DETERMINATION OF THMFP OF THE RESERVOIRS IN TURKEY : KINETICS ASPECT

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MİNE ARTUĞ

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Prof. Dr. Canan Özgen
Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

Prof. Dr. Filiz B. Dilek
Head of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Assoc. Prof. Dr. Dilek Sanin
Co-Supervisor

Prof. Dr. Filiz B. Dilek
Supervisor

Examining Committee Members

Asst. Prof. Dr. Ayşegül Aksoy	(METU,ENVE)	
Prof. Dr. Filiz B. Dilek	(METU,ENVE)	
Assoc. Prof. Dr. Dilek Sanin	(METU,ENVE)	
Asst. Prof. Dr. İpek İmamoğlu	(METU,ENVE)	
Fikriye Baltacı	(DSİ)	

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this wok.

Name, Last Name : MİNE ARTUĞ

Signature :

ABSTRACT

DETERMINATION OF THMFP OF THE RESERVOIRS IN TURKEY: KINETICS ASPECT

ARTUĞ, Mine
M.Sc., Department of Environmental Engineering
Supervisor: Prof. Dr. Filiz B. Dilek
Co-Supervisor: Assoc. Prof. Dr. Dilek Sanin
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Chlorine is still the most commonly used disinfectant in many water treatment plants all over the World. However, studies conducted demonstrated that the chlorine reacts with the natural organic matter (NOM) in source waters, and leads to the formation of a variety of chlorinated organic compounds, disinfection by-products (DBPs). Among these, the most common are the trihalomethanes (THMs).

In this study, kinetics of the THM formation was investigated. Kinetic experiments were carried out with the raw waters from Devegeçidi and Atatürk Reservoirs as well as with water containing a model compound, humic acid. THM and Chlorine concentrations were measured for 6 weeks on a seasonal basis. The simulation model developed by USEPA was used for predicting THM concentrations.

The results of this study have shown that THM formation increases with increasing time and higher chlorine doses result in higher THM formation. Also, higher organic matter concentrations resulted in higher chlorine demands and both these parameters increased the TTHM concentrations. But, on the contrary to the standard THMFP testing, THM formation did not complete in seven days. In addition, THM formation and chlorine consumption were very rapid during the first 24 hr followed by a more gradual formation and decay after 24 hr. THM formation rates ranged between 35-66 µg/L.day for Atatürk Reservoir, between 80-167 µg/L.day for Devegeçidi Reservoir and between 85-248 µg/L.day for humic acid during the first 24 hr, and ranged between 2-6 µg/L.day for Atatürk Reservoir, between 7-16 µg/L.day for Devegeçidi Reservoir and between 3-14 µg/L.day for humic acid after 24 hr.

Keywords: Trihalomethanes (THMs), Natural Organic Matter, Drinking Water Sources, Kinetics

ÖZ

TÜRKİYEDEKİ BARAJLARDA THM OLUŞMA POTANSİYELİ: KİNETİK YÖNÜ

ARTUĞ, Mine
Yüksek Lisans, Çevre Mühendisliği Bölümü
Tez Danışmanı: Prof. Dr. Filiz B. Dilek
Ortak Tez Danışmanı: Doç. Dr. Dilek Sanin
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Dünyada pek çok içmesuyu arıtma tesisinde en yaygın dezenfektan olarak kullanılan klor, baraj sularındaki doğal organik maddelerle (DOM) reaksiyona girerek dezenfeksiyon yan ürünleri (DYÜ) olarak tanımlanan ve kanserojen oldukları bilinen klorlu-organik bileşiklerin oluşumuna yol açmaktadır. Bu bileşikler arasında en yaygını trihalometan (THM) bileşiklerdir.

Bu çalışmada, THM oluşma kinetiği araştırılmış ve bu amaçla Devegeçidi ve Atatürk barajları ile bir model bileşik (hümik asit) içeren su örneği ile 6 hafta süren kinetik deneyleri yürütülmüştür. 6 haftalık süre boyunca THM ve klor konsantrasyonları ölçülmüş ve mevsimsel bazda değerlendirmeler yapılmıştır. USEPA tarafından geliştirilmiş olan simülasyon modeli ile THM konsantrasyonları tahmin edilmeye çalışılmıştır.

Bu çalışmanın sonucunda reaksiyon süresinin ve uygulanan klor dozunun artmasının THM oluşumunu arttırdığı belirlenmiştir. Ayrıca, yüksek organik madde konsantrasyonlarının su kaynağının klor ihtiyacını arttırdığı ve dolayısıyla daha çok THM oluşumuna neden olduğu görülmüştür. Fakat, standard THMFP metodunda belirtilenin aksine THM oluşumunun yedi günde tamamlanmadığı gözlenmiştir. Bunlara ek olarak, THM oluşumunun ve klor tüketiminin ilk 24 saatte çok hızlı olduğu daha sonra ise daha düşük bir hızda gerçekleştiği saptanmıştır. THM oluşum hızları ilk 24 saatte; Atatürk Barajı örneklerinde 35-66 µg/L.day, Devegeçidi Barajı örneklerinde 80-167 µg/L.day ve hümik asit çözeltilerinde 85-248 µg/L.day; daha sonraki sürelerde ise sırasıyla 2-6 µg/L.day, 7-16 µg/L.day ve 3-14 µg/L.day arasında değişmiştir.

Anahtar Kelimeler: Trihalometanlar (THM), Doğal Organik Madde, İçme Suyu Kaynakları, Kinetik

To my sister …

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ABBREVIATIONS

AROM	: Aquagenic Refractory Organic Matter
BDM	: Bromodichloromethane
D/DBP	: Disinfectant/Disinfection By-Products
DBM	: Dibromochloromethane
DBPs	: Disinfection By-Products
DOC	: Dissolved Organic Carbon
DOM	: Dissolved Organic Matter
EPA	: Environmental Protection Agency
ESWTR	: Enhanced Surface Water Treatment Rule
GAC	: Granular Activated Carbon
GC	: Gas Chromatography
HAAs	: Haloacetic Acids
HANs	: Haloacetonitriles
IC	: Inorganic Carbon
MCL	: Maximum Contaminant Level
NOM	: Natural Organic Matter
NPOC	: Non-purgeable Organic Carbon
PROM	: Pedogenic Refractory Organic Matter
SDS	: Simulated Distribution System
SOCs	: Synthetic Organic Chemicals
SUVA	: Specific Ultraviolet Absorbance
TC	: Total Carbon
THMs	: Trihalomethanes
TOC	: Total Organic Carbon
TOX	: Total Organic Halides
TTHM	: Total Trihalomethanes
THMFP	: Trihalomethane Formation Potential

TTHMFP : Total Trihalomethane Formation Potential

USEPA : United States Environmental Protection Agency

UV(A)$_{254nm}$: Ultraviolet Absorbance at 254 nm

WHO : World Health Organization

CHAPTER 1

INTRODUCTION

1.1. General

The final step of water purification is disinfection, a procedure for protecting drinking water during distribution against external contamination and re-growth of bacteria (Minear and Amy, 1996). Since the early 1900s, chlorine, being easy and ready to use, especially in its most common form of hypochlorite, has been the major disinfectant introduced into drinking water for preventing waterborne diseases (Houston, 1913).

On the other hand, it is known that the use of chlorine for disinfection purposes of drinking water leads to the formation of many byproducts potentially harmful for human health. Among all the chlorinated by-products, trihalomethanes, which exhibit potentially carcinogenic activity, are certainly the class of compounds that has been investigated most thoroughly during the last 20 years. Classical trihalomethanes consist of chloroform ($CHCl_3$), dichlorobromoform ($CHCl_2Br$), dibromochloroform ($CHBr_2Cl$) and bromoform ($CHBr_3$). They are formed through the reactions of hypochlorous acid (HOCl) with natural organic matter (NOM) in presence or absence of bromide (Gallard and von Gunten, 2002).

Trihalomethanes are listed as priority pollutants by the Environmental Protection Agency of the United States due to their tumorigenic properties and deleterious effects to the nervous system of test animals (Walter and Tassos, 1997).

Depictive epidemological studies have consistently suggested increased risk of cancer of bladder, stomach, large intestine and rectum in areas where chlorinated surface waters have been used (Golfinopoulos et al., 1996). Therefore, extensive importance is given on the regulations covering DBPs in different countries such as USA, Canada, Japan etc. However, there has not been much awareness on this topic and for now there is no regulatory limit for THM concentrations in Turkey.

Although THMs are known carcinogens and their concentration in water should be monitored, it is difficult and time-consuming to measure their concentrations. So, to predict or monitor THM, surrogate parameters such as TOC, $UV(A)_{254nm}$, THMFP, etc. are used.

Surrogate parameters are good substitutes for the measurement of some parameters which are difficult and time consuming to measure. However, surrogate parameters have some limitations because they are the substitute measurements and often are nonspecific. Hence, correlations between the surrogate parameters and THM are often poor.

THMFP (surrogate parameter of THM) is an index of the potential extent of THM formation after the application of chlorine. According to Standard Methods (1998) THMFP test is conducted by a 7 day-test which determines the THMFP of the water sample after a reaction time of 7 days. This time period is believed to allow the reaction to approach completion. However, THM formation may not finish in 7 days, and this, in turn, may result in underestimation of the ultimate potential of the water for producing trihalomethanes.

In order to achieve minimization of the formation of such harmful disinfection by-products (DBPs), while maintaining proper disinfection, the parameters affecting their formation should be well understood. THM formation has been shown to be a function of many water quality parameters, including total organic carbon (TOC), pH of chlorination, temperature, reaction time etc. Also, organic matter nature or composition is thought to play an important role on THM formation. Various researchers have qualitatively or semi-quantitatively evaluated the effects of these factors on THM formation. However, there is still remarkable gap in existing literature concerning kinetics of THM formation which may provide better understanding of the effect of reaction time on THM formation that may in turn be of value for the design and optimization of the chlorination conditions.

1.2. Objective and Scope of the Study

This study aims to determine the kinetics of THM formation. Within this scope; the effects of chlorine dose and the seasonal variation of THM precursors on the rates and yields of THM formation and chlorine decay are investigated.

For these purposes, kinetic experiments were conducted with raw water samples of two reservoirs (Atatürk and Devegeçidi) in Turkey as well as with synthetic water containing a model compound, humic acid. Humic acid was used to compare with reservoir waters since humic acid is the main precursor of THM formation. Within the scope of the study, non-purgeable organic carbon (NPOC), UV absorbance at 254 nm [$UV(A)_{254nm}$] and specific ultraviolet absorbance (SUVA) of the raw waters were investigated to monitor the natural organic matter content/nature of the water supplies. In addition THM formation and chlorine decay rates were investigated. Finally, a kinetic model simulated by USEPA was used to compare the predicted and observed results.

CHAPTER 2

THEORETICAL BACKGROUND

2.1. Disinfection By-Products and THMs

The disinfection process has been routinely carried out since the dawn of the 20th century to eradicate and inactivate the pathogens from water used for drinking purposes. In addition to inactivating pathogens in the source water, disinfectants are also used as oxidants in drinking water treatment to:

- Remove taste and odors,
- Oxidize iron and manganese,
- Maintain a residual to prevent biological regrowth in the distribution system,
- Improve coagulation and filtration efficiency,
- Prevent algal growth in sedimentation basins and filters (USEPA, 1999a).

Chlorine and its compounds are the most commonly used disinfectants for water treatment. Chlorine's popularity is not only due to lower cost, but also to its higher oxidizing potential, which provides a minimum level of chlorine residual throughout the distribution system and protects against microbial recontamination (Sadiq and Rodriguez, 2004; Huang and Smith, 1984). Advantages and disadvantages of chlorine usage for disinfection process is given in Table 2.1.

Over the years, chlorine has remained the most popular disinfecting agent due to its ability to kill most pathogens. However, in 1974, it was discovered that the chlorination of drinking waters resulted in the production of chloroform and other trihalomethanes (THMs) due to the reaction of chlorine with the organics in the water. Since then hundreds of additional disinfection by-products (DBPs) have been identified, including haloacetic acids and haloacetonitriles (Moudgal et al., 2000; Bellar et al., 1974; Rook, 1976). 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). The adverse health effects of DBPs will be addressed in Section 2.4. Depending on the process of disinfection (i.e. the type of disinfectant used), different DBPs are formed. Table 2.2 presents a summary of these disinfection by-products. It is convenient from the regulatory and industry standpoint to categorize the related DBPs. Such grouping is represented in Table 2.3.

Table 2.1 Advantages and Disadvantages of Chlorine (Rook, 1976; El-Shafy and Grünwald, 2000; Clark, 1998)

Advantages	**Disadvantages**
Provides a strong residual in the distribution system	Formation of disinfection by-products (DBPs) especially trihalomethanes (THMs)
Easily applied, controlled, and monitored	Provides poor Cryptosporidium* and Giardia** control
Relatively inexpensive	
Effective at low concentrations	
Highly effective against most pathogens	

* *Cryptosporidium parasite is the cause of gastrointestinal diseases (USEPA, 1997).*

** *Giardia lamblia parasite is the cause of gastrointestinal illness (e.g. diarrhea, vomiting, cramps) (USEPA, 1997).*

Table 2.2. Different Disinfection Processes and Their Resultant DBPs (Marhaba and Washington, 1998)

Disinfection Process	**Disinfection By-Products**
Chlorination	Trihalomethanes, Haloacetic acids, Haloacetonitriles
Chloramination	Chloral Hydrate
Chlorine Dioxidation	Chlorate, chlorite, chlorophenols, quinones
Ozonation	Aldehydes, carboxylic acids, quinones, peroxides, Bromates, Brominated products
Titanium Dioxide	3-methyl-2,4-hexanedione, dihydro-4,5-dichloro-2(3H)
Photocatalysis	Furanone

Table 2.3. DBP Grouping and the Associated DBP Constituents (Marhaba and Washington, 1998; Krasner et al., 1989)

DBPs	**Formula**
Trihalomethanes (THMs)	
Chloroform	$CHCl_3$
Bromodichloromethane	$CHCl_2Br$
Dibromochloromethane	$CHClBr_2$
Bromoform	$CHBr_3$
Haloacetic acids (HAAs)	
Monochloroacetic acid	$CH_2ClCOOH$
Dichloroacetic acid	$CHCl_2COOH$
Trichloroacetic acid	CCl_3COOH
Monobromoacetic acid	$CH_2BrCOOH$
Dibromoacetic acid	$CHBr_2COOH$
Chloral hydrate	$CCl_3CH(OH)_2$
Haloacetonitriles (HANs)	
Bromochloroacetonitrile	$C_2HNClBr$
Dibromoacetonitrile	C_2HNBr_2
Dichloroacetonitrile	C_2HNCl_2
Trichloroacetonitrile	C_2NCl_3
Haloketones	
1,1-Dichloropropanone	$C_3H_4Cl_2O$
1.1.1-Trichloropropanone	$C_3H_3Cl_3O$

THMs often represent the largest (by mass) of identified DBPs in treated water. Krasner et al. (1989) in a study of 35 American water treatment plants, representing a variety of treatment processes and raw water qualities, reported that 54% (by mass) of the identified disinfection by-products were THMs.

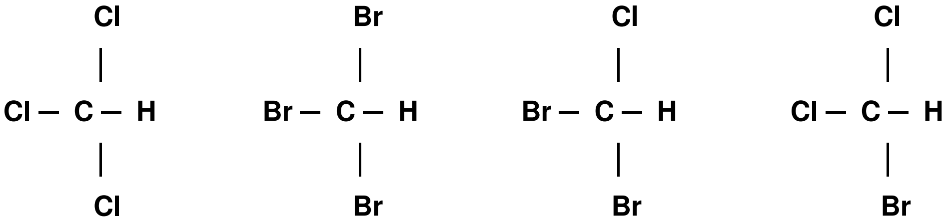
Trihalomethanes are organohalogen compounds; they are named as derivatives of the compound methane. Trihalomethanes are formed when three of the four hydrogen atoms attached to the carbon atom in the methane compound are replaced with atoms of chlorine, bromine and/or iodine (Vogt and Regli, 1981). Physical and chemical properties of THMs are presented in Table 2.4 (Gang, 2001).

Table 2.4. Properties of THMs (Gang, 2001)

Name	**Structure**	**Molecular Weight (g/mol)**	**Boiling Point (^oC)**
Chloroform (Trichloromethane)	$CHCl_3$	119.5	61
Bromodichloromethane	$CHBrCl_2$	163.9	87
Chlorodibromomethane	$CHBr_2Cl$	208.3	116
Bromoform	$CHBr_3$	252.7	151

THMs include chloroform ($CHCl_3$), dibromochloromethane ($CHBr_2Cl$), bromodichloromethane ($CHBrCl_2$), and bromoform ($CHBr_3$) (Figure 2.1). Chloroform is the THM most commonly found in drinking water and is usually present in the highest concentration (Vogt and Regli, 1981).

THMs appear to be the most prevalent halogenated by-products of chlorination and the chemistry underlying their formation is well understood. THM formation patterns are generally applicable to other by-product forms; however there is more data on occurrence and health effects for THMs which are the most widely studied forms of DBPs (Black et al., 1996).



$$\begin{array}{c}Cl\\|\\Cl-C-H\\|\\Cl\end{array}\qquad\begin{array}{c}Br\\|\\Br-C-H\\|\\Br\end{array}\qquad\begin{array}{c}Cl\\|\\Br-C-H\\|\\Br\end{array}\qquad\begin{array}{c}Cl\\|\\Cl-C-H\\|\\Br\end{array}$$

Chloroform Bromoform Dichlorobromo methane Dichlorobromo methane

Figure 2.1 Molecular Structure of THMs

2.2. THM Precursors

Organic matter present in water supplies reacts with chlorine and leads to the formation of THMs. Therefore, the amount, type and characteristics of organic precursors directly affect the formation of THMs.

Organic chemical contaminants in drinking water supplies are classified into three main groups;

- Natural organic matter (NOM): This group of organics includes humic substances, microbial exudate and other organic materials dissolved into the water from sources as plant tissues and animal wastes,
- Synthetic organic chemicals (SOCs): This class includes chemicals from point sources (volatile organic carbons, etc.) and nonpoint sources (pesticides, etc.),
- Chemical by-products or additives formed through reactions during treatment or transmission in the distribution system such as trihalomethanes (Randtke, 1988).

Water throughout the world contains natural organic matter (NOM) 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' biogeochemical cycles (Murray and Parsons, 2004).

Natural organic matter (NOM) affects significantly many aspects of water treatment, including the performance of unit processes (i.e., oxidation, coagulation, and adsorption), application of disinfectants, and biological stability. As a result, NOM acts upon potable water quality by contributing to disinfection by-products (DBP), biological regrowth in the distribution system, colour, taste, and odour (Matilainen et al., 2002).

NOM in dissolved, colloidal, or particulate form is ubiquitous in surface and ground waters. The dissolved and colloidal forms (i.e., DOM, those constituents passing a 0.45-mm filter) constitute the major fraction of NOM in natural waters. DOM in aquatic environments is derived from both external and internal sources of organic materials as a result of various complex biotic and abiotic reactions. It is composed of a heterogeneous mixture of humic substances, hydrophilic acids, proteins, lipids, carbohydrates, carboxylic acids, amino acids and hydrocarbons (Kitis et al., 2001).

Humic substances are the major constituents (approximately 50%) of DOM. About 30% of the DOM is comprised of hydrophilic acids. The remaining 20% is carbohydrates (including polysaccharides), carboxylic acids, proteins, amino acids, low molecular weight acids, lipids and peptides (Imai et al., 2003; Fan et al., 2001; Nikolaoua and Lekkas, 2001).

Naturally occurring humic and fulvic substances which constitute a large fraction of the organic matter in water, are major THM precursors (Singer, 1999; Pomes et al., 1999). Yamada et al. (1998) investigated the behavior of humic substances as precursors of THM in river-water samples. The total THM formed and the concentration of humic substances showed a high correlation (r^2=0.932). Also, they observed that the trends for the seasonal changes in the concentrations of the trihalomethane formation potential (THMFP) were almost consistent with those of humic substances.

Humic substances are amorphous, acidic, predominantly aromatic, hydrophobic, chemically complex polyelectrolytes that range in molecular weight from a few hundred to tens of thousands. Humic materials are negatively charged macromolecules under the pH conditions of most natural waters. Although these macromolecules may be truly dissolved, they can be classified as colloids because of their colloidal dimensions. (AWWA Committee Report, 1979)

Humic substances are commonly classified on the basis of solubility. If a material containing humic substances or humus is extracted with a strong base and the resulting solution is then acidified, the products are a) a nonextractable plant residue that is not soluble at any pH value, called humin, b) a material called humic acid that precipitates from the acidified ($pH < 2$) solution, and c) an organic material called fulvic acid that is soluble over the entire pH. Another classification proposed by Oden (1919) also includes hymatomelanic acid which is soluble in NaOH and alcohol but insoluble in mineral acid. However, many investigators consider only fulvic acid and humic acid and tend not to seperate the hymatomelanic acid component from the humic acid fraction (AWWA Committee Report, 1979; Nikolaoua and Lekkas 2001).

Substantial evidence shows that humic substances consist of a skeloton of alkyl/aromatic units cross-linked mainly by oxygen and nitrogen groups with the major functional groups being carboxylic acid, phenolic and alcoholic hydroxyls, ketone, and quinone groups. The structures of fulvic acids are somewhat more aliphatic and less aromatic than humic acids; and fulvic acids are richer in carboxylic acid, phenolic, and ketonic groups (Wu, 1998).

Oliver and Thurman (1984) studied the THMFP associated with fulvic and humic acid fractions of various aquatic humic substances. They found that, in general, groundwater fulvic acids had the lowest THMFP, with surface water fulvic acids having greater THMFP and marsh-bog fulvic acids having the largest THMFP.

Because groundwater contains the oldest organic material and marsh-bog water the youngest, they reasoned that structural changes that occur during the maturation process must lead to a lowering of THMFP. In comparing fulvic with humic acids they found that 18-52% percent more THMs were produced by humic acids.

It is also possible to subdivide humic substances 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 (Kitiş, 2001).

The high molecular weight and polyelectrolytic humic substance macromolecules range from a molecular weight of a few hundred for fulvic acid to tens of thousands for the humic acid and humin fractions. Humic substances are excellent chelating agents that bind with and hold metal ions in water, and they also effectively exchange cations with water. (Wu, 1998). The gross chemical and physical properties of humic acid and fulvic acid are listed in Table 2.5 (AWWA Committee Report, 1979).

Table 2.5. Physical and Chemical Properties of Humic and Fulvic Acids

Property	Humic Acids	Fulvic Acids
Elemental Composition (% by weight)		
C	50-60	40-50
H	4-6	4-6
O	30-35	44-50
N	2-4	<1-3
S	1-2	0-2
Solubility in strong acid (pH=1)	Not soluble	Soluble
Molecular weight range	Few 100 → Several million	180 → 10,000
Functional group distribution	Percent of oxygen in indicated functional group	

There are also non-humic THM precursor sources which generate THMs at concentrations comparable to those obtained from the chlorination of humic materials (Imai et al. 2003; Marhaba and Van, 2000; Lin and Hoang, 2000).

Imai et al. (2003) conducted a research on the THMFP of dissolved organic matter in a shallow eutraphic lake in Japan. Dissolved organic matter (DOM) in water samples from the Lake Kasumigaura, the second largest lake in Japan, was fractionated and characterized by using resin adsorbents into 5 classes: aquatic humic substances (AHS), hydrophobic neutrals, hydrophilic acids (HiA), bases (BaS) and hydrophilic neutrals (HiN). When the trihalomethane formation potential (THMFP) of AHS and hydrophilic fractions (HiF) (HiF=HiA+BaS+HiN) were examined, the THMFP of HiF, normalized on a DOC basis, was found to be comparable to that of AHS (0.176 µmolTHM/mgC for HiF and 0.195 µmolTHM/mgC for AHS). When THMFP was evaluated in terms of concentration, THMFP of HiF was much greater than that of AHS (0.374 μmolTHM/L for HiF and 0.229 μmolTHM/L for AHS) showing the importance of HiF over AHS as a THM precursor.

Marhaba and Van (2000) fractionated dissolved organic material (DOM) from a conventional surface water treatment plant in northern New Jersey and found that the hydrophilic acid fraction was the most reactive THM precursor. Removing the hydrophilic acid fraction removed 70 percent of the THMFP.

2.3. THM Formation

2.3.1. Factors Affecting THM Formation

There are several factors affecting the formation potential of THMs. Previous research studies have shown that the major variables that affect THM formation are: chlorine dose and residual, concentration and nature of NOM (mainly humic substances), contact time, pH, temperature of water, and the presence of inorganic ions like bromide (Amy et al., 1987; Nikolaou et al., 2004; Elshorbagy et al., 2000; Golfinopoulos and Arhonditsis, 2002). In general, higher THM concentrations are expected at higher levels of the above mentioned parameters (Sadiq and Rodriguez, 2004).

Increase of chlorine dose has been reported to have positive influence of DBPs yield. The same is true for increased concentrations of natural organic matter and increased temperature. The presence of bromide ion shifts the speciation of DBPs to more brominated analogues, while increased pH can enhance the formation of some categories of DBPs, e.g. THM, and inhibit the formation of some others, e.g. haloacetonitriles and haloketones (Nikolau et al., 2004).

The type of raw water also affects the THM levels. Generally, ground waters are naturally protected from runoff NOM, while the difference in occurrence of DBP precursors in river and lakes depends on geological, physical and environmental factors (trophic stage, watershed soil characteristics and land use, lake size, river flow rate, etc.) (Sadiq and Rodriguez, 2004).

Chlorine dose: Studies that have been investigating the effect of disinfectant concentration on DBP formation have shown that as the disinfectant concentration increases, DBP formation also increases (Montgomery, 1993; Rathbun, 1996). For example, Singer et al. (1995) conducted a study on eight conventional water treatment plants that practiced chlorine disinfection in North Carolina. Results showed that the treatment plant that used the largest chlorine dose had average TTHM (total trihalomethane) and HAA (haloacetic acids) levels of 52 µg/L and 80 µg/L, respectively. The plant which used the smallest chlorine dose had mean TTHM and HAA levels of 19 µg/L and 39 µg/L, respectively.

