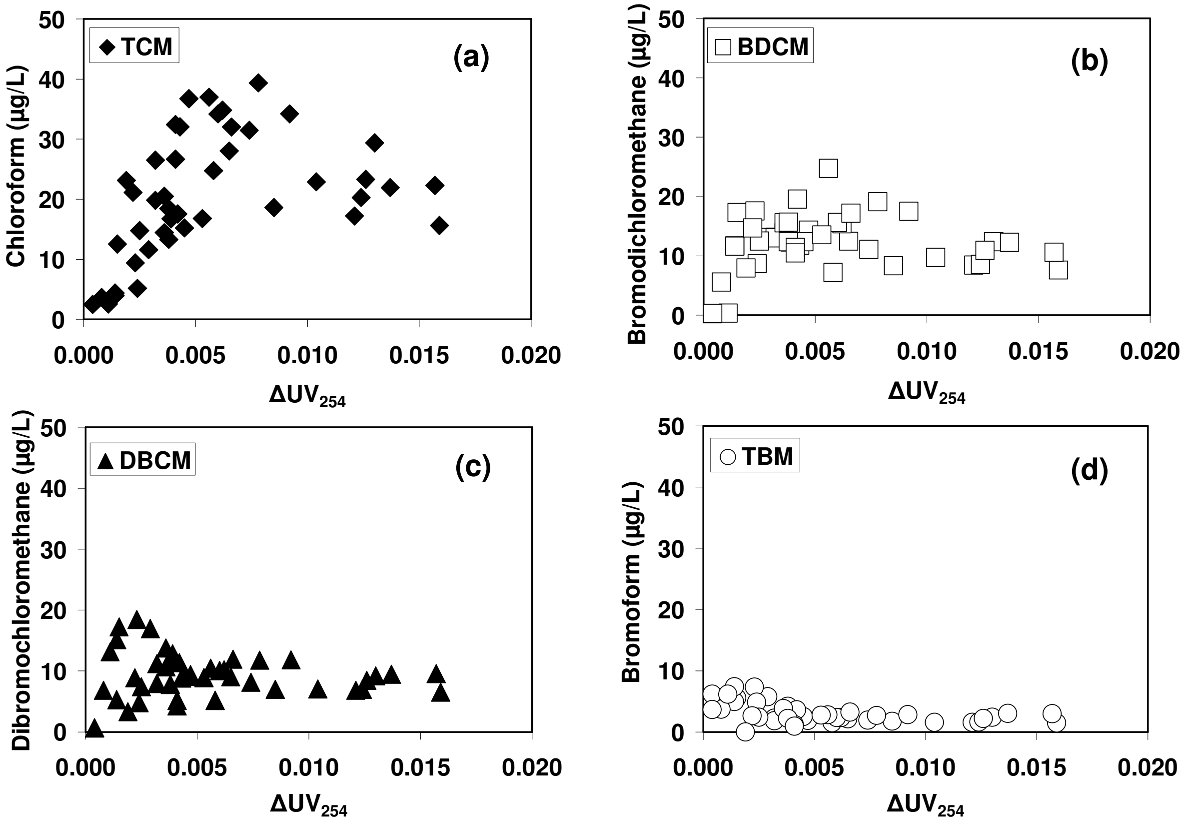

Figure 5.14. The impact of ΔUV on THM species in all NOM fractions of Alibeyköy water.

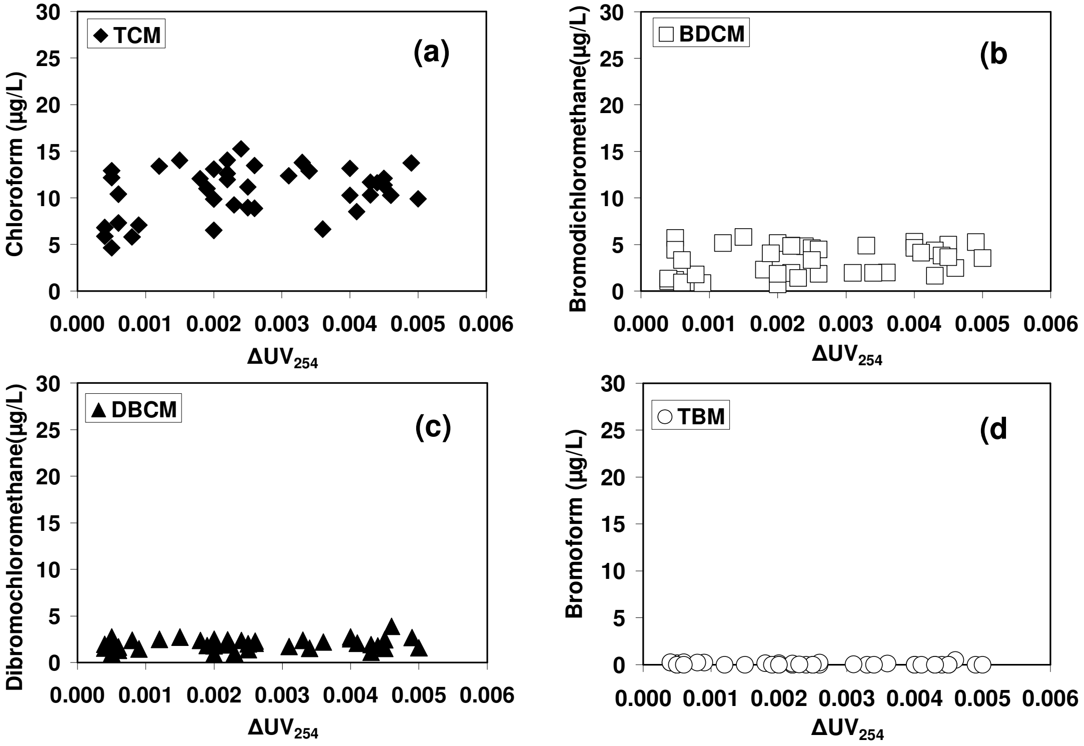

Figure 5.15. The impact of ΔUV on THM species in all NOM fractions of Karacaören water.

5.3.6. Impact of Bromide Concentration on DBP Formation and Speciation

During fractionation with XAD-8, XAD-4 and GAC adsorption and MIEX® ion exchange (for only Alibeyköy water), DOC concentration was decreased in different levels by increasing adsorbent or resin dose in NOM fractions of Alibeyköy and Karacaören. No significant change was expected in the bromide concentrations by XAD and GAC adsorption. However, MIEX® resin is not limited to only DOC removal and will remove other negatively charged ions (anions) from water such as sulfates, sulfides and arsenate (Bourke, 2001). Bromide concentrations in MIEX® fractions were measured by DPD method using HACH instrument. Because this method was not sensitive for very low bromide levels (<0.2 mg/L); the measured data did not give any reasonable changes in bromide concentration. In case of high concentration of bicarbonate ions in the high alkalinity water and relatively low bromide concentrations, bromide is unable to compete effectively for the exchange sites on the strong base anion exchange resin. On the other hand, Singer and Bilyk (2002) stated that removal of bromide ion decreased as the alkalinity of the raw water increased. They found a small increment in bromide ion concentration in MIEX-treated water with respect to raw water having 155 mg/L as $CaCO_3$ alkalinity. In this study, Alibeyköy raw water had 225 mg/L as $CaCO_3$ alkalinity. Thus, no removal of bromide ion was assumed in MIEX-treated samples. Therefore, in all NOM fractions for both Alibeyköy and Karacaören waters, the Br^-/DOC ratios were calculated assuming no bromide removal, the change in bromide concentrations were due to dilution of samples by adjusting constant DOC concentration. Figure 5.14 and 5.15 show the impact of bromide concentrations on THMs and HAAs formations of NOM fractions in all NOM fractions of Alibeyköy and Karacaören waters, respectively. As seen from Figure 5.16 and 5.17, no reasonable correlations were observed between Br/DOC ratio and THMs and HAAs formations. As discussed in Chapter 4, even low levels of bromide in raw waters affected the formation and distribution of THM species. In this study, although two surface waters having different characteristics moiety and distribution of organic compounds were tested, THMs and HAAs formations did not correlate with bromide ion. Similarly, no impact of bromide ion was obtained on AOX formations in both Alibeyköy and Karacaören waters (in Appendix B, Figure B.15 and B.16).

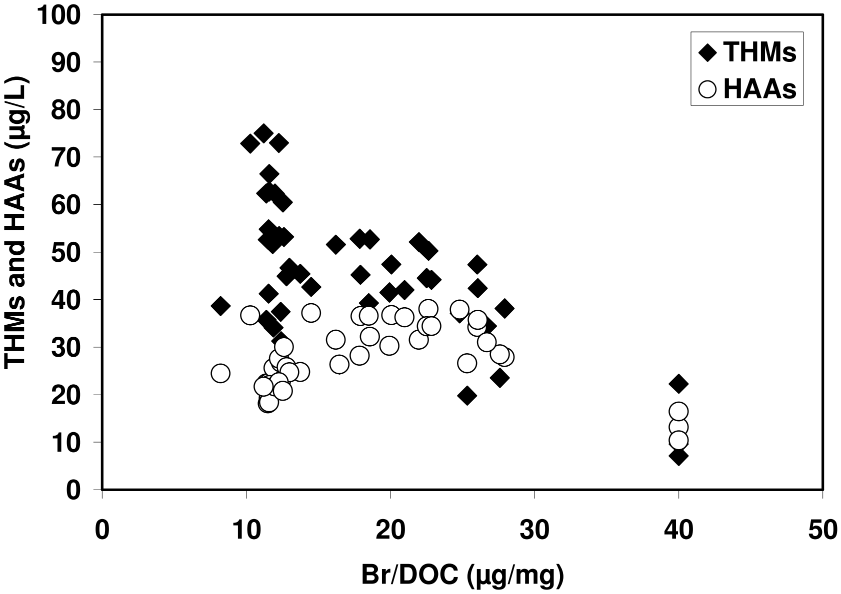

Figure 5.16. The impact of bromide concentrations on THMs and HAAs formation in all NOM fractions of Alibeyköy water.

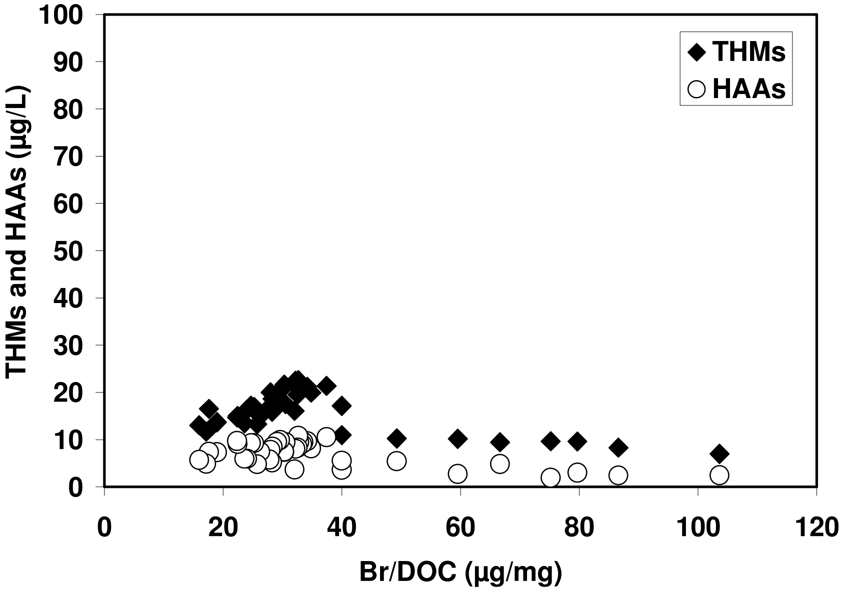

Figure 5.17. The impact of bromide concentrations on THMs and HAAs formation in all NOM fractions of Karacaören water.

In Figure 5.18 and 5.19, Br$^-$/DOC values versus bromine incorporation factors were plotted for all NOM fractions of Alibeyköy and Karacaören waters, respectively. The bromine incorporation factors varied between 0.3 and 1.8 for THM and between 0.2 and 0.8 for HAA among all NOM fractions for Alibeyköy water. On the other hand, bromine incorporation factors were from 0.2 to 0.5 for THM and from 0.1 to 0.6 for HAA among all NOM fractions for Karacaören water. It was expected that brominated species increased with increasing Br$^-$/DOC ratio. A small increase in bromine incorporation factors by increasing Br$^-$/DOC for THM in Alibeyköy fractions (Figure 5.18) showed that bromide ion had tendency to form brominated-THM species. On the contrary, there was no significant difference observed between THM and HAA with respect to bromine incorporation factors among Karacaören fractions. This was probably due to very low level of organic content in Karacaören fractions corresponding to Alibeyköy fractions. Nevertheless, for both tested waters, there were no strong correlations between bromine incorporation factors and bromide ion concentration. This result was seen more clearly in Karacaören fractions (Figure 5.19).

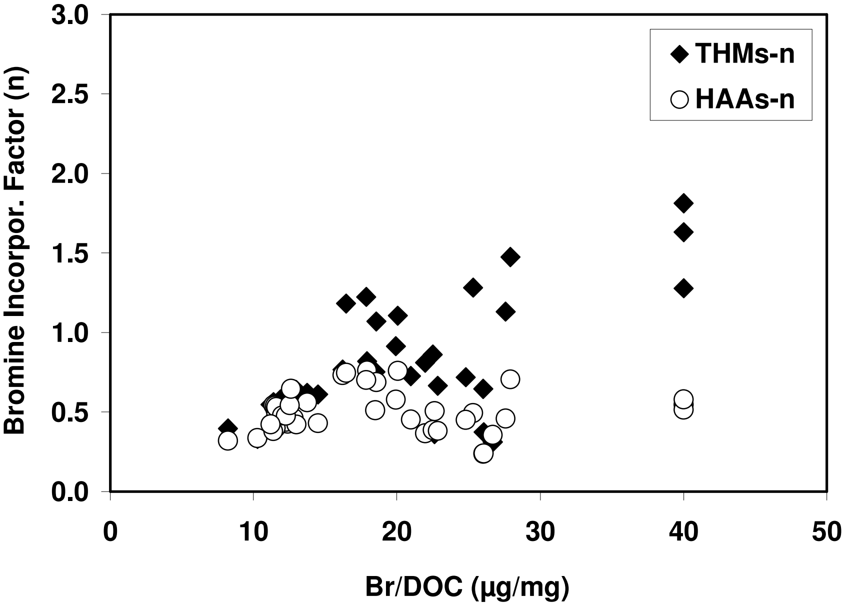

Figure 5.18. The impact of bromide concentrations on THM and HAA speciation in all NOM fractions of Alibeyköy water.

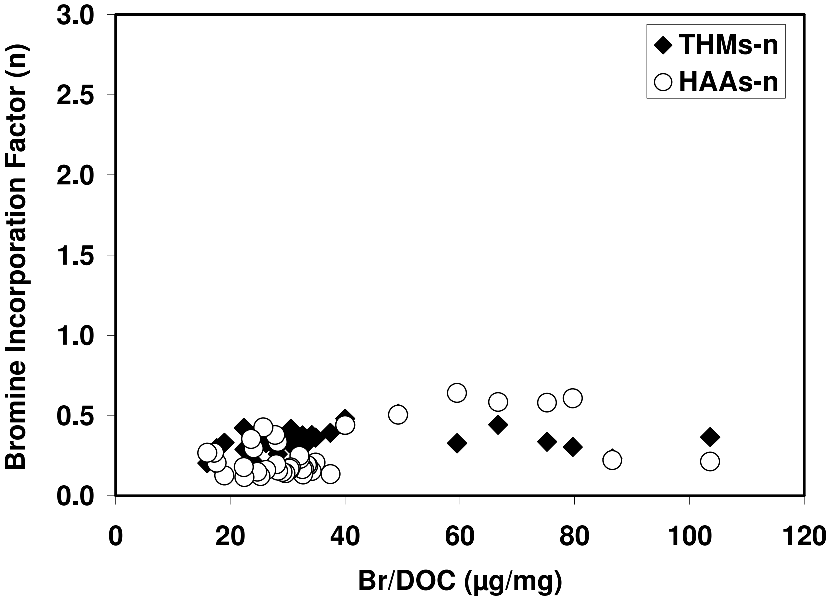

Figure 5.19. The impact of bromide concentrations on THM and HAA speciation in all NOM fractions of Karacaören water.

5.4. Conclusions

The majority of NOM in both waters was found to have average molecular weights <2000 Da as PSS and $SUVA_{254}$ values <2 L/mg org-C.m, indicating that NOM in the tested waters contained dominantly LMW fractions and low aromaticity. A total of 83 bulk water NOM fractions with a wide range of $SUVA_{254}$ values were obtained from two source waters by batch XAD-8, XAD-4, MIEX® resin and GAC adsorption. XAD-8 resin preferentially removed high- SUVA NOM components from both waters. However, no consistent trend was found for XAD-4 resin. UV absorbing fractions were preferentially removed by GAC in Alibeyköy water. On the other hand, for Karacaören water having a DOC concentration of only 1.2 mg/L, no consistent trend was observed with respect to fractionation based on SUVA. Similar to XAD-8 and GAC adsorption, MIEX® resin also preferentially removed higher UV-absorbing fractions in Alibeyköy water although the extent of fractionation based on SUVA was not as large as that obtained by the GAC.

In all fractions, concentrations of THMs were generally higher than those of HAAs. Fractions with low-$SUVA_{254}$ values (<1 L/mg C.m) resulted in THMs and HAAs concentrations as high as 35 and 40 µg/mg DOC, respectively. Chlorinated species dominated over brominated ones in both waters, a consistent trend found for both THMs and HAAs. This is expected since the bromide concentrations in Alibeyköy and Karacaören fractions were only <40 and <20 µg/L, respectively. Chloroform and dichloroacetic acid were the most abundant THM and HAA species, respectively. Interestingly, the relative concentration of trichloroacetic acid, usually found to be a major HAA specie especially in high-SUVA waters (Liang and Singer, 2003), was very low in both of the studied waters. The higher yields of dichloroacetic acid over trichloroacetic acid further indicated that organic nature of these water sources were mostly non-humic and hydrophilic in character.

SUVA did not correlate well with the formation of total THMs, HAAs and AOX in the fractions of both waters. Furthermore, SUVA also did not correlate with the formations of any THM or HAA species in either water source. All these results basically suggest that the effectiveness of SUVA in correlating with DBP formation is water specific. In other words, SUVA as a bulk parameter may not capture the reactive sites on NOM moieties responsible for DBP formation in all source waters, given the high degree of NOM heterogeneity among waters. Apparently, the DBP formation prediction capability of SUVA is weak in waters with low-SUVA values and containing LMW NOM fractions. The destruction in UV_{254} absorbance after chlorination (i.e., differential UV spectroscopy) did not correlate with total

THM or HAA formations in both of the tested waters. Same trend was also observed for single THM and HAA species, indicating that the formation of THMs and HAAs are not directly dependent on the destruction in UV_{254}-absorbing sites after chlorination. It seems that other NOM moieties not absorbing UV light also play important roles in DBP formations in waters with low-SUVA values, i.e., waters hydrophilic in character. Overall, consistent with the findings for SUVA, it is apparent that formation of DBPs in low-SUVA and low-DOC waters may not be estimated by simple UV absorbance measurements.

CHAPTER 6

REMOVAL OF DISINFECTION BY-PRODUCT PRECURSORS BY UF AND NF MEMBRANES IN LOW-SUVA WATERS

6.1. Introduction

Previous research has shown that DBP precursor reductions can be succeeded in different efficiencies by membrane filtration processes (Taylor et al., 1987; Amy et al., 1990; Weisner et al., 1991; Laine et al., 1993; Jacangelo et al., 1995a; Scanlan et al., 1997; Siddiqui et al., 2000; Lin et al., 2006). This is mainly due to the variations in the characteristics of DBP precursors and different types of membranes used in various studies. Although several researchers investigated the performances of membrane processes on the removal of DBP precursors, majority of the studies was conducted on waters with relatively high DOC concentration (>3 mg/L) and high $SUVA_{254}$ (specific ultraviolet absorbance at 254 nm wavelength) values (>2-3 L/mg org-C.m). This is mainly caused by the fact that waters with high DOC and SUVA levels are considered to be problematic from the DBP formation point of view. However, there is limited information in the literature on the performance of membrane filtration in removing DBP precursors in waters with relatively low DOC and SUVA levels. Such waters may be characterized by having NOM dominantly in hydrophilic character and less aromaticity. In this context, the main objective of this work was to evaluate the performances of NF and UF membranes on DBP precursor removal in waters having low-to-medium DOC and SUVA levels. In addition, the fouling behavior of such membranes was investigated. A total of four different membranes was tested for DBP formation reduction and fouling control. In addition; for a selected membrane, the effect of CFV was investigated. HPSEC measurements were conducted in the raw water and permeate samples to determine the MWD of NOM moieties after membrane filtration and to link such information to DBP formation in permeate samples after chlorination. The measured DBPs were THMs, HAAs and AOX.

6.2. Materials and Methods

6.2.1. Source water and Membrane Filtration Unit

The tested surface water in this part of the study was Alibeyköy reservoir (İstanbul) sampled in June 2006. A total of 550 L water sample was collected headspace free in 25-L polyethylene bottles and shipped overnight to the laboratory. Table 6.1 presents the physico-chemical characteristics of Alibeyköy source water. Alibeyköy water had DOC concentration and $SUVA_{254}$ value of 3.4 mg/L and 2.5 L/mg org-C.m, respectively, representing natural water with low-to-medium DOC and SUVA levels.

A lab-scale cross-flow flat-sheet configuration test unit (as described in Section 3.1.3) was used for all membrane separation experiments, which simulates the flow dynamics of larger, commercially available spiral-wound membrane elements.

Table 6.1. Characteristics of Alibeyköy raw water

Parameter	**Value**[1]
pH	7.95 ± 0.09
Turbidity (NTU)[2]	3.0 ± 0.5
Conductivity (µS)	514 ± 3
TDS (mg/L)	257 ± 2
DOC (mg/L)	3.4 ± 0.3
UV_{254} Absorbance	0.085 ± 0.002
$SUVA_{254}$ (L/mg org-C.m)	2.5 ± 0.2
Bromide (µg/L)	50 ± 10

[1] The values represent average of triplicate measurements of ten membrane filtration tests with standard deviations.
[2] Unfiltered raw water. All other parameters were quantified after filtration.

6.2.2. Experimental Procedures

Experimental matrix for membrane filtration is given in Table 3.4. Clean water and feed water fluxes (Eq. 6.1) were determined by collecting permeate samples in a graduated cylinder at t: 0, 1, 2, 4, 6, 8, 10, 12, and 24 h during the operation. Besides, TMP and membrane resistance were calculated for each membrane test.

$$J = \frac{dV/dt}{A} \qquad \text{(Eq. 6.1)}$$

where, J is the flux (L/m^2-h), dV/dt is the permeate flowrate (L/h) and A is the effective membrane area (m^2).

Trans-membrane pressure (TMP) is defined as:

$$\mathrm{TMP\ (bar)} = \frac{(P_{feed} + P_{conc})}{2} - P_{perm} \qquad \text{(Eq. 6.2)}$$

where, P_{feed} is the feed pressure (bar), P_{conc} is the concentrate pressure (bar), and P_{perm} is the permeate pressure which is equivalent to 0.93 bar atmospheric pressure.

Membrane resistance (R) is calculated according to the following equations:

$$\mathrm{R\ (m^{-1})} = \frac{\mathrm{TMP}}{\mu * J} \qquad \text{(Eq. 6.3)}$$

where, μ is the dynamic viscosity of water at 20 ^{0}C (1.002x10^{-3} N.s/m^2), and J is the permeate flux (L/m^2-h).

Chlorination of the raw waters and permeate samples was performed according to the uniform formation condition (UFC) protocol (Summers et al., 1996) as described in detail in Section 3.2.3.

6.2.3. Analytical Methods

Analyses of all parameters were performed according to the methods described in Section 3.3.

6.3. Results and Discussion

Figure 6.1 illustrates the MWD of organic compounds in filtered Alibeyköy raw water obtained by HPSEC measurements. MWD analysis showed that two main different organic fractions were present in Alibeyköy water. Average molecular weights of these fractions were 12,216 Da (M_z) (M_n=8,981; M_w=10,690; ρ=1.14) and 1,822 Da (M_z) (M_n=1,704; M_w=1,766; ρ=1.04). Since different organic components in their nature give different responses with respect to calibration standards (PSS), the actual amounts of such organic fractions in water samples could not be determined. Therefore, the proportions of organic fractions could be estimated. The responses of these two types of organic fractions demonstrated that 28 and 72% of NOM in Alibeyköy water were of HMW and LMW, respectively (Ates et al., 2007). The $SUVA_{254}$ value of Alibeyköy water was 2.5 L/mg org-C.m (Table 6.1). It is generally indicated in the literature that natural waters with high $SUVA_{254}$ values, e.g., ≥4 L/mg org-C.m, have relatively high content of hydrophobic, aromatic and HMW NOM fractions, while waters with $SUVA_{254}$ at ≤2-3 L/mg org-C.m contain mostly hydrophilic, non-humic and LMW fractions (Edzwald and Van Benschoten, 1990; White et al., 1997; Edzwald and Tobiason, 1999). Thus, based on the SUVA and HPSEC measurements, NOM in the tested water contained dominantly LMW fractions and low aromaticity.

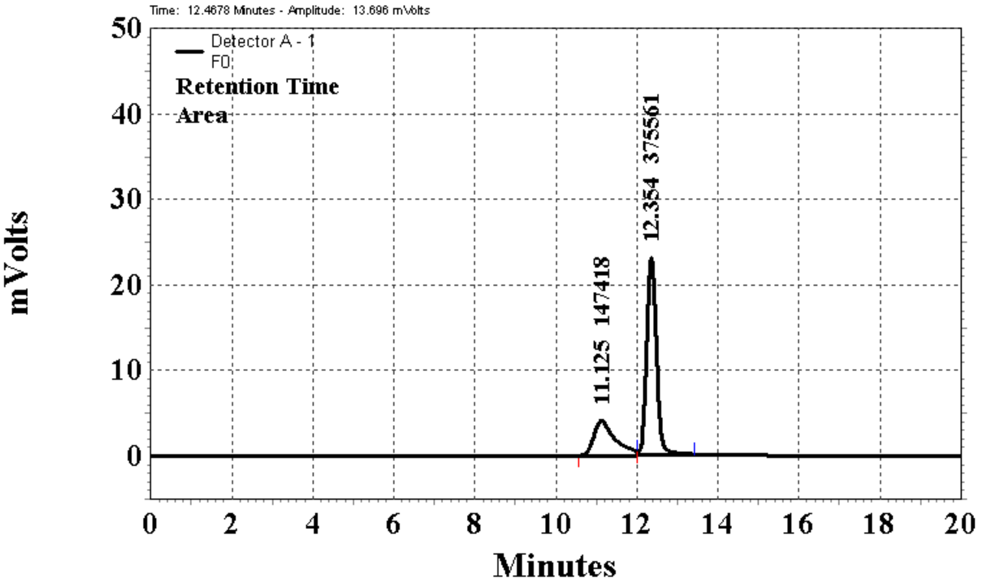

Figure 6.1. MWDs of organic compounds in filtered Alibeyköy raw water. Sampling date for Alibeyköy water is June 2006.

6.3.1. Flux Development and Fouling

Clean water fluxes at steady state for GH-UF, DK-NF and DL-NF membrane tests were 36.3, 32.9 and 42.6 L/m^2-h, respectively (Table 6.2). Clean water fluxes for these three membranes were similar to fluxes provided by manufacturer which were 34 L/m^2-h for GH-UF membrane, 37 L/m^2-h for DK-NF membrane and 53 L/m^2-h for DL-NF membrane. On the other hand, clean water flux of PT-UF membrane was 42.8 L/m^2-h. This value is highly different from typical manufacturer value (153 L/m^2-h) even the same filtration condition was applied. This may be due to the variations in as-received membrane characteristics.

In Figure 6.2, the change of feed water normalized fluxes based on time at different type of membrane, pressure and CFV were given. The highest flux decline with 0.71 corresponding to their initial flux (at time zero) was observed for DK-NF membrane test. PT-UF, GH-UF and DL-NF membranes displayed similar flux decline trends with respect to time and their normalized fluxes at steady state were 0.91, 0.97 and 0.95, respectively (Figure 6.2a). On the other hand, similar flux development trends were observed at different pressures using DK-NF membrane and increasing in pressure increased normalized flux (Figure 6.2b). The normalized fluxes were 0.95, 0.86 and 0.71 for 13.8, 10.4 and 6.9 bar, respectively. No significant difference was observed on normalized flux among CFVs (Figure 6.2c).

Since NF membranes reject smaller molecules than UF membranes, higher flux reductions were observed with the tested NF membranes than with the UF membranes for the Alibeyköy water (Table 6.2). At a cross-flow velocity of 1.2 m/s, DK-NF membrane presented a slightly higher equilibration flux decline (9.4%) than DL-NF membrane (8.5%). On the other hand, UF membranes displayed similar flux decline trends as 7.4% and 6.9%. In filtration with DK-NF membrane, an increase in TMP from 6.3 to 13.8 bar resulted in a 41% increase in flux decline. This finding was in agreement with Tu et al. (2005) who also stated that higher permeate flux reductions were observed at higher TMPs. It is generally agreed that high initial flux results in severe flux reduction. Since the initial flux of a membrane is proportional to the applied TMP, flux loss typically increases at higher pressures (Tang et al., 2007).

The flux development of DK-NF membrane was evaluated at the CFVs of 0.7 and 1.2 m/s and it was observed that CFV did not have a significant impact on flux decline (9.3 vs 9.4%). This finding indicates that CFV of 1.2m/s was not high enough to further reduce concentration polarization existing on the membrane surface. In a recent study, Tang et al (2007) reported a 20% reduction in permeate conductivity when CFV was increased from 0.2 to 0.35 m/s in the filtration of NOM with ESPA3 membrane.

Table 6.2. TMP and membrane resistance of feed water at steady state conditions (Phase I and II).

Membrane Type	**CFV (m/s)**	**Clean Water Flux (L/m^2-h)**	**Feed Flux (L/m^2-h)**	**Flux Decline (%)**	**TMP (bar)**	**R (1/m)**	**Clean Water Flux Recovery (%)***
PT-UF	1.2	42.8	39.9	6.9	2.9	7.2	92
GH-UF	1.2	36.3	33.6	7.4	10.1	29.9	100
DL-NF	1.2	42.6	39.0	8.5	6.3	16.1	103
DK-NF	1.2	70.6	61.2	13.3	13.8	21.7	106
	1.2	59.8	53.1	11.4	10.1	19.8	101
	1.2	32.9	29.8	9.4	6.3	21.2	102
	0.7	33.5	30.4	9.3	6.1	19.4	102

* After feed water processing of used membranes.

As presented in Table 6.2, after the filtration of natural water, clean water fluxes were recovered back to their initial values (i.e., for new membranes) for GH-UF, DK-NF and DL-NF membranes but not for PT-UF. This finding indicated that fouling of GH-UF, DK-NF and DL-NF membranes is more likely by cake/gel layer formation (surface coverage). However, fouling of PT-UF was partly irreversible which is attributed to internal pore blockage and adsorption of HMW organics (>5KDa MWCO). Tu et al. (2005) stated that gel layer formation and internal pore blockage are affected by the membrane hydrophobicity; as the hydrophobicity of membrane increases the tendency of less hydrophilic organic solute molecules to leave aqueous phase and get adsorbed or deposited on membrane surfaces or pores increases. The nature of PT-UF membrane is PES which is hydrophobic and therefore susceptible to irreversible fouling.

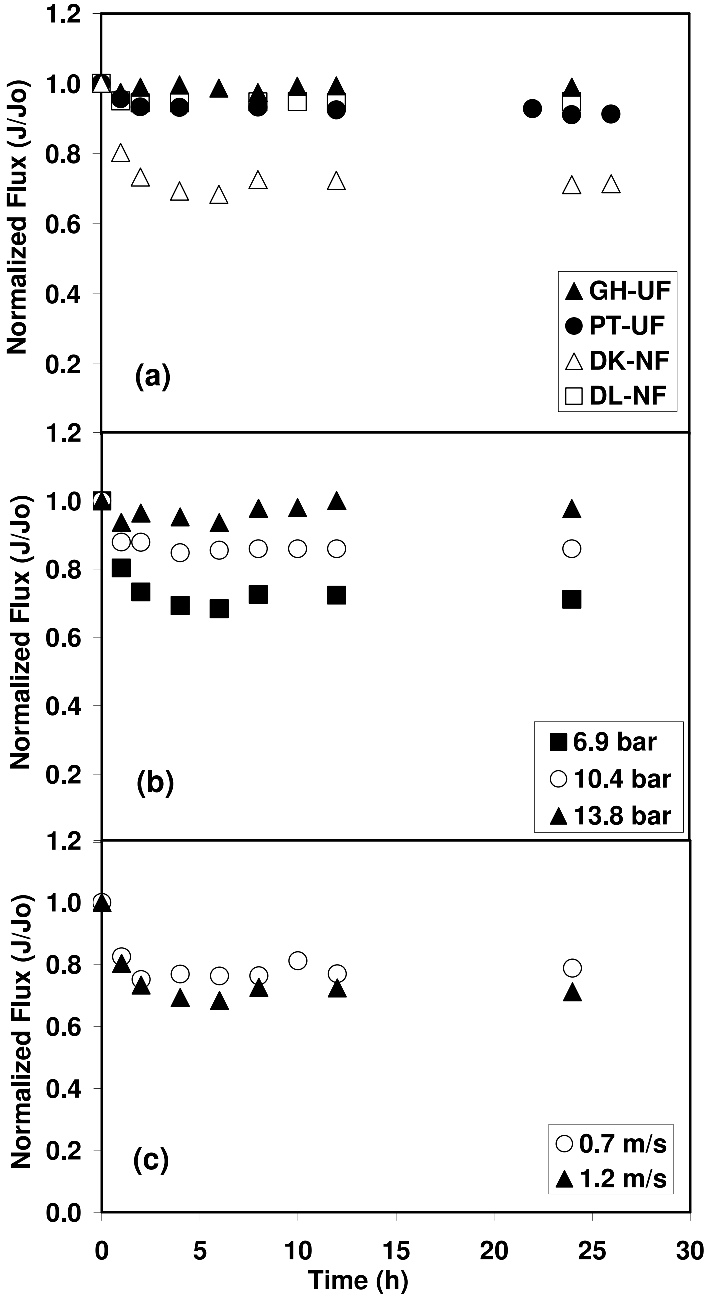

Figure 6.2. Flux development curves using feed water:
(a) membrane type effect, (b) pressure effect (DK-NF membrane), (c) CFV effect (DK-NF membrane).

6.3.2. Effect of Membrane Type

In Figures 6.3a and 6.3b, time dependent DOC and UV_{254} absorbance rejection performances of different membranes are illustrated. At equilibration, all UF and NF membranes removed organic matter significantly indicating rejection of NOM not only by the pore size exclusion mechanism, but also by other separation mechanisms such as adsorption onto the membrane surface, adsorption onto particles in the cake layer or sieving as a result of physical constriction of the membrane pores due to irreversible fouling as indicated by several other investigators (Jacangelo et al., 1995c; Walsh et al, in press). As can be seen from Figure 6.3, more or less similar DOC and UV_{254} absorbance rejections were observed with all the membranes except, PT-UF which provided the lowest equilibration DOC and UV_{254} absorbance rejections (61 and 74% respectively). With GH-UF, DK-NF and DL-NF membranes, DOC rejections were at or above 85% while UV_{254} absorbance rejections were at or above 90% indicating similar high NOM removal efficiencies. This finding indicates that all the membranes tested removed preferentially aromatic/hydrophobic organics to which UV_{254} absorbance is attributed to. Amy and Cho (1999) reported similar findings and indicated that UF preferentially removed UV_{254} absorbance over DOC and thus removed organics were hydrophobic (fulvic and humic) acids. Similar results were also indicated by Rubia et al. (2008).

The efficiencies of UF and NF membranes in rejecting HMW and LMW organic fractions are given in Figures 6.3c and 6.3d. HMW organic fraction was almost completely removed from the feed water with all the membranes (HMW organic fraction rejections were 89, 92, 98 and 98% with PT-UF, GH-UF, DK-NF and DL-NF, respectively). This result is expected, as the MWCOs of all the membranes were lower than the average molecular size of the HMW organics (~12,000 Da) present in the feed water. On the other hand, for LMW organic fraction, different rejection efficiencies were observed with different membranes tested (Figure 6.3d). The lowest rejection (1.5%) was observed with PT-UF membrane. LWM organic fraction was removed from the feed water by the other UF membrane (GH-UF) with 11% rejection efficiency. On the other hand, both of the NF membranes displayed similar rejection efficiency of 30% on this organic fraction. Indeed, much higher rejection efficiencies were expected in the removal of LMW organic fraction with all the membranes tested except PT-UF as the MWCO of these membranes provided by the manufacturer are much lower than the average MW of LMW organic fraction (~1,800 Da) in feed water. The MWCOs and the rejection sizes provided by manufacturer are 5000 Da for PT-UF membrane and 1000 Da for GH-UF membrane and 98% $MgSO_4$ for DK-NF membrane and 96% $MgSO_4$ for DL-NF membrane. Similar result was observed by Amy and Cho (1999) whom reported significantly lower rejection of NOM of MW of 1,650 Da using UF membrane having a MWCO of 8,000 Da. According to these findings, although NF and UF membranes with a MWCO less than 2000 Da are highly successful on the removal of NOM from a low SUVA, low bromide surface water, these membranes could not efficiently remove LMW organics.

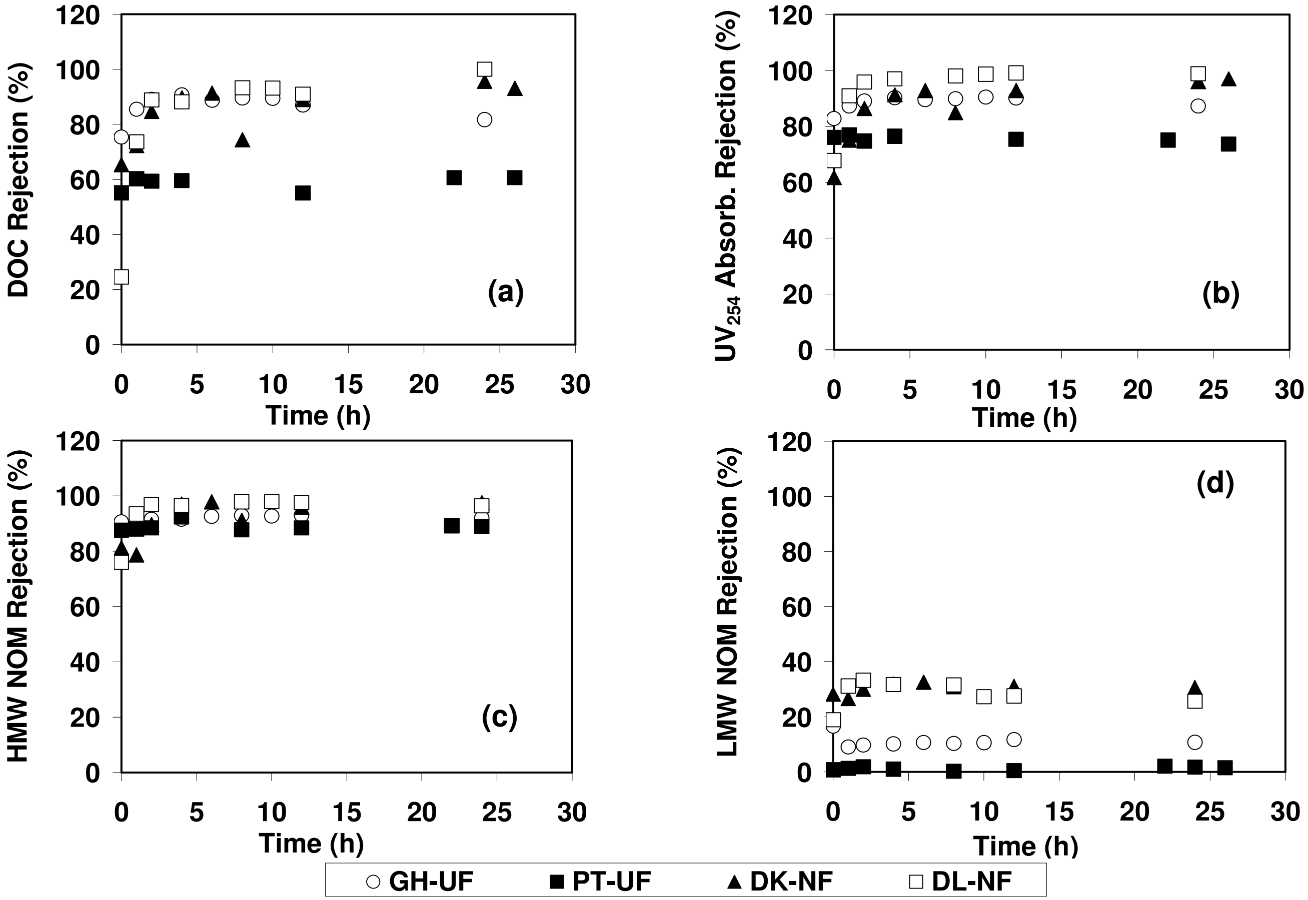

Figure 6.3. The impact of membrane type on time dependent rejection of DBPs precursors (Phase I).