With increasing chlorine dose and residual, formation of haloacetic acids becomes greater than trihalomethane formation. Also, more trihalogenated than mono- and di-halogenated species and more chlorinated than brominated species are formed (Singer, 1994). Depletion of the free chlorine residual ceases THM and haloacetic acid formation. However, limited formation of some other DBPs continues due to hydrolysis reactions (Singer, 1994).

Urano et al. (1983) studied with different initial chlorine doses and concluded that rates of THM formation at a same Cl_2 value were not equal and THM concentrations depended upon initial Cl_2 concentration. This result showed that THM formation might be controlled by the amount of chlorinated intermediates which were produced fast and were dependent on initial chlorine concentration.

Nature and Concentration of NOM: Properties of NOM play an important role, since activated aromatic content of NOM increases DBP formation (Reckow et al., 1990, Harrington, 1997). Singer (1999) conducted a study on five humic and fulvic extracts. The extracts were chlorinated under uniform conditions and analyzed for their DBP production. The chlorine consumption and yields of each of the DBPs, including overall TOX (total organic halides) production, is relatively higher for the humic acid fraction, presumably because of the greater aromatic carbon content of the fraction. Their work showed a linear relationship between chlorine consumption and the activated aromatic carbon content of the various humic and fulvic acid. In addition, NOM contains hydrophobic and hydrophilic materials, the nature and distribution of which may vary with different types of vegetation in the watershed and different species of algae in water. This results in varying influence of NOM on DBP formation (Singer, 1994).

Singer et al. (1995) showed that as toc concentrations increased so did TTHM and HAA levels in a study conducted on eight North Carolina water supply systems. At a TOC concentration of 5.4 mg/l, an average of 82 µg/l of TTHMs was produced and an average of 106 µg/l of HAA was formed. At a TOC level of 2.4 mg/l, a mean of 39 µg/l of TTHMs were created and a mean of 36 µg/l of HAA were produced.

DOM from a conventional surface water treatment plant in Northern New Jersey was isolated and fractionated using resin adsorption chromatography into six different fractions. These fractions are operationally categorized as hydrophobic acid (a soil fulvic), hydrophobic neutral (a mix of hydrocarbon and carbonyl compounds), hydrophobic base (portion of humic substance retined by the resin), hydrophilic acid (organic compound of the hydroxyl acid group), hydrophilic neutral (organic compound of polysaccharides) and hydrophilic base (proteinaceous materials). The hydrophilic acid fraction was found to be the most abundant fraction in the source water. Seven-day chlorine DBP formation potential (FP) tests were performed on all DOM fractions through the water treatment plant. For the source water studied, the hydrophilic acid fraction was found to be the most reactive precursor to the THM formation. The contributions of humic (hydrophobic) and non-humic (hydrophilic) substances toward the formation of THMs were 28% and 72%, respectively (Marhaba and Van, 2000).

Reaction time: Studies conducted to examine the effect of residence time on DBP formation have shown that longer reaction time increases the formation of THMs. On the other hand, DBPs such as haloacetonitriles and haloketones, which were initially formed, decay as a result of hydrolysis and reactions with residual chlorine (Singer, 1994; Chen and Weisel, 1998; Gang et al., 2003; Gallard and von Gunten, 2002; Boccelli et al., 2003; Urano et al., 1983; Rodriguez and Serodes, 2001).

Chen and Weisel (1998) conducted experiments at a conventional treatment plant using chlorine disinfection to investigate the concentrations of DBPs. Over 100 samples were collected in four groups, each group representing an increasing residence time from the point of disinfection. The average concentrations for TTHMs at days zero, one, two and three or more were 25±14 µg/L, 30±16 µg/L, 29±15 µg/L, and 30±14 µg/L, respectively.

Gallard and von Gunten (2002) conducted experiments with natural waters and solutions of humic materials during the investigation of the kinetics of the formation of THMs and of chlorine consumption. As the reaction time increased, formation of THM also increased. Initial THM formation potential corresponding to the THMs formed during the first hours of reaction time accounted for 28% of the final THM concentration.

LeBel et al. (1997) conducted an experiment on a conventional water treatment system that used chlorine for primary and secondary disinfection processes. Four sampling points were used at an increasing distance from the treatment plant. At the first, second, third, and fourth points, TTHM levels were analyzed and the results were 24.8 µg/L, 37.5 µg/L, 48.4 µg/L, and 61.4 µg/L, respectively.

Temperature/Season: When temperature increases, reactions are faster and a higher chlorine dose is required, leading to higher formation of DBPs. Subsequently, DBP concentrations are expected to be higher in summer than in winter (Williams et al., 1997; Golfinopoulos et al., 1996; LeBel et al., 1997; Arora et al., 1997; Chen and Weisel, 1998; Rodriguez and Serodes, 2001). In the winter months and in some cases where the ice cover protects surface raw waters, the THM concentrations are lower due to lower water temperature and NOM. In these conditions, the chlorine demand is lower, therefore, the chlorine dose required to maintain adequate residual in the distribution system is also less.

Nieminski et al. (1993) examined TTHM and HAA concentrations (during all four seasons) in 14 conventional water treatment plants which disinfect with chlorine. In this study, the mean TTHM levels for summer, fall, winter, and spring were

32.1 µg/L, 28.7 µg/L, 17.6 µg/L, and 16.5 µg/L, respectively. This study showed that the highest TTHM concentrations were found in the summer and fall seasons, and the lowest TTHM concentrations were present in the winter and spring.

Golfinopoulos (2000) investigated the occurrence of THMs in public water supplies of Greece. Samples were collected from three treatment plants in Athens and from the distribution systems of Athens, Mytilene and Chalkida. Each of the systems followed a pattern, generally having the lowest TTHMs concentrations during the winter and spring seasons and the highest during the summer and fall seasons. Since higher doses of chlorine were used in the warm summer and fall months to ensure prevention of microbiological problems, it was to be expected that this, in combination with warmer water temperatures, would lead to higher TTHMs concentration during the summer and fall seasons.

pH: Several studies have been made to investigate the effect of pH on DBP concentrations. The studies have shown that THM concentrations increases with increasing pH.

With increasing pH, trihalomethane formation increases, whereas haloacetic acid formation decreases (Krasner et al., 1989; Pourmoghaddas and Stevens, 1995). At high pH values, hydrolysis of many halogenated DBPs occurs (Krasner et al., 1989). As a result, total organic halide (TOX) concentration is lower at pH>8 (Singer, 1994).

Urano et al. (1983) has investigated the influence of pH change on the rates of THM formation. Initial pH of the sample was 7.3 and was increased to 10.3 with the addition of sodium hydroxide. THM concentration increased rapidly after adding sodium hydroxide and the rates of THM formation soon became equal to the rate as that in the case when initial pH was 10.3. The results showed that THM formation is mainly attributed to the reactions of the chlorinated intermediates with hydroxide ion in the presence of a small amount of free chlorine.

Bromide: Recent studies have examined the relationship between bromide concentration in a drinking water supply and DBP formation. Based on the differences in bromide concentration, it is inferred that substantial variations in THM formation (and THM species) can be expected. Studies have shown that as the concentration of bromide increases, the concentration of TTHMs increases and more brominated THMs forms because there is more bromide present in the water source for the organics to react with.

In the presence of bromide ion (Br^-), more brominated and mixed chloro-bromo derivatives are formed (Krasner et al., 1993; Heller-Grossman et al., 1993; Pourmoghaddas and Stevens, 1995). When bromide is present, chlorine in the form of hypochlorous acid-hypochlorite ion ($HOCl^-OCl^-$) oxidizes bromide ion to hypobromous acid-hypobromite ion ($HOBr^-OBr^-$). A mixture of HOCl and HOBr can lead to the formation of both chlorinated and brominated by-products (Pourmoghaddas et al., 1993).

Nikolaou et al., (2004a) investigated 24 DBPs in chlorinated water from three different sources and the study showed that in the case of presence of excess bromide ion, the total bromide incorporation into the detected DBPs also increased significantly with increasing chlorine dose. The percentage bromide incorporation into the THMs was 2.2% for chlorine dose of 2 mg/L, while for chlorine dose of 4 mg/L it was significantly higher, 10.0%. Since there was excess bromide ion in the water, increase of chlorine dose shifted the speciation of DBPs to brominated species, thus increasing bromide incorporation.

Duong et al. (2003) investigated the occurrence and the fate of trihalomethanes (THMs) in the water supply system of Hanoi City, Vietnam from 1998 to 2001. With regard to THM formation, three types of groundwater resources were identified: (I) high bromide, (II) low bromide, and (III) high bromide combined with high ammonia and high dissolved organic carbon (DOC) concentrations. The THM speciation showed >80% of bromo-THMs in type I water due to the noticeable high bromide level (50-140 µg/L). In type II water, the bromo-THMs still accounted for some 40% although the bromide concentration is significantly lower (20-30 µg/L). In contrast, only traces of bromo-THMs were formed (~ 5%) in type III water, despite bromide levels were high (70-240 µg/L). This observation could be explained by competition kinetics of chlorine reacting with ammonia and bromide.

2.3.2. Surrogate Parameters and THM Formation Potential

It is difficult and time-consuming to measure THM concentrations. Measurements require skilled personnel as well as high technical instrumentation. So, to predict or monitor THM or its precursor concentrations surrogate parameters are used. Surrogate parameter is one, concentration of which is linearly proportional to the concentration of the target parameter that is less easily measured. Parameters that are measured more easily, rapidly and inexpensively than the parameter of interest are chosen as surrogates. However they have some limitations as they are substitute measurements and are often nonspecific (Edzwald et al., 1985).

The research in the last 2 decades has been aimed principally at linking DBP concentrations (mainly THMs) with total or dissolved organic matter (TOC or DOC), UV-absorbance at 254 nm (UV- 254), pH, water temperature (T), concentration of bromide ion (Br), chlorine dose (D) and reaction time of residual chlorine (t). TOC (or DOC), UV-254 and specific UV absorbance, i.e. SUVA (specific ultraviolet absorbance, the ratio between UV-254 and TOC) are the common surrogates of NOM. Surrogate parameters for monitoring THM precursor concentrations are listed in Table 2.6 (Edzwald et al., 1985).

Table 2.6. Surrogate Measurements for Monitoring THMs (Edzwald et al., 1985)

Surrogate Parameter	**Measurement**
Color	Surrogate measure of humic matter; traditional aesthetic parameter
TOC	Collective or group measure of organic matter
TTHMFP	Indirect measure of THM precursors
$UV(A)_{254}$	Surrogate measure of TOC and THM precursors
TOX	Surrogate measure of potentially harmful halogenated organics

TOC and DOC are indicators of mass of organic substance whereas UV-254 accounts for specific structure and functional groups (Edzwald et al., 1985; USEPA, 2001a). The magnitude of absorbance at a particular wavelength is a function of the amount of organic carbon present in solution. Therefore, in order to compare the characteristics of different DOMs, UV absorbance at a particular wavelength must be normalized by dividing by the DOC concentration. This normalized value is called absorptivity or specific ultraviolet absorbance (SUVA). The SUVA is an indicator of NOM reactivity (Kitiş, 2001).

A study was conducted to evaluate the characteristics of NOM that contribute to DBPs in 17 different drinking water systems in Alaska (White et al., 2003). In order to determine the nature of the organic matter contributing to DBPs, DBP formation potential was compared with standard water quality parameters such as UV-254, color and dissolved organic carbon (DOC), as well as pyrolysis-gas chromatography/mass spectrometry (GC/MS). Results showed strong correlations (r^2 values between 0.89-0.99) between UV-254 and DBP formation potential for all waters studied. DOC, on the other hand, was less strongly correlated to DBP formation potential.

SUVA provides a quantitative measure of the aromatic content within organic carbon. One possible reason that SUVA has been shown to correlate well with DBP formation is the likelihood that "activated" 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 (Kitiş et al., 2001).

Singer (1999) showed that THM formation and TOX formation potential correlate well with SUVA for a variety of different materials. Because the hydrophilic components of NOM have a lower aromatic content and a correspondingly lower SUVA than the hydrophobic components, they tend to produce lower amounts of halogenated DBPs upon chlorination. Because SUVA is relatively easy to measure, it can be used as a surrogate for the aromatic content of bulk waters.

Singer et al. (1995) showed that as TOC is a good surrogate for TTHM in a study conducted on eight North Carolina water supply systems. At a TOC concentration of 2.4 mg/l and 5.4 mg/l, an average of 39 µg/l and 82 µg/l of TTHMs was produced, respectively and linear coefficients better than 0.86 were obtained. Although TOC may be a good surrogate for THM, its measurement is at least as time consuming and labor intensive as analysis of THMs.

The organic precursors in the water source can be indirectly measured by the THMFP test. THMFP is an index of the potential extent of THM formation after the application of chlorine. THMFP test is conducted under standard conditions, samples are buffered at pH 7.0 ± 0.2, chlorinated with an excess of free chlorine and stirred at 25 ± 2 ^{o}C for 7 days to allow the reaction to approach completion. A free residual chlorine of 3 to 5 mg/L exits at the end of reaction time (Standard Methods, 1998).

Besides the THMFP test, simulated distribution system (SDS) testing method is also used to provide an estimate of the THMs formed in a distribution system after disinfection by using bench-scale techniques. Chlorine dose and the incubation time are the primary differences between THMFP and SDS testing methods. The disinfectant concentrations and incubation time in SDS test samples are intended to mimic conditions in a distribution system. The chlorine dosage used in this method is one that results in a chlorine residual at the end of incubation period that is comparable to the chlorine residuals measured in operating full scale distribution systems (commonly between 0.5-2 mg/L) and the incubation period of 12 or 48 hr which is comparable to the average hydraulic residence time in a distribution system. Therefore higher chlorine doses and incubation periods at the standardized formation potential procedures (THMFP testing method) would result in higher THM concentrations than the ones measured by SDS tests (Standard Methods, 1998, Najm et al., 1994).

2.4. Adverse Health Effects

The concern surrounding DBPs formed during disinfection process is based on evidence that these by-products have some adverse health effects, in particular cancer and reproductive disorders (Cantor et al., 1988; Graves et al., 2002).

2.4.1. Human Studies

Sources and routes of human exposure to DBPs could be;

- Drinking water (ingestion)
- Bathing (ingestion, inhalation, dermal)
- Showering (ingestion, inhalation, dermal)
- Swimming pool use (ingestion, inhalation, dermal)
- Foods and beverages (ingestion)

Lin and Hoang (2000) developed exposure models to consider the three major scenarios associated with probable inhalation exposure of THMs, including shower, pre- and post-cooking activities, and cooking processes. The model results show that the mean inhalation exposure of THMs for shower, pre- and post-cooking activities, and cooking processes are 26.4, 1.56, 3.29 µg/day, respectively. The total inhalation exposure (summation of the three scenarios) was found to be comparable with that for direct ingestion, indicating that inhalation is an important pathway for THM exposure from drinking water.

Depictive epidemiologic studies have consistently suggested increased risks of bladder, stomach, large intestine and rectum cancer in areas where chlorinated surface waters have been used. 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).

Morris et al. (1992) used a statistical method to compile the results of many studies conducted between 1966 and 1991 to evaluate the effects of chlorination by-products. They found that the studies supported a strong association between bladder cancer and exposure to disinfection byproducts in drinking water and also further indicated a fairly strong relationship between rectal cancer and chlorination by-products.

A considerably richer literature reporting adverse health effects through toxicological laboratory studies is available. Adverse effects of some of the important DBPs are summarized in Table 2.7.

Support for an association between by-products of chlorination and measures of fetal growth is found in two European studies that used method of disinfection as the exposure marker. A hospital-based study in Italy showed lower mean birthweights among women greater than 30 years of age consuming chlorinated water and reported associations with low birth weight and somatic parameters (Kanitz et al., 1996). Källén and Robert (2000) also reported an effect of chlorine treated systems on somatic parameters of body length and head circumference as well as an association with low birth weight and preterm delivery. However, another study conducted in Taiwan found no evidence of an association between low birth weight and chlorination, but municipalities using chlorination had a significantly higher rate of preterm delivery (Yang et al., 2000).

Table 2.7. Toxicological Information for DBPs (modified after USEPA,1999b)

DBPs	Compound	Rating*	Detrimental effects
THM	$CHCl_3$	B2	Cancer,liver,kidney,and reproductive effects
	$CHClBr_2$	C	Nervous system,liver,kidney and reproductive effects
	$CHCl_2Br$	B2	Cancer,liver,kidney,and reproductive effects
	$CHBr_3$	B2	Cancer,nervous system,liver and kidney effects
HAN	C_2NCl_3	C	Cancer,mutagenic and clastogenic effects
HAAs	$CHCl_2COOH$	B2	Cancer,reproductive and developmental effects
	CCl_3COOH	C	Liver,kidney,spleen and developmental effects
Inorganic compounds	Bromate	B2	Cancer
	Chlorite	D	Developmental and reproductive effects

** A:Human carcinogen; B1:Probable human carcinogen (with some epidemiological evidence); B2:Probable human carcinogen (sufficient laboratory evidence); C:Possible human carcinogen; D:Non classifiable.*

2.4.2. Animal Studies

Among all DBPs, THMs received a lot of attention because chloroform was shown to be an animal carcinogen (Fayad, 1993; Simpson and Hayes, 1998). Animal studies showed that chloroform has produced kidney tumors in male mice (Table 2.8) and rats, liver tumors in female rats and liver tumors in mice (both sexes). The International Agency for Research on Cancer (IARC) has evaluated the evidence as "sufficient" for the carcinogenicity of chloroform in experimental animals (IARC, 1999b). There has been a consistent, tissue-, species-, strain- and sex-specific pattern in the rate of metabolism, cytotoxicity and cell proliferation in the liver and kidneys, the target organs of carcinogenicity. These findings have suggested that the mode of action for tumorigenesis of chloroform has involved cytotoxicity in the liver and kidneys and that the cytotoxicity induced cell proliferation may be a key component in the carcinogenesis in these tissues (Komulainen, 2004).

Table 2.8. Target Organs of Tumorigenesis of Chlorinated By-Products in Mice And The Main Types of Tumors (IPCS, 1994; IARC, 1999b; IARC, 1991; IARC, 1999a)

By-product	**Sex**	**Strain**	**Tissue**	**Tumors**
$CHCl_3$	Male, female Male	$B6C3F_1$ ICI, BDF_1	Liver Kidney	Adenoma, carcinoma Adenoma, carcinoma
$CHCl_2Br$	Male Female	$B6C3F_1$ $B6C3F_1$	Kidney Liver	Adenoma, adenocarcinoma Adenoma, carcinoma
$CHClBr_2$	Male Female	$B6C3F_1$ $B6C3F_1$	Liver Liver	Carcinoma Adenoma, carcinoma

Bromodichloromethane has been also reported to be carcinogenic both in rats and mice. In rats, after gavage dosing, it has caused tumors in the large intestine and kidneys, in both sexes, and after exposure in drinking water, liver tumors but only in male rats (IARC, 1991; IARC, 1999a; George et al., 2002).

Studies with mice also showed that, bromodichloromethane increased the liver weight, induced cell proliferation and caused DNA hypomethylation in the liver in female mice like chloroform but the liver damage looked histologically different (Coffin et al., 2000).

Like bromodichloromethane, bromoform produced tumors in the large intestine of rats, adenomatous polyps and adenocarcinomas. It also induced aberrant crypt foci in the colon of male rats like other brominated trihalomethanes (DeAngelo et al., 2002).

In the female mouse liver, chlorodibromomethane induced a similar type of liver toxicity as chloroform, such as increased liver weight, enhanced cell proliferation and c-myc-hypomethylation (Coffin et al., 2000).

2.5. Regulatory Standards for THMs

In the early 1970s, scientists discovered that DBPs were produced during the disinfection process. As the DBPs were investigated, scientists also discovered the harmful health effects of these halogenated byproducts on animals and humans. Since the discovery, several regulations have been promulgated by the regulation agencies of various countries to monitor and control DBPs.

The first legislation (*interim total trihalomethane standard*) to limit the concentration of total THMs (TTHMs) in drinking waters was promulgated on November 29, 1979 by USEPA. This rule set a maximum contaminant level (MCL) of 100 µg/L for TTHMs including chloroform, bromodichloromethane, dibromochloromethane and bromoform as an annual average based on quarterly measurements in the distribution system. This standard is applicable to all community water systems, serving at least 10,000 people, that disinfect water using Cl compounds.

The *Information collection rule (ICR)* was promulgated by USEPA in May, 1996. Information collected under this rule would be used with research to support the development of the regulations. According to ICR, large public systems would be required to collect approximately $130 million of occurrence and treatment information concerning pathogens and DBPs. (USEPA, 1997). The ICR applied to three types of public water systems including surface water systems serving more than 100,000 people, groundwater serving more than 100,000 people and groundwater serving 50,000 to 100,000 people. (Xie, 2004).

Disinfectant / disinfection by-products (D/DBP) regulations have been proposed by USEPA in two stages (Stage I and Stage II). One goal of the proposed D/DBP rule is to balance the risk of disease associated with the presence of pathogenic microorganisms with the chemical toxicity risks associated with disinfectants and DBPs.

The Stage 1 D/DBP Rule was promulgated by the USEPA on December 18, 1999. This rule covers many areas including DBP monitoring and reporting, best available technologies (BAT) for DBP control and coagulation provisions. This rule lowered the TTHM maximum contaminant levels (MCLs) to 80 µg/L and regulated five haloacetic acids (HAAs), bromate, and chlorite for the first time. MCLs for the sum of five HAAs, bromate ion and chlorite ion were set at 60 µg/L, 10 µg/L and 1,000 µg/L, respectively. Compliance with Stage 1 regulations for THMs and HAAs is based on the running annual averages, which represent averages of all samples collected in a utility's distribution system over a one-year period. The BATs for THM and HAA control involve enhanced coagulation, enhanced softening or using granular activated carbon.

The proposed Stage 1 DBP rule also included lower MCLs for TTHMs (40 ug/L) and HAA5 (30 ug/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 repropose, as appropriate, depending on the criteria agreed on in a second regulatory negotiation (USEPA, 1997).

With the proposal in Stage 2, the spatial averaging components have been eliminated; that is, utilities will have to comply with the MCLs at each sampling location in the distribution system which is a phenomenon called “water quality equity” (Wilkes, 2002).

In addition to Total Trihalomethanes Rule, Information Collection Rule and Stage 1/Stage 2 Disinfectant/Disinfection by-products Rules, several rules (Total Coliform Rule, Surface Water Treatment Rule, Long Term 1 Enhanced Surface Water Treatment Rule, etc.), have been promulgated or proposed by the USEPA in order to balance the chemical and microbial risks in disinfected drinking water. For example; Surface Water Treatment Rule (SWTR), promulgated in June 1989, is applicable to all public water systems using surface water sources or ground water sources under the direct influence of surface water. In order to comply with this regulation, systems must achieve at least 3 log (99.9%) combined removal and inactivation of *Giardia* and 4 log (99.99%) of viruses.

Not only USEPA but also the other governmental agencies of various countries have focused on DBPs and have promulgated regulations. The World Health Organization (WHO, 1993) published drinking water guidelines for a few DBPs including THMs, haloacetic acids (HAAs), haloacetonitriles (HANs), chlorite, chloral hydrate, formaldehyde and cyanogen chloride. In addition to individual THM guidelines, the WHO has also suggested that the sum of the ratios of the THM levels to the guideline values should not exceed 1 (Table 2.9) (Sadiq and Rodriguez, 2004).

Health Canada has set 0.10 mg/L for total THM as an interim maximum acceptable concentration, which serves as a guideline for Provincial regulations in 2001. No Canadian drinking water quality guideline exists for other DBPs for the time being. The Aus–NZ (2000) and UK (2000) drinking water standards are also summarized in Table 2.9 for comparison (Sadiq and Rodriguez, 2004).

Table 2.9. Standards/Guidelines related to THMs (mg/L) in various jurisdictons of the World (Sadiq and Rodriguez, 2004)

Compound	**WHO (1993)**	**USEPA (2001)**	**Health Canada (2001)**	**Aus-NZ (2000)**	**UK (2000)**
Chloroform (Trichloromethane)	0.200	0.000*	-	-	-
Bromodichloromethane	0.060	0.060*	-	-	-
Dibromochloromethane	0.100	0.000*	-	-	-
Bromoform	0.100	0.000*	-	-	-
Total Trihalomethanes	(THM/WHO)≤1**	0.080	0.100	0.250	0.100

** Maximum Contaminant Level Goals (MCLG)*

*** the sum of the ratios of the THM levels to the guideline values should not exceed 1*

As it can be seen in Table 2.9, much concern is given on DBPs in developed and developing countries. Although the standards become more and more stringent all over the world, in Turkey there is no attempt to regulate THMs yet.

2.6. Kinetics of THM Formation

The presence of organic disinfection by-products (DBPs) in drinking water has caused great public health concerns. Chlorine consumption and THM formation were very rapid during the first hours of the reaction followed by a more gradual decay and formation after 10 hr (Gang et al., 2003; Gallard and von Gunten, 2002; Boccelli, et al., 2003; Urano et al., 1983). The rapid and slow decay rates are likely due to different competing reactants, such as the oxidation of inorganic compounds (rapid) and substitution reactions with NOM (relatively slow) (Boccelli et al., 2003).

Also, one of the most important factors affecting their formation during the disinfection procedure is reaction time. Investigation of the influence of reaction time on DBPs formation is critical in order to determine the final concentrations to which people could be exposed. The kinetics of the formation of DBPs can be different for the different categories or species of compounds, depending also on the chlorine dose and organic matter content. (Nikolaou et al., 2004).

Gallard and von Gunten (2002) investigated the kinetics of the formation of THMs and of chlorine consumption for the chlorination of natural organic matter with an excess of chlorine (50 μM > $[Cl_2]_0$ > 210 μM). The study showed that THM precursors could be divided into a fast (formed within the first hours of reaction time) and a slow reacting fraction. Kinetics of formation of THMs from slow reacting precursors verified a second order model, first order in chlorine concentration and first order in reactive sites.