Conductivity and TDS of feed water did not change considerably during filtration for all membrane types (Figure B.17 and B.18, respectively). As the rejection efficiencies for conductivity and TDS were 20% in PT-UF permeates, those efficiencies were 81% in DK-NF permeates. As expected, the lowest rejection efficiencies were obtained by PT-UF membrane having the highest MWCO or rejection size (5000 Da). DK-NF membrane was followed by DL-NF and GH-UF with the efficiencies of 71% and 45%, for conductivity and TDS, respectively. The reason of higher rejection efficiency obtained in DK-NF permeates was probably that DK-NF membrane had higher specified rejections (98% $MgSO_4$) than DL-NF membrane (96% $MgSO_4$).

6.3.3. Effect of TMP and CFV

The effects of TMP on the rejection of DBP precursors in permeate samples with respect to time are given in Figure 6.4. Although TMP variation affected rejection of DOC, UV_{254} absorbance and HMW NOM at the first few hours of the filtration, there was no significant pressure effect observed at steady state. On the other hand, the rejection of LMW organic fraction increased with an increase in TMP. Organic contents based on both DOC and UV_{254} absorbance of feed water were almost all removed with all the membrane tested independent of TMP at steady state. When the effect of CFV on DOC, UV_{254} absorbance, HMW NOM and LMW NOM was investigated, it was observed that the results are similar (Figure 6.5), and an increase in CFV does not significantly influence the rejections.

As shown in Figure 6.4c, DK-NF membrane was highly successful in removing HMW organic fraction with almost 98-100% efficiency independent of TMP. However, this membrane provided a low LMW organic matter rejection and moreover an increase in rejection with an increase in TMP (30, 35, 41% rejection at 6.9, 10.4 and 13.8 bar TMP, respectively) (Figure 6.4d).

As seen from Figure 6.5, similar to the TMP effect, higher LMW organic matter rejections were obtained by increasing CFV. The rejection efficiencies were 25% and 30% at 0.7 and 1.2 m/s CFV, respectively (Figure 6.5d). Thus, at all conditions tested, some portion (60-70 %) of LMW organic fraction could not be removed and was still in permeates. The presence of this portion of NOM in permeates was not apparent from DOC data presented in Figure 6.5a possibly due to its low concentration.

The rejections of conductivity and TDS in permeate with respect to time at different pressures were given in Figure B.19 and B.20, respectively. Although small differences were observed among different pressures, even so increasing in pressure increased the rejections of conductivity and TDS. The rejection efficiencies were 86, 84 and 81% at 13.8, 10.4 and 6.9 bar, respectively. On the other hand, the rejections of conductivity and TDS were lower at 0.7 m/s (76%) than at 1.2 m/s (80%) (Figure B.21 and B.22).

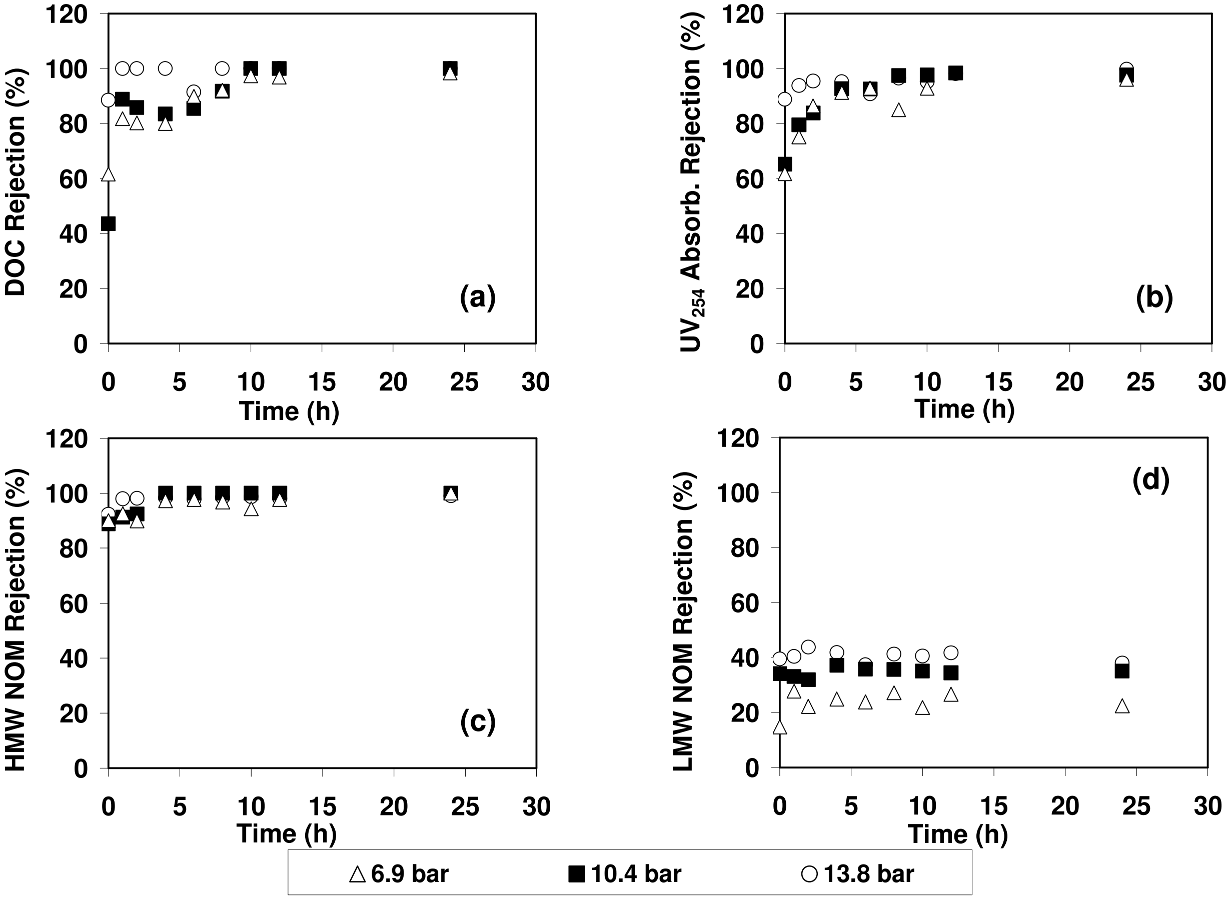

Figure 6.4. The impact of pressure on time dependent rejection of DBPs precursors by DK-NF membrane filtration (Phase II).

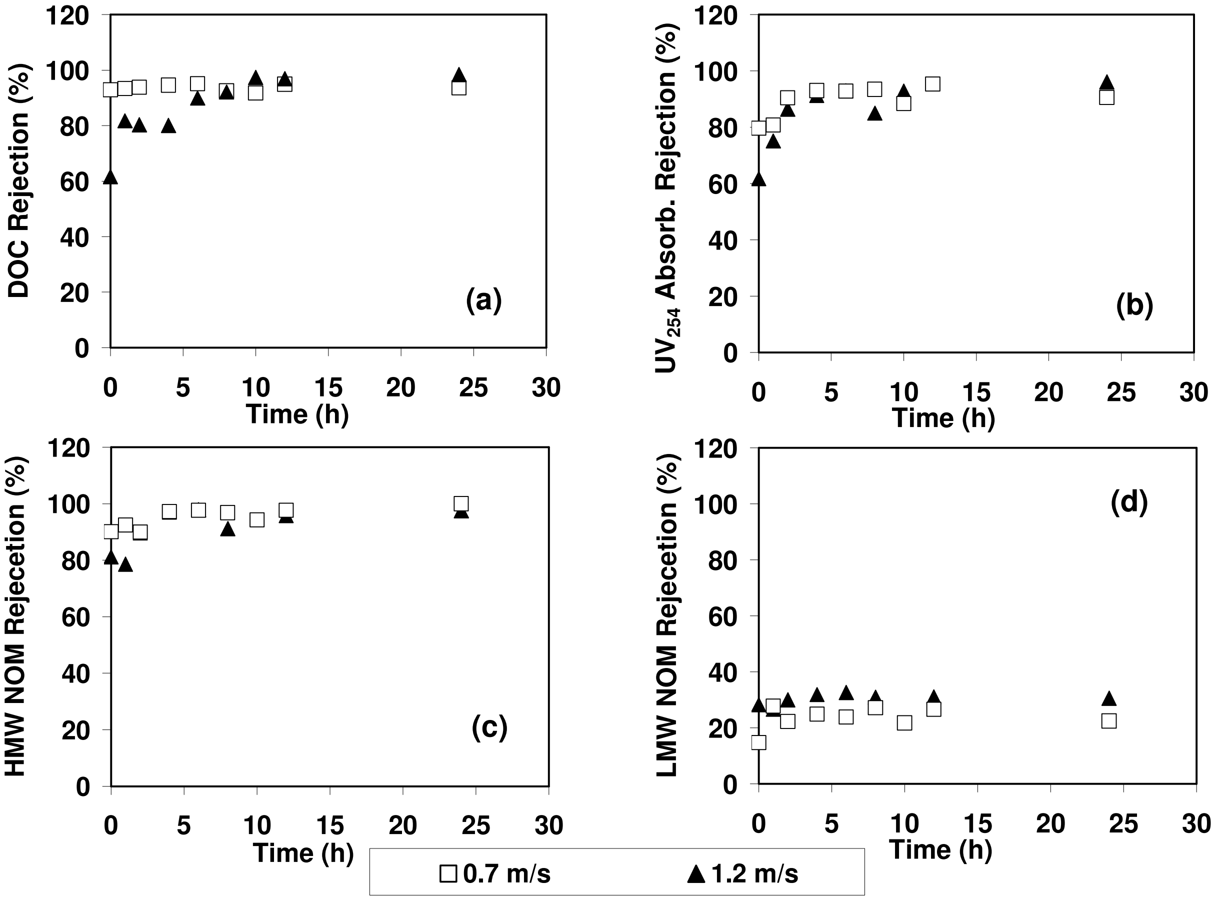

Figure 6.5. The impact of CFV on time dependent rejection of DBPs precursors by DK-NF membrane filtration (Phase II).

6.3.4. DBP Reactivity of NOM in Permeates

In Table 6.3, DBP formation in the chlorinated feed water and the permeate samples from different membranes are presented. In general, NOM in all water samples led to higher THM concentrations than those of HAAs. But, this difference was more pronounced for PT-UF membrane than for other membranes. The highest THMs and HAAs (and also AOX) formations were observed in permeates from PT-UF membrane while the lowest formations were in permeates from DL-NF. Corresponding reductions in THMs, HAAs and AOX formations as compared to the formations in the feed water were 63, 38 and 61% respectively for the PT-UF membrane, and 93, 89 and 75% for the DL-NF membrane. The reductions in THM formation by all UF and NF membranes were proportional to the reductions in DOC and UV_{254} absorbance (Figure 6.2 and Table 6.4) However, the reductions in HAAs formation was low compared to UV_{254} absorbance removals for both UF and NF membranes. The reductions in HAA formation in permeates from UF membranes were much lower than the reductions in DOC removal indicating the association of HAAs with LMW organic matter. This further points out that organic fraction removed by UF which is mostly HMW, corresponds to reactive sites of NOM that form more THMs than HAAs.

In case of NF membranes, DOC and UV_{254} absorbance removals (Figure 6.2) were similar to the reductions in THMs and HAAs formation potentials (Table 6.3), but not to AOX. As indicated before, THMs and HAAs are mostly associated with HMW organics; therefore increased removal of THMs and HAAs precursors is expected with an increase in DOC removal. As a consequence, THMs and HAAs reductions were as high as the DOC and UV_{254} absorbance removals in permeates obtained from NF membranes and UF membrane (with 1000 Da MWCO). This result is consistent with the study of Lee et al. (2005). In contrast, Rubia et al. (2008) reported that DBP reactivity reduction was not as high as NOM removal.

Table 6.3. DBP formations and formation reductions in permeates from UF and NF membranes

Water Source	**DBP Formations (µg/L)**			**DBP Reductions (%)**		
	AOX	**THMs**	**HAAs**	**AOX**	**THMs**	**HAAs**
Feed Water	355	128	53	-	-	-
PT-UF	140	60	34	61	63	38
GH-UF	100	22	21	71	82	60
DL-NF	81	6	5	78	96	91
DK-NF	83	10	6	75	93	89

Values presented are the averages of the last three consecutive permeates.

It was surprising and noteworthy to find AOX concentrations as high as 80 µg/L in DK-NF and DL-NF permeates. This result supported that LMW organic fraction played important role in forming other DBPs than THMs and HAAs. It has been indicated in the literature that about 30-60% of total organic halides (TOX) can be assigned to identified individual DBPs, mostly THMs and HAAs (Christman et al., 1983; Reckhow and Singer, 1984; Singer, 1994). On the other hand, in this study, the contribution of THMs and HAAs to AOX as halogens was lower at permeates than that of feed water except PT-UF membrane test. Although the halogen contributions of THMs and HAAs to AOX was 48% in feed water, it was 57% in PT-UF permeates. The contribution to AOX was lowered as much as 12% at DL-NF test.

As presented in Table 6.4, DBPs formations in the permeates from DK-NF membrane at different pressures were not different at all. Variation in DBP rejections based on CFV was also negligible. Nevertheless, over 90% rejection performances for THMs and HAAs associated with reduced NOM were obtained for all pressure and CFV using DK-NF membrane. Similarly, THM and HAA species shifted from chlorinated to brominated ones based on pressure and CFV. In addition, contribution of THMs and HAAs presented parallel trend with the membrane type effect.

Table 6.4. DBPs formation and formation reductions in Alibeyköy feed water and permeates from DK-NF membrane (Phase II)

Water Source	**Pressure (Bar)/ CFV (m/s)**	**DBPs Formations (µg/L)**			**DBPs Reduction (%)**		
		AOX	**THMs**	**HAAs**	**AOX**	**THMs**	**HAAs**
Feed Water	-	355	128	53	-	-	-
DK-NF	13.8/1.2	48	7	4	87	94	92
	10.4/1.2	56	9	4	85	92	92
	6.9/1.2	83	10	6	75	93	89
	6.9/0.7	87	12	5	77	92	87

Values presented are the averages of the last three consecutive permeates.

6.3.5. DBP Speciation in Chlorinated Permeates

Among THMs, chloroform was the dominant specie in the chlorinated feed water with an average percentage of 54% (Table 6.5). Bromodichloromethane, dibromochloromethane and bromoform followed chloroform with the averages percentages of 28, 17, 1%, respectively. In chlorinated permeate samples from all the membranes, the dominant THMs were dibromochloromethane (48%) and bromoform (34%) followed by bromodichloromethane (13%) and chloroform (4%). Among HAAs (Table 6.6); in the chlorinated feed water samples, trichloroacetic acid (42%) and dichloroacetic acid (20%) were the most abundant species followed by bromochloro- (16%), bromodichloro- (11%), dibromochloro- (8%) and dibromoacetic acid (3%). On the other hand; monochloro-, monobromo- and tribromoacetic acids were under detectable levels. In chlorinated permeates, the relative abundance of HAA species were in the following order: trichloro- (41%), dibromochloro- (15%), bromochloro- (14%), dibromo- (11%), dichloro- (10%), bromodichloro- (9%); monochloro-, monobromo- and tribromoacetic acids were under detectable level.

Table 6.5. The average formation of THM species and their percentages in Alibeyköy feed water and permeates from all the membranes

Water	**THM Species (µg/L)***			
Source	**TCM**	**BDCM**	**DBCM**	**TBM**
FW	65	40	22	1
PT-UF	8	11	28	13
GH-UF	1	3	10	9
DK-NF	0	2	6	2
DL-NF	0	1	3	2
% in FW	54	28	17	1
% in Permeates	4	13	48	34

* THM species; chloroform (TCM), bromodichloromethane (BDCM), Dibromochloromethane (DBCM), bromoform (TBM).
Pressure: 3.5 bar (PT-UF), 10.4 bar (GH-UF), 6.9 bar (DK-NF) and 6.9 bar (DL-NF), CFV: 1.2 m/s for all the membranes.

Table 6.6. The average formation of HAA species and their percentages in Alibeyköy feed water and permeates from all the membranes

Water Source	HAA Species (µg/L)*								
	CAA	**BAA**	**DCAA**	**TCAA**	**BCAA**	**DBAA**	**BDCAA**	**DBCAA**	**TBAA**
FW	0	0	11	22	9	1	6	4	0
PT-UF	0	0	3	7	8	3	5	7	0
GH-UF	0	0	1	3	6	3	3	4	1
DK-NF	0	0	0	2	1	1	1	1	0
DL-NF	0	0	1	2	1	0	0	1	0
% in FW	0	0	20	41	16	3	11	8	0
% in Permea.	0	0	10	41	14	11	9	15	0

* HAA species; monochloro-AA (MCAA), monobromo-AA (MBAA), dichloro-AA (DCAA), trichloro-AA (TCAA), bromochloro-AA (BCAA), dibromo-AA (DBAA), bromodichloro-AA (BDCAA), dibromochloro-AA (DBCAA), tribromo-AA (TBAA).
Pressure: 3.5 bar (PT-UF), 10.4 bar (GH-UF), 6.9 bar (DK-NF) and 6.9 bar (DL-NF), CFV: 1.2 m/s for all the membranes.

Brominated species is discussed in terms of bromine incorporation factor (n). While bromine incorporation factor was as high as 2.16 for THMs in DL-NF permeates and 1.09 for HAAs in GH-UF permeates, it was only 0.45 (THMs) and 0.39 (HAAs) in feed water. In the literature, it was reported that bromide ion could be removed by UF and NF membranes with 40-80% (Siddiqui et al., 2000). On the contrary, Laine et al. (1993) reported that NF membranes were effective for DBP precursor removal but ineffective for removing bromide, thereby resulting increase in the bromide to TOC ratio and proportion of brominated to chlorinated THMs. Similar trend was also reported by Jacangelo et al. (1995b) using combined powdered activated carbon (PAC) and UF treatment that increasing of the bromide-to-TOC ratio was observed as TOC was removed by the PAC. In this study, increase in brominated species indicated that no significant rejection efficiency was developed on bromide and bromide to DOC ratio was increased. Furthermore, increase in bromide to DOC ratio dominantly affected to form of brominated THM species.

3.6. Effect of Molecular Size of NOM on DBP Formation and Speciation

To evaluate the distribution of NOM among LMW and HMW groups and also the rejection of these organics during the course of UF and NF for a low-SUVA water; timely permeate samples were collected during PT-UF and DK-NF membrane filtration tests, chlorinated and analyzed for DBPs and also for molecular size of organics present. The data obtained is presented in Figure 6.6. There was a decrease in the permeate organic matter as filtration proceeded for both PT-UF and DK-NF membranes. Similar to the first phase membrane tests, the rejections of HMW and LMW NOM were 90 and 7% by PT-UF membrane (Figure 6.6a), and 98 and 29% by DK-NF membrane (Figure 6.6b), indicating better removal of LMW organics by DK-NF. Among different DBP groups, the highest rejection was for AOX and the lowest was for HAAs in PT-UF permeates. THM reactivity is greater than HAA reactivity in the presence of HMW organics in hydrophobic character (e.g. HS). Moreover, although the removal of HMW NOM was almost complete, the rejections of THMs and HAAs were never above 50-55%. This finding indicates that, the LMW organics are responsible for about 50% of the DBPs formation. On the other hand, in DK-NF membrane permeates, there was a better removal of LMW NOM and consequently almost complete rejection of THMs (97 %) and HAAs precursors (90%) (Figure 6.6b). A-20% increase in LMW NOM rejection provided a 40 to 50% additional decrease in THM and HAA formations and thus their rejections increased to about 90-95%. However, DK-NF membrane was not that satisfactory in the removal of all other DBPs, hence there was no significant improvement in the rejection of AOX formation, and therefore considerable amount of AOX formed (70 µg/L) in the permeate from DK-NF.

All above-mentioned findings from the present study indicate that the contribution of organic compounds with MW less than 2000 Da was much higher than HMW organics for the formation of THMs and HAAs for such water. This result was also consistent with the literature. Some researchers reported that most organic matter responsible for the formation of major DBPs are small to medium compounds with MW of close or less than 1 KDa in Taiwan source waters (Chang et al., 2001; Chiang et al., 2002; Chow et al., 2004). Amy et al. (1990) stated that apparent MW fractions less than 1 KDa were the majority of the THM precursors. Some other investigators also reported that NF with relatively lower MWCO of 400-800 Da was more effective in controlling the formation of DBPs than UF with high membrane-MWCO, which could resulted only a portion of THM (Jacangelo et al., 1995a; Lin et al., 1999).

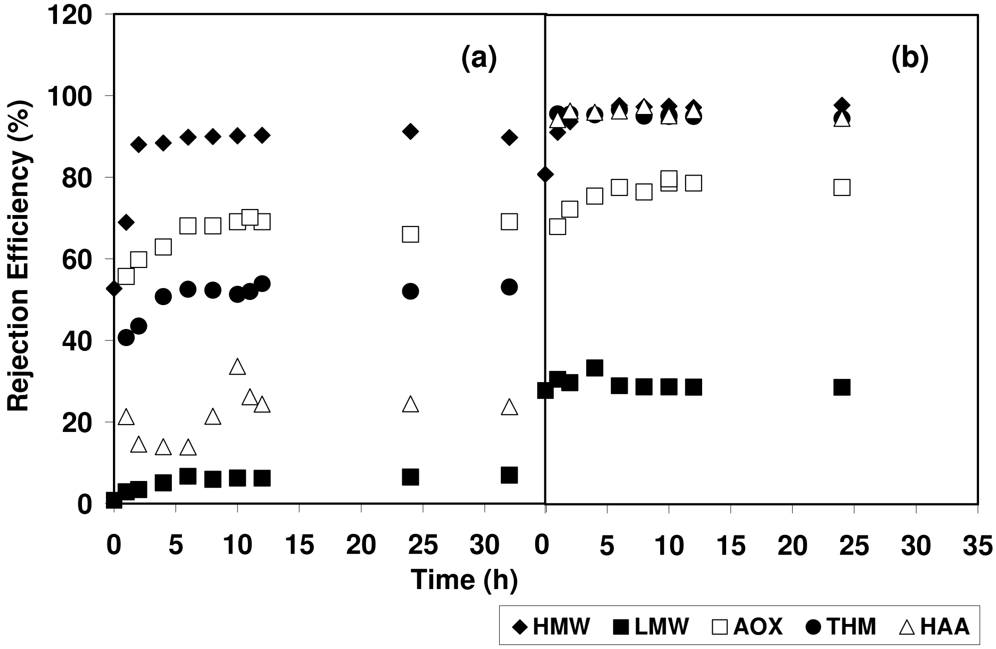

Figure 6.6. The impacts of HMW and LMW NOM in permeates on DBP rejections (AOX, THMs and HAAs): (a) UF permeates, (b) NF permeates.

In an effort to investigate the relative effectiveness of PT-UT and DK-NF membranes in the removal of brominated and chlorinated THM and HAA species, for all permeate samples from both PT-UF and DK-NF membranes, bromine incorporation factors were calculated after evaluating the distribution of brominated THMs and HAAs among other species and plotted against Br/DOC ratio (Figure 6.7). From the figure, it is clearly seen that NOM in Alibeyköy water is more susceptible to the formation of brominated THM species as opposed to brominated HAAs. A comparison of bromine incorporation factor for THMs in permeates from both PT-UF (2.0) and DK-NF (2.2) and for the feed water (0.5) indicates that the bromine incorporation factor increased by both UF and NF. This increase is obviously due to the reduction in NOM content while there is no removal in bromide content by UF and NF.

Although bromine incorporation factor for HAAs in permeates from PT-UF membrane gradually increased to 1.2 from its earlier value of 0.4 (in the feed water) as Br/DOC ratio increased, it decreased from 0.4 to 0.20 in DK-NF permeates (Figure 6.7). The decrease in bromine incorporation factor for HAA is mainly caused by very low level of organic content in DK-NF permeates. In such a way that bromide ion could not find chance to react with NOM to form HAAs over to form THMs. As mentioned Section 6.3.5, bromide rejection is insignificant during to membrane filtration by both membranes.

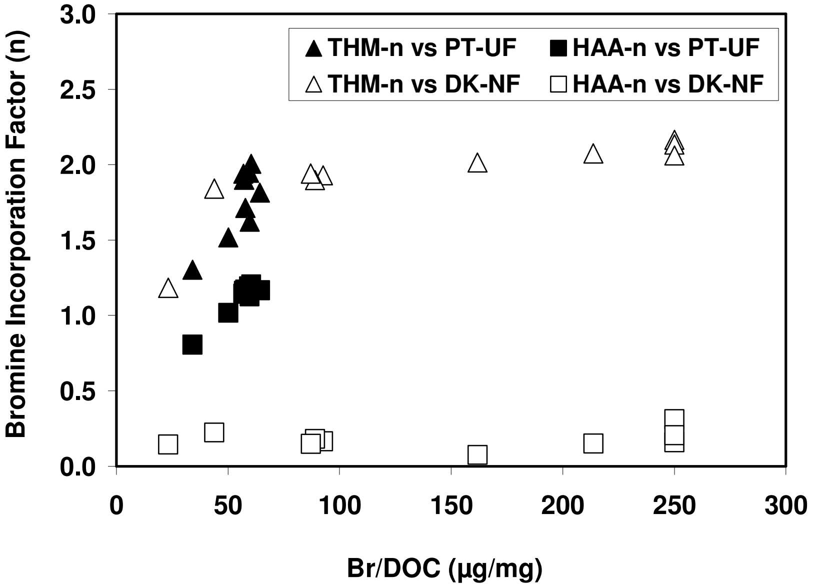

Figure 6.7. The impact of bromide concentrations on THM and HAA speciation in PT-UF and DK-NF permeates of Alibeyköy water.

6.4. Conclusions

In this study, lab-scale cross-flow membrane filtration tests have been performed using two UF (GH-UF and PT-UF) and two NF (DK-NF and DL-NF) membranes with Alibeyköy source water having low DOC and low SUVA values. HPSEC analysis showed that water has two different organic fractions having average MWs of 12,216 Da and 1,822 Da. When this water was subjected to UF and NF separation, the highest flux decline was observed as 9.4%, with filtration through DK-NF membrane. Fouling investigations revealed that the fouling of GH-UF, DK-NF and DL-NF membranes is more likely affected by cake/gel layer formation (surface coverage) while that of PT-UF membrane could be partly attributable to pore blockage and adsorption of HMW organics.

All UF and NF membranes tested except PT-UF membrane (having 5000 Da rejection size) were found to be suitable for the elimination of NOM from a surface water in low DOC and SUVA character. Whereas rejection efficiencies of organic matter in terms of DOC and UV_{254} absorbance were all over 90%, LMW organics could be removed up to 30%. Apparently, NF membranes led to higher rejection of NOM and correspondingly higher reduction of DBPs precursors than those of UF membranes.

Increasing Br^-/DOC ratio with decreasing organic content of water led to dominance of brominated species over chlorinated ones especially among THM species. Increase in brominated species in permeates corresponding to feed water revealed that bromide rejection is insignificant during to membrane process independent on membrane type.

CHAPTER 7

CONCLUSIONS

This study systematically investigated the impacts of low-bromide and low NOM levels on the formations and speciations of DBPs. The applicability of surrogate parameters (i.e., SUVA and ΔUVA spectroscopy), shown to be well correlated with DBP formation in the literature, was investigated in terms of the estimation of DBPs formations were put forward. Besides, the performances of UF and NF membranes for removal of DBP precursors were presented. Two low-SUVA and low-bromide source waters (Alibeyköy and Karacaören) were utilized throughout the experimental studies. The important conclusions drawn from this study can be presented as follows:

- The majority of NOM in the tested waters, Alibeyköy and Karacaören, was found to have average MWs <2000 Da as PSS and $SUVA_{254}$ values <2 L/mg org-C.m, indicating that NOM contained dominantly LMW fractions and low aromaticity.
- In general, bulk water NOM fractions with a wide range of $SUVA_{254}$ values were obtained from Alibeyköy and Karacaören waters by batch XAD-8, XAD-4, MIEX® resin and GAC adsorption. XAD-8 resin preferentially removed high-SUVA NOM components from both waters. However, no consistent trend was found for XAD-4

resin. As UV absorbing fractions were preferentially removed by GAC in Alibeyköy water, no consistent trend was observed with respect to fractionation based on SUVA. MIEX® resin also preferentially removed higher UV-absorbing fractions in Alibeyköy water although the extent of fractionation based on SUVA was not as large as that obtained by the GAC.

- In all fractions, concentrations of THMs were generally higher than those of HAAs in chlorinated raw waters and NOM fractions. Chlorinated species dominated over brominated ones in low level bromide concentration in both Alibeyköy and Karacaören waters (<40 and <20 µg/L, respectively), a consistent trend found for both THMs and HAAs. Chloroform and dichloroacetic acid were the most abundant THM and HAA species, respectively. In higher bromide concentrations (500 µg/L), chloroform and dichloroacetic acid were shifted to bromoform and dibromo acetic acid in Alibeyköy water.
- Mass balance calculations on halogens using THMs, HAAs and AOX data indicated that significant amounts of either identifiable or unidentifiable halogenated by-products (>50% of AOX) other than THMs and HAAs were formed in the both of tested waters with low bromide concentrations. However, the contribution of halogens in THMs and HAAs to AOX was significantly higher, i.e., values as high as 84% were found at 500 µg/L bromide.
- No correlations were found between SUVA and DBP (THMs, HAAs and AOX) formations in the fractions of Alibeyköy and Karacaören waters. Furthermore, SUVA also did not correlate with the formations of any THM or HAA species in either water source. Apparently, capability of SUVA for prediction of the DBP formation is weak in waters with low-SUVA values and containing LMW NOM fractions.

- The destruction in UV_{254} absorbance after chlorination (i.e., differential UV spectroscopy) did not correlate with total THM or HAA formations in both of the tested waters. Same trend was also observed for single THM and HAA species, indicating that the formation of THMs and HAAs were not directly dependent on the destruction in UV_{254}-absorbing sites after chlorination.
- All tested UF (PT-UF, GH-UF) and NF (DK-NF, DL-NF) membranes except PT-UF membrane (having 5000 Da rejection size) were found to be suitable for the elimination of NOM from a surface water in low DOC and SUVA character. Whereas rejection efficiencies of organic matter in terms of DOC and UV_{254} absorbance were all over 90%, LMW organics could be removed up to 30%. Apparently, NF membranes led to higher rejection of NOM and correspondingly higher reduction of DBP precursors than those of UF membranes.
- Fouling investigations revealed that the fouling of GH-UF, DK-NF and DL-NF membranes is more likely affected by cake/gel layer formation (surface coverage) while that of PT-UF membrane could be partly attributable to pore blockage and adsorption of HMW organics.
- Increasing Br/DOC ratio with decreasing organic content of water led to dominance of brominated species over chlorinated ones especially among THM species. Increase in brominated species in permeates corresponding to feed water revealed that bromide rejection is insignificant during to membrane process independent of membrane type.

CHAPTER 8

RECOMMENDATION

The disinfection of drinking water in public facilities primarily uses chemical disinfectants such as chlorine, ozone, chlorine dioxide, chloramines. Although more than 500 DBPs have been reported in the literature for these disinfectants used as well as their combinations, only small percentage of these DBPs has been quantified in drinking waters. Most of the studies in the literature have focused on formation of THMs and HAAs and relation of certain surrogate parameters to quantify and predict their formation. However, many other groups of organic compounds are formed in chlorinated waters: halogenated ketones, aldehydes, acetonitriles, and nitromethanes. Moreover, new generation DBPs such as halonitromethanes, iodo-acids, iodo-THMs, brominated forms of mixed-halogens and bromoamides have gained interests.

In this study, THMs and HAAs among DBPs were quantified in low-SUVA and low-bromide waters. Additionally, AOX, adsorbable portion of organic halides, was investigated. However, mass balance calculations on halogens using THMs, HAAs and AOX data indicated that significant amounts of either identifiable or unidentifiable halogenated by-products (>50% of AOX) other than THMs and HAAs were formed in NOM fractions of tested waters having low-SUVA and low-bromide concentration.

Therefore, further investigation is necessary to determine and quantify these unknown DBPs in waters with low-SUVA and low-bromide levels and to link the formation of such unknown DBPs to surrogate parameters. Additionally, the formation mechanisms and their stability of these unknown DBPs in distribution systems should be studied.

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APPENDIX A

ADDITIONAL INFORMATION FOR MATERIALS AND METHODS

This appendix provides supplementary information for the experimental procedure that includes calibration curves.

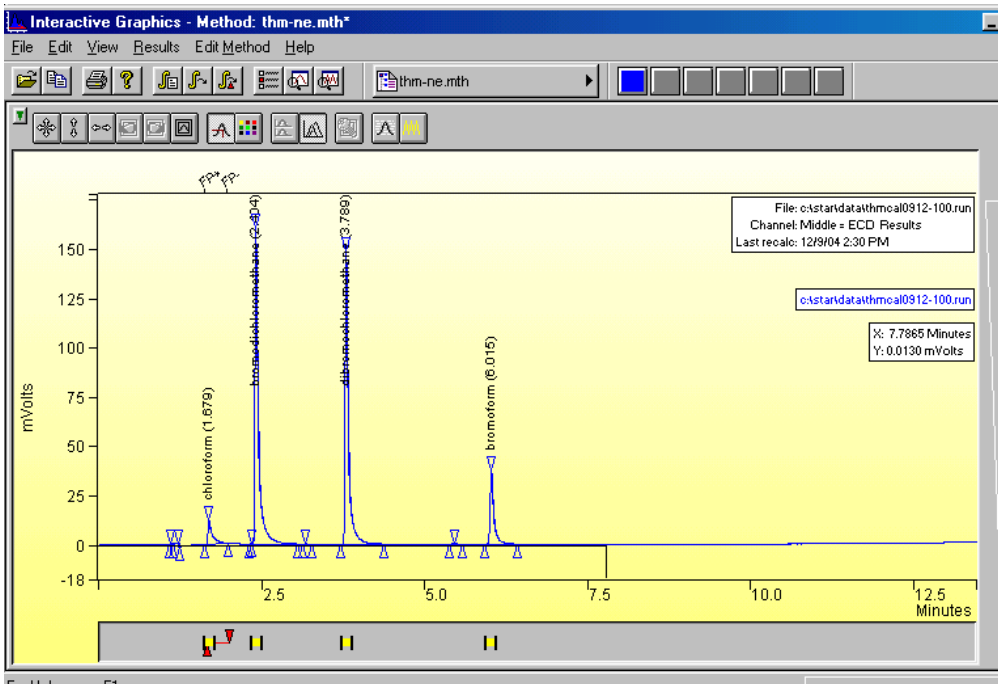

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Figure A.1. A representative chromatogram of a 250 µg/L standard of THMs.

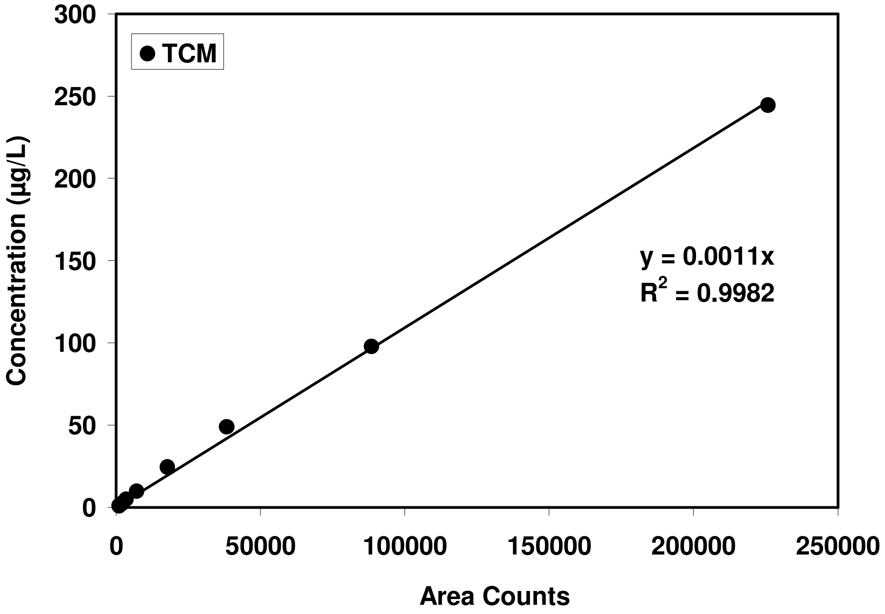

Figure A.2. A representative calibration curve of Chloroform.

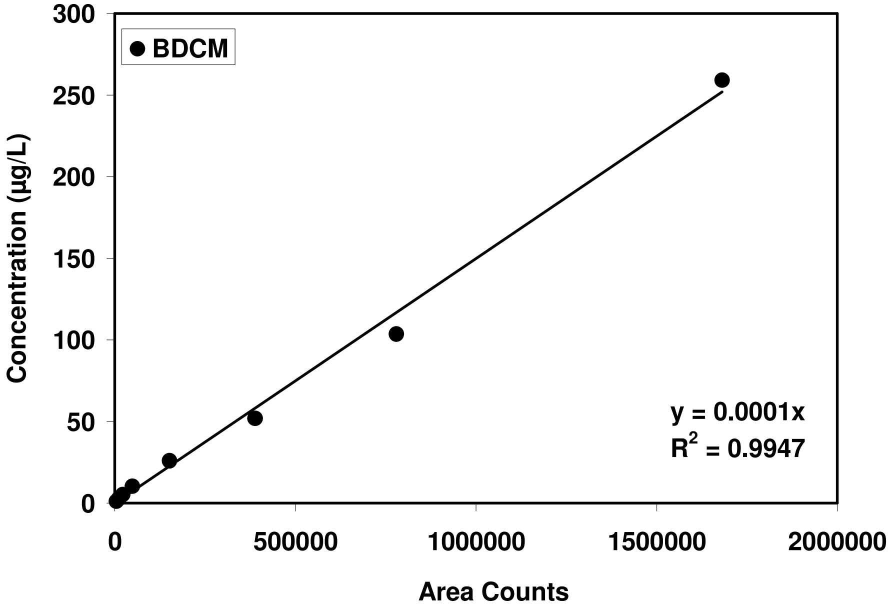

Figure A.3. A representative calibration curve of Bromodichloromethane.

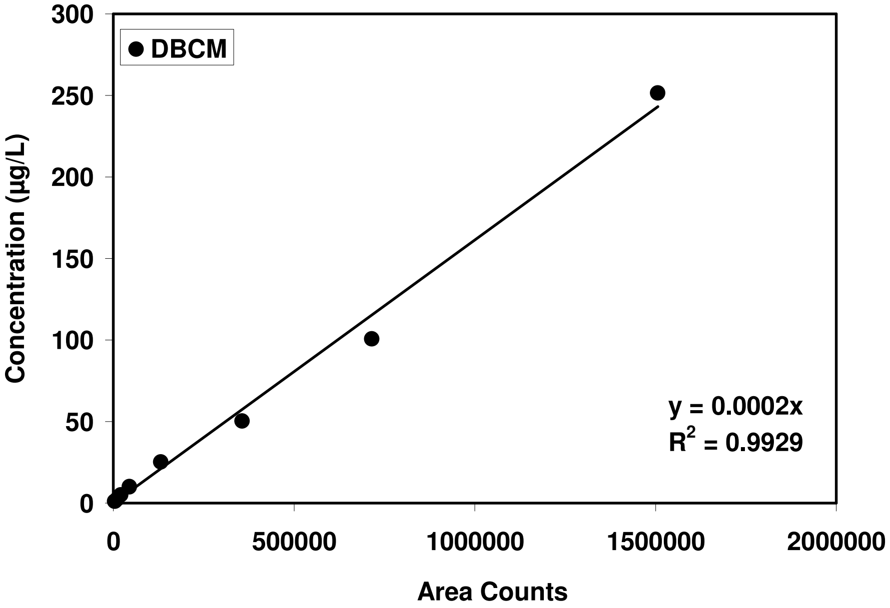

Figure A.4. A representative calibration curve of Dibromochloromethane.