Nikolaou et al. (2004) investigated the kinetics of the formation of different species of DBPs including THMs in the three river (Evergetoulas, Mylopotamos, Tsiknias) samples of Greece. The formation of THMs were completed within 24 hr reaction time in all chlorinated waters. For $CHCl_3$, $CHCl_2Br$ and $CHClBr_2$ in chlorinated water from river Evergetoulas the formation rates were highest during the first hours of the reaction and then decreased. However, for waters from rivers Mylopotamos and Tsiknias the opposite behavior was observed, with the formation rates increasing after the first hours of the reaction. Bromoform was the only compound with formation rate increasing with time in all three rivers. Increase of chlorine dose resulted in increase of the THMs formation rates, especially for $CHCl_3$ and $CHCl_2Br$ in water from river Evergetoulas. Regarding the rate of formation of the different species of THMs, in chlorinated waters from river Evergetoulas and Tsiknias the order followed was $CHCl_3 > CHCl_2Br > CHClBr_2 > CHBr_3$, while for chlorinated water from river Mylopotamos, in significant presence bromide ion, the order was $CHCl_2Br > CHClBr_2 > CHCl_3 > CHBr_3$ at the low chlorine dose, and became $CHClBr_2 > CHBr_3 > CHCl_2Br > CHCl_3$ at the higher chlorine dose.

El-Shafy and Grünwald (2000) investigated the THM formation in a water supply South Bohemia and found out a very good correlation between the residence time and THM and chloroform formation (r^2 of 0.89 for the chloroform and 0.91 for the THM). The increase of THM and chloroform concentrations were formulated as exponential functions of the residence time t (first-order) as;

- $THM_t = THM_0 \exp(kt)$ (Eq. 2.1)
- $CHCl_{3t} = CHCl_{30} \exp(kt)$ (Eq. 2.2)

The reaction rates of chlorine are dependent on several factors such as source water characteristics, treatment type (which can effect the amount and type of reactive material available for reaction), contact time (both in the treatment plant and distribution system) and the characteristics of the distribution system (pipe material, pipe age, etc.) (Boccelli et al., 2003).

Adin et al., (1991) suggested THM formation occurs in a stepwise fashion: fast formation of a chlorinated intermediate, followed by slow formation of a second intermediate, followed by THM formation.

Rossman et al., (2001) investigated the DBP formation kinetics in a simulated distribution system by conducting experiments in a simulated pipe environment and glass bottles. They found out a much more rapid decay of chlorine in the pipe than in the bottle resulting in different THM production. Over a 24-hr time period, the production of THM in the pipe was on average 15% higher than for the bottles which suggested that there was a reservoir of available THM precursor material attached to the pipe wall.

Kavanaugh et al., (1980) investigated a two-parameter kinetic model of trihalomethane formation for predicting THM formation. They found that the order of THM formation reaction with respect to applied chlorine dose has been shown to be approximately three.

Besides the kinetics of THM formation, consumption of chlorine was also investigated by different researchers. Haas and Karra (1984) evaluated the reliability and performance of five different chlorine decay models. They investigated first-order decay, power-order decay, first-order decay with stable component, power law decay with stable component and parallel first-order decay. They found that the parallel first-order decay model, which assumes parallel decay of two components of chlorine residual (one decaying more rapidly than the other), provided the best results.

The Water Treatment Plant model used three models in sequence to describe chlorine decay: zero-order from t=0 to t=5 min, second order from t= 5 min to 5 h, and first order for t>5 h (USEPA, 1992).

Koechling (1998) investigated the impacts of source water quality and reaction conditions on chlorine reactions with natural organic matter. The results showed that chlorine decay and demand was highly correlated to DOC concentration and UV absorbance for eleven different raw waters chlorinated at the same Cl_2/DOC ratio: the higher the DOC or UVA, the larger the extent and the faster the chlorine decay.

CHAPTER 3

EXPERIMENTAL METHODS

This chapter explains the experimental plan, sample collection and how each experiment was conducted. This chapter also examines the analytical procedures that were used in the experiments.

Experiments were carried out with two reservoir (Atatürk and Devegeçidi) samples and humic acid, the model compound, in order to determine the kinetics of THM formation. Reservoir waters were selected according to the results of a project of Regional Directorate of State Hydraulic Works. In this study, twenty nine surface waters, which are used as drinking water supply for public, have been examined with respect to formation potential of DBPs. Humic acid was used for comparison with the reservoir samples which in turn provide information on the organic matter characteristics of reservoir waters. Kinetic experiments lasted for six weeks at various reaction times detailed in Section 3.3.

3.1. Materials

3.1.1. Sample

In this study, water samples were taken monthly from the raw waters of Devegeçidi and Atatürk Reservoirs which are located in Diyarbakır and Şanlıurfa, respectively. Water samples were preserved at 4 ^{o}C until analysis and without adding any preservatives. In laboratory, kinetic experiments were carried out after the chlorination of the samples. Raw water characteristics of Atatürk and Devegeçidi reservoir waters are provided in Table 3.1 and Table 3.2 on a seasonal basis, respectively.

Table 3.1. Raw Water Characteristics of Atatürk Reservoir Water

	Spring 2003	**Summer 2003**	**Fall 2003**	**Winter 2003**
NPOC (mg/L)	0.677	0.927	0.884	0.080
Bromide (µg/L)	283.3	150.0	450*	20.0
$UV(A)_{254nm}$	0.0175	0.0135	-	0.0165

** measured only in September 2003*

Table 3.2. Raw Water Characteristics of Devegeçidi Reservoir Water

	Spring 2003	**Summer 2003**	**Fall 2003**	**Winter 2003**
NPOC (mg/L)	2.926	2.621	2.784	2.823
Bromide (µg/L)	26.7	23.3	10.0*	65.0
$UV(A)_{254nm}$	0.0880	0.0678	-	0.0688

** measured only in September 2003*

3.1.2. Reagents

The chlorine solution used in this study was sodium hypochlorite solution produced by Fluko with the following specifications:

- Chemical formula: NaOCl
- Molecular weight: 74.44 g/mole
- Density (d_{20}): 1.25 g/m^3

Characteristics of the solid humic acid, the model compound, are provided below:

- Humic acid
- Content: 5gr
- CAS: 68131-04-4
- Produced by Acros Organics

3.1.3. Glassware

All the glassware used during the experiments were cleaned using chromic acid. The chromic acid solution is prepared by mixing 100 g of $K_2Cr_2O_7$ with 5 L of H_2SO_4. The cleaning procedure comprised the washing of glassware with chromic acid solution, rinsing several times with tap water and then two times with distilled water. Then, the glassware were dried at 105 ^{o}C for two hours and cooled to room temperature.

3.2. Analytical Techniques

This section provides detailed methods used in the experiments and discusses how each parameter was analyzed.

UV(A)$_{254nm}$ Measurement

UV absorbance measurements were carried out by VARIAN Cary-100 Model Spectrophotometer which is a UV/Visible spectrophotometer covering wavelength range from 190 to 920 nm. The bandwith is 5 nm.

The UV measurements were performed at 254 nm in order to eliminate or minimize the interferences of compounds such as nitrate, nitirite, ferrous iron and bromide (Standard Methods, 1998). Also, samples were filtered to control variations in UV absorption caused by particles. Calibration of the spectrophotometer was made with distilled water. UV measurements were performed using quartz cells of 1 cm width. One of the cells was filled with distilled water and used as a reference during the measurements.

Non-purgeable Organic Carbon (NPOC) Measurement

Non-purgeable organic carbon (NPOC) measurements were carried out by Shimadzu 5000A TOC Analyzer. This analyzer can measure total carbon (TC), total organic carbon (TOC) and inorganic carbon (IC) as well as non-purgeable organic carbon. Its operation is based on the combustion/non-dispersive infrared gas analysis method widely employed for TOC measurements.

For NPOC measurements, pH of the samples were adjusted to 2 with dilute (1/50) HCl. The acidified sample was purged with high purity air at a flow rate of 150 ml/min for 10 minutes to remove the inorganic carbon content.

Each sample was measured at least three times and at most five times to decrease the coefficient of variation below 2%. The NPOC of the samples were determined using the calibration curves given in Appendix A.

In order to obtain the calibration curves, the stock standard solution for total carbon was prepared by dissolving 106.06 mg potassium hydrogen phthalate ($C_8H_5KO_4$) in 250 ml organic free (distilled) water. The TC concentration of this solution was 200 mg/L. Then, the stock solution was diluted in appropriate amounts with deionized water to obtain standard solutions with concentrations of 1, 2, 4, 6 mg/L. The peak areas of these solutions were measured and calibration curve was plotted.

<u>THM Measurement</u>

THM measurements were carried out by VARIAN CP-3380 Gas Chromotograph with an autosampler. A capillary column was used to determine the THM compounds; chloroform, dibromochloromethane, bromodichloromethane and bromoform. The characteristics of the column, autosampler and the operating conditions are given in Table 3.3, Table 3.4 and Table 3.5, respectively.

Table 3.3. Characteristics of the Capillary Column

Column Type	WCOT fused silica
Stationary Phase	CP-Sil 13 CB for halocarbons
Column Length	25 m
Outside Diameter	0.32 mm
Inside Diameter	0.45 mm
Film Thickness	1.20 µm

Table 3.4. Characteristics of the Autosampler

Autosampler Type	8400
Syringe size	5 µL
Injection Mode	Standard on Column
Sample Depth	90 %
Solvent Depth	90 %

Table 3.5. Operating Conditions

Detector	Electron Capture Detector (ECD)
Detector Temperature	290 °C
Injector	Front CP 1177
Injector Temperature	280 °C
Column Temperature	50-110 °C (increasing 5 °C/min)

The analyses were carried out according to Liquid-Liquid Extraction Gas Chromotographic Method 6232B (Standard Methods, 1998). According to this method, 10 mL of sample was extracted with 2 mL of n-pentane by shaking for one minute in a seperation funnel of 25 mL volume. The samples and pentane were added to the funnel using syringes of 10 mL and 2 mL volumes, respectively, to avoid the loss of THMs during sampling. Phase separation occurred in 2 minutes and the upper phase was collected into 2 mL vials having PFTE septa screw caps.

The standard THM solutions were prepared using the THM test mixtures produced by SUPELCO. The THM mixture contained 99.5 µg/L of chloroform, 97.0 µg/L of bromodichloromethane, 104.5 µg/L of dibromochloromethane and 101.4 µg/L of bromoform in 1 mL of methanol. The standards were prepared for the range of 0-500 µg/L. For THM standard preparation; 50, 100, 300, 500 µg/L of samples were taken from the THM test mixture and diluted to 100 mL by organic free water. The corresponding standard concentrations are given in Table 3.6.

Table 3.6. THM Standard Solution Concentrations

$CHCl_3$ (μg/L)	$CHCl_2Br$ (μg/L)	$CHClBr_2$ (μg/L)	$CHBr_3$ (μg/L)
49.75	48.50	52.25	50.70
99.50	97.00	104.50	101.40
298.50	291.00	313.50	304.20
497.50	485.00	522.50	507.00

In the analysis of THM samples, samples of 1 μL volume were injected into the gas chromatography (GC) column by autosampler and four peaks were observed belonging to the four THM compounds. Calibration curves were obtained by plotting the areas under the peaks of each standard THM solutions versus their concentrations, as shown in Appendix B. The THM concentrations of the samples were determined using these calibration curves.

THMFP

Trihalomethane Formation Potential (THMFP) is an index of the potential extent of THM formation after the application of chlorine; that is, THMFP test is conducted in order to determine the maximum potential of the sample to form trihalomethanes. THMFP of a water sample is determined by subtracting the initial total THM ($TTHM_i$) concentration from the final total THM ($TTHM_f$) concentration.

THMFP test comprises of the following steps:

- Determination of the sample's chlorine demand by DPD Colorimetric Method (Standard Methods, 1998),
- Dosing of excess chlorine,
- Adjusting pH to 7 by adding phosphate buffer,
- Incubating the samples at 25 °C till the end of reaction period,
- Determination of THM by liquid-liquid extraction followed by gas chromatography and residual chlorine concentration by DPD Colorimetric Method.

Chlorine demand of the sample is determined by adding an initial chlorine (C_i) dose close to the previous chlorine demands of the sample. After incubating it overnight at 25 °C, residual chlorine (C_R) of the sample is measured using DPD (N,N-diethyl-p-phenylenediamine) colorimetric method [DPD free chlorine reagent (powder pillow) method] (Standard Methods, 1998). In this method, DPD reagent is added to the sample paying close attention to color development. Then, the absorbance of the sample is quickly measured at 530 nm by spectrophotometer. The total chlorine demand of the water sample is; $D_{Cl} = C_i - C_R$. In the standard 7-day THMFP tests, the volume of chlorine to be dosed to the sample, so as to assure that the reaction is not Cl-limited (free chlorine residual of 3 to 5 mg/L existing at the end of reaction time), is calculated as follows:

$$V_D\ (\mathrm{mL}) = [(D_{Cl} + 3) / (C_{stock}/1000)] \times (V / 1000) \qquad \text{(Eq. 3.1)}$$

where;

V_D: volume of chlorine to be dosed to the sample (mL),
D_{Cl}: chlorine demand of the water sample (mg/l),
C_{stock}: concentration of stock solution (mg/l),
V: volume of the sample bottle (mL).

Chlorine Analysis

Chlorine ion concentration was measured colorimetrically according to Standard Method 4500F using a Hach Dr 2000 analyzer. A-25 ml cell was filled with samples and added DPDs free chlorine reagent (powder pillow). After mixing, chlorine ion concentration was read at 530 nm wavelength.

Bromide Analysis

Bromide ion concentration was measured colorimetrically according to Standard Method 4500 Br^- B using a Hach Dr 2000 analyzer. A-25 ml cell was filled with samples and added DPD free bromide reagent (powder pillow). After mixing and 3 minutes detention period, bromide ion concentration was read at 590 nm wavelength.

3.3. Experimental Methods

The water samples were taken from Atatürk and Devegeçidi Reservoir waters. The experiments were carried out for the samples of May 2003, June 2003, July 2003, September 2003 and February 2004. The same experiments were also carried out with a solution of humic acid, the model compound, for comparison with the reservoir samples. The reservoir water samples were kept at 4 °C until the experiments were conducted.

In order to compare the kinetics of THM formation due to humic acids in synthetic water sample with the reservoir waters, NPOC values of the humic acid solutions were selected as similar to Atatürk and Devegeçidi Reservoir waters. Therefore, two humic solutions were prepared: The first which has a low organic content (low NPOC) had an NPOC value of 0.7 mg/L which is representative of Atatürk Reservoir waters and the second solution which has an NPOC value of 2.5 mg/L (high NPOC) that would be used to represent the experiments conducted with Devegeçidi Reservoir waters.

Each kinetic experiment lasted 6 weeks (upto the completion of THM formation). During the 6-week long experiments, THM and residual chlorine concentrations were measured in the same hour of the day (except for the measurements within the first 24 hours) at the following reaction times:

- 3 hours, 6 hours, 9 hours, 22 hours, daily in the first week, 10th day, 14th day, 17th day, 21th day, 28th day, 35th day and 42th day (the last day).

For each reaction time, separate sample bottles were used rather than dosing into one bottle in order to prevent THM losses through sampling while opening the bottles at each time interval.

Two different initial chlorine doses (low dose and high dose) were applied to each water sample to determine the effect of chlorine dose on THM formation. Low dose and high dose were chosen as 25% and 75% excess of the chlorine demand, respectively. At each reaction time, THM and residual chlorine concentrations were measured by gas chromatography after liquid-liquid extraction and spectrophotometer, respectively.

These measured THM concentrations were compared with the predicted values of a kinetic model simulated by USEPA and the following equations were used to compute the TTHM levels (Hutton, 1993, Amy et. al., 1987):

$TTHM = 0.00309\ [(TOC)(UVA_{254nm})]^{0.44}\ (Cl_2)^{0.409}\ (t)^{0.265}\ (T)^{1.06}\ (pH\text{-}2.6)^{0.715}\ (Br)^{0.036}$
(Eq. 3.2)

$AWM = 105(UVA)^{-0,089}\,(Br+1)^{0.48}$ (Eq. 3.3)

where;

TTHM: total trihalomethane concentration (µmole/L),
TOC: total organic carbon concentration (mg/L),
$UV(A)_{254nm}$: ultraviolet absorbance at 254 nm,
Cl_2: chlorine dose (mg/L),
t: reaction time (hr),
T: temperature (^oC),
Br: bromide ion concentration (mg/L)
AWM: apparent molecular weight (µg/µmole).

The general strategy adopted in formulating this model was to include single terms to describe the roles of precursor, chlorine, temperature, pH, bromide and reaction time in the formation of THMs because when the various parameters are considered, either molar basis or weight basis, THMs could theoretically serve as the dependent variable whereas the other variables in either their arithmetic or transformed state, represent candidate independent variables. This modeling approach was applied to the entire database consisting of 1090 reservoir cases for predicting total THMFP and kinetics during the chlorination of natural waters.

CHAPTER 4

RESULTS AND DISCUSSION

In this study, raw water samples collected from Devegeçidi and Atatürk reservoirs were used to determine the kinetics of THM formation. Also, seasonal variation of THM formation and the effect of chlorine dose on THM formation were examined. In order to determine the seasonal variation, experiments were conducted with raw water samples collected in May 2003 (representing Spring), June 2003 and July 2003 (representing Summer), September 2003 (representing Fall) and February 2004 (representing the Winter). Also, kinetics of THM formation of humic acid, the model compound, was investigated to compare with reservoir samples.

Devegeçidi and Atatürk reservoirs were selected for this study due to the difference in their organic content. Devegeçidi reservoir waters have a high organic matter concentration, averaging to 2.918 mg/L NPOC in the selected months where kinetic experiments have been conducted. Atatürk reservoir waters have a lower organic content, 1.053 mg/L NPOC on the average for the sampled months.

In order to determine the effect of chlorine dose on THM formation, two different initial chlorine doses were applied to each water sample. These are referred to as the low dose (25% excess of chlorine demand) and the high dose (75% excess of the chlorine demand). At the end of each of the pre-determined time intervals THM and residual chlorine concentrations were measured by gas chromatography after liquid-liquid extraction and spectrophotometer, respectively. Results of the kinetics experiments were compared with the predicted values obtained by the equation of the USEPA model.

4.1. Organic Matter Content

The main parameter that affects the quantity of THMs formed during chlorination is the organic matter content of the raw water. In this study, the organic content was measured in terms of NPOC and UV(A)$_{254nm}$. The results of NPOC measurements carried out with Atatürk and Devegeçidi Reservoir waters are presented in Figure 4.1 and Figure 4.2, respectively. The organic matter content of both reservoir waters was below 5.0 mg NPOC/L which is typical for unpolluted-fresh surface waters. Throughout the experimental period (May 2003-February 2004), NPOC content values varied around 1.0 mg/L and reached its maximum of 1.9 mg/L for Atatürk Reservior and varied around 2.5 mg/L and reached its maximum of 4.0 mg/L for Devegeçidi Reservoir. Maximum values were observed in February 2004 within the kinetic study period for both reservoirs.

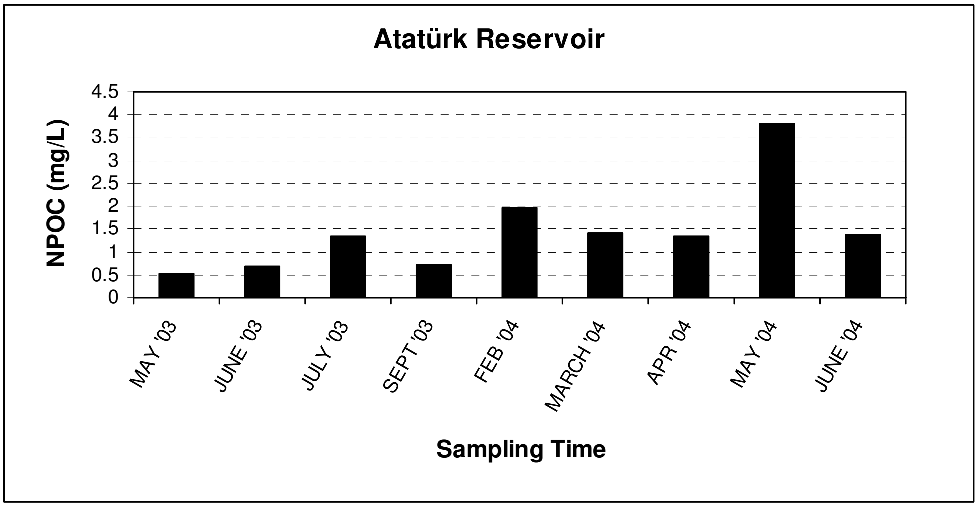


Figure 4.1. NPOC Content of Atatürk Reservoir Water

** Kinetic study has covered the period between May 2003-February 2004.*

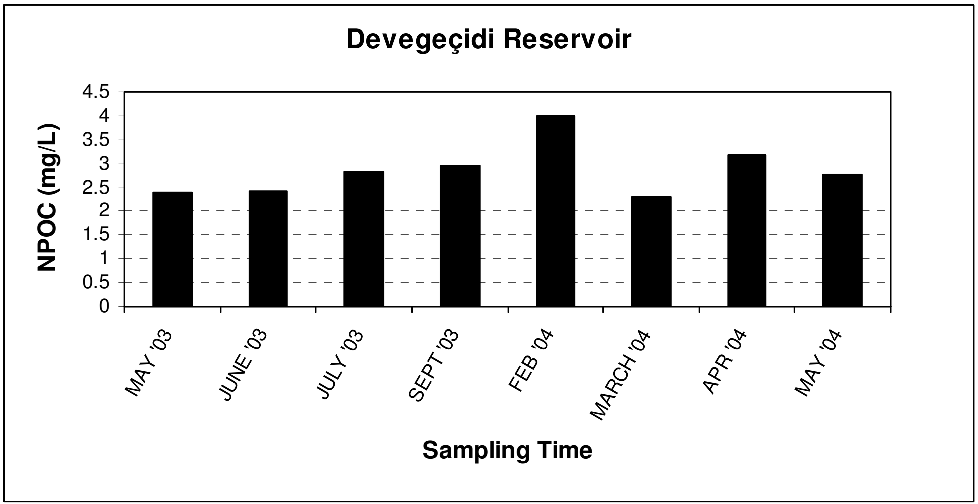


Figure 4.2. NPOC Content of Devegeçidi Reservoir Water

** Kinetic study has covered the period between May 2003-February 2004.*

The organic matter content of the water supplies typically starts to increase in Spring, reaches a maximum in early Fall and then decreases in Winter months. The highest NPOC values are usually observed in Summer and early Fall due to primary biological production (algal growth) which is enhanced as the temperature and the light intensity are increased. Also, the leaching of humic substances from the watershed is another reason for the higher values in Summer. NPOC variation of both reservoir waters throughout the months generally complied with the expected situation. Although the NPOC values for both reservoir waters increased from Spring to Summer, the highest values were both measured in February 2004 (1.987 mg/L for Atatürk Reservoir and 4.004 mg/L for Devegeçidi Reservoir) within the study period for kinetic experiments. These values were unexpectedly higher than the ones measured in Summer 2003. Therefore, NPOC measurements were continued and it was observed that organic matter content is high in all measured months in 2004. These results can be explained by the difference in meteorological conditions (temperature and precipitation) between these two years. When the meteorological conditions were investigated, it was found out that in 2004, less precipitation amount and higher temperature values were observed in the region (State Meteorological Institute, 2004). Higher temperature values increase the algal productivity and reaction rates of THM formation. In addition, higher precipitation values in 2003 results in the dilution of aquatic NOM and therefore in lower values of organic matter. Therefore, higher NPOC values were observed during 2004.

In addition to NPOC, UV absorbance was measured at 254 nm as an indicator of organic matter content. $UV(A)_{254nm}$ measurements were performed for filtered raw water samples in order to prevent the interferences of colloidal particles. The results of $UV(A)_{254nm}$ measurements carried out with Atatürk and Devegeçidi Reservoir waters are presented in Figure 4.3 and Figure 4.4, respectively. $UV(A)_{254nm}$ measurement is suitable for the determination of humic and fulvic content of raw water which are expected to be higher during Summer. In Atatürk Reservoir waters although the highest $UV(A)_{254nm}$ value, 0.0143, was measured in February 2004 during the kinetic experiments (similar to trend exhibited by NPOC), the one observed in July 2003 was also high (0.0139) which is an expected situation since higher $UV(A)_{254nm}$ values are observed during Summer.

The results of $UV(A)_{254nm}$ measurements carried out in Devegeçidi Reservoir Water showed that $UV(A)_{254nm}$ values did not significantly change among all seasons ranging between 0.0615 and 0.0678 during the sampled months. The highest value was observed in February 2004 during Winter. $UV(A)_{254nm}$ and NPOC values followed the same trend.

Besides NPOC and $UV(A)_{254nm}$, SUVA (specific ultraviolet absorbance) is a common surrogate parameter for monitoring NOM. In order to compare the characteristics of different DOMs, UV absorbance at a particular wavelength must be normalized by dividing by the DOC concentration. This normalized value is called absorptivity or specific ultraviolet absorbance (SUVA). The SUVA is an indicator of NOM reactivity (Kitiş, 2001). SUVA values determined for Atatürk Reservoir waters and Devegeçidi Reservoir waters are presented in Figure 4.5 and Figure 4.6, respectively.