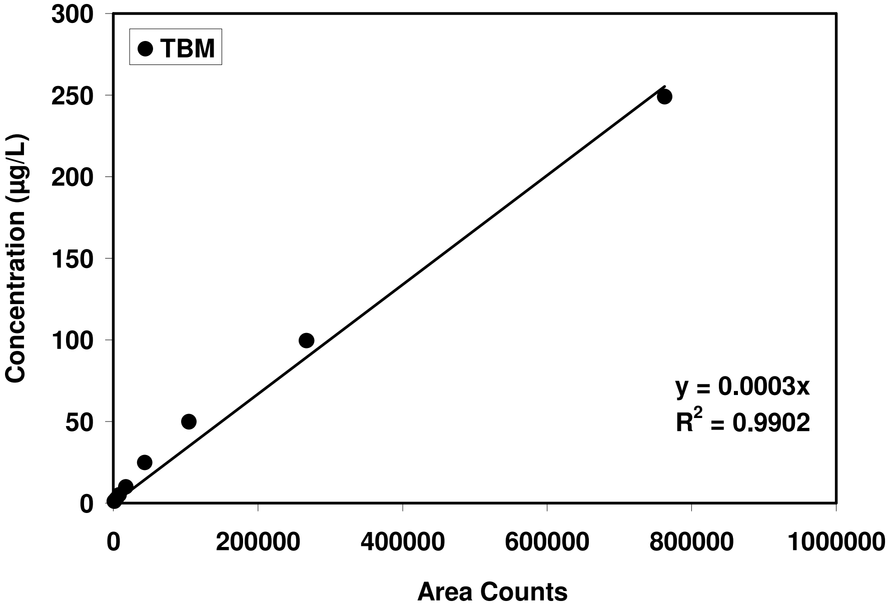

Figure A.5. A representative calibration curve of Bromoform.

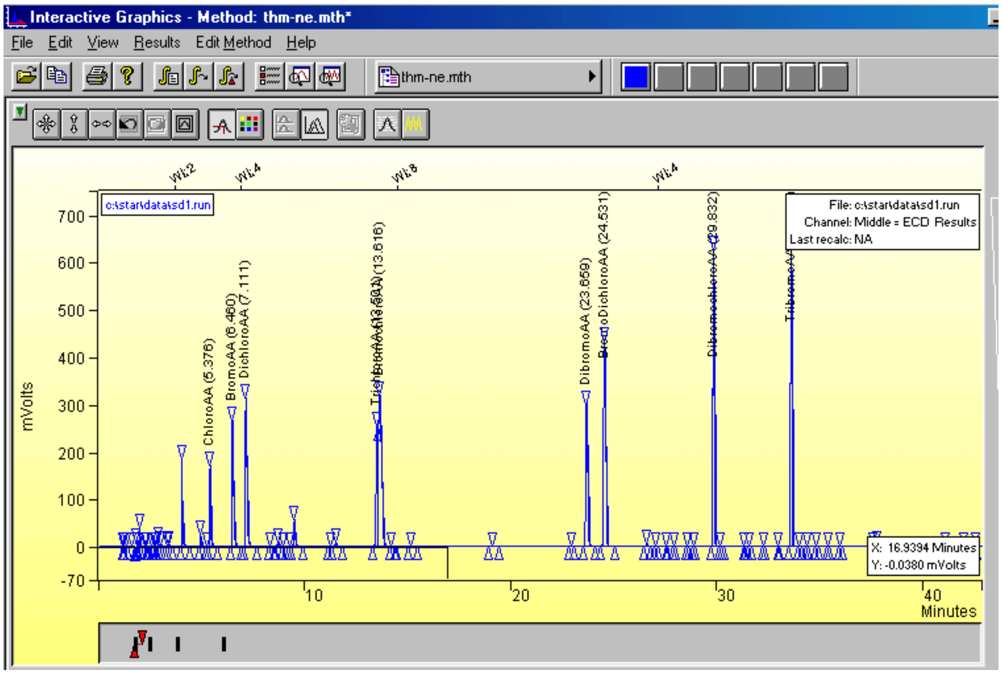

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Figure A.6. A representative chromatogram of a 600 µg/L standard of HAAs.

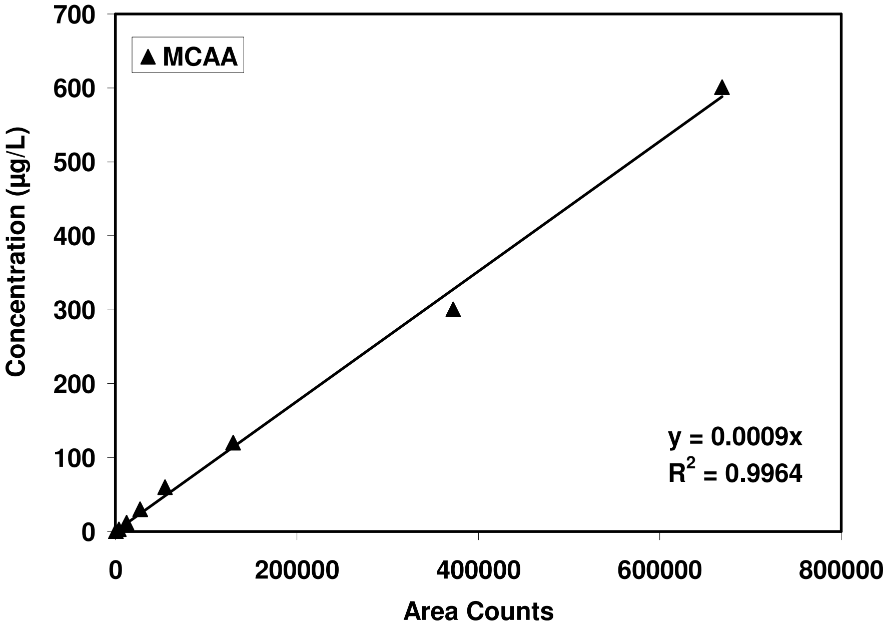


Figure A.7. A representative calibration curve of Monochloroacetic Acid.

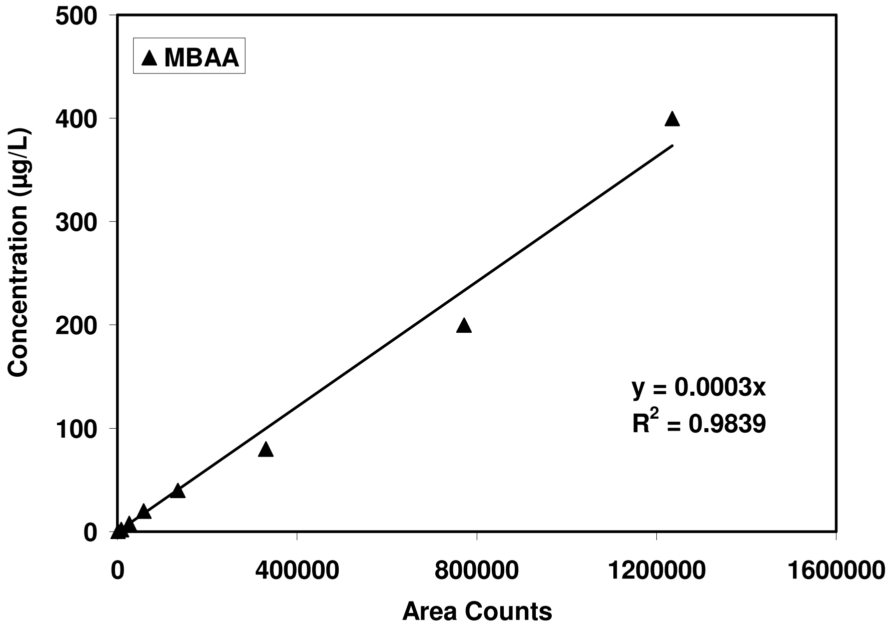


Figure A.8. A representative calibration curve of Monobromoacetic Acid.

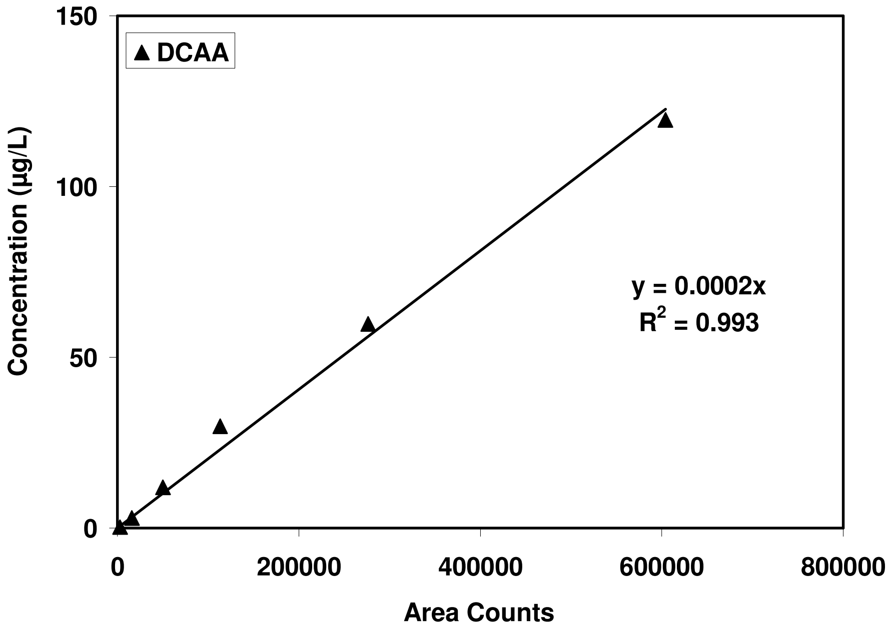


Figure A.9. A representative calibration curve of Dichloroacetic Acid.

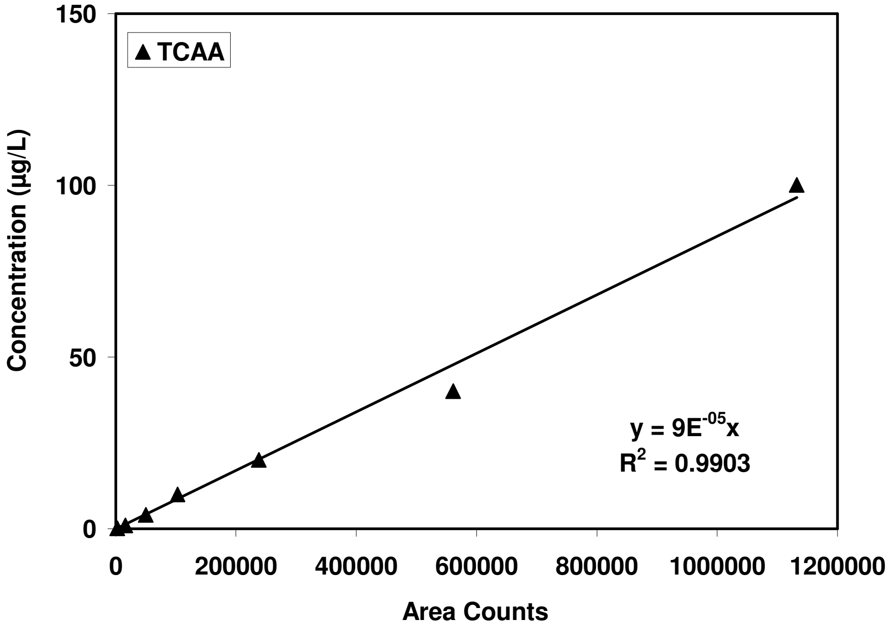


Figure A.10. A representative calibration curve of Trichloroacetic Acid.

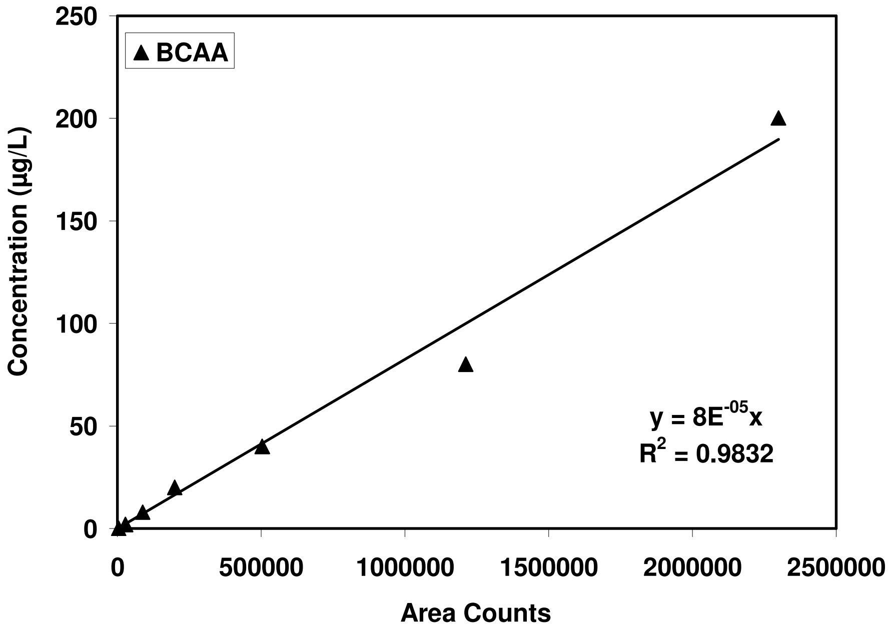


Figure A.11. A representative calibration curve of Bromochloroacetic Acid.

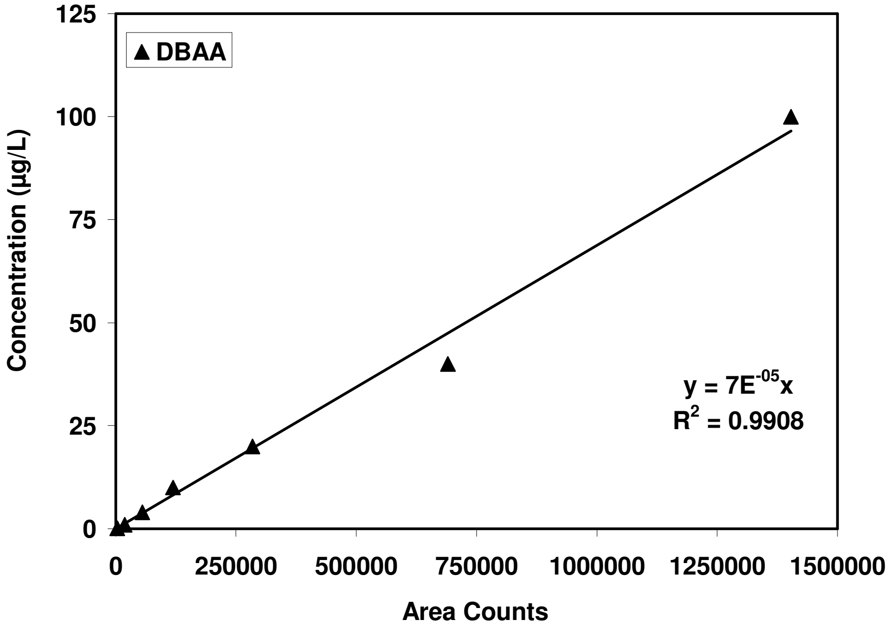


Figure A.12. A representative calibration curve of Dibromoacetic Acid.

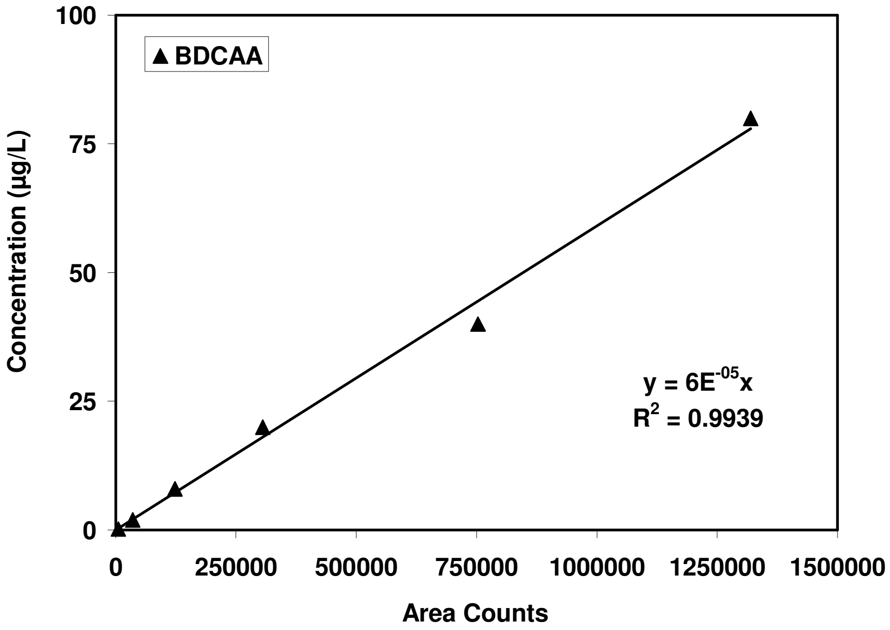


Figure A.13. A representative calibration curve of Bromodichloroacetic Acid.

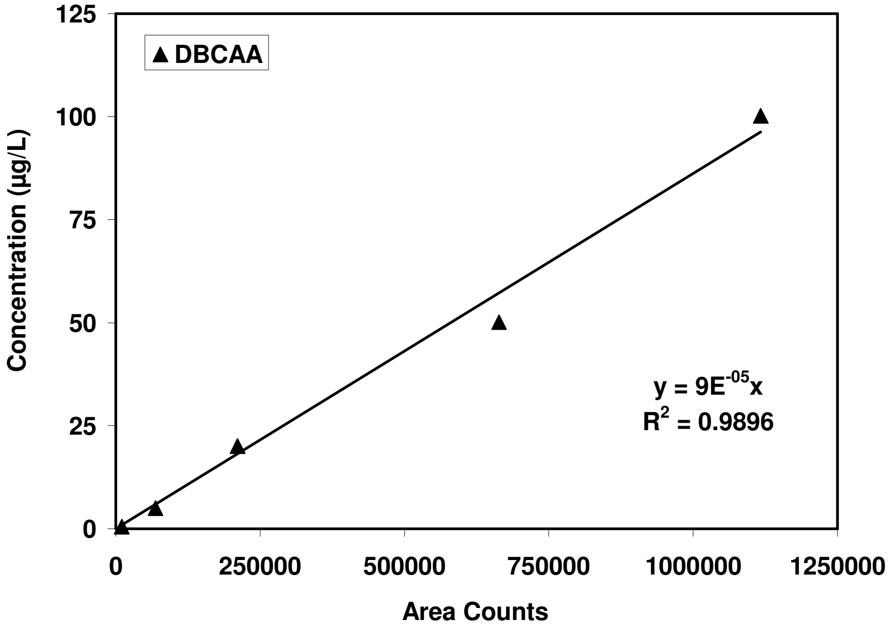


Figure A.14. A representative calibration curve of Dibromochloroacetic Acid.

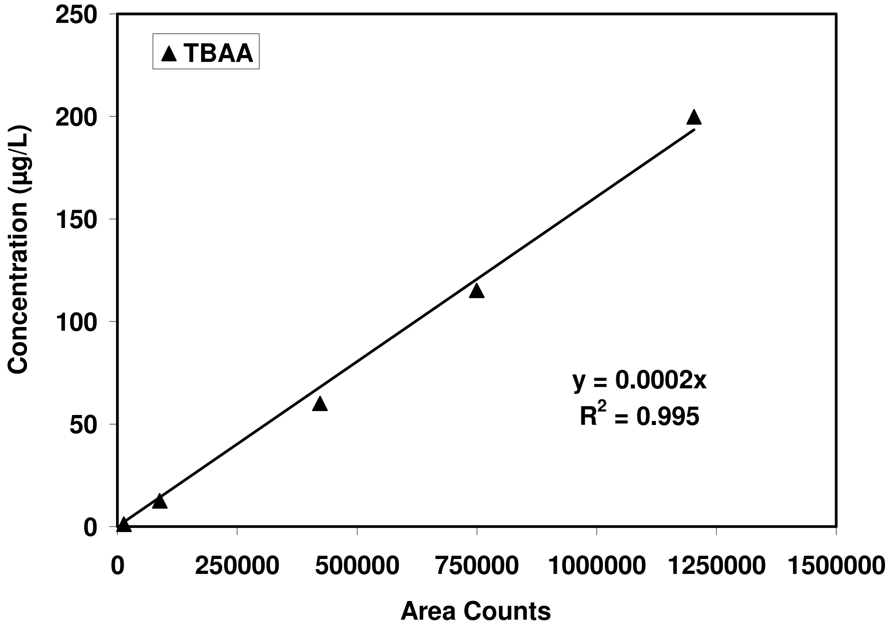
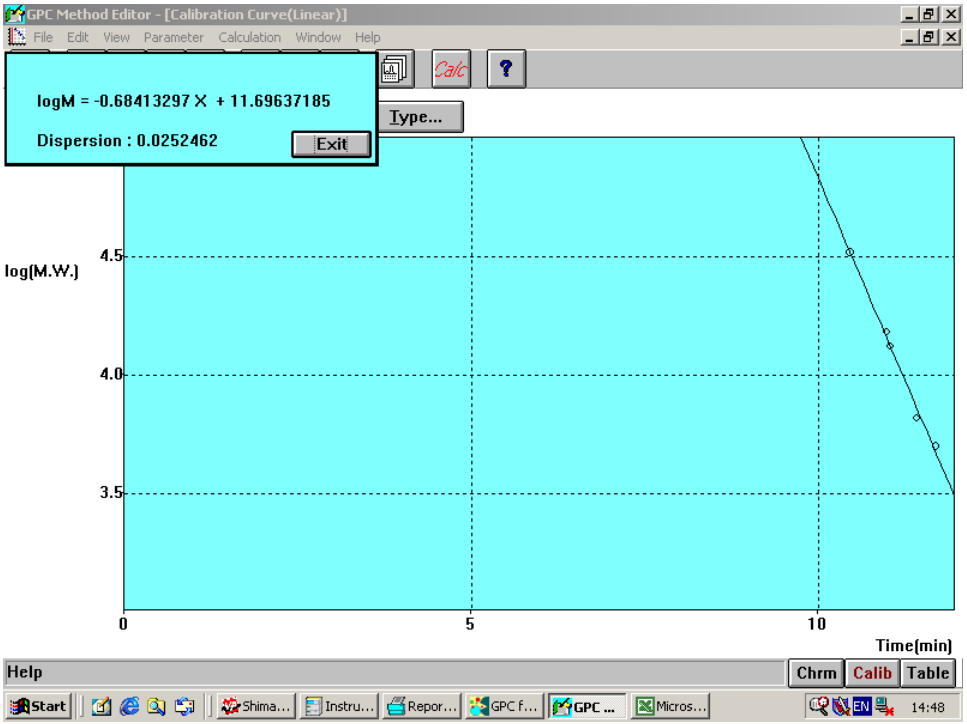


Figure A.15. A representative calibration curve of Tribromoacetic Acid.



logM = -0.68413297 X + 11.69637185

Dispersion : 0.0252462

Figure A.16. Calibration curve for MWD.

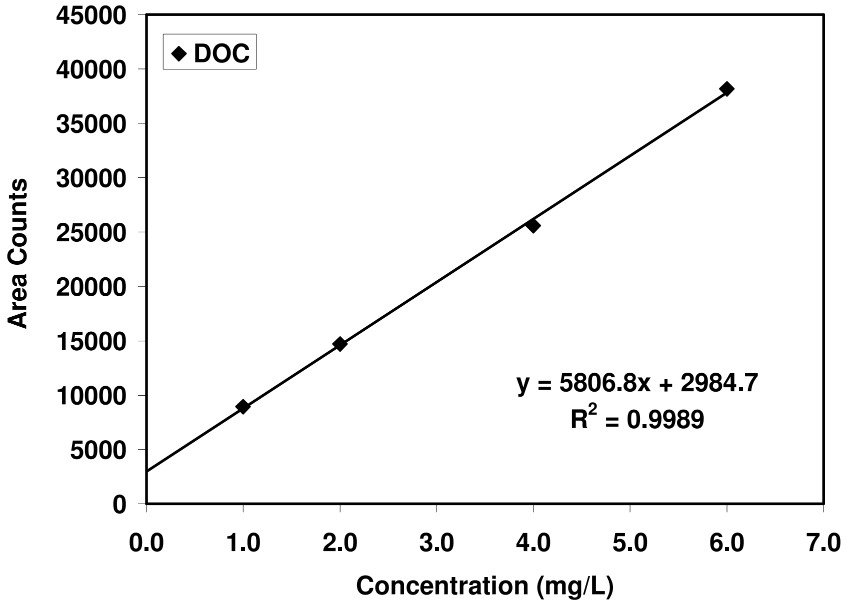


Figure A.17. A representative calibration curve for DOC measurement.

APPENDIX B

ADDITIONAL INFORMATION FOR RESUTS AND DISCUSSION

This appendix provides supporting figures and tables for discussion of results in Chapters 4, 5 and 6.

Table B.1. SUVA values and formations of DBPs in all Alibeyköy fractions*

	SUVA (L/mg org C-m)	THM (µg/L)	HAA (µg/L)	AOX (µg/L)
XAD-8	1.99	36	22.3	85
	1.85	41	21.8	88
	1.86	34	25.7	118
	2.31	31	22.9	143
	2.07	38	26.7	77
	1.93	53	27.7	162
	1.82	45	25.9	125
	2.12	46	24.9	180
	1.76	47	24.7	118
	0.70	39	24.5	51
XAD-4	1.76	52	20.4	121
	1.80	55	19.2	70
	2.17	66	22.1	143
	1.89	62	21.7	96
	1.68	53	18.2	151
	1.75	63	18.3	81
	1.80	62	21.7	88
	1.87	73	22.8	143
	1.61	64	20.7	151
	1.05	75	21.8	118
GAC	2.11	53	29.9	279
	2.08	52	31.7	246
	1.95	45	36.4	224
	1.77	48	36.7	257
	1.41	53	32.3	55
	1.18	53	28	129
	0.74	26	26.3	37
	1.03	38	27.7	62
	0.71	24	28.6	103
	0.45	20	26.5	33
	0.44	10	13.1	26
	0.41	22	16.4	40
	0.34	7	10.4	29
MIEX	1.21	43	37.2	62
	1.23	39	36.6	70
	1.13	42	30.4	140
	1.32	42	36.1	73
	1.15	52	31.6	224
	1.16	50	38	96
	1.18	45	34.4	73
	1.19	44	34.4	169
	1.13	37	37.8	353
	1.05	47	34.2	235
	1.11	42	35.8	246
	1.12	34	30.9	92

* SUVA values were measured after dilution of all fractions.

Table B.2. SUVA values and formations of DBPs in all Karacaören fractions*

	SUVA (L/mg org C-m)	THM (µg/L)	HAA (µg/L)	AOX (µg/L)
XAD-8	2.10	14	7	66
	2.70	20	8	59
	2.70	22	7	81
	2.70	21	10	143
	2.80	21	10	40
	2.60	22	11	73
	2.50	21	11	99
	2.30	18	10	51
	2.20	19	9	29
	2.30	15	7	18
	2.00	17	9	136
XAD-4	2.30	15	10	40
	2.48	17	9	18
	2.12	15	9	17
	2.36	18	10	15
	2.44	18	10	48
	2.86	21	10	33
	2.80	20	8	81
	2.70	21	9	107
	2.80	21	8	114
	2.64	22	8	129
	2.72	20	8	143
GAC	1.76	12	5	29
	1.78	16	6	26
	2.08	16	5	81
	2.66	16	4	55
	1.64	14	6	48
	1.90	17	6	37
	1.54	13	5	37
	1.82	17	4	22
	1.94	11	6	44
	1.07	9	5	15
	1.06	10	6	33
	1.52	10	3	15
	1.83	10	3	15
	1.95	10	2	26
	1.82	8	3	55
	0.78	7	3	54

* SUVA values were measured after dilution of all fractions.

Table B.3. Formation of THM species (µg/L) in all Alibeyköy fractions*

	TCM	BDCM	DBCM	TBM
XAD-8	18.6	8.4	7.0	1.8
	22.9	9.7	7.0	1.6
	17.2	8.5	6.9	1.6
	15.6	7.6	6.5	1.5
	20.3	8.6	7.0	1.6
	29.4	12.4	9.2	2.4
	23.3	10.9	8.5	2.2
	22.3	10.6	9.6	3.0
	21.9	12.3	9.5	3.0
	24.8	7.2	5.2	1.5
XAD-4	28.0	12.5	9.1	2.1
	32.0	11.8	8.8	2.1
	34.2	17.5	11.9	2.8
	36.7	14.3	9.4	1.9
	31.5	11.1	8.1	1.9
	34.8	15.4	10.2	2.4
	34.2	15.7	10.1	2.4
	39.3	19.1	11.8	2.7
	32.0	17.2	11.9	3.2
	37.0	24.8	10.4	2.8
GAC	26.5	13.2	11.2	2.3
	20.5	13.9	13.8	3.4
	16.7	12.3	12.8	3.3
	11.6	13.1	17.0	5.8
	12.5	17.3	17.2	5.6
	9.4	17.6	18.4	7.3
	4.4	11.7	5.3	5.0
	4.0	11.6	15.1	7.4
	5.2	8.7	4.8	4.9
	3.7	5.6	6.8	3.7
	2.5	0.3	0.6	6.2
	2.6	0.4	13.1	6.2
	2.5	0.3	0.7	3.7
MIEX	19.8	13.0	8.0	1.8
	15.2	12.4	9.1	2.5
	13.3	12.4	11.6	4.2
	16.8	13.5	8.9	2.8
	17.5	19.6	11.4	3.6
	32.4	11.5	5.2	1.2
	14.4	15.6	10.7	3.9
	18.4	15.7	7.8	2.2
	14.8	12.5	7.4	2.4
	21.1	14.7	8.9	2.7
	26.7	10.5	4.3	0.9
	23.1	8.0	3.3	0.0

*THM species; chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM).

Table B.4. Formation of HAA species (µg/L) in all Alibeyköy fractions*

	CAA	BAA	DCAA	TCAA	BCAA	DBAA	BDCAA	DBCAA	TBAA
XAD-8	0.7	0.2	8.7	0.7	8.2	1.7	0.9	1.0	0.2
	1.2	0.2	9.5	0.8	6.5	1.6	0.9	0.9	0.2
	1.5	0.2	10.1	1.1	8.2	1.8	1.3	1.3	0.2
	1.0	0.2	9.0	1.0	7.6	1.6	1.2	1.2	0.1
	4.4	0.2	8.9	1.0	7.7	1.8	1.3	1.2	0.2
	4.4	0.2	9.4	0.8	8.4	1.9	1.0	1.2	0.4
	3.1	0.2	9.2	1.1	7.4	1.8	1.3	1.4	0.4
	1.5	0.2	8.7	1.0	8.5	2.1	1.1	1.3	0.5
	3.5	0.1	8.9	1.3	6.6	1.6	1.1	1.2	0.4
	5.2	0.2	8.7	1.6	5.5	1.1	1.0	0.9	0.3
XAD-4	2.1	0.3	7.6	0.8	6.0	1.3	1.0	1.0	0.3
	1.9	0.1	7.6	1.5	5.6	1.1	0.6	0.6	0.2
	0.8	0.1	9.4	0.9	7.1	1.6	0.9	1.0	0.3
	1.2	0.1	10.1	1.6	5.8	1.2	0.8	0.7	0.2
	0.4	0.1	7.4	0.7	6.2	1.5	0.8	0.8	0.3
	0.7	0.1	7.2	0.6	6.4	1.5	0.8	0.8	0.2
	1.4	0.1	8.9	0.8	6.7	1.5	1.0	1.1	0.2
	2.2	0.1	8.6	0.7	6.8	1.6	1.3	1.2	0.3
	1.1	0.2	7.8	0.6	6.8	1.7	1.0	1.2	0.3
	1.5	0.2	10.3	0.7	5.9	1.8	0.1	1.0	0.3
GAC	1.8	0.2	9.4	1.0	9.6	2.2	1.3	3.1	1.3
	1.2	0.3	9.4	1.0	9.9	2.7	1.6	3.8	1.8
	1.9	0.3	9.4	1.3	10.8	2.9	2.2	5.8	1.8
	3.8	0.3	8.4	0.8	9.4	3.4	2.0	6.4	2.2
	5.5	0.3	6.4	0.7	7.6	2.7	1.6	5.6	1.9
	2.3	0.2	8.8	0.4	6.0	2.6	1.1	4.7	1.9
	2.6	0.2	7.1	0.6	5.4	2.4	1.0	4.7	2.3
	3.4	0.2	7.9	0.3	5.0	2.7	0.9	5.0	2.3
	9.2	0.3	5.7	0.4	6.4	3.5	0.3	1.8	1.0
	6.7	0.3	6.6	0.7	5.1	2.0	0.7	2.8	1.6
	3.4	0.1	3.1	0.1	2.5	1.1	0.2	1.3	1.3
	4.0	0.1	4.5	0.3	2.4	0.8	0.2	2.6	1.5
	2.7	0.9	1.7	0.2	2.1	0.6	0.2	1.2	0.8
MIEX	6.0	0.9	11.0	6.8	1.9	5.2	1.6	1.1	2.7
	6.0	1.2	10.0	5.4	1.8	6.2	1.6	1.3	3.1
	6.0	1.1	6.8	3.6	1.6	6.1	1.2	1.1	2.9
	6.5	1.1	10.7	5.3	1.6	5.4	1.5	1.1	2.9
	7.1	1.1	11.0	3.2	1.3	4.4	1.0	0.8	1.7
	7.4	1.3	10.3	4.7	1.6	5.9	1.4	1.3	4.1
	6.1	0.7	12.2	4.9	1.3	3.8	1.3	1.0	3.1
	7.3	0.8	11.2	4.6	1.3	4.2	1.3	1.0	2.7
	6.3	1.0	10.8	7.3	1.3	4.0	1.2	0.9	5.0
	4.9	0.4	15.8	6.4	0.9	1.8	1.0	0.6	2.4
	3.9	0.5	16.7	7.7	1.0	1.9	1.1	0.7	2.3
	0.6	0.6	13.7	8.2	0.9	2.0	1.0	0.6	3.3

* HAA species; monochloro-AA (MCAA), monobromo-AA (MBAA), dichloro-AA (DCAA), trichloro-AA (TCAA), bromochloro-AA (BCAA), dibromo-AA (DBAA), bromodichloro-AA (BDCAA), dibromochloro-AA (DBCAA), tribromo-AA (TBAA).

Table B.5. Formation of THM species (µg/L) in all Karacaören fractions*

	TCM	BDCM	DBCM	TBM
XAD-8	8.9	3.3	1.4	0.0
	12.1	5.0	2.5	0.0
	13.7	5.2	2.7	0.0
	13.1	5.3	2.8	0.0
	13.1	5.2	2.5	0.0
	14.0	5.8	2.7	0.0
	12.9	5.7	2.8	0.0
	11.2	4.6	2.0	0.0
	12.2	4.4	2.0	0.0
	9.9	3.5	1.6	0.0
	11.6	3.8	1.8	0.0
XAD-4	8.5	4.1	2.1	0.0
	11.0	4.1	1.8	0.0
	10.4	3.3	1.3	0.0
	11.7	4.3	1.9	0.0
	10.3	4.6	2.6	0.0
	13.8	4.9	2.4	0.0
	12.6	4.9	2.4	0.0
	13.4	5.2	2.5	0.0
	14.0	4.9	2.3	0.0
	15.3	4.8	2.4	0.0
	13.5	4.5	2.1	0.0
GAC	9.2	1.4	1.0	0.0
	12.9	2.0	1.5	0.0
	12.0	1.9	1.9	0.1
	12.4	2.0	1.7	0.0
	9.9	1.9	1.8	0.0
	12.1	2.3	2.4	0.2
	8.9	1.9	2.3	0.2
	10.3	2.5	3.9	0.5
	6.6	2.0	2.2	0.1
	5.9	1.3	2.0	0.2
	5.8	1.8	2.4	0.2
	7.3	0.9	1.7	0.3
	7.1	0.8	1.5	0.2
	6.8	1.0	1.6	0.2
	6.5	0.7	0.9	0.1
	4.6	1.2	1.0	0.1

*THM species; chloroform (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM).

Table B.6. Formation of HAA species (µg/L) in all Karacaören fractions*

	CAA	BAA	DCAA	TCAA	BCAA	DBAA	BDCAA	DBCAA	TBAA
XAD-8	0.9	0.0	4.7	0.6	0.5	0.3	0.4	0.0	0.0
	0.9	0.0	5.0	0.7	0.7	0.4	0.5	0.0	0.0
	0.7	0.0	4.9	0.6	0.3	0.5	0.4	0.0	0.0
	0.8	0.0	6.6	0.8	0.4	0.6	0.5	0.0	0.0
	0.8	0.0	6.5	0.6	0.6	0.5	0.5	0.0	0.0
	1.2	0.0	6.8	1.1	0.6	0.4	0.6	0.0	0.0
	1.1	0.0	6.8	1.0	0.4	0.6	0.7	0.0	0.0
	1.0	0.0	6.5	0.8	0.6	0.4	0.7	0.0	0.0
	1.0	0.0	5.5	0.5	0.6	0.4	0.5	0.0	0.0
	0.8	0.0	4.7	0.6	0.4	0.4	0.5	0.0	0.0
	1.1	0.0	5.7	0.9	0.5	0.5	0.5	0.0	0.0
XAD-4	1.1	0.0	5.9	0.8	0.8	0.6	0.6	0.0	0.0
	1.0	0.0	6.0	1.0	0.2	0.5	0.6	0.0	0.0
	1.0	0.0	5.8	1.1	0.4	0.3	0.5	0.0	0.0
	1.0	0.0	6.1	0.8	0.6	0.5	0.5	0.0	0.0
	1.2	0.0	5.8	0.6	0.7	0.7	0.6	0.0	0.0
	0.8	0.0	6.0	0.8	0.9	0.6	0.5	0.0	0.0
	0.8	0.0	4.8	0.7	0.8	0.6	0.5	0.0	0.0
	1.0	0.0	5.4	0.7	0.8	0.6	0.5	0.0	0.0
	0.7	0.0	4.7	0.7	0.5	0.4	0.5	0.0	0.0
	0.3	0.0	5.2	0.5	1.1	0.6	0.4	0.0	0.0
	0.6	0.0	5.3	0.2	0.9	0.4	0.4	0.0	0.0
GAC	0.4	0.0	2.5	0.7	0.5	0.2	0.2	0.1	0.3
	0.4	0.0	2.9	0.9	0.8	0.2	0.3	0.1	0.3
	0.9	0.0	2.1	0.5	0.8	0.4	0.2	0.1	0.3
	0.6	0.0	1.8	0.4	0.3	0.1	0.1	0.1	0.3
	0.5	0.0	2.7	0.8	0.9	0.3	0.3	0.2	0.4
	0.4	0.0	2.6	0.7	0.9	0.4	0.3	0.2	0.3
	0.4	0.0	2.0	0.6	0.8	0.4	0.2	0.2	0.3
	0.3	0.0	1.9	0.3	0.6	0.5	0.2	0.2	0.3
	0.3	0.0	2.4	0.6	0.8	0.6	0.3	0.2	0.3
	0.7	0.0	1.3	0.5	0.6	0.8	0.2	0.3	0.4
	0.5	0.0	2.0	0.6	0.7	0.7	0.3	0.3	0.4
	0.5	0.0	0.6	0.2	0.3	0.4	0.1	0.2	0.4
	0.5	0.0	0.7	0.3	0.4	0.3	0.2	0.2	0.4
	0.4	0.0	0.5	0.2	0.2	0.2	0.1	0.1	0.3
	0.2	0.0	1.2	0.5	0.2	0.1	0.1	0.1	0.1
	0.2	0.0	1.2	0.5	0.2	0.1	0.1	0.1	0.1

* HAA species; monochloro-AA (MCAA), monobromo-AA (MBAA), dichloro-AA (DCAA), trichloro-AA (TCAA), bromochloro-AA (BCAA), dibromo-AA (DBAA), bromodichloro-AA (BDCAA), dibromochloro-AA (DBCAA), tribromo-AA (TBAA).