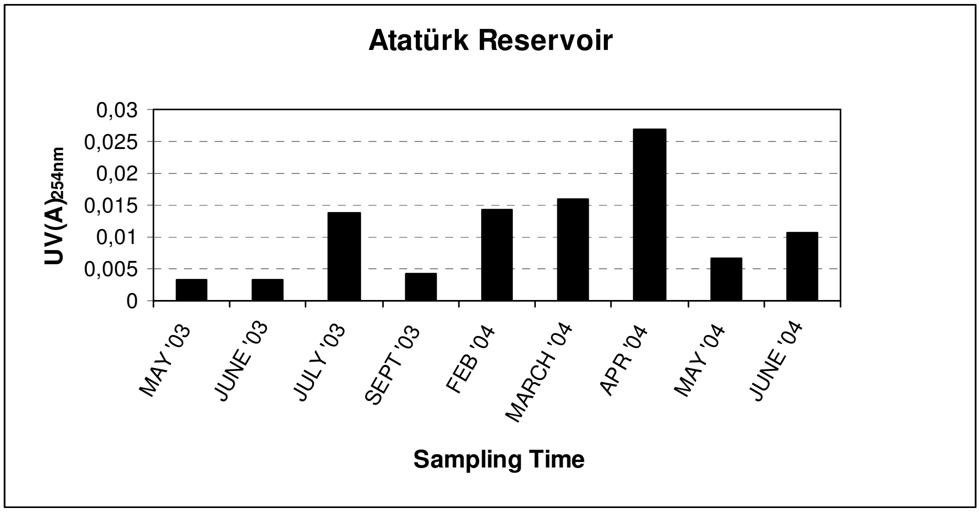


Figure 4.3. UV(A)$_{254nm}$ values of Atatürk Reservoir Water

** Kinetic study has covered the period between May 2003-February 2004.*

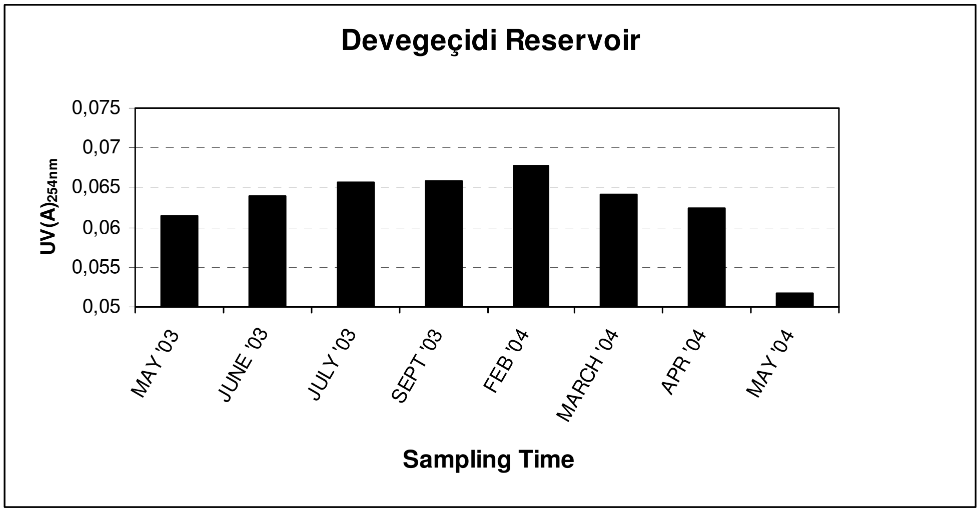


Figure 4.4. UV(A)$_{254nm}$ values of Devegeçidi Reservoir Water

** Kinetic study has covered the period between May 2003-February 2004.*

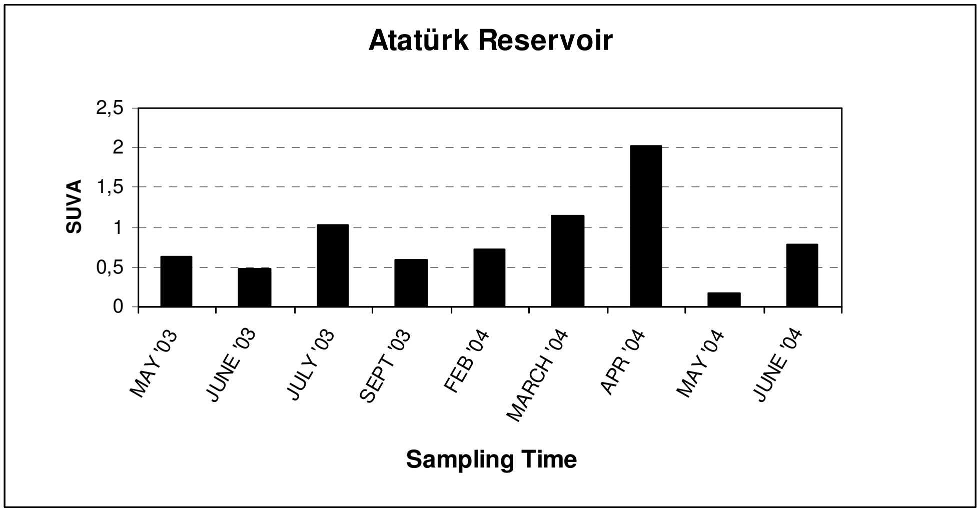


Figure 4.5. SUVA Values for Atatürk Reservoir Water

** Kinetic study has covered the period between May 2003-February 2004.*

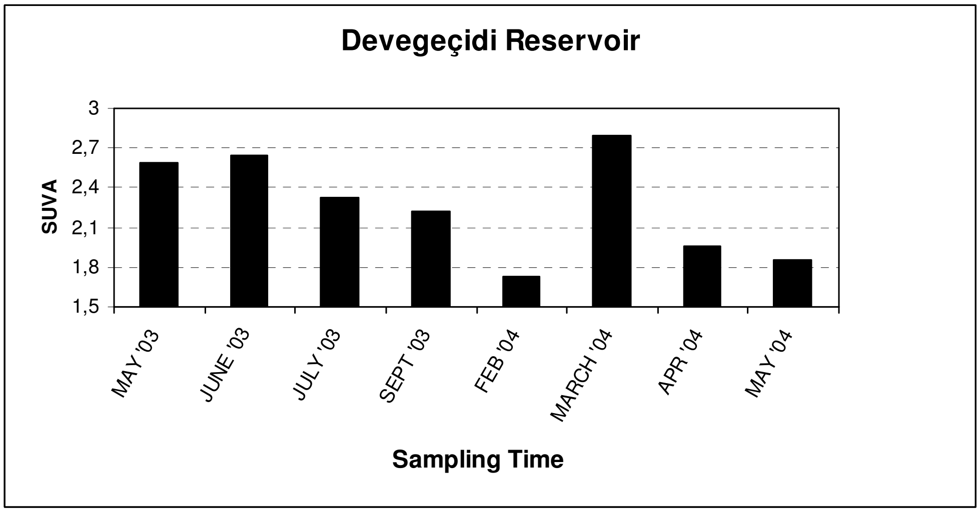


Figure 4.6. SUVA Values for Devegeçidi Reservoir Water

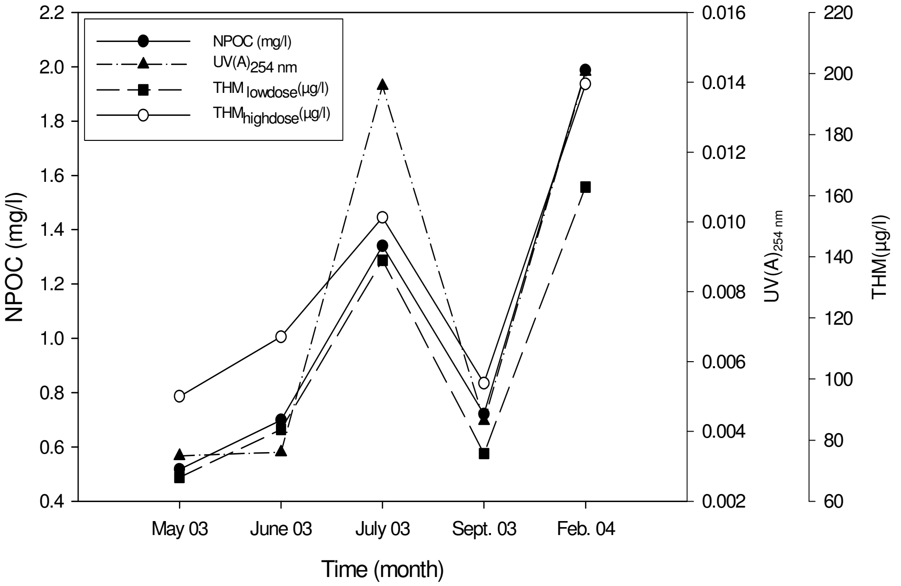
** Kinetic study has covered the period between May 2003-February 2004.*

NOM is a heterogeneous mixture of various complex organic molecules having different SUVA values. Edzwald (1993) has shown that SUVA in the 4 to 5 L/mg-m range is characteristic of waters with a relatively high content of hydrophobic, aromatic, and high molecular weight DOM fractions, such as humic and fulvic acids, whereas SUVA in the <3 L/mg-m range is characteristic of waters with non-humic (hydrophilic) carbon. SUVA values in Atatürk Reservoir waters are generally lower than 2 L/mg corresponding to hydrophilic carbon. In Devegeçidi Reservoir waters SUVA values are higher than the ones observed in Atatürk Reservoir waters, generally ranging between 2.0 and 2.7 L/mg, but showing also hydrophilic characteristics. Also, changes in SUVA values among sampling months show the changes in the nature/composition of natural organic matter. These changes can be attributed to the seasonal variations in organic matter due to meteorological conditions such as temperature and precipitation as well as algal growth/productivity etc.

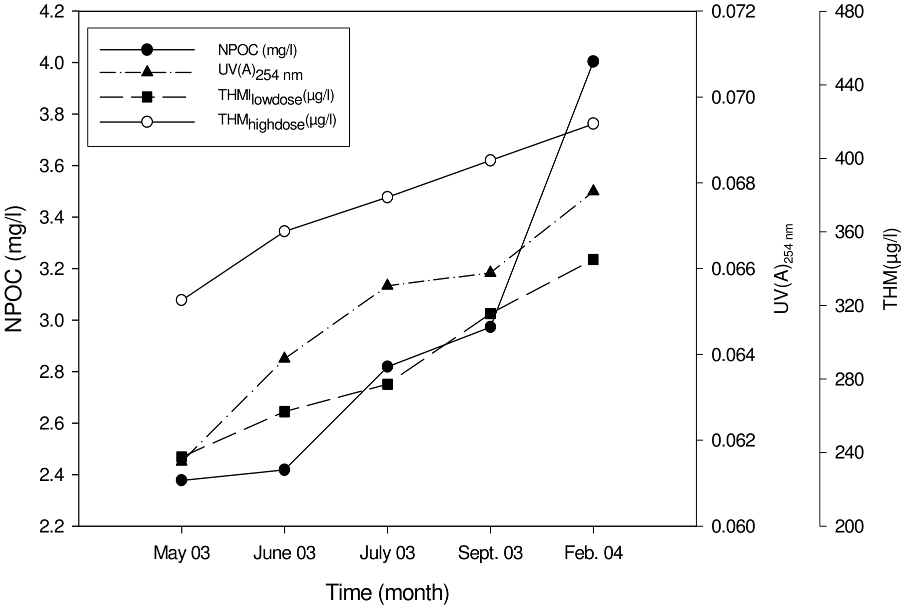
Seasonal variation of TTHM concentration (THMFP) for low and high chlorine doses applied in Atatürk and Devegeçidi Reservoir waters are presented in Figure 4.7a and Figure 4.7b respectively, together with corresponding NPOC and $UV(A)_{254nm}$ values. As seen in Figure 4.7, the seasonal variations of TTHM, NPOC and $UV(A)_{254nm}$ follow the same trend throughout the months studied in both reservoirs.

In Atatürk Reservoir waters, the highest ultimate TTHM and NPOC and $UV(A)_{254nm}$ values were measured in February 2004. The ultimate THM concentrations increased from May 2003 to July 2003 then decreased at September 2003 and finally reached its maximum value on February 2004 which is similar to the trends exhibited by NPOC and $UV(A)_{254nm}$. In Devegeçidi Reservoir waters, the highest ultimate TTHM, NPOC and $UV(A)_{254nm}$ values were measured in February 2004. The ultimate THM concentrations showed an increasing trend from May 2003 to February 2004 similar to the trends of NPOC and $UV(A)_{254nm}$.

Increasing trend in Spring through Summer is an expected situation since the algal activity and temperature increases during Summer months. In addition, less precipitation amounts during Summer results in more accumulation of available organic matter for THM formation reaction. In Winter months, due to heavy rains and low temperature values THM and organic matter concentrations are expected to be low. However, in February 2004, unexpected situation occurred which can be attributed to the changes of meteorological conditions (high temperature and low precipitation).



(a)



(b)

Figure 4.7. Seasonal Variation of Ultimate TTHM (for Low and High Chlorine Doses), NPOC and UV(A)$_{254nm}$ Values in Atatürk (a) and Devegeçidi Reservoirs (b)

Since natural waters are complex in nature, it is generally difficult to understand and analyze the THM formation and factors affecting it. Using a model compound such as humic acids in pure water is thought to eliminate some of the complexities of the system and make it easier to understand the mechanism of THM formation.

Also, as the organic matter composition (humic, fulvic, etc. nature) of the both reservoirs are not known, behavior of the model compound was investigated in order to obtain a general idea about the NPOC structure/organic nature of the reservoir waters and to explain the differences in THM formation observed between two reservoirs.

So, in order to compare the kinetics of THM formation due to humic acids in synthetic water sample with the reservoir waters, NPOC values of the humic acid solutions were selected as similar to Atatürk and Devegeçidi Reservoir waters. Therefore, two humic solutions were prepared: The first which has a low organic content (low NPOC) had an NPOC value of 0.7 mg/L which is representative of Atatürk Reservoir waters and the second solution which has an NPOC value of 2.5 mg/L (high NPOC) that would be used to represent the experiments conducted with Devegeçidi Reservoir waters. $UV(A)_{254nm}$ measurements were performed for filtered raw water samples in order to prevent the interferences of colloidal particles. The results of $UV(A)_{254nm}$ measurements carried out with humic acids showed 0,0471 and 0,165 for low NPOC and high NPOC solutions, respectively.

4.2. Kinetics of THM Formation

In order to determine the kinetics of THM formation, experiments were continued upto the completion of formation (for 6 weeks), with sampling for THM and residual chlorine measurements at pre-determined time intervals. The initial THM concentrations of the raw water samples before chlorination was measured as zero in all months. Concentration of each THM compound, TTHM and residual chlorine as a function of time in May 2003, June 2003, July 2003, September 2003 and February 2004 for low and high chlorine doses are presented in Figure 4.8 – Figure 4.12, respectively for Atatürk Reservoir and in Figure 4.13 – Figure 4.17, respectively for Devegeçidi Reservoir.

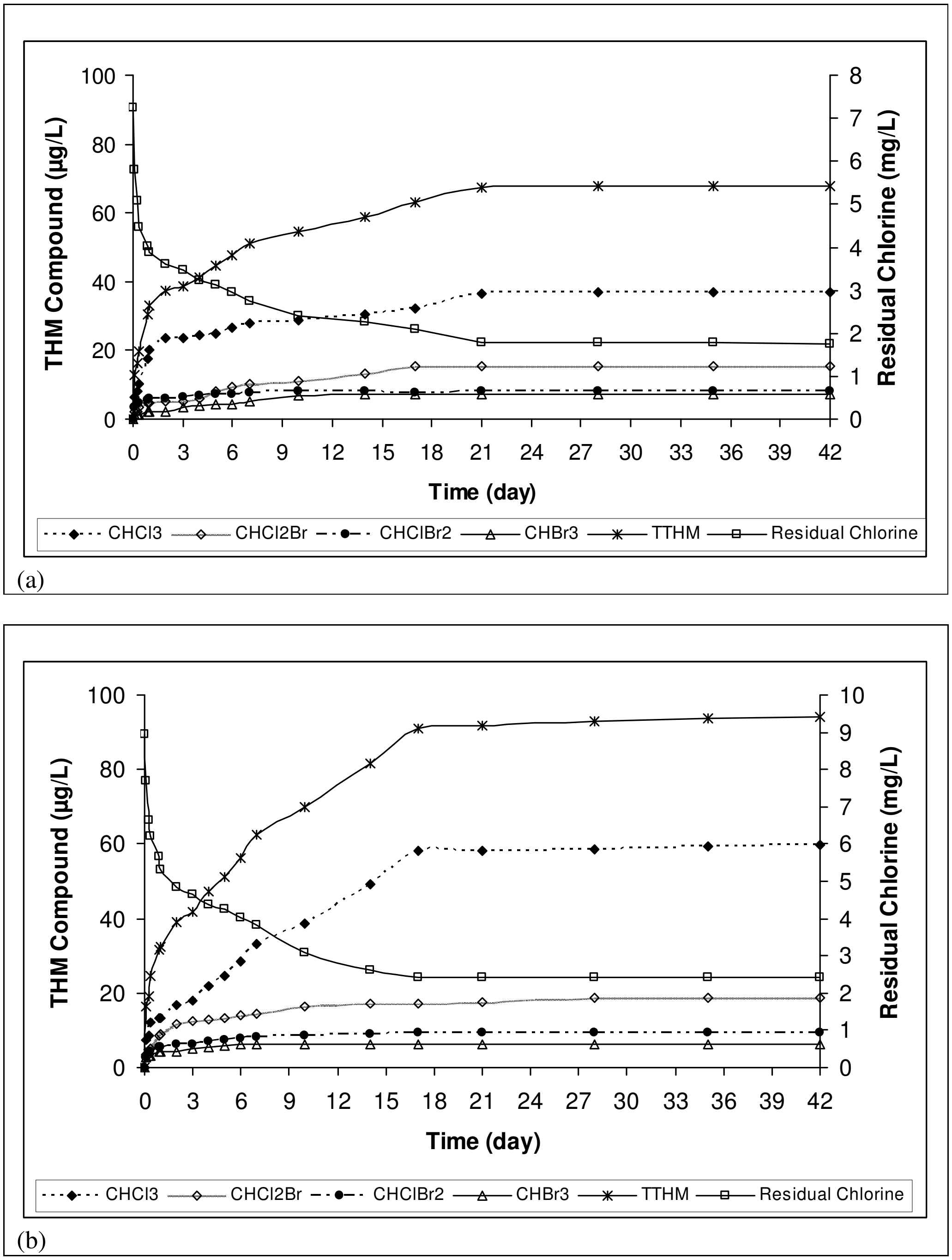


Figure 4.8. Formation of each THM compound/TTHM and Consumption of Chlorine in Atatürk Reservoir in May 2003 (a) Low Dose (Initial Chlorine Conc.= 7.25 mg/L) (b) High Dose (Initial Chlorine Conc.= 8.95 mg/L)

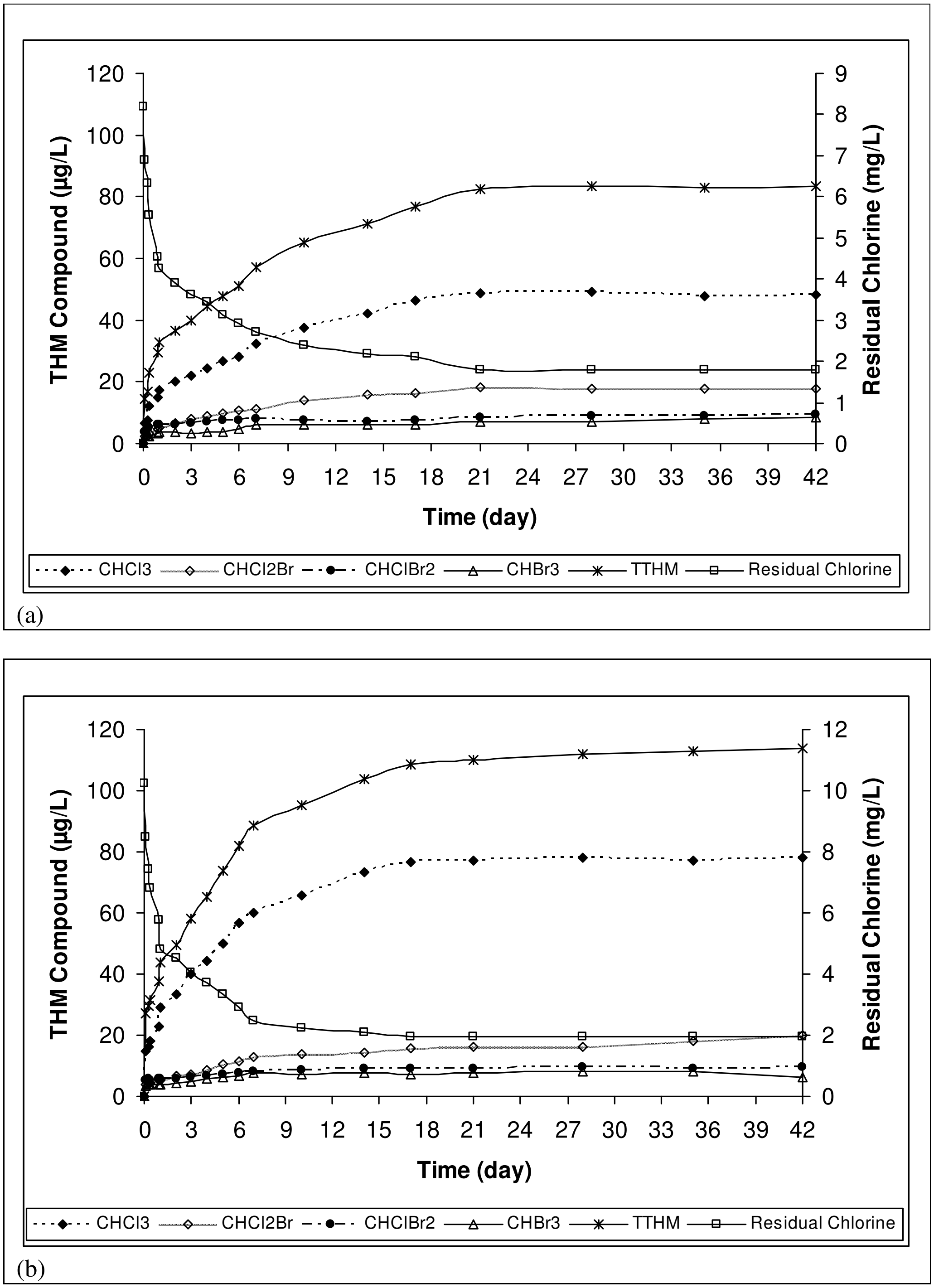


Figure 4.9. Formation of each THM compound/TTHM and Consumption of Chlorine in Atatürk Reservoir in June 2003 (a) Low Dose (Initial Chlorine Conc.= 8.18 mg/L) (b) High Dose (Initial Chlorine Conc.= 10.25 mg/L)

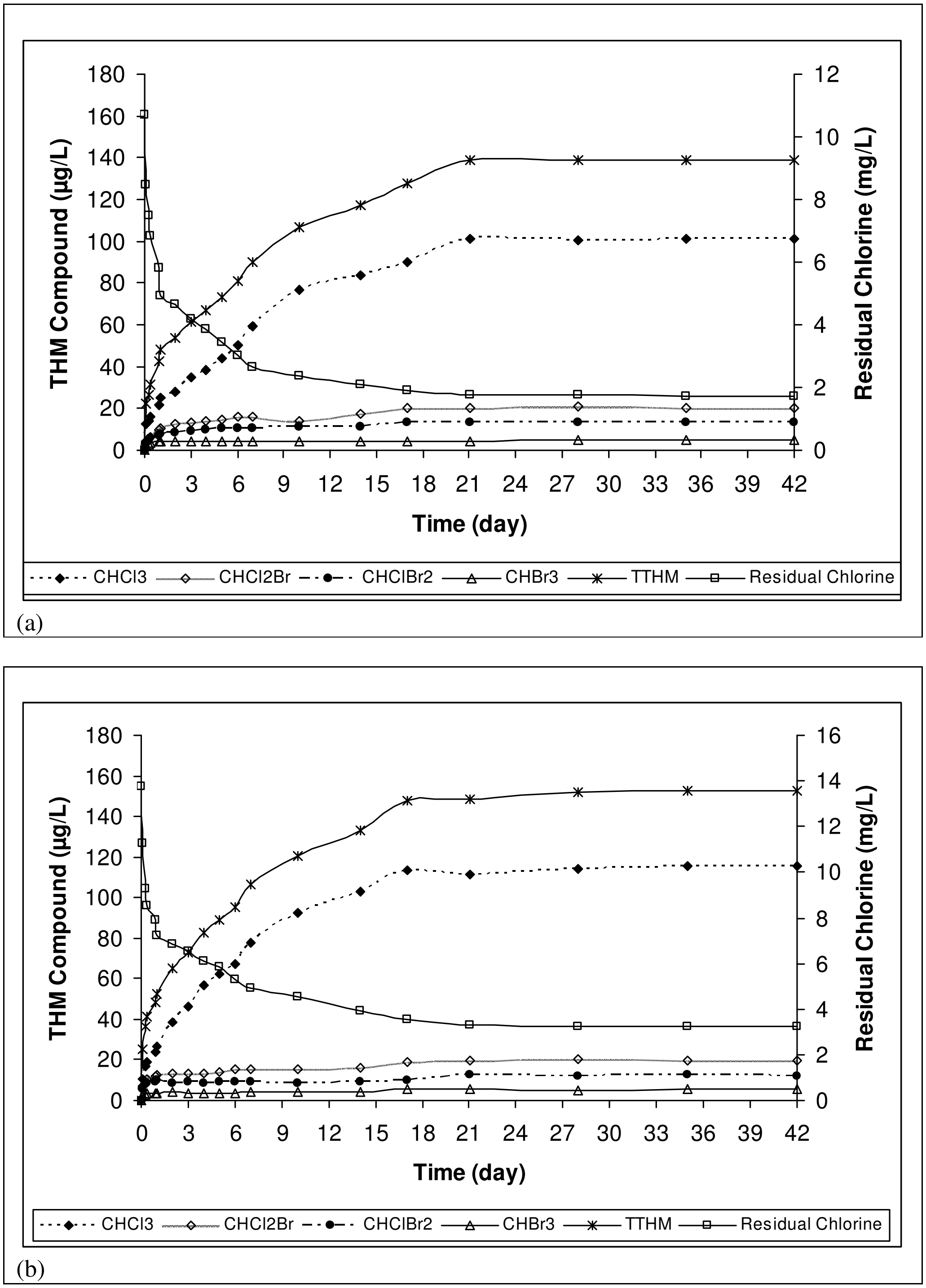


Figure 4.10. Formation of each THM compound/TTHM and Consumption of Chlorine in Atatürk Reservoir in July 2003 (a) Low Dose (Initial Chlorine Conc.= 10.68 mg/L) (b) High Dose (Initial Chlorine Conc.= 13.75 mg/L)

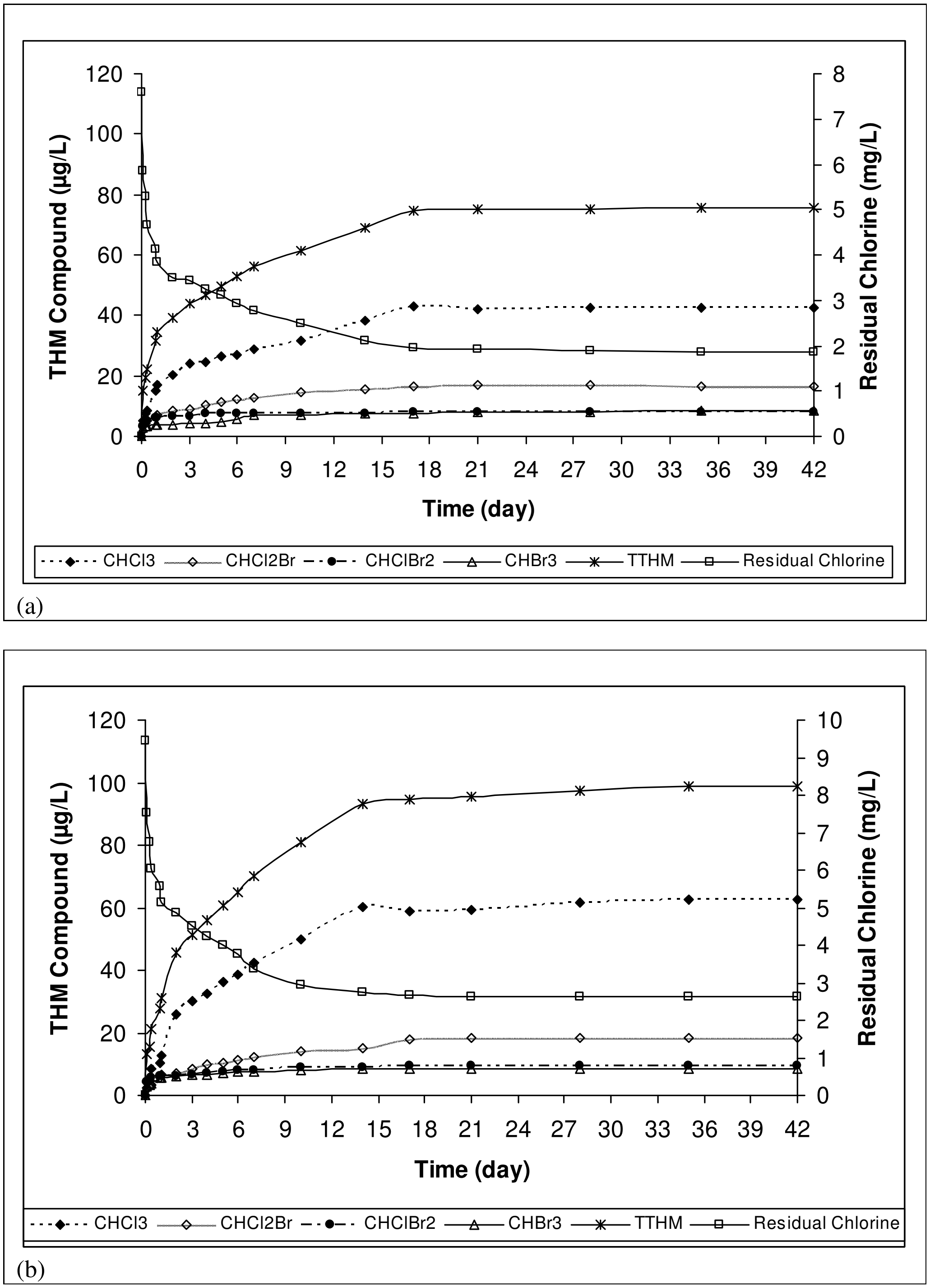


Figure 4.11. Formation of each THM compound/TTHM and Consumption of Chlorine in Atatürk Reservoir in September 2003 (a) Low Dose (Initial Chlorine Conc.=7.6 mg/L) (b) High Dose (Initial Chlorine Conc.=9.44 mg/L)

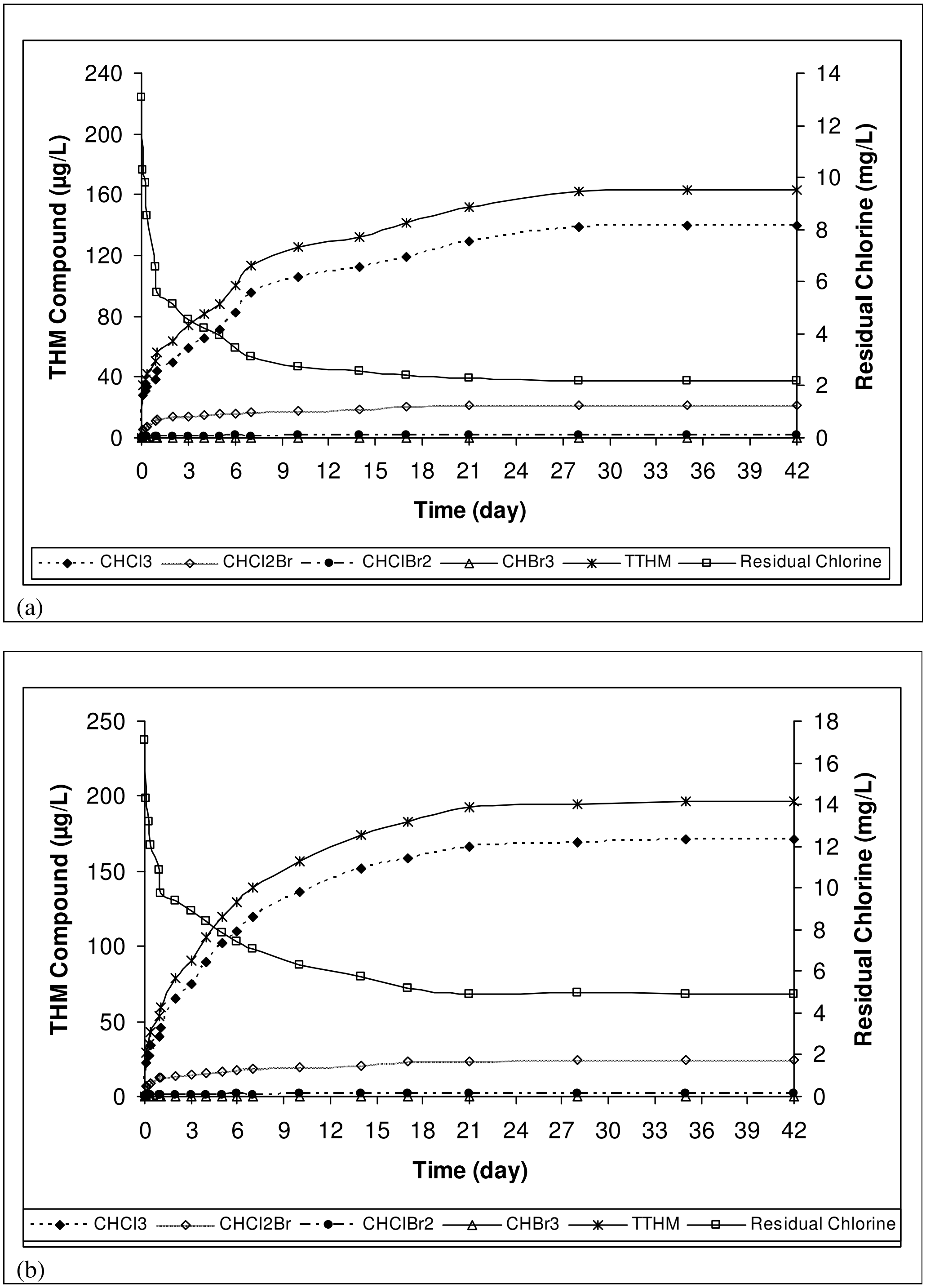


Figure 4.12. Formation of each THM compound/TTHM and Consumption of Chlorine in Atatürk Reservoir in February 2004 (a) Low Dose (Initial Chlorine Conc.=13.1 mg/L) (b) High Dose (Initial Chlorine Conc.=17.07 mg/L)

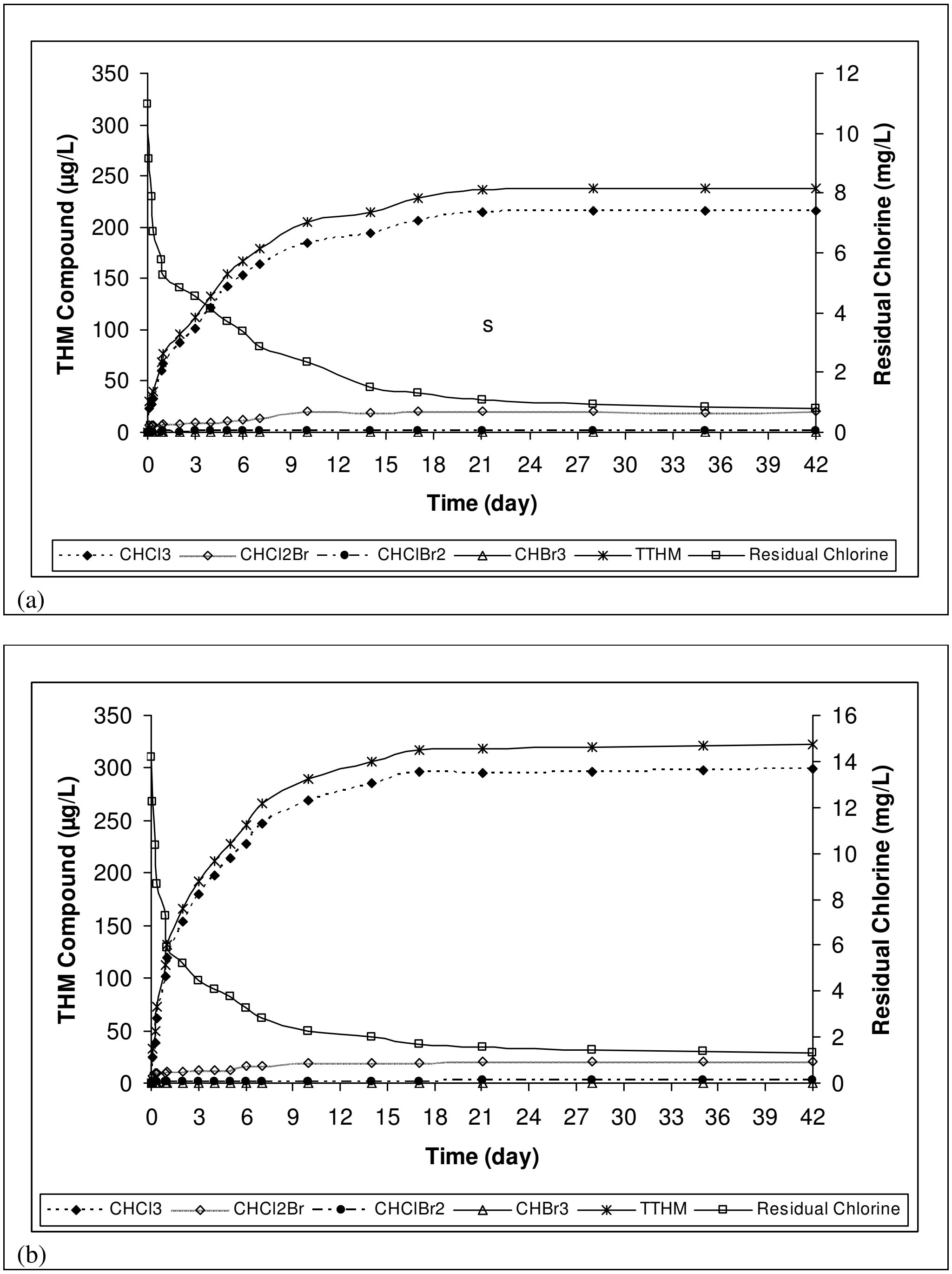


Figure 4.13. Formation of each THM compound/TTHM and Consumption of Chlorine in Devegeçidi Reservoir in May 2003 (a) Low Dose (Initial Chlorine Conc.=10.99 mg/L) (b) High Dose (Initial Chlorine Conc.=14.18 mg/L)

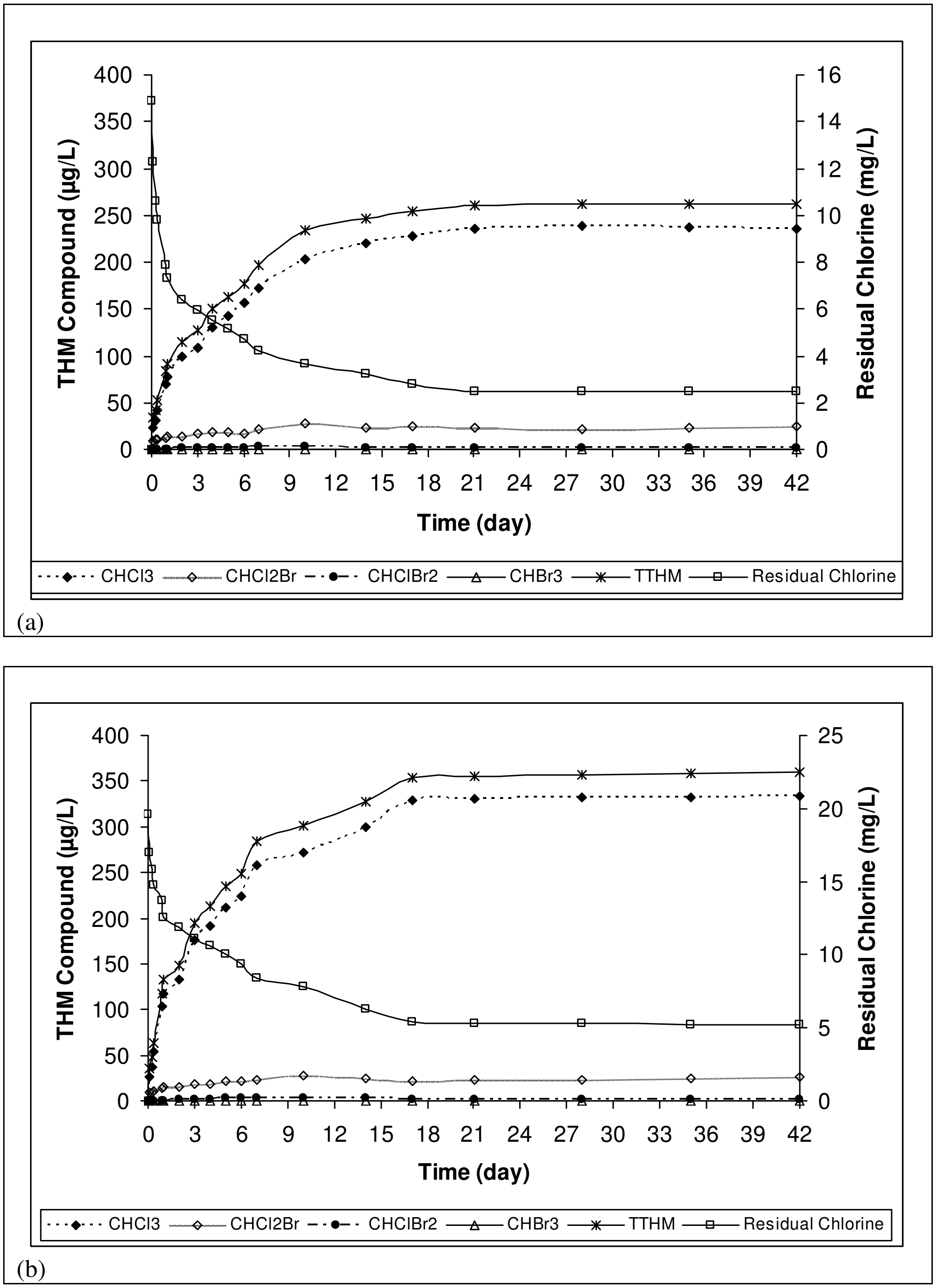


Figure 4.14. Formation of each THM compound/TTHM and Consumption of Chlorine in Devegeçidi Reservoir in June 2003 (a) Low Dose (Initial Chlorine Conc.=14.88 mg/L) (b) High Dose (Initial Chlorine Conc.=19.63 mg/L)

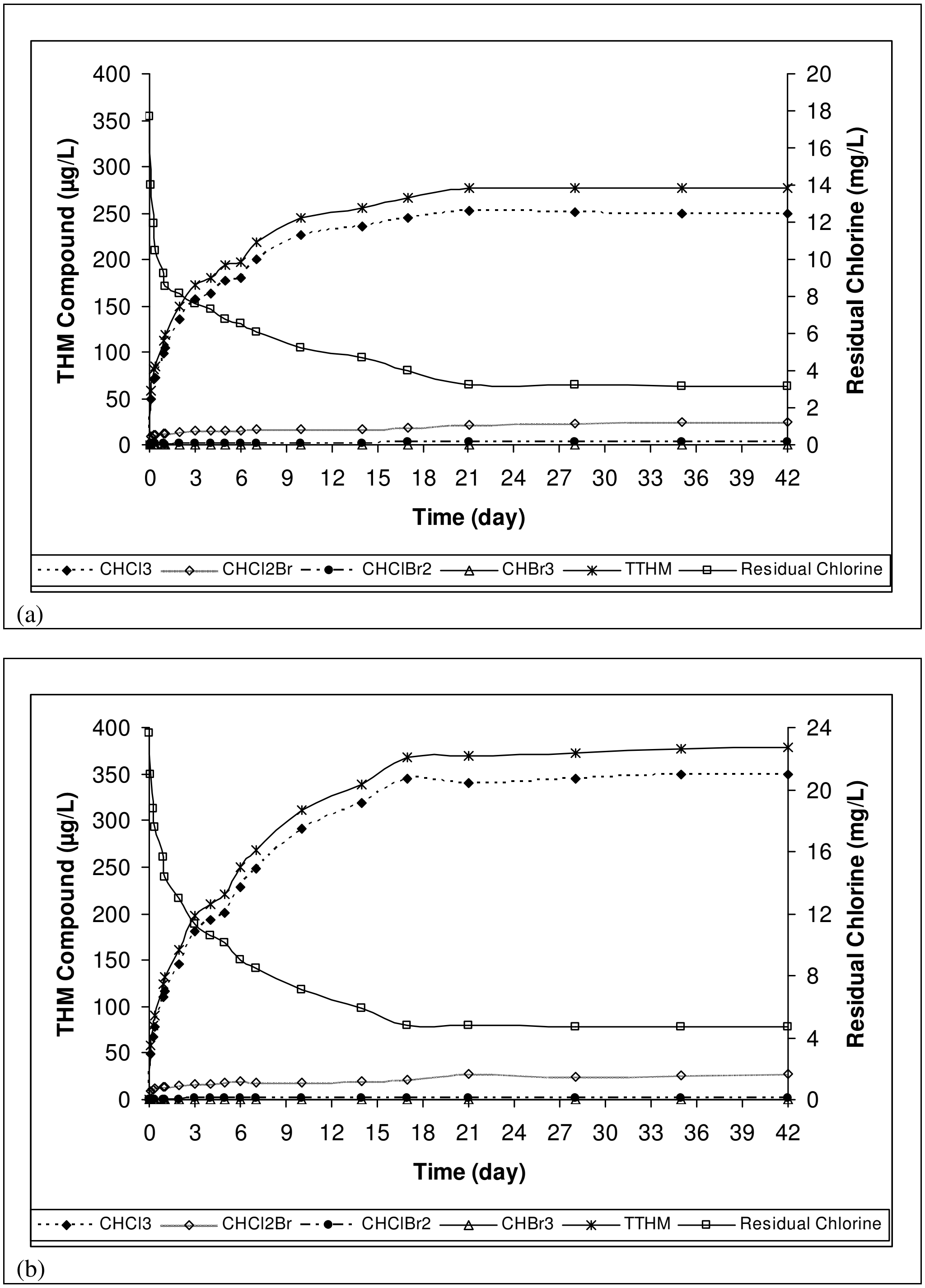
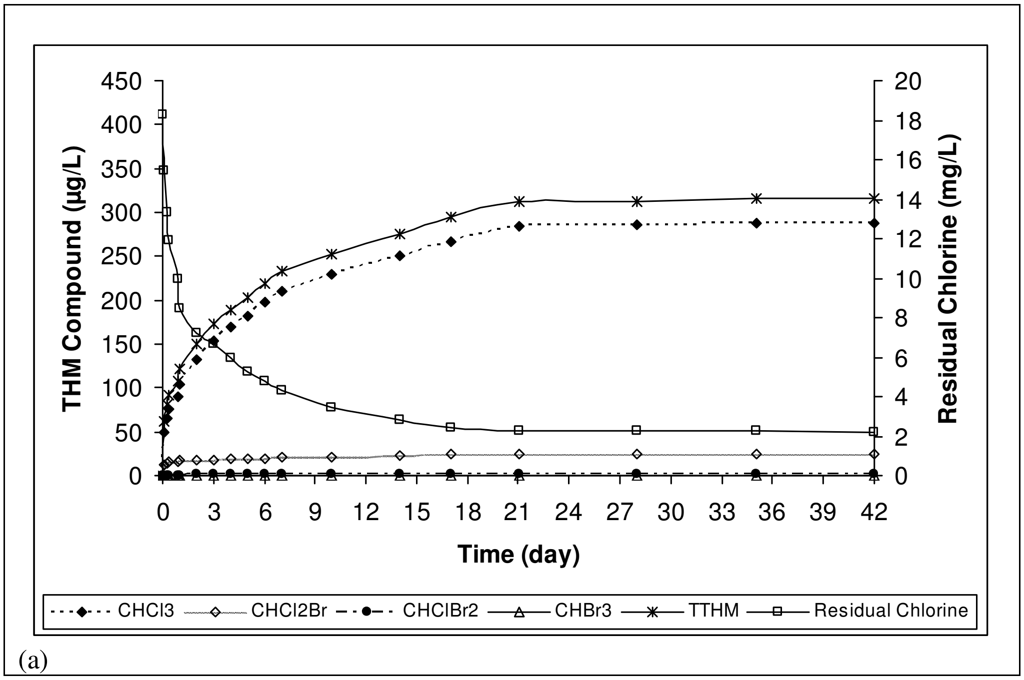


Figure 4.15. Formation of each THM compound/TTHM and Consumption of Chlorine in Devegeçidi Reservoir in July 2003 (a) Low Dose (Initial Chlorine Conc.=17.73 mg/L) (b) High Dose (Initial Chlorine Conc.=23.62 mg/L)



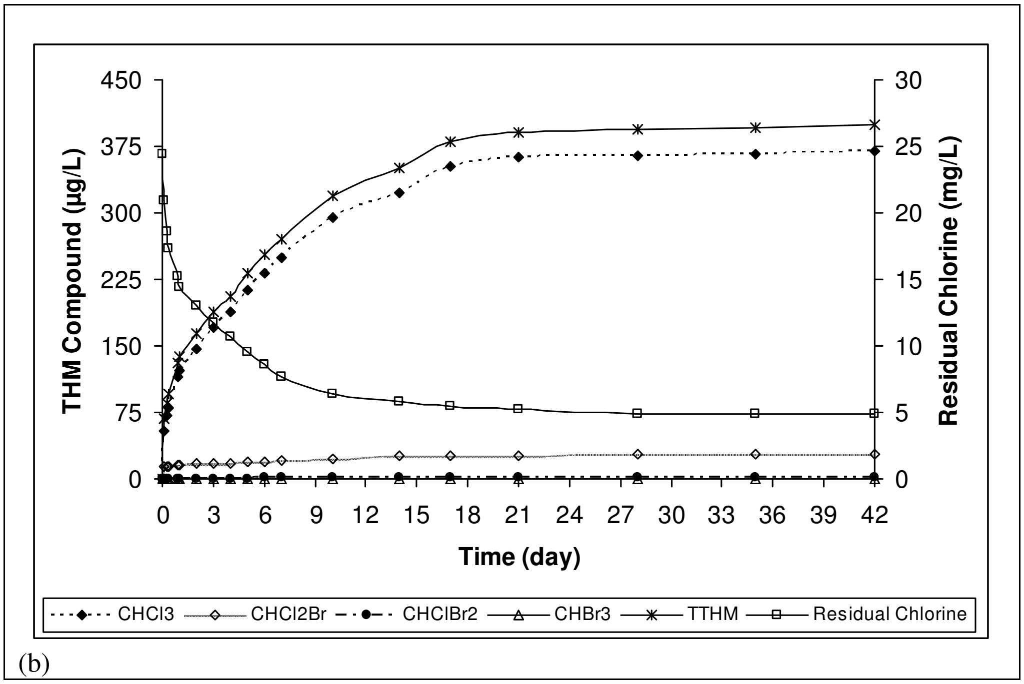


Figure 4.16. Formation of each THM compound/TTHM and Consumption of Chlorine in Devegeçidi Reservoir in September 2003 (a) Low Dose (Initial Chlorine Conc.=18.31 mg/L) (b High Dose (Initial Chlorine Conc.=24.44 mg/L)

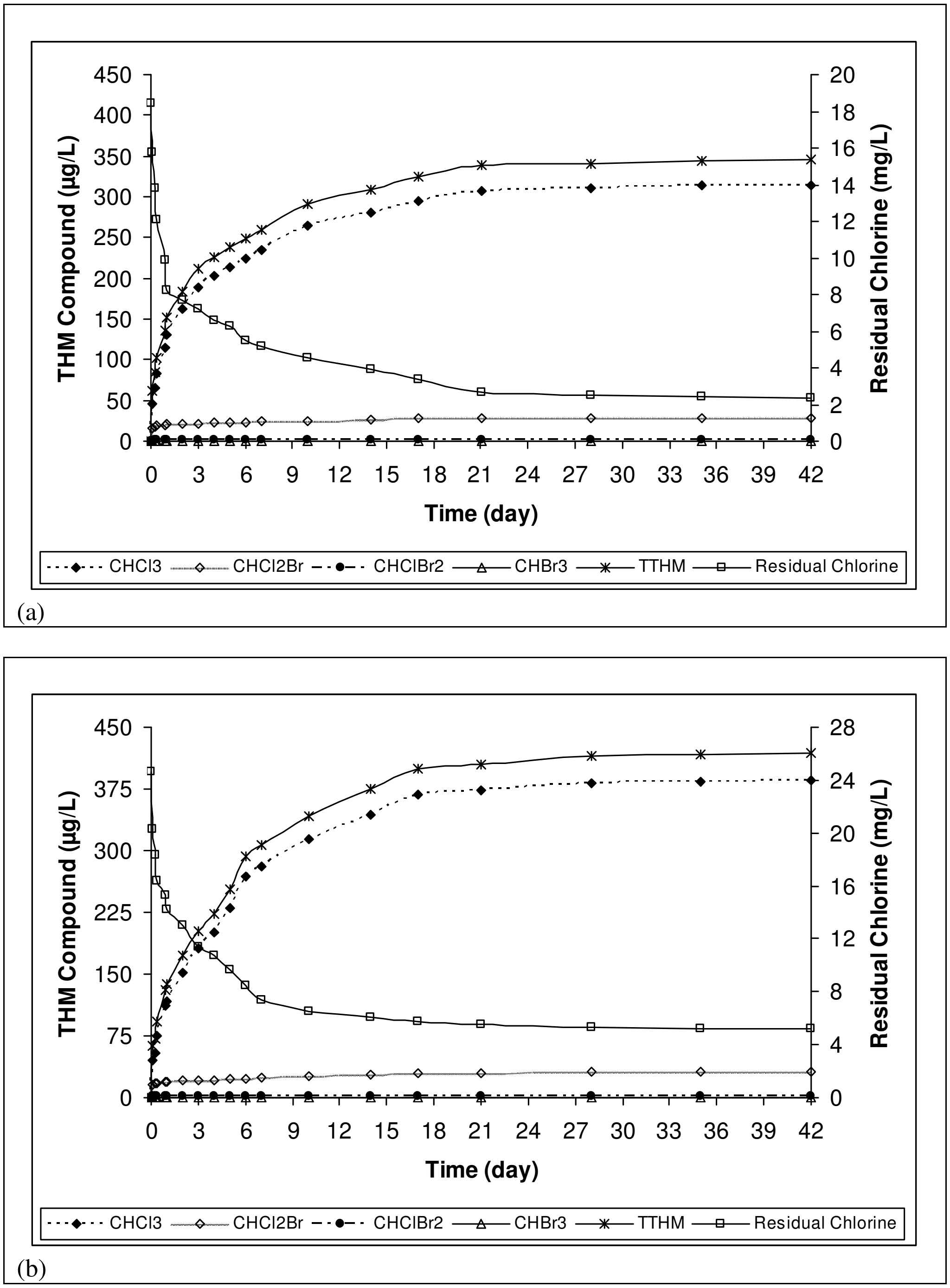


Figure 4.17. Formation of each THM compound/TTHM and Consumption of Chlorine in Devegeçidi Reservoir in February 2004 (a) Low Dose (Initial Chlorine Conc.=18.43 mg/L) (b) High Dose (Initial Chlorine Conc.=24.60 mg/L)

As seen in Figure 4.8 through Figure 4.17, concentration of each THM compound and TTHM increases with increasing time and final THM concentrations for high doses were always higher than the ones observed in low chlorine doses for both reservoir waters although both doses are higher than the chlorine demand of the water samples which in turn emphasizes the importance of chlorine dose on THM formation. TTHM concentrations observed at high chlorine doses in May, June, July, September and February are 39%, 36%, 10%, 31% and 48% higher, respectively in Atatürk Reservoir waters and 26%, 37%, 37%, 26% and 21% higher, respectively in Devegeçidi Reservoir waters than the ones observed in low chlorine doses that are similar to the results of studies that have been investigating the effect of disinfectant concentration on DBP formation. These studies have shown that as the disinfectant concentration increases, DBP formation also increases (Montgomery, 1993; Rathbun, 1996; Singer et. al, 1995, Singer, 1994). Singer et al. (1995) conducted a study on eight conventional water treatment plants that practiced chlorine disinfection in North Carolina. Results showed that the treatment plant that used the largest chlorine dose and the one which used the smallest dose had average TTHM (total trihalomethane) levels of 52 µg/L and 19 µg/L, respectively. Also, higher NPOC content of Devegeçidi Reservoir waters than the Atatürk reservoir waters resulted in higher chlorine demand and therefore higher THM formation in all the sampled months

In addition increase in chloroform ($CHCl_3$) concentration over time was higher compared to the other THM species in all months. In Atatürk Reservoir waters; chloroform concentration after 7-day reaction time became approximately 5-fold, 5-fold, 3-fold, 11-fold and 4-fold higher than its concentration at 3-hours in May, June, July, September and February, respectively for low doses. However, bromoform ($CHBr_3$) concentrations did not significantly increase after 24-hr reaction time period and no $CHBr_3$ was detected in February '04 due to the low bromide content of the raw water (30 µg/L).

In Devegeçidi Reservoir waters; for low chlorine doses, chloroform concentration after 7-day reaction time became approximately 10-fold, 9-fold, 6-fold, 5-fold and 7-fold higher than its concentration at 3-hours in May, June, July, September and February, respectively. Bromoform have not been observed in any month due to the low bromide content of the raw water (average of 24 µg/L).

Also, according to Standard Methods (1998), THMFP test is conducted by a 7-day test which determines the THMFP of the water sample after a reaction time of seven days. This time period is believed to allow the reaction to approach completion. However, as seen in Figure 4.8-Figure 4.17, THM formation did not finish in seven days in both reservoir waters, and this, in turn, may result in underestimation of the ultimate potential of the water for producing trihalomethanes. On the contrary to these results, Nikolaou et al. (2004) found out that formation of THMs were completed within 24 hr reaction time in all chlorinated waters in his study at which he investigated the kinetics of the formation of different species of DBPs including THMs in the three river (Evergetoulas, Mylopotamos, Tsiknias) samples of Greece. This can be explained by the differences in the nature/composition of the NOM in water samples as well as the applied chlorine doses and concentrations of NOM.

In addition, these figures also showed that while THM formation increases, chlorine concentration decreases with increasing time due to the chlorine reaction with organic precursors to form THMs. For a given initial chlorine dose, the formation of THMs and consumption of chlorine were both completed at the same reaction time, however, the time period required for the completion of THM formation varied with the applied chlorine dose and season. At high chlorine doses, THM formation was complete earlier than that for the low doses due to the fact that initial chlorine concentration is an important factor affecting the time of completion of the reaction as well as the amount and rate of THM formation (higher values of initial chlorine also results in higher reaction rates). In Atatürk Reservoir waters; in May, June and July, THM formation and chlorine consumption were complete in 21 days for the low dose and in 17 days for the high dose. In February 2004 and September 2003, the reactions were complete in 28 and 17 days for the low dose and in 21 and 14 days for the high dose, respectively. In Devegeçidi Reservoir waters, THM formation and chlorine consumption were complete in 21 days for the low chlorine dose and 17 days for the high chlorine dose in all sampled months. In addition, THM concentrations at the same residual chlorine value were not equal for low and high doses due to the difference in the rates of THM formation which was also seen in the study of Urano et. al. (1983). He explained this by the rapid formation of chlorinated intermediates during the initial stages of the reaction which is dependent on initial chlorine concentration and THM formation might be controlled by the amount of these chlorinated intermediates.

In addition, when the correlations between the $UV(A)_{254nm}$ and chlorine demand of the water samples are investigated, r^2 values of 0.88 and 0.91 were fpund which is similar to the findings of Zamora et.al. (2004) (r^2 of 0.94). Although the NPOC content and chlorine demand of the Atatürk Reservoir samples show high correlation (r^2 of 0.98), this is not observed at Devegeçidi Reservoir samples (r^2 of 0.50). This may be attributed to the changes in organic matter characteristics through the sampled months. Organic nature can show alterations according to the geographical structure, position, age of the reservoir, meteorological conditions, etc. (Oliver and Thurman, 1983).

Moreover, although there is still residual chlorine available for the reaction, THM formation and chlorine consumption cease and residual chlorine concentrations at the completion of the reaction differ at the low and high initial doses. Table 4.1and Table 4.2 present the residual chlorine concentrations together with NPOC, $UV(A)_{254nm}$, SUVA and overall yield values for Atatürk and Devegeçidi Reservoir waters, respectively. Residual chlorine concentrations during the completion of THM formation reaction are always higher for the high doses as the residual concentration are dependent on the applied doses and concentrations differ through the sampling months. Furthermore, the overall yield values (total THM formed/total Chlorine consumed during the entire reaction periods) as well as the average yield values (µg TTHM formed/mg Chlorine consumed between two reaction times) differ through sampled months (Figure 4.18 and Figure 4.19).

These can be attributed to the different unit chlorine demand of the water supplies which can be explained by the differences in natural organic matter composition in the sampled months. This can also be supported by the changes in SUVA values which are also indicators of NOM characteristics. SUVA values differ through sampled months for both reservoirs changing from 0.49 through 1.04 for Atatürk Reservoir waters and from 1.69 to 2.64 for Devegeçidi Reservoir waters.

Table 4.1. NPOC, UV(A)$_{254nm}$, SUVA, Yield and Residual Chlorine Values in Atatürk Reservoir Waters

	NPOC (mg/L)	UV(A)$_{254}$	SUVA	Yield (µgTHM/mg Cl$_2$)		Residual Chlorine (mg/L)	
				Low Dose	High Dose	Low Dose	High Dose
May 2003	0.517	0.0033	0.63	12.35	14.44	1.80	2.44
June 2003	0.699	0.0034	0.49	13.29	13.70	1.81	1.96
July 2003	1.34	0.0139	1.04	15.50	14.55	1.75	3.57
Sept. 2003	0.721	0.0043	0.60	13.15	14.48	1.95	2.74
February 2004	1.987	0.0143	0.72	14.99	16.14	2.20	4.93

Table 4.2. NPOC, UV(A)$_{254nm}$, SUVA, Yield and Residual Chlorine Values in Devegeçidi Reservoir Waters

	NPOC (mg/L)	UV(A)$_{254}$	SUVA	Yield (µgTHM/mg Cl$_2$)		Residual Chlorine (mg/L)	
				Low Dose	High Dose	Low Dose	High Dose
May 2003	2.378	0.0615	2.59	23.36	25.10	1.1	1.7
June 2003	2.418	0.0639	2.64	21.12	24.97	2.6	5.4
July 2003	2.819	0.0656	2.33	18.99	20.00	3.3	4.8
Sept. 2003	2.973	0.0659	2.21	19.61	20.36	2.3	5.4
February 2004	4.004	0.0678	1.69	21.42	21.54	2.7	5.7

The overall yield values obtained with Devegeçidi Reservoir waters are higher than the ones obtained with Atatürk Reservoir waters that can be attributed to the high organic content of Devegeçidi Reservoir waters which result in higher THM formation. When the overall yield values in Atatürk Reservoir waters at all sampled months were calculated, it was observed that overall yields range between 12.35 µg TTHM formed/ mg Cl$_2$ consumed and 15.50 µg TTHM formed/ mg Cl$_2$ consumed for the low dose and 13.70-16.14 µg TTHM formed/ mg Cl$_2$ consumed for the high doses (Table 4.1). In Devegeçidi Reservoir waters, the overall yield values at all sampled months range between 18.99-23.36 µg TTHM formed/ mg Cl_2 consumed for the low chlorine dose and 20.00-25.10 µg TTHM formed/ mg Cl_2 consumed for the high doses (Table 4.2).

Gang et al. (2003) investigated the correlation of chlorine decay and THM formation to NOM molecular size and and results indicated that the TTHM yield coefficients ranged from 31 to 42 µg TTHM/ mg Cl_2. These values are higher than the ones shown in Table 4.1 and Table 4.2 which could be explained by the differences in source water qualities (concentration and nature/characteristics of natural organic matter, temperature) as well as in the applied chlorine doses.

Figure 4.18 and Figure 4.19 represent the average yields (µg THM formed/mg Cl_2 consumed between two reaction times) versus time for May, June, July, September 2003 and February 2004 at low chlorine dose and for high chlorine dose in Atatürk Reservoir waters and Devegeçidi Reservoir waters, respectively. In all months, the formation yields were highest during the first hours of reaction time and then decreased; which is in parallel with the findings of various other studies (Gang et al., 2003; Gallard and von Gunten, 2002; Boccelli, et al., 2003; Urano et al., 1983). Chlorine consumption and THM formation were very rapid during the first hours of the reaction followed by a more gradual Cl_2 decay and THM formation after 10 hr. Boccelli et al. (2003) explained this phenomenon (rapid chlorine consumption) by the competing reactants, such as the oxidation of inorganic compounds (rapid) and substitution reactions with NOM (relatively slow). However as there is THM formation during the initial hours and these can not be attributed to the inorganic compounds, the rapid consumption during initial hours can be explained by the nature of NOM. Gang et. al. (2003) explains this by the two instinct types of reactive functionalities existing in NOM which result in two parallel first order reactions. One functionality, possibly attributed to aldehyde and phenolic hydroxyl groups, results in a very rapid rate of chlorine consumption and THM formation. The other NOMs functionality is less reactive, such as expected for activated double bonds and methyl groups and results in a slow, long-term chlorine consumption and THM formation. Also, at low chlorine doses, the maximum yield values obtained were higher than for the high doses. This may be due to the excess chlorine concentrations in high doses which have not been used during the reaction yet.

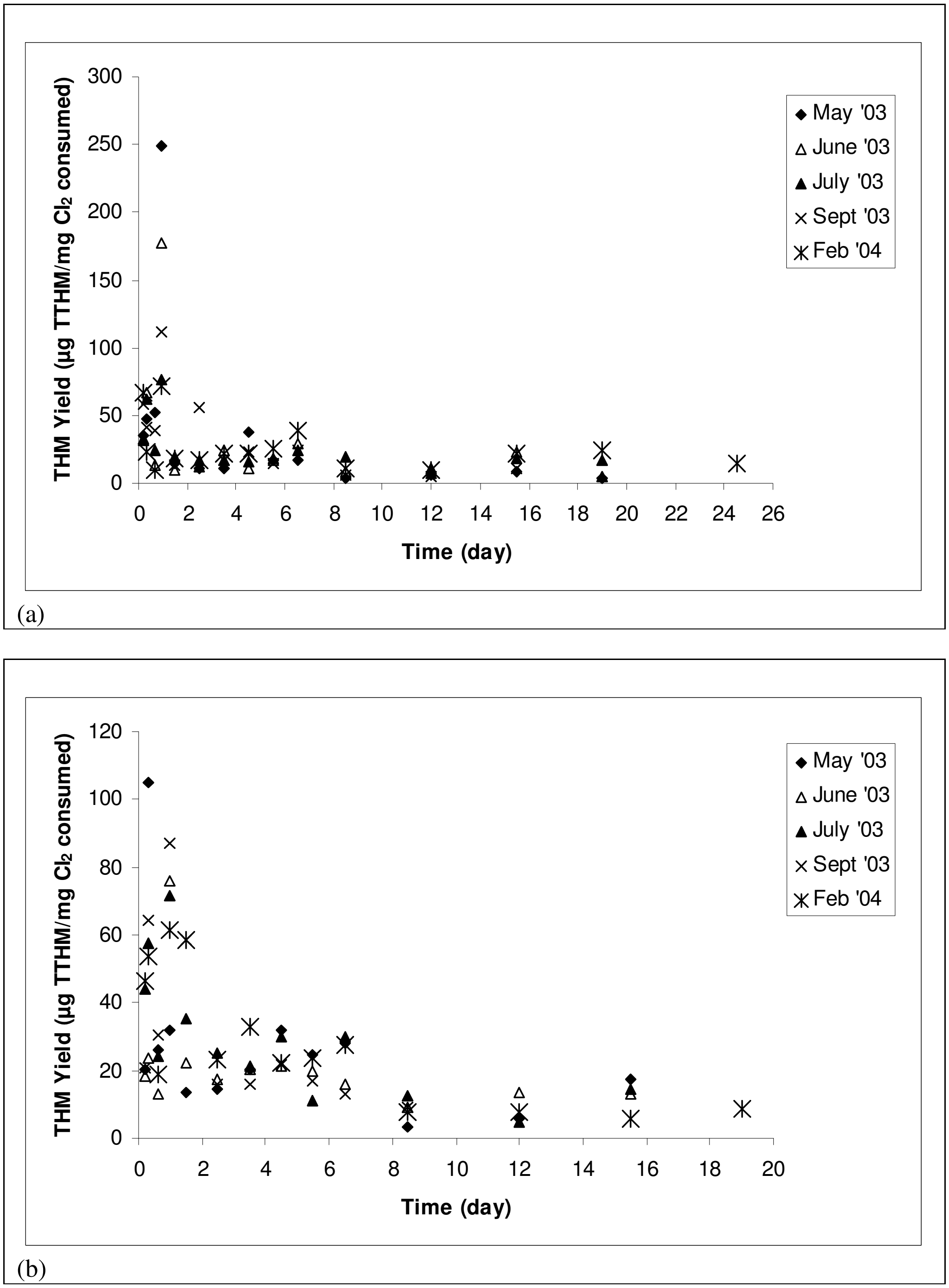
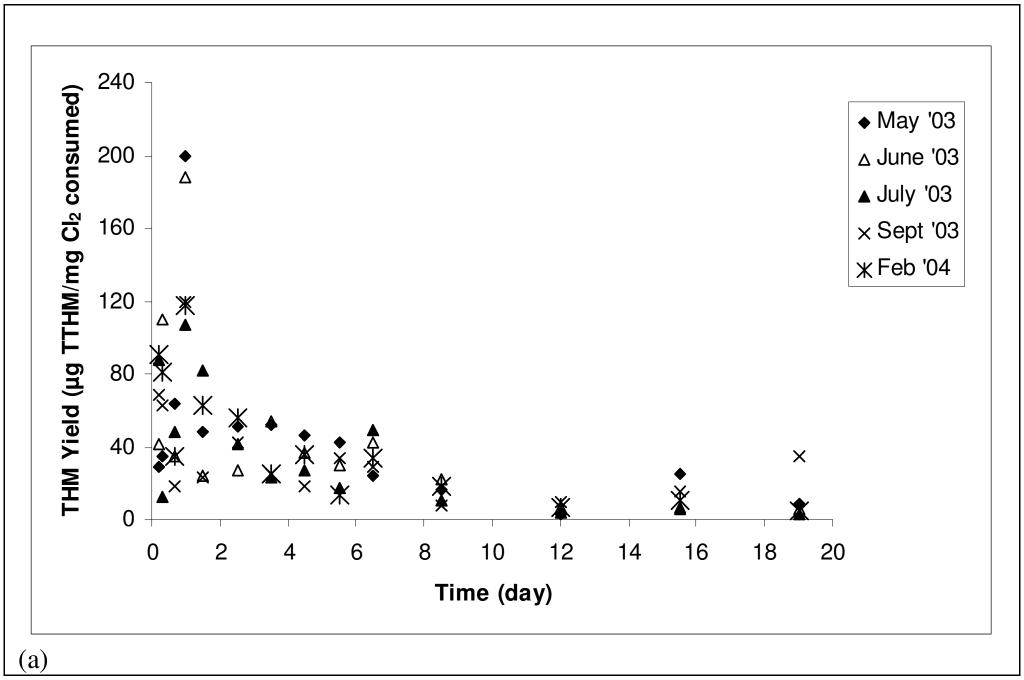


Figure 4.18. Yield Values in Atatürk Reservoir (a) Low Dose (b) High Dose



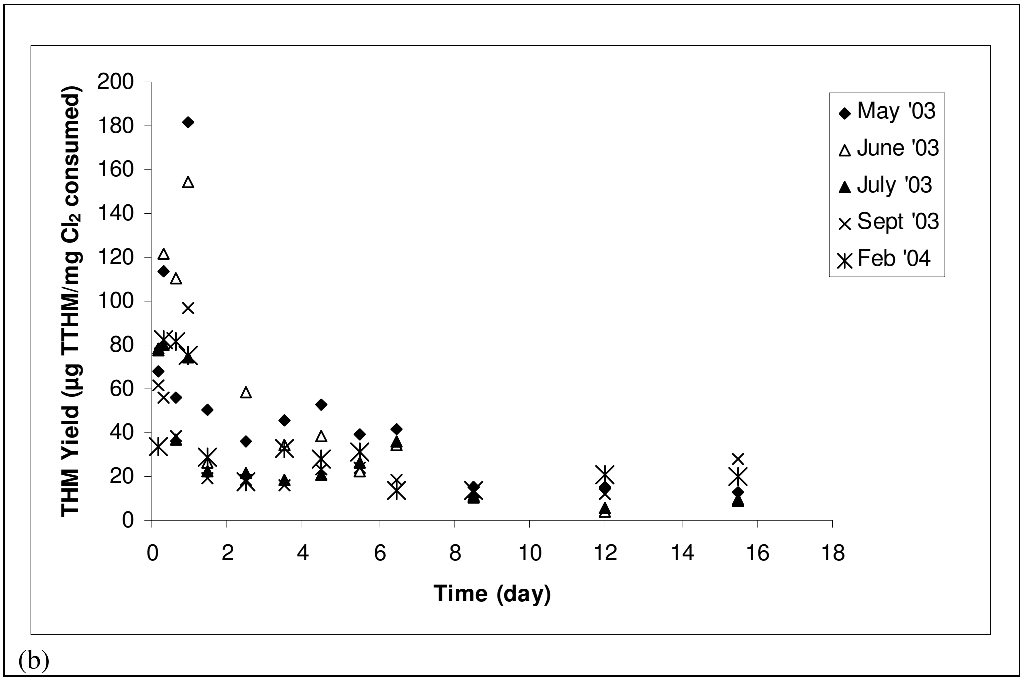


Figure 4.19. Yield Values in Devegeçidi Reservoir (a) Low Dose (b) High Dose

The same procedure as in the case of Atatürk and Devegeçidi Reservoirs was applied to water containing humic acids for the determination of THM formation and chlorine consumption kinetics. Similar to the reservoir waters, the initial THM concentrations of the humic acid solutions before chlorination were measured as zero. Concentration of THM species and residual chlorine as a function of time for low NPOC and high NPOC solutions, both for low and high chlorine doses, are presented in Figure 4.20 and Figure 4.21, respectively.

As seen in Figure 4.20 and Figure 4.21, TTHM concentration increases with increasing time and ultimate THM concentrations for high doses were higher than the ones observed in low chlorine doses which is similar to the findings with the reservoir waters. As there is no bromide ion present in the humic acid solutions, no brominated specie was formed. TTHM concentration comprise of only the chloroform. Although the organic matter concentration of low NPOC is similar to the ones in Atatürk Reservoir waters and the same situation between high NPOC and Devegeçidi Reservoir waters, the ultimate TTHM concentration of low NPOC humic acid solutions were higher than the ones in Atatürk Reservoir waters as well as concentrations of high NPOC containing humic acid solutions were higher than the ones obtained with Devegeçidi Reservoir waters. This is an expected result since humic acids are the main precursors of THM formation. In addition, similar to the results obtained with the reservoir waters, these figures also showed that while THM formation increases, chlorine concentration decreases with increasing time due to the chlorine reaction with organic precursors to form THMs.

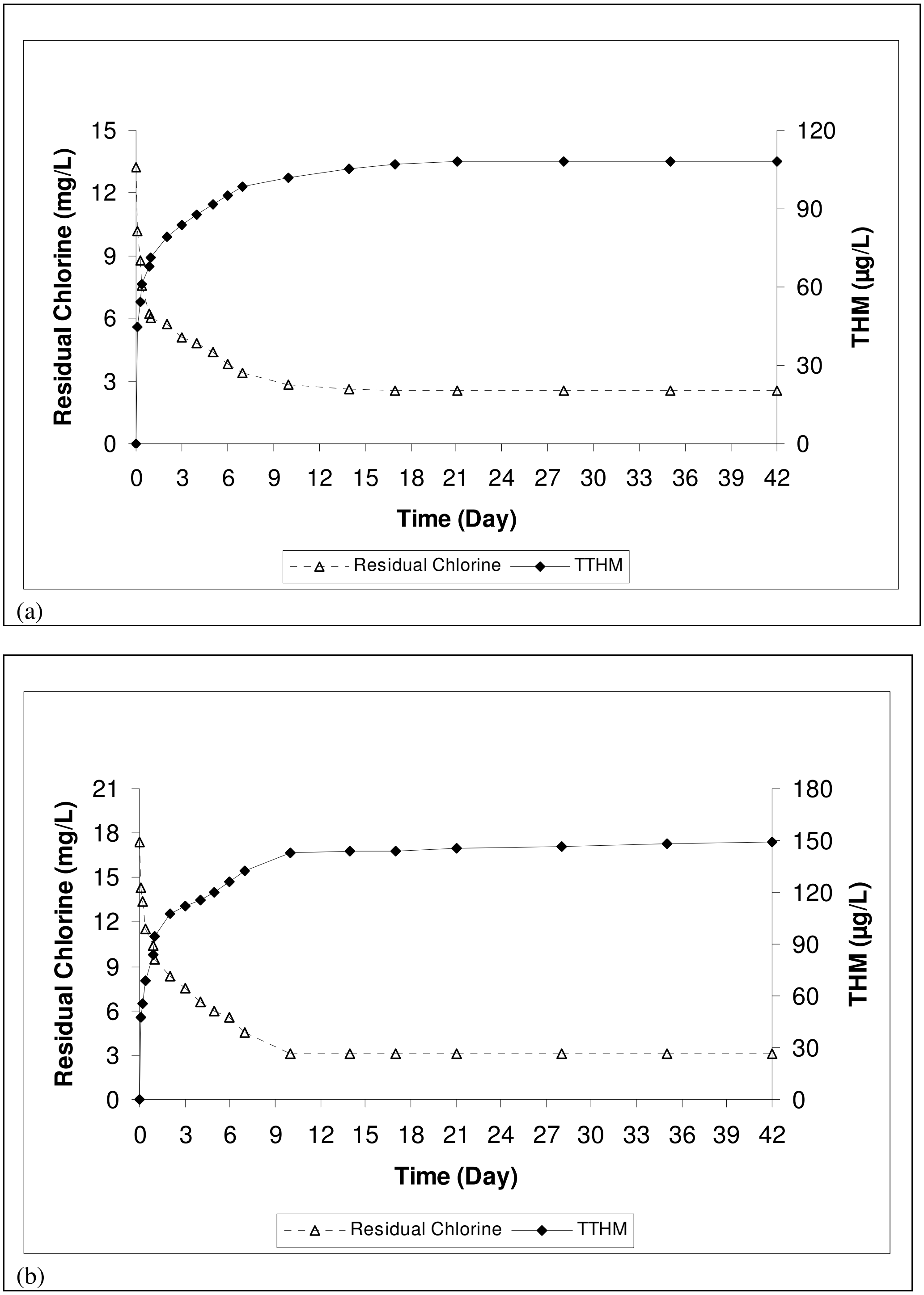


Figure 4.20. Formation of TTHM and Consumption of Chlorine for Low NPOC Humic Acids (a) Low Dose (Initial Chlorine Conc.=13.25 mg/L) (b) High Dose (Initial Chlorine Conc.=17.35 mg/L)

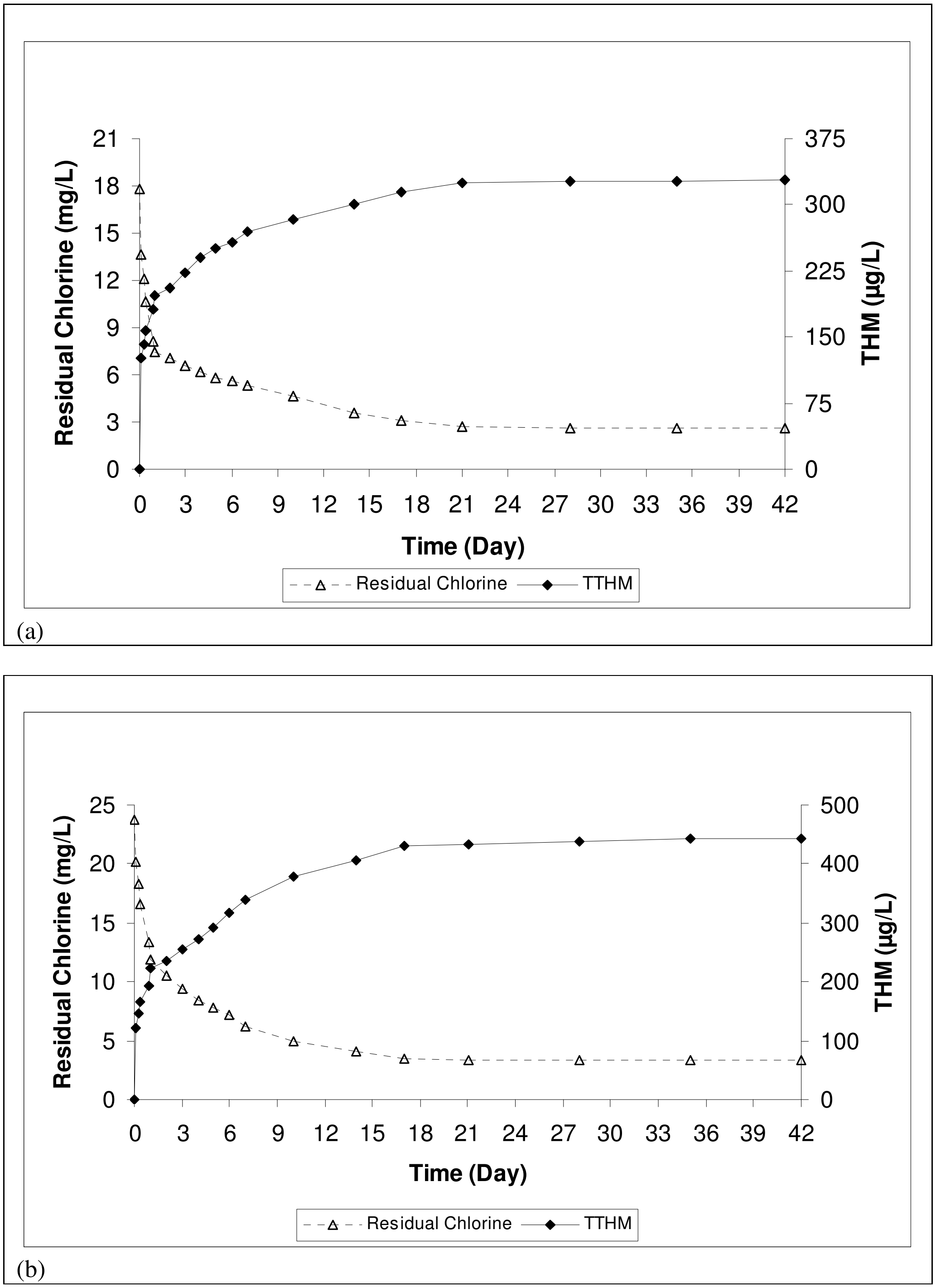


Figure 4.21. Formation of TTHM and Consumption of Chlorine for High NPOC Humic Acids (a) Low Dose (Initial Chlorine Conc.=17.82 mg/L) (b) High Dose (Initial Chlorine Conc.=23.75a mg/L)

Moreover, similar to reservoir waters; although there is still residual chlorine available for the reaction, THM formation and chlorine consumption cease and residual chlorine concentrations at the completion of the reaction differ at the low and high initial doses. On the contrary to the results obtained with reservoir waters, residual chlorine concentrations during the completion of THM formation reaction do not change between the low and high NPOC content. This can be explained by the same natural organic matter composition/nature in both solutions which in turn verifies the attributions done for the reservoir cases, related to the different unit chlorine demands due to the differences in NOM composition in the sampled months. Table 4.3 presents the residual chlorine concentrations at low and high chlorine doses for low NPOC and high NPOC humic acids.

Table 4.3. Residual Chlorine Concentrations After the Completion of THM Formation at Humic Acid Solutions

	Residual Chlorine (mg/L)	
	Low Dose	**High Dose**
Low NPOC	2,61	3,12
High NPOC	2,74	3,45

Overall yields for low NPOC humic acid solution were 10.11 µg TTHM formed/ mg Cl_2 consumed for the low dose and 10.02 µg TTHM formed/ mg Cl_2 consumed for the high dose which are similar to the values obtained with Atatürk Reservoir samples. When the results of high NPOC humic acid solution were investigated overall yields for low and high chlorine doses were 21.58 µg TTHM formed/ mg Cl_2 consumed and 21.69 µg TTHM formed/ mg Cl_2 consumed, respectively which are similar to the values obtained with Devegeçidi Reservoir samples. The difference observed in the yield values between low NPOC and high NPOC solutions (higher values in high NPOC solution) can be attrributed to the higher organic content consequently higher THM formation reaction rates in high NPOC humic solution.

Therefore, in the light of these findings; yield variation during the sampled months in the reservoir waters can be explained both by the differences in organic matter concentrations as well as variations in the organic matter nature. However, as the NPOC content of the reservoir samples donot vary as much as the ones of humic acid solutions (low NPOC and high NPOC), the variations in the overall yield values may be attributed to the changes in the nature/characteristics of organic matter rather than its concentration.

Figure 4.22 and Figure 4.23 represent the average yields (μg TTHM formed/ mg Cl_2 consumed) for low NPOC and high NPOC humic acid solutions, respectively. In both solutions, the formation yields were highest during the first hours of reaction time and then decreased; which is in parallel with the findings of reservoir waters and various other studies (Gang et al., 2003; Gallard and von Gunten, 2002; Boccelli, et al., 2003; Urano et al., 1983). As the THM formation were very rapid during the first hours of the reaction followed by a more gradual formation after 10 hr, yield values during the first hours were high.

Also, at low chlorine doses, the maximum yield values obtained were higher than for the high doses that may be due to the excess chlorine concentrations in high doses which have not been used during the reaction yet.

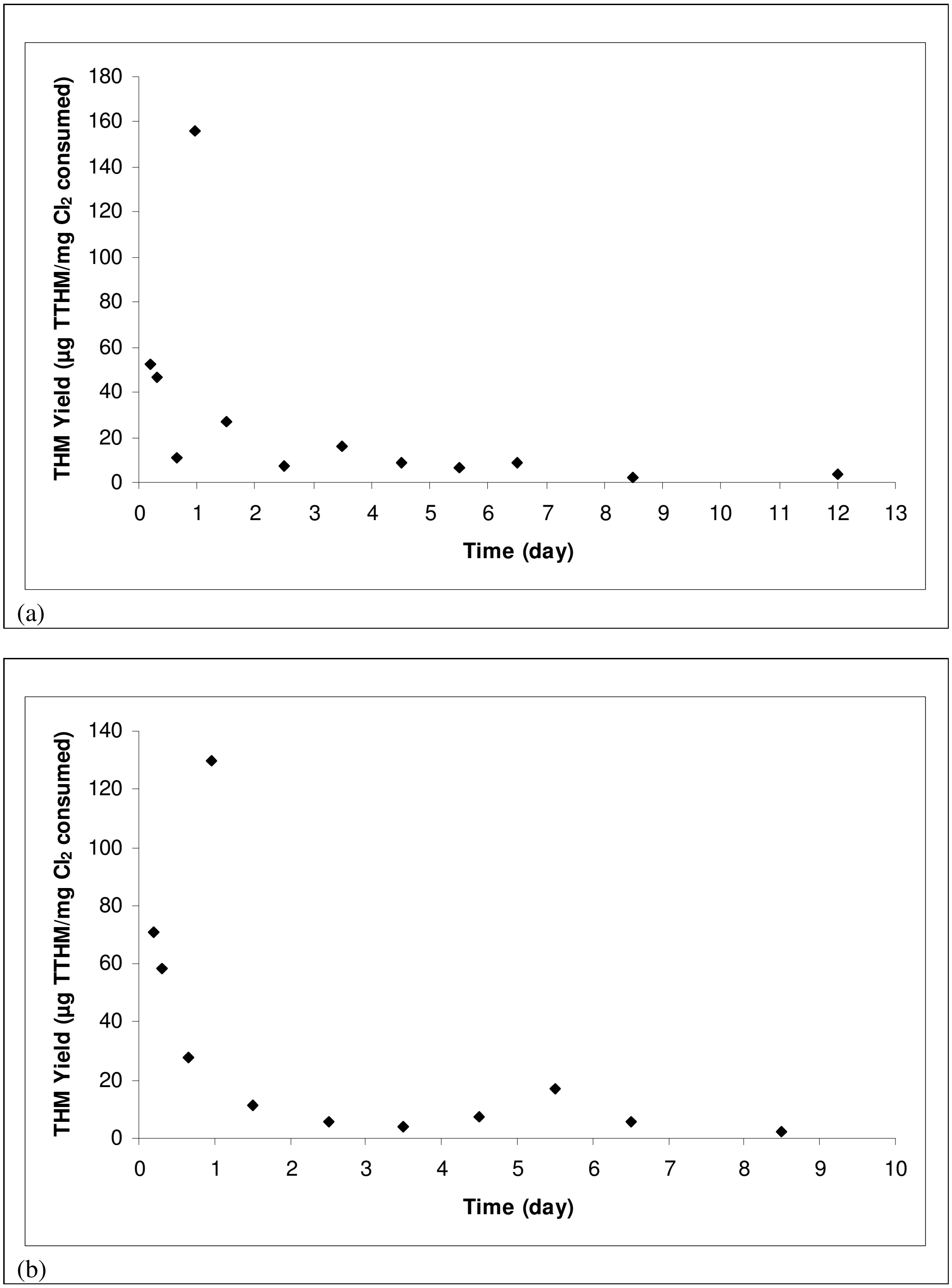
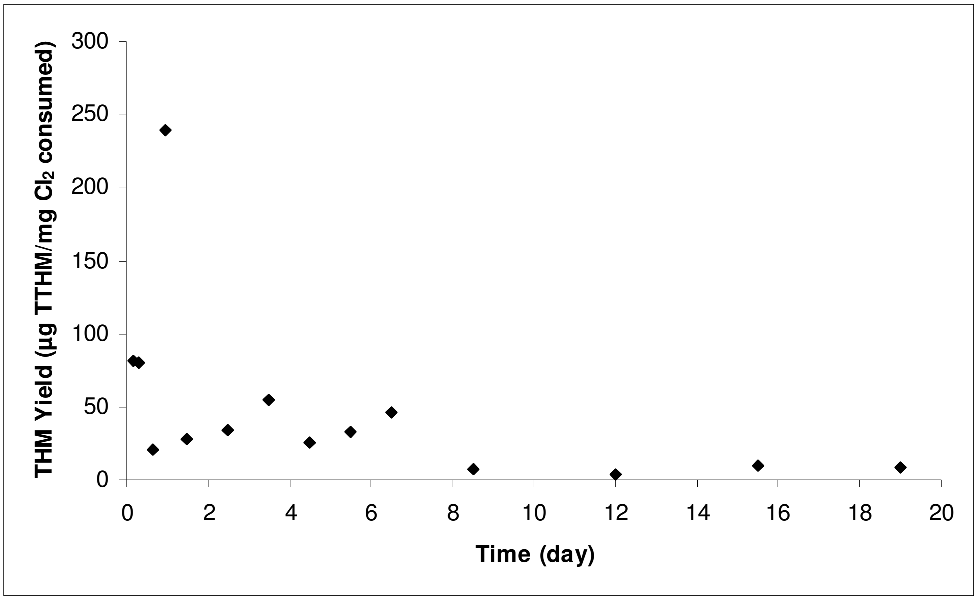
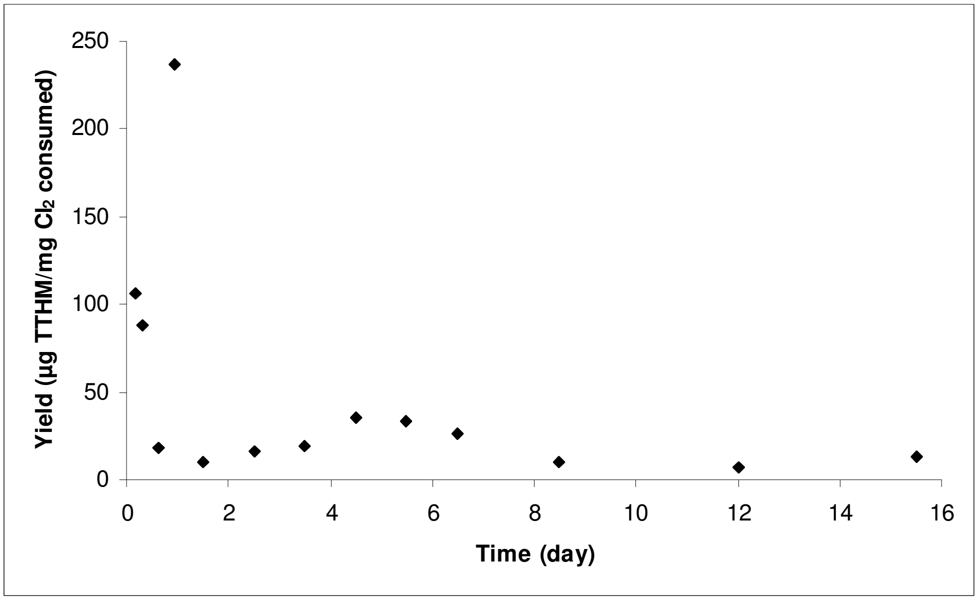


Figure 4.22. Yield Values for Low NPOC Humic Acid (a) for Low Dose (b) for High Dose



(a)



(b)

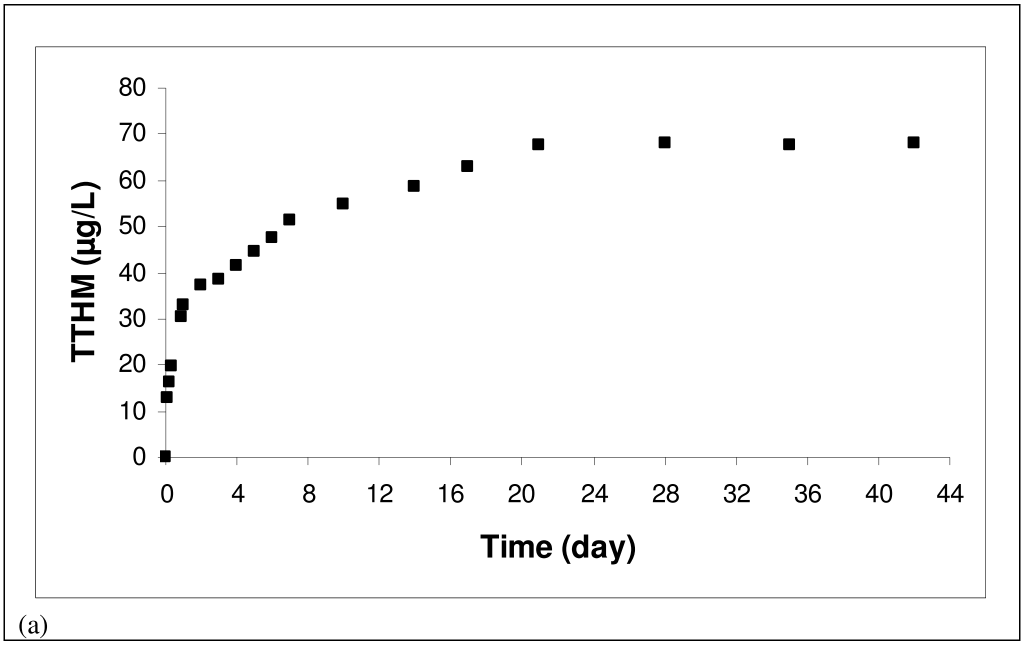
Figure 4.23. Yield Values for High NPOC Humic Acid (a) for Low Dose (b) for High Dose

4.2.1. THM Formation Rate Analysis

Chlorine consumption and THM formation are very rapid during the first hours of the reaction followed by a more gradual decay and formation after 24 hr similar to the results obtained by various researchers (Gang, et al., 2003; Gallard and von Gunten, 2002; Boccelli, et al., 2003; Urano et al., 1983). Gallard and von Gunten (2002) divided the THM precursors into a fast reacting (formed within the first hours of reaction time) and a slowly reacting fraction. Kinetics of formation of THMs from slowly reacting precursors verified a second order model, first order in chlorine concentration and first order in reactive sites.

Figure 4.24 and Figure 4.25 present the THM formation during the entire reaction period in May 2003 for Atatürk and Devegeçidi Reservoirs, respectively. In addition, THM formation rate for Low NPOC and High NPOC humic acid solutions are presented in Figure 4.26 and Figure 4.27, respectively.

All these figures show that THM formation rates are different at each reaction time, But, in order to simplify and explain the formation rates of THM and as the studies conducted before and the shape of the THM formation curves state that the chlorine consumption and THM formation differ at the initial hours and the rest of the reaction time (very rapid during the first hours of the reaction followed by a more gradual decay and formation after 24 hr), the reaction period is divided into two fractions; the first 24 hr and the period starting from the 1st day upto the completion of THM formation (Figure 4.28 – Figure 4.33). Rate constants and r^2 values for Atatürk Reservoir, Devegeçidi Reservoir and the Humic acid solutions are provided in Table 4.4, Table 4.5 and Table 4.6, respectively.



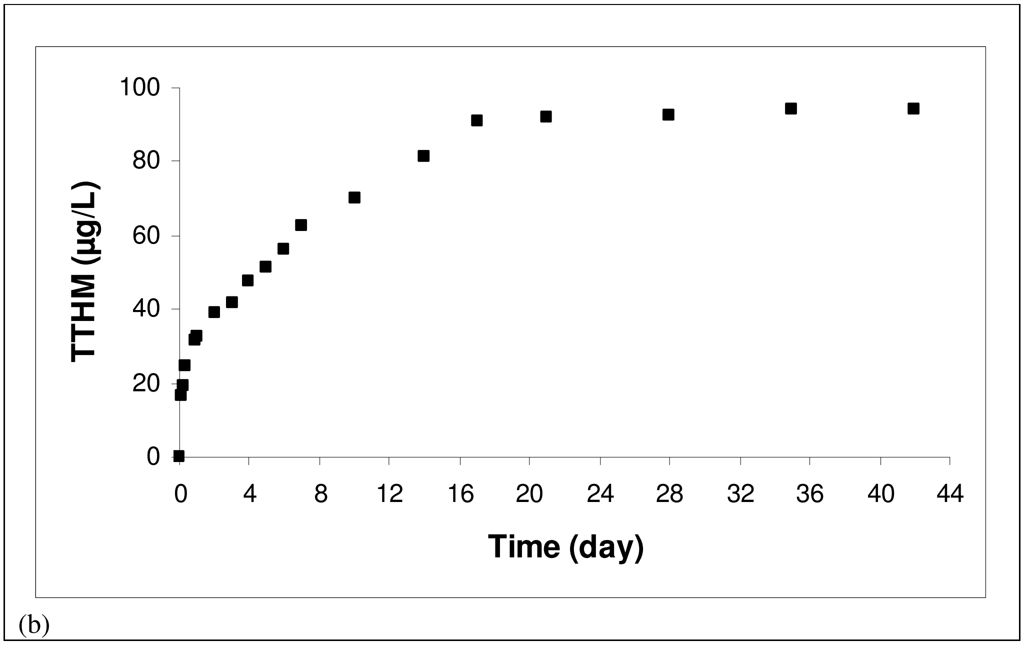
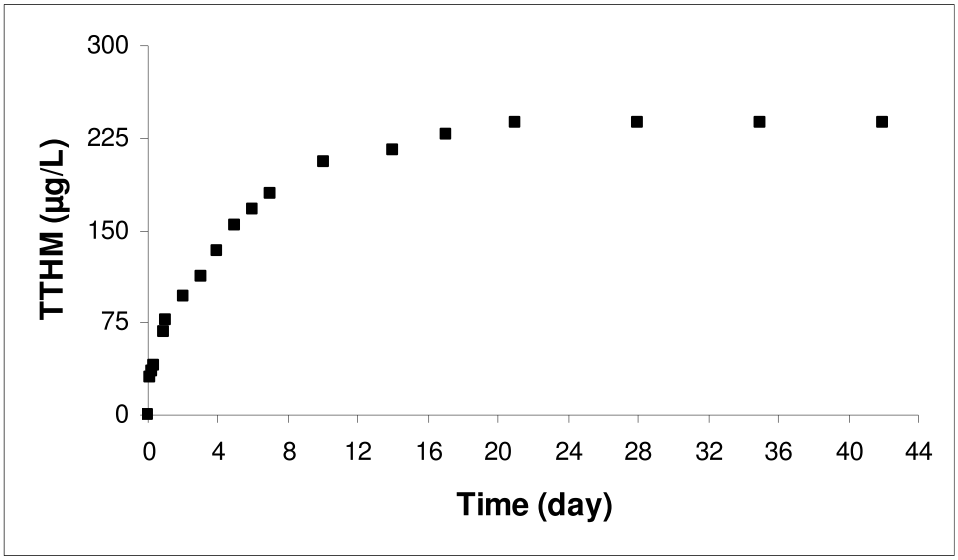
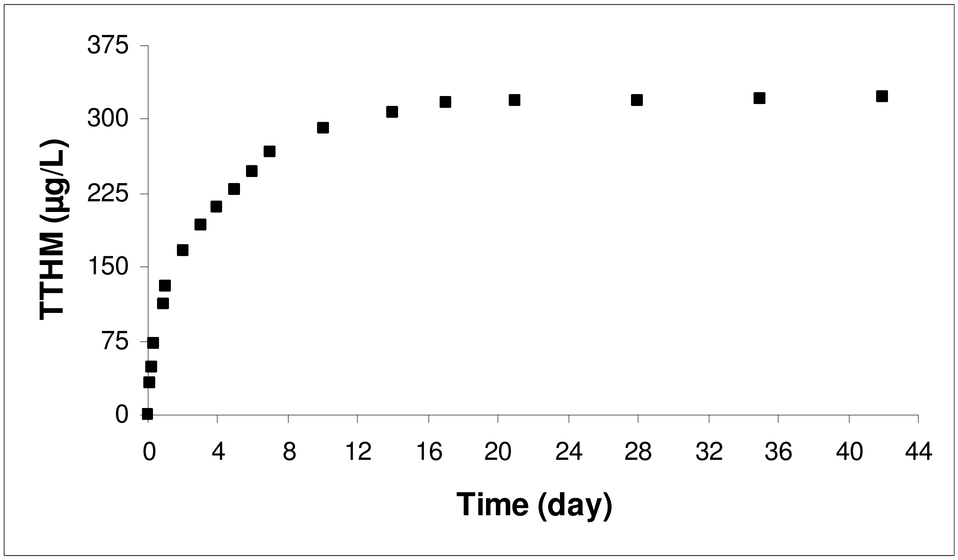


Figure 4.24. TTHM Formation in Atatürk Reservoir in May 2003 (a) for Low Dose (b) for High Dose



(a)



(b)

Figure 4.25. TTHM Formation in Devegeçidi Reservoir in May 2003 (a) for Low Dose (b) for High Dose

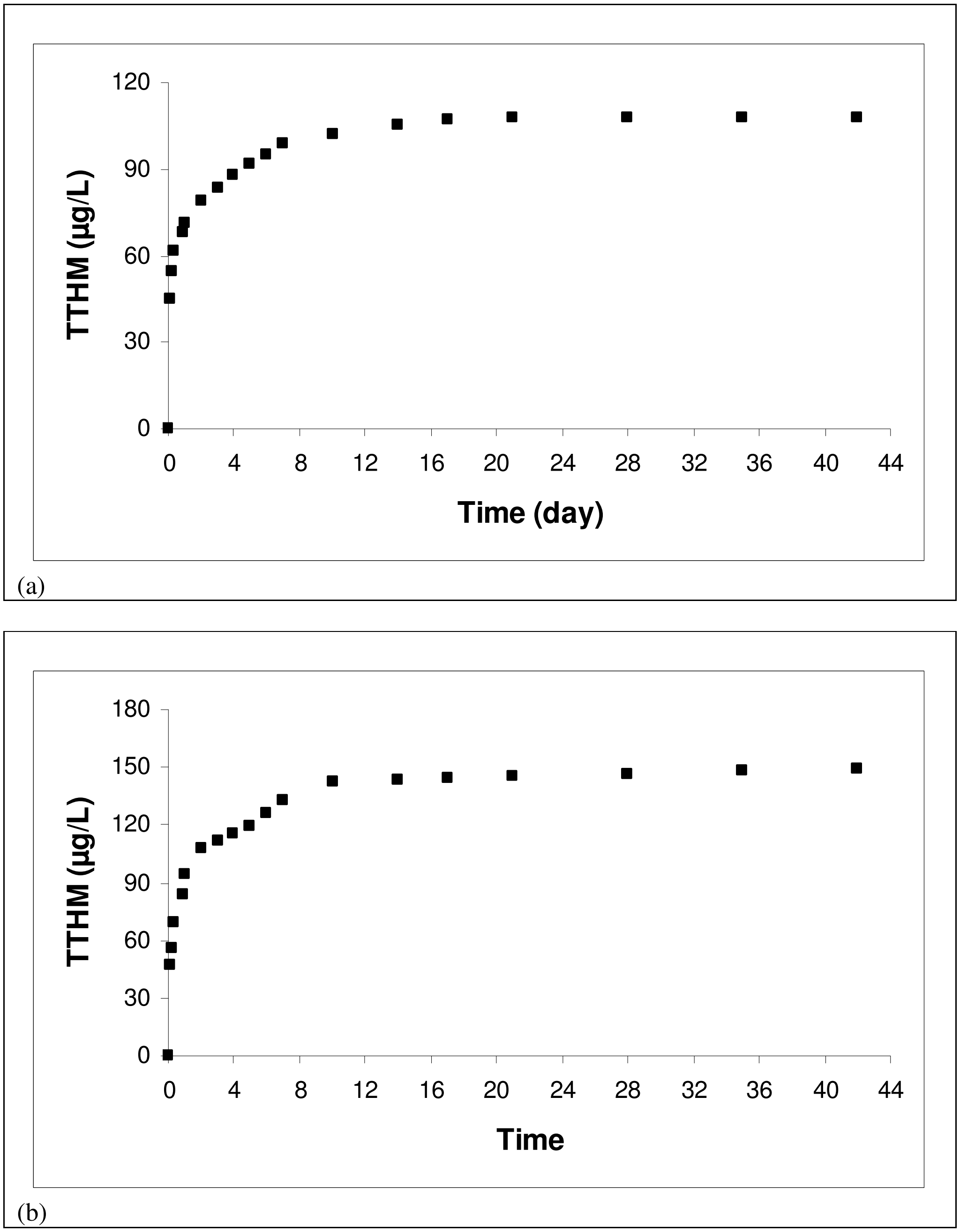


Figure 4.26. TTHM Formation for Low NPOC Humic Acid (a) for Low Dose (b) for High Dose

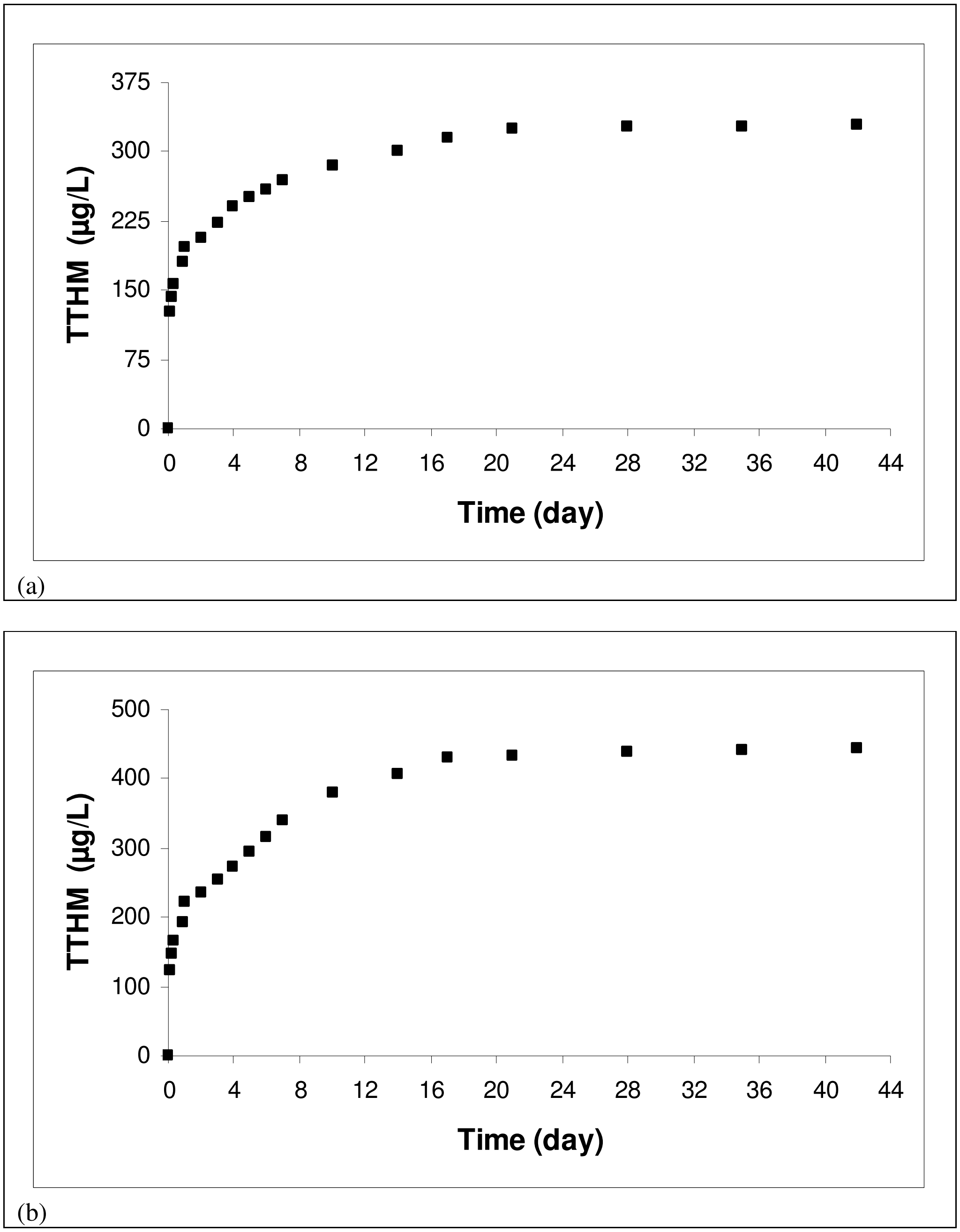
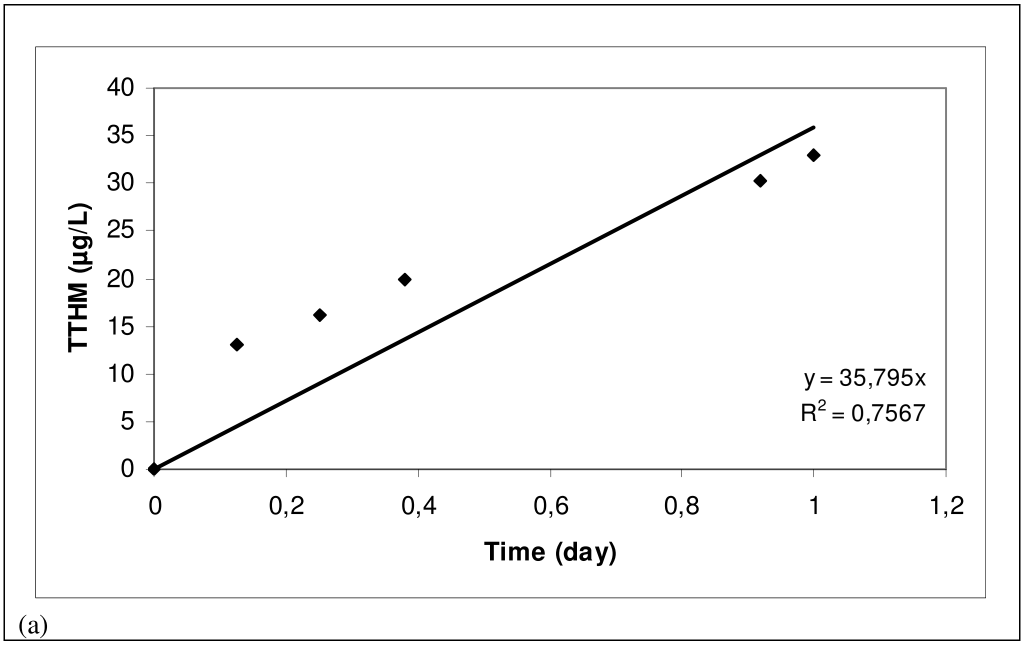
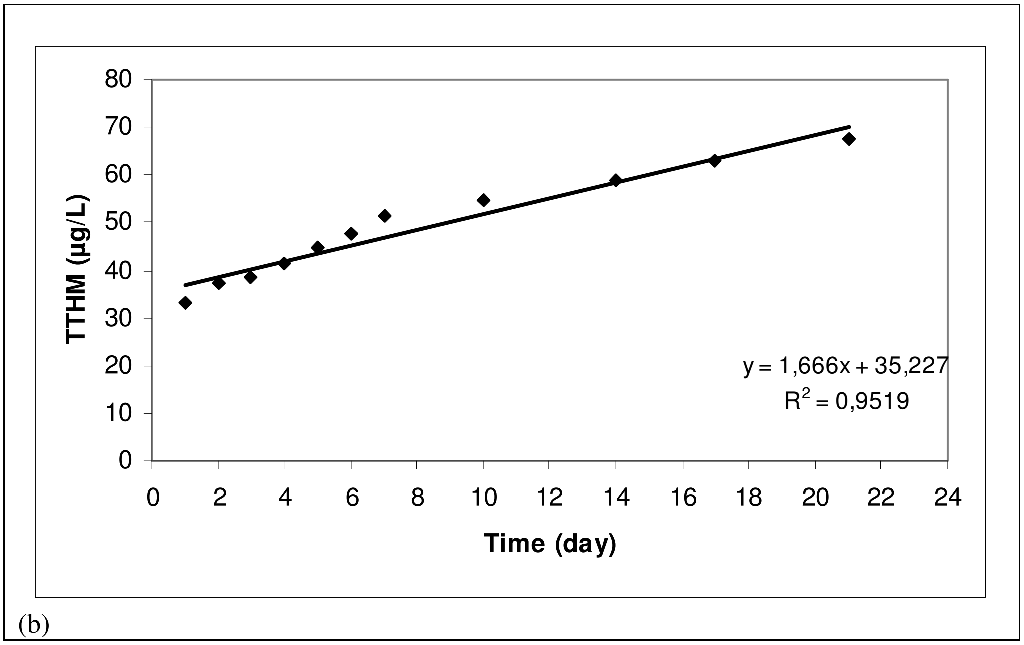


Figure 4.27. TTHM Formation for High NPOC Humic Acid (a) for Low Dose (b) for High Dose



(a)



(b)

Figure 4.28. TTHM Formation Rate in Atatürk Reservoir in May 2003 for Low Dose (a) First 24 hr (b) between 1st day-Completion of THM formation

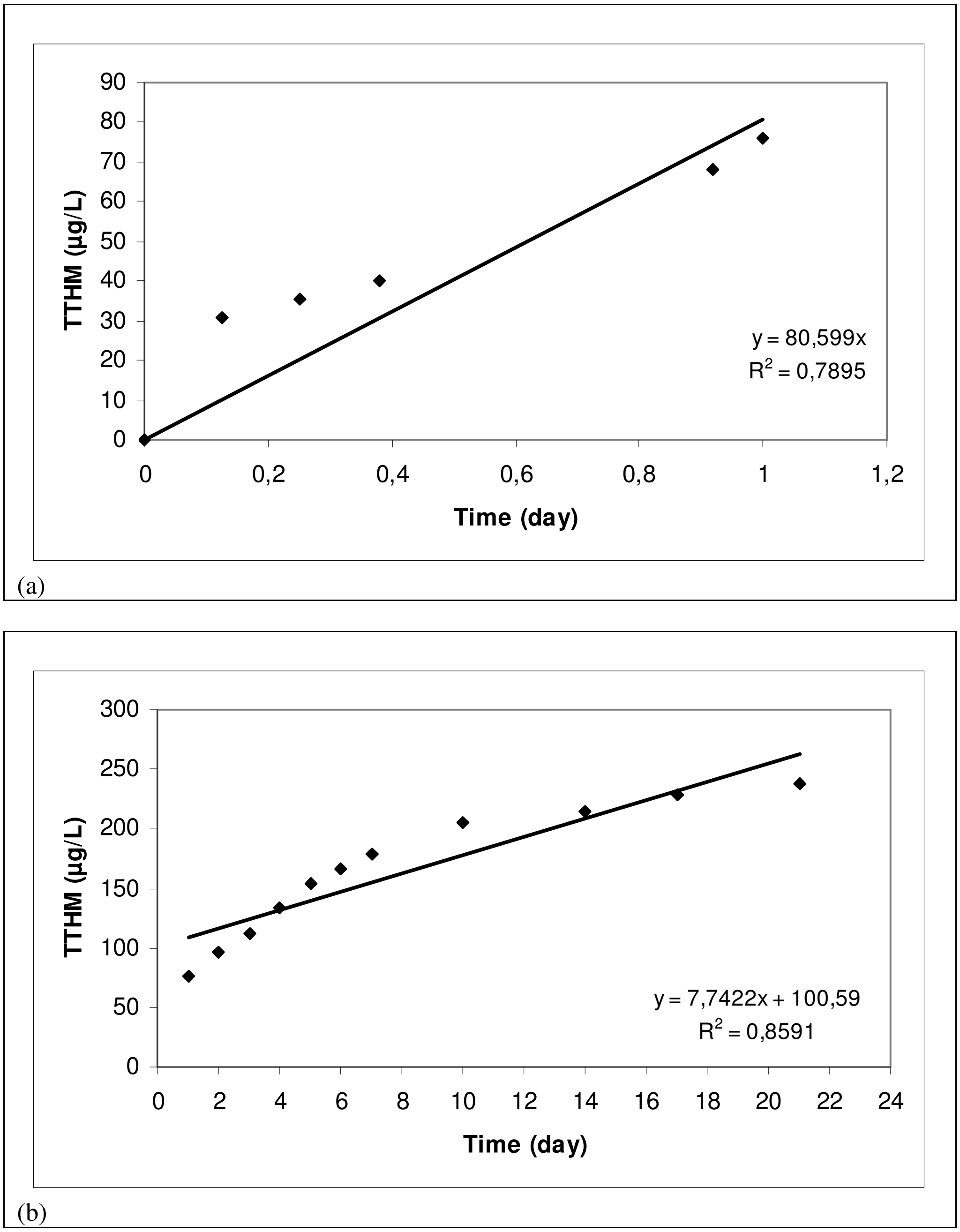


Figure 4.29. TTHM Formation Rate in Devegeçidi Reservoir in May 2003 for the Low Dose (a) First 24 hr (b) between 1st day-Completion of THM formation

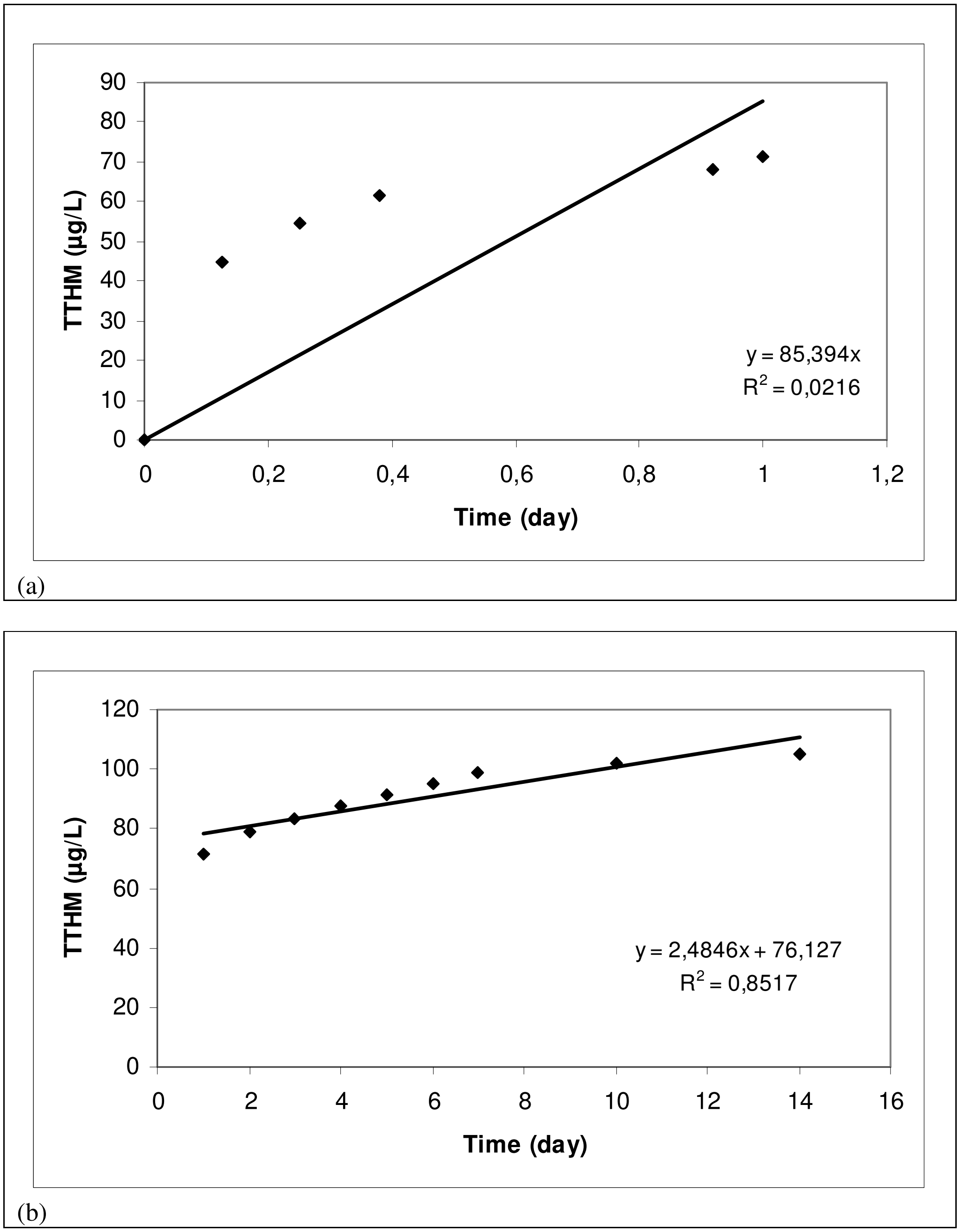


Figure 4.30. TTHM Formation Rate for Low NPOC Humic Acid at Low Chlorine Dose (a) for the First 24 hr (b) between 1st day-Completion of THM formation

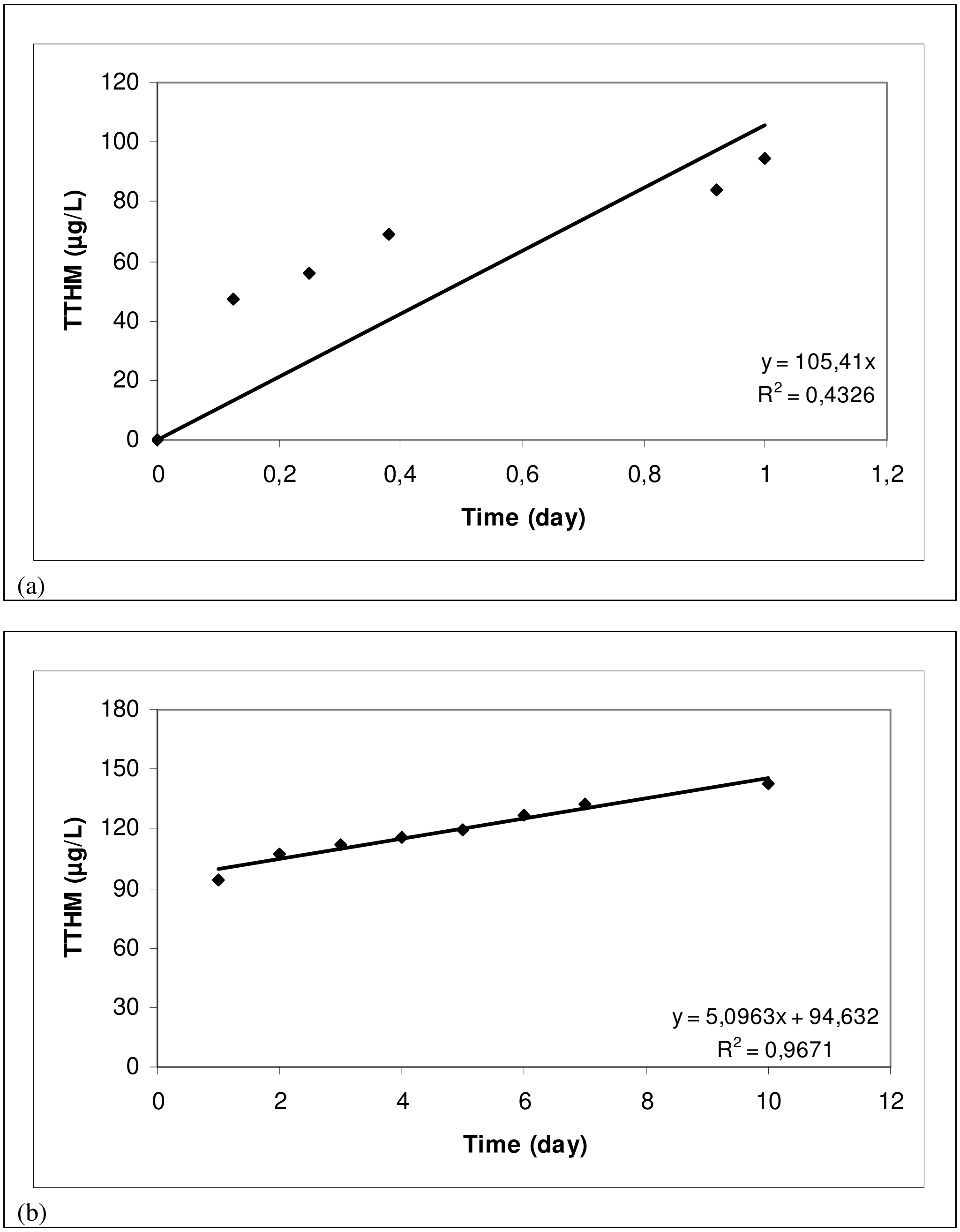


Figure 4.31. TTHM Formation Rate for Low NPOC Humic Acid at High Chlorine Dose (a) for the First 24 hr (b) between 1st day-Completion of THM formation

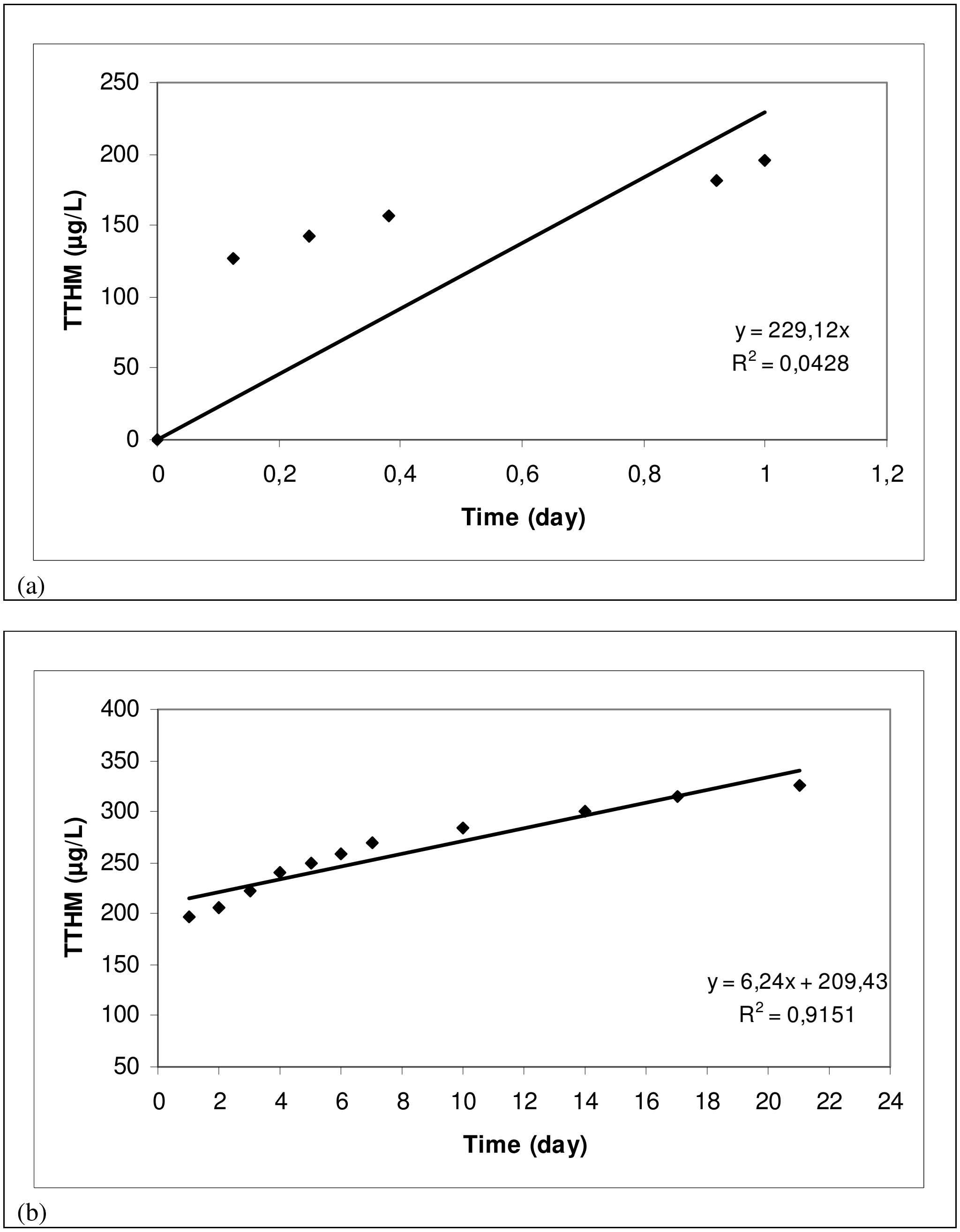