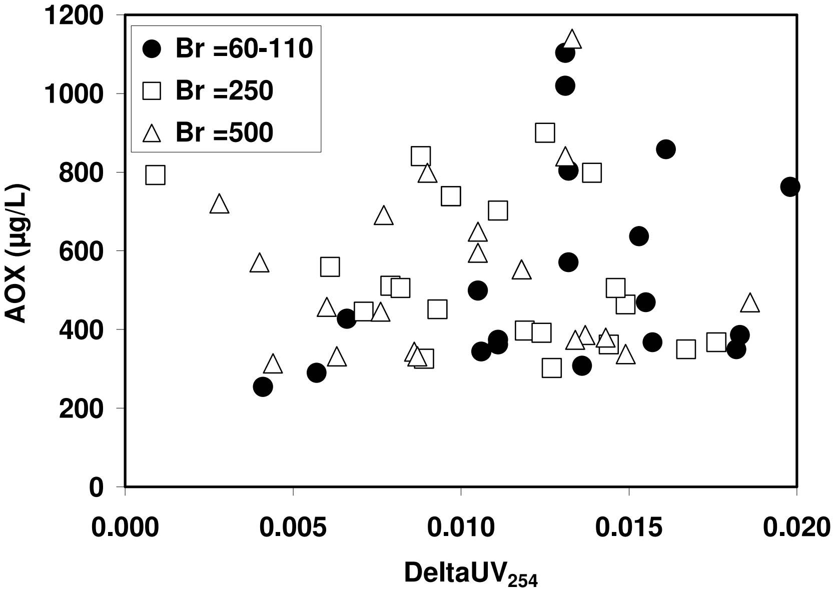


Figure B.1. Relations between AOX formation and ΔUV (differential UV spectroscopy) of all NOM fractions at different bromide levels.

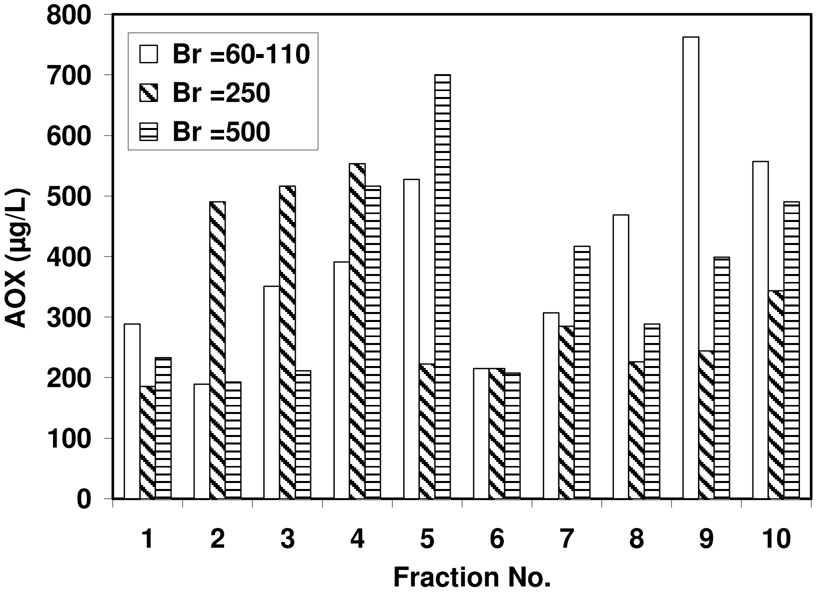


Figure B.2. The impact of bromide concentrations on AOX formation of NOM fractions in Alibeyköy water (XAD-8 fractions).

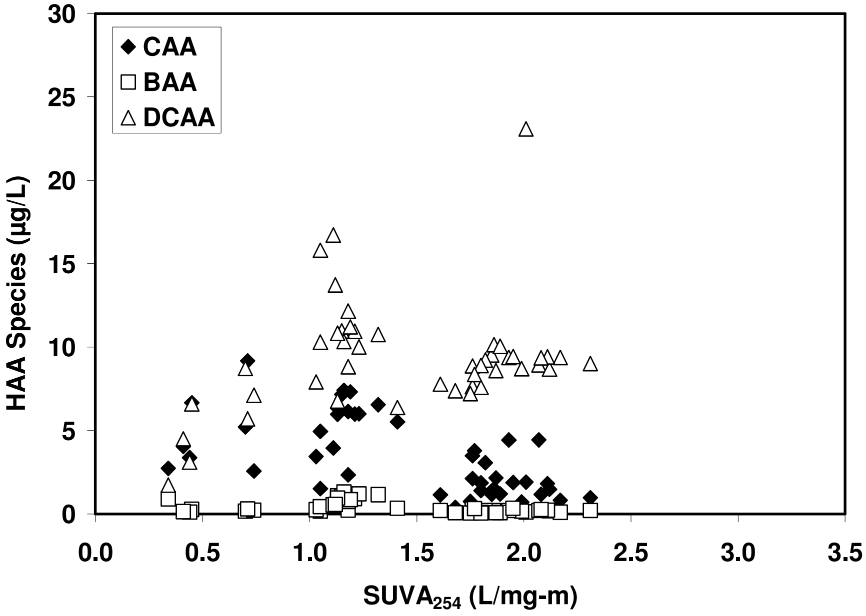


Figure B.3. The impact of SUVA on HAA species (CAA, BAA, DCAA) in all NOM fractions of Alibeyköy water.

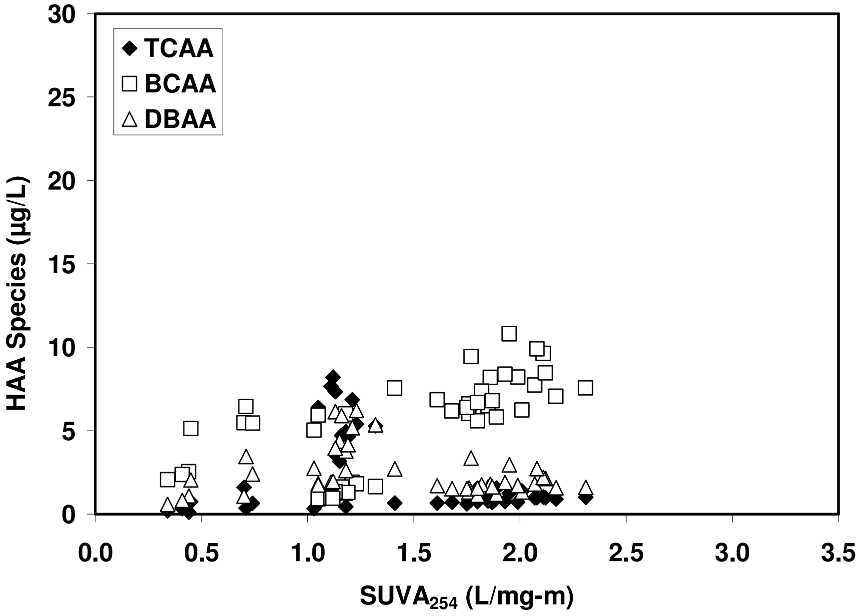


Figure B.4. The impact of SUVA on HAA species (TCAA, BCAA, DBAA) in all NOM fractions of Alibeyköy water.

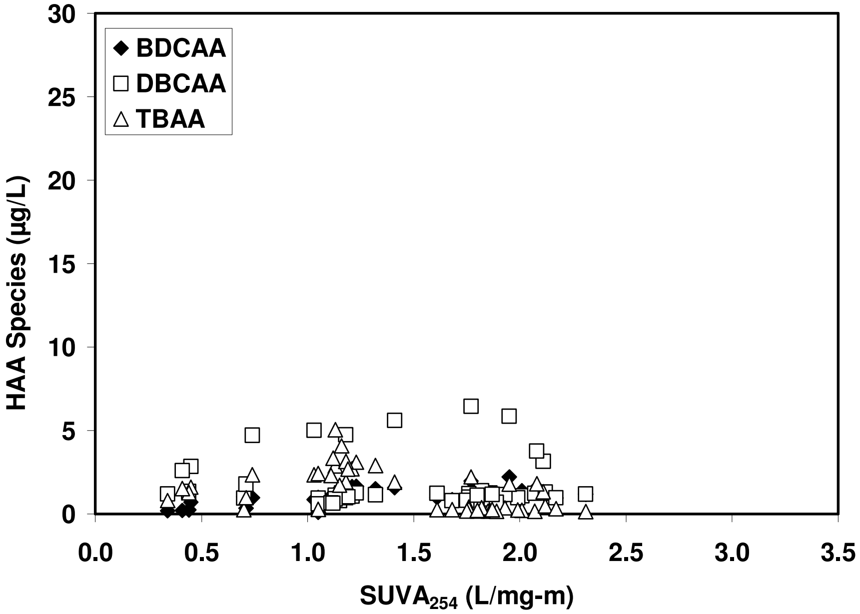


Figure B.5. The impact of SUVA on HAA species (BDCAA, DBCAA, TBAA) in all NOM fractions of Alibeyköy water.

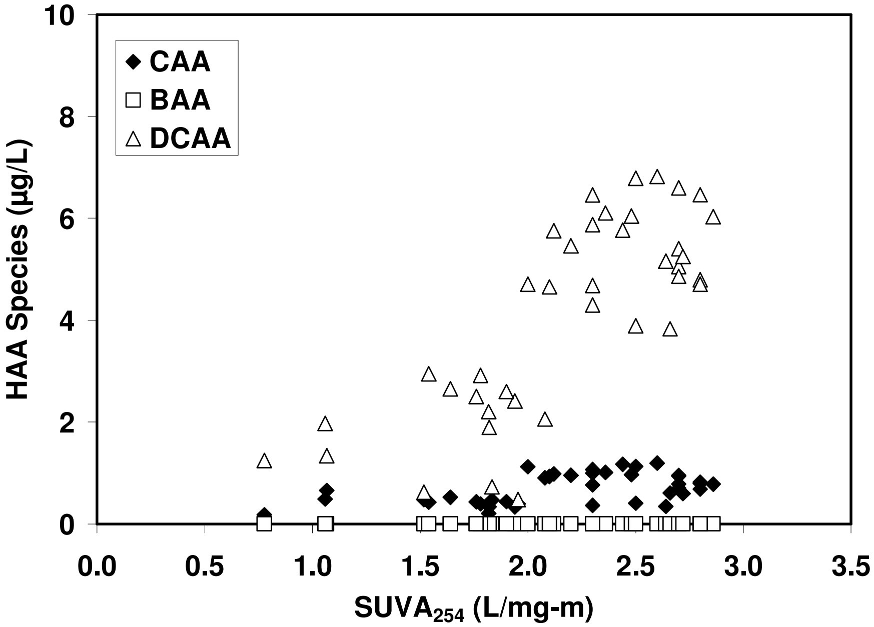


Figure B.6. The impact of SUVA on HAA species (CAA, BAA, DCAA) in all NOM fractions of Karacaören water.

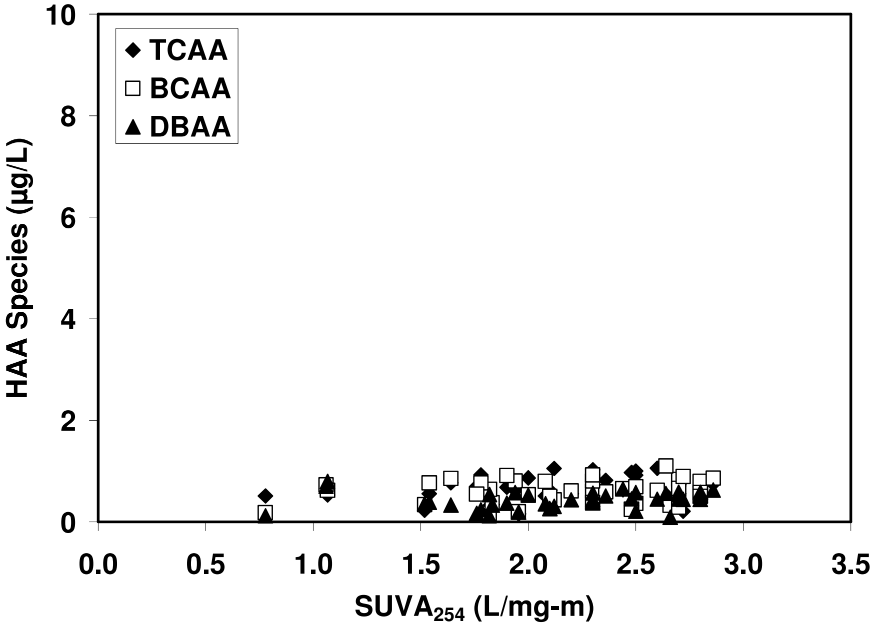


Figure B.7. The impact of SUVA on HAA species (TCAA, BCAA, DBAA) in all NOM fractions of Karacaören water.

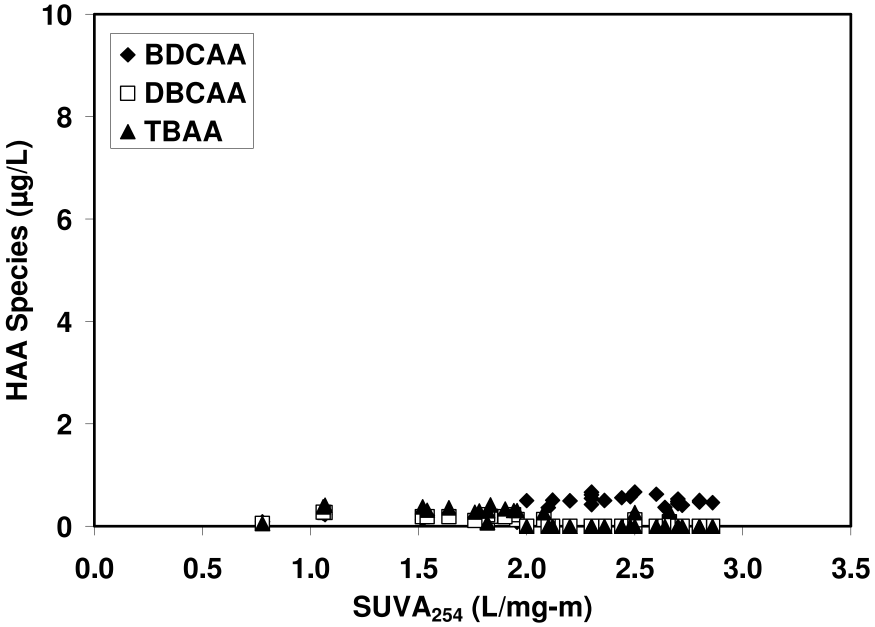


Figure B.8. The impact of SUVA on HAA species (BDCAA, DBCAA, TBAA) in all NOM fractions of Karacaören water.

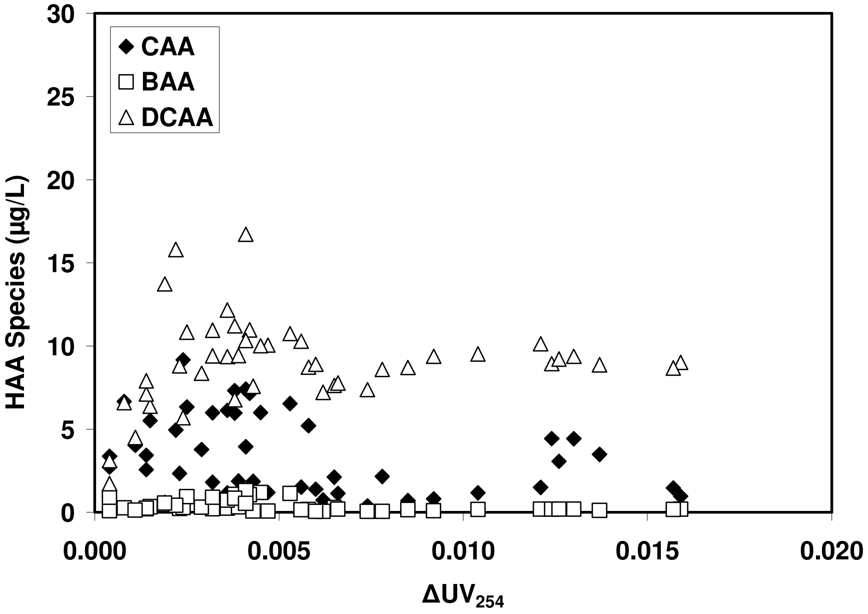


Figure B.9. The impact of ΔUV on HAA species (CAA, BAA, DCAA) in all NOM fractions of Alibeyköy water.

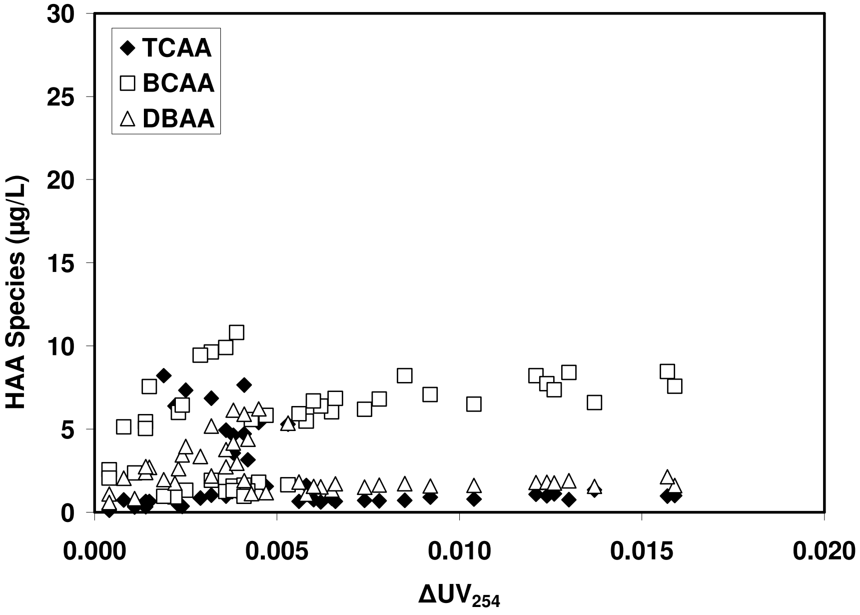


Figure B.10. The impact of ΔUV on HAA species (TCAA, BCAA, DBAA) in all NOM fractions of Alibeyköy water.

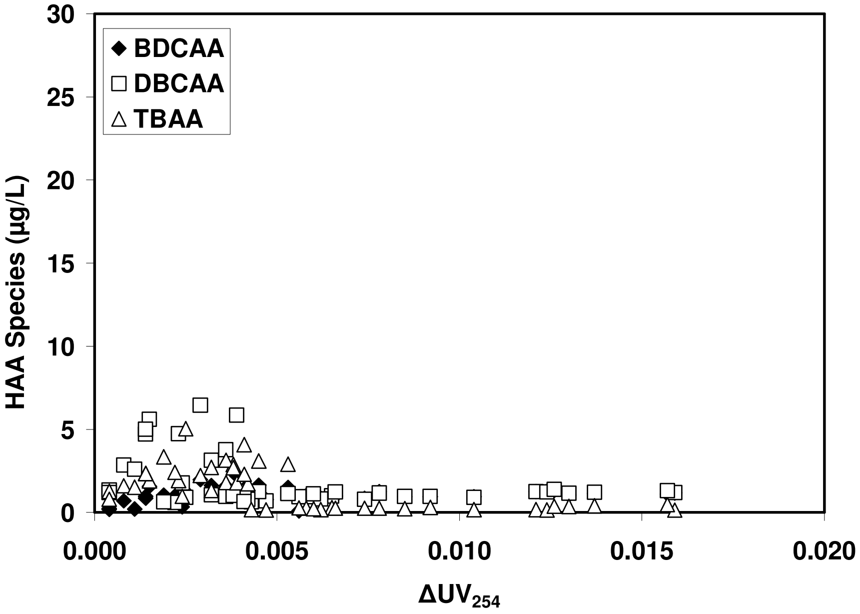


Figure B.11. The impact of ΔUV on HAA species (BDCAA, DBCAA, TBAA) in all NOM fractions of Alibeyköy water.

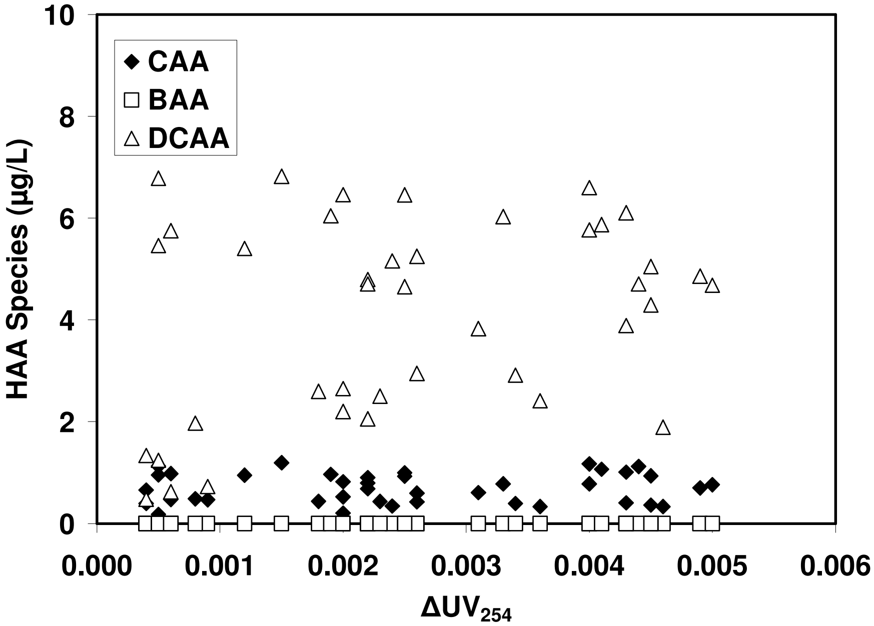


Figure B.12. The impact of ΔUV on HAA species (CAA, BAA, DCAA) in all NOM fractions of Karacaören water.

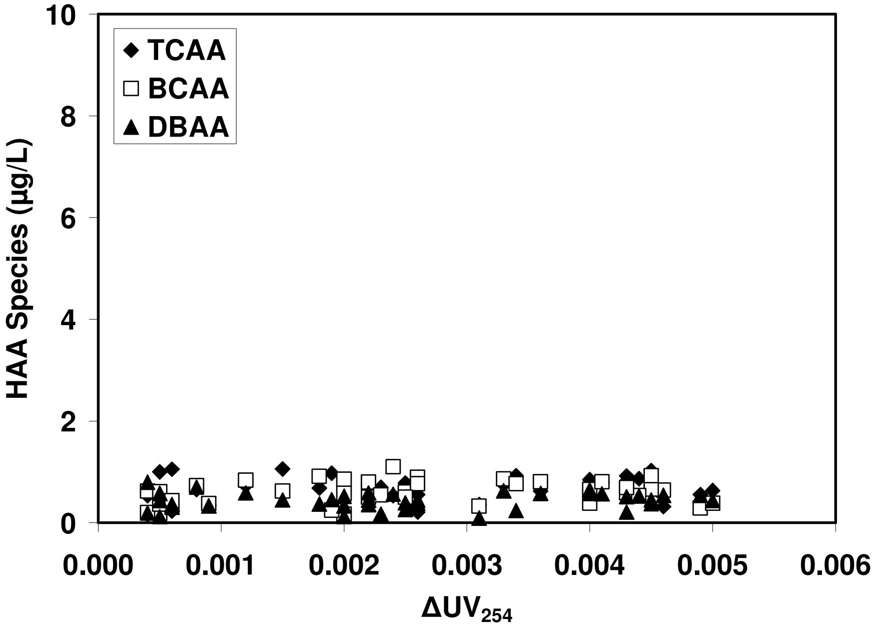


Figure B.13. The impact of ΔUV on HAA species (TCAA, BCAA, DBAA) in all NOM fractions of Karacaören water.

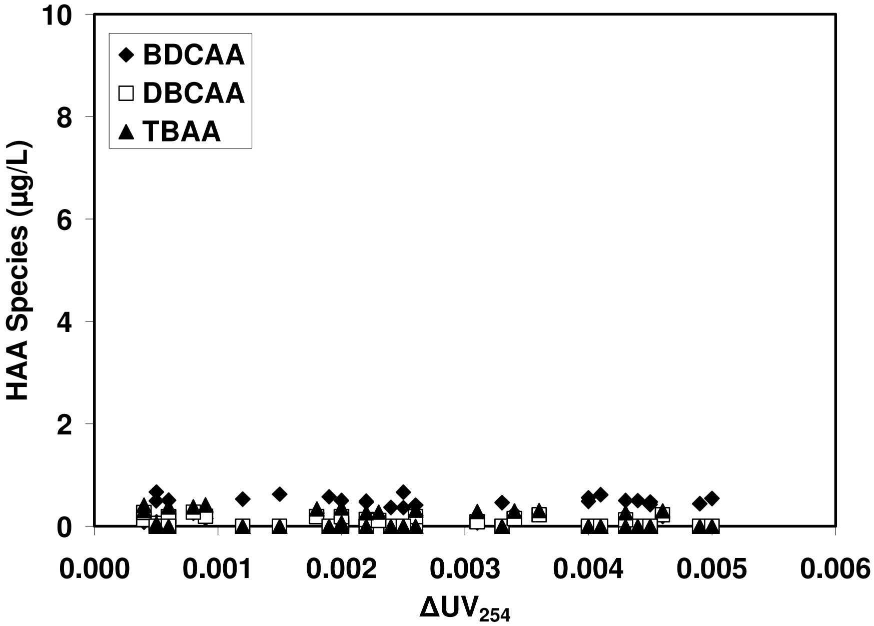


Figure B.14. The impact of ΔUV on HAA species (BDCAA, DBCAA, TBAA) in all NOM fractions of Karacaören water.

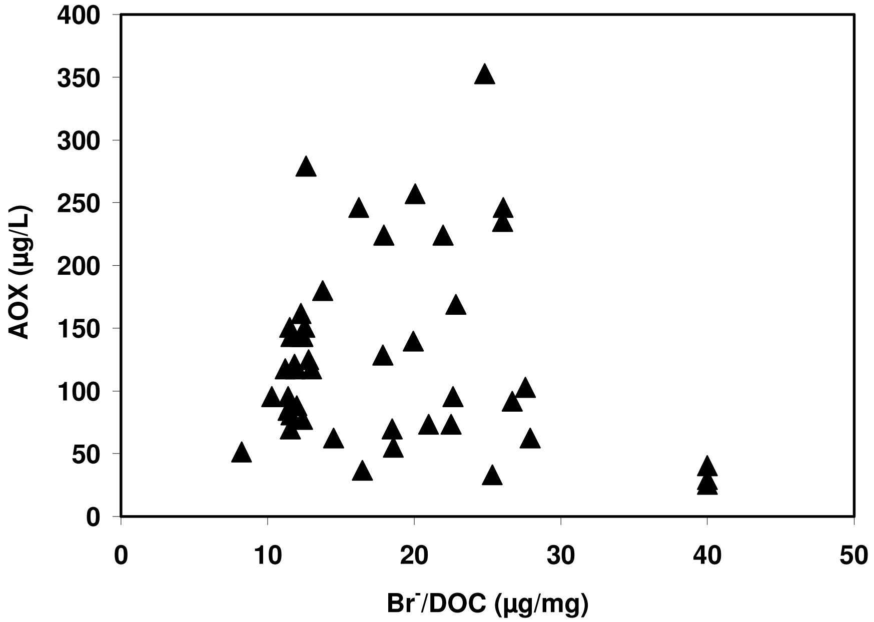


Figure B.15. The impact of bromide concentrations on AOX formation in all NOM fractions of Alibeyköy water.

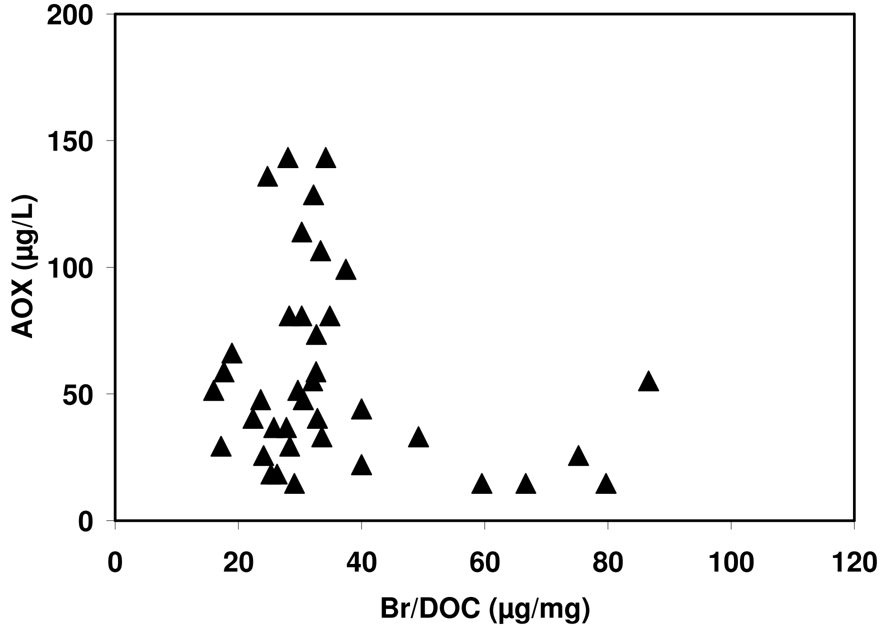


Figure B.16. The impact of bromide concentrations on AOX formation in all NOM fractions of Karacaören water.

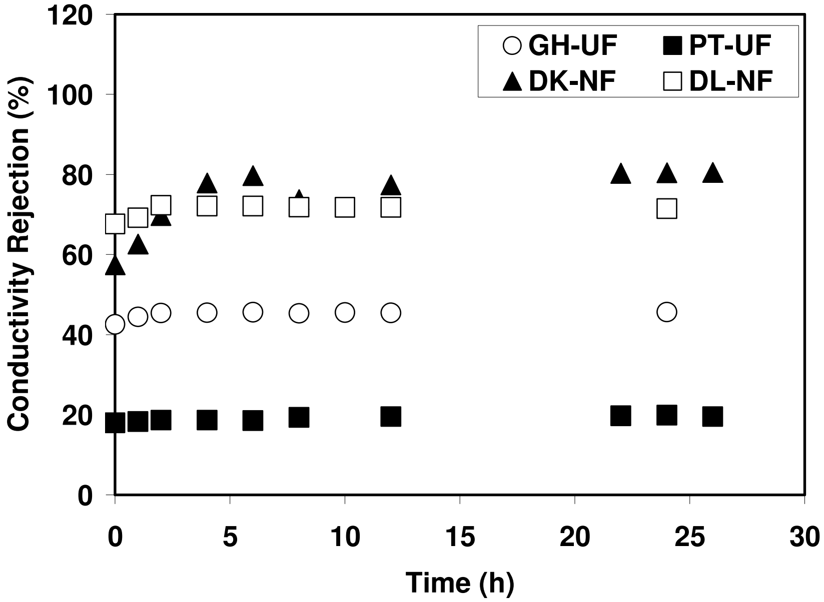


Figure B.17. The impact of membrane type on time dependent rejection of conductivity.

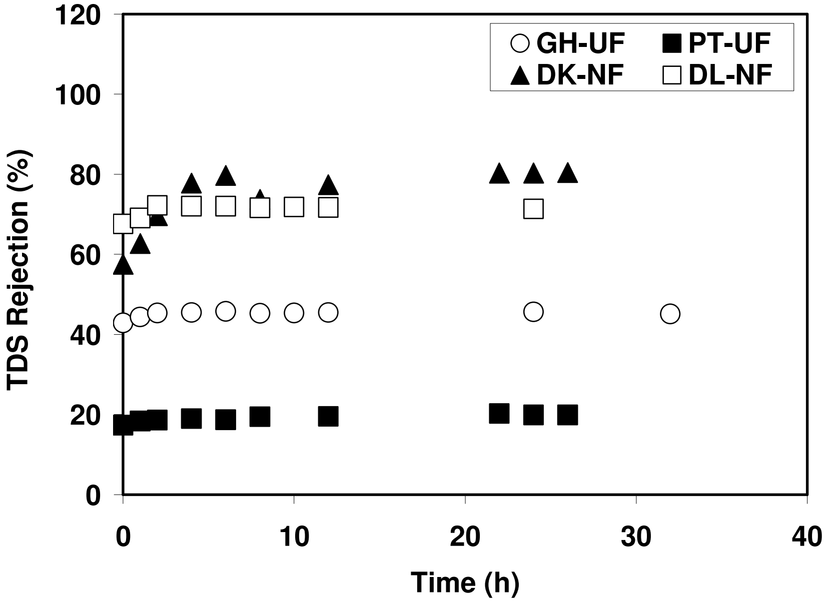


Figure B.18. The impact of membrane type on time dependent rejection of TDS.

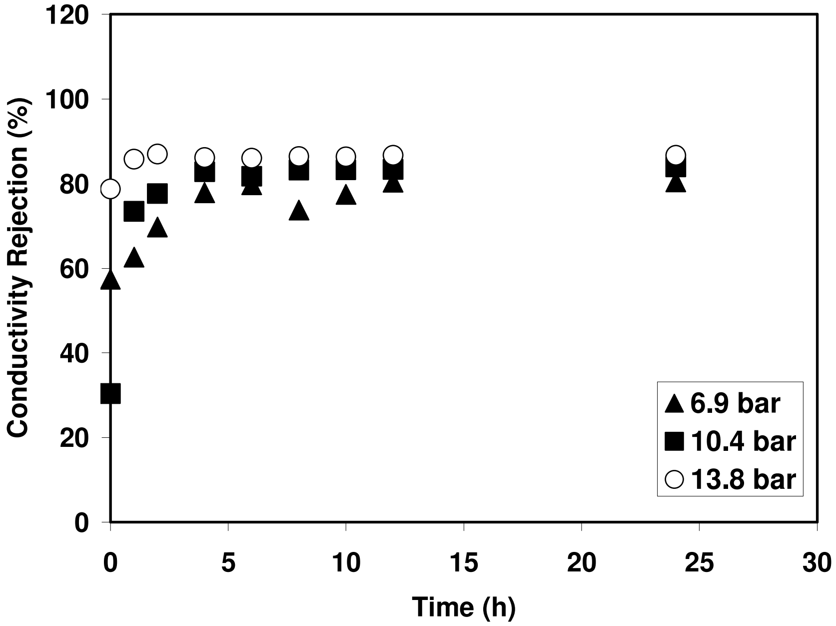


Figure B.19. The impact of pressure on time dependent rejection of conductivity.

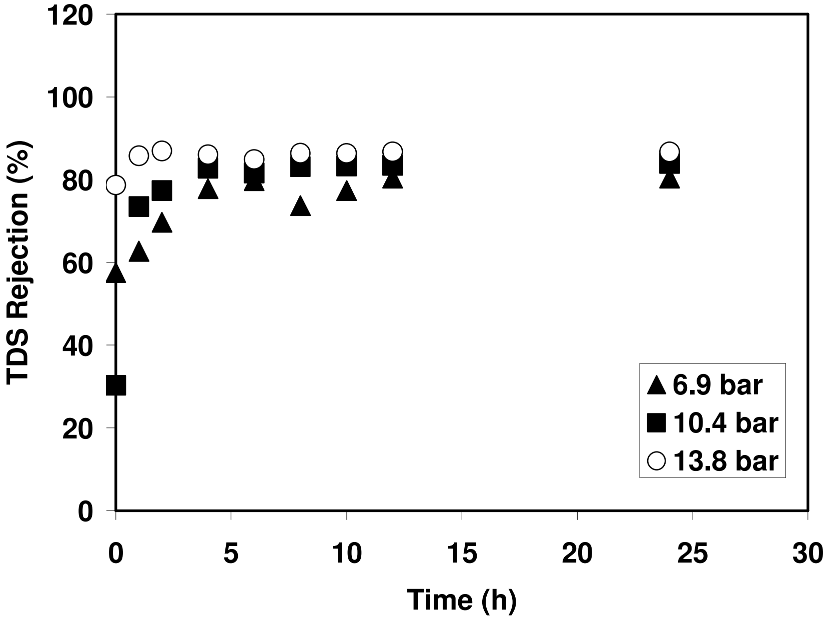


Figure B.20. The impact of pressure on time dependent rejection of TDS.

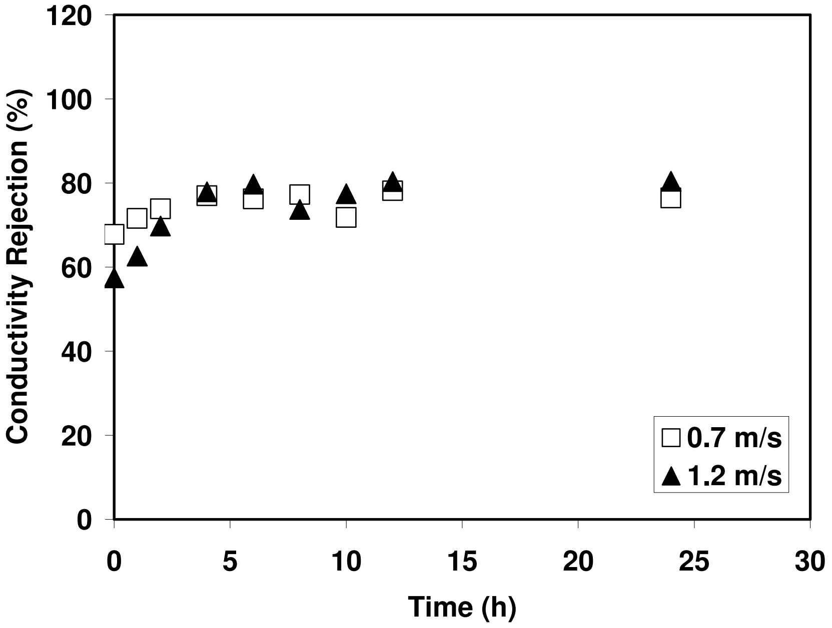


Figure B.21. The impact of CFV on time dependent rejection of conductivity.

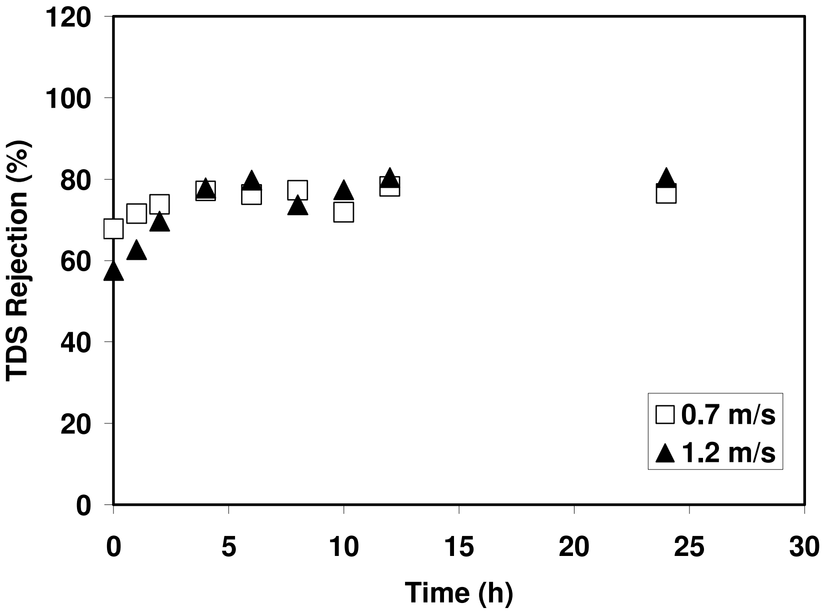


Figure B.22. The impact of CFV on time dependent rejection of TDS.

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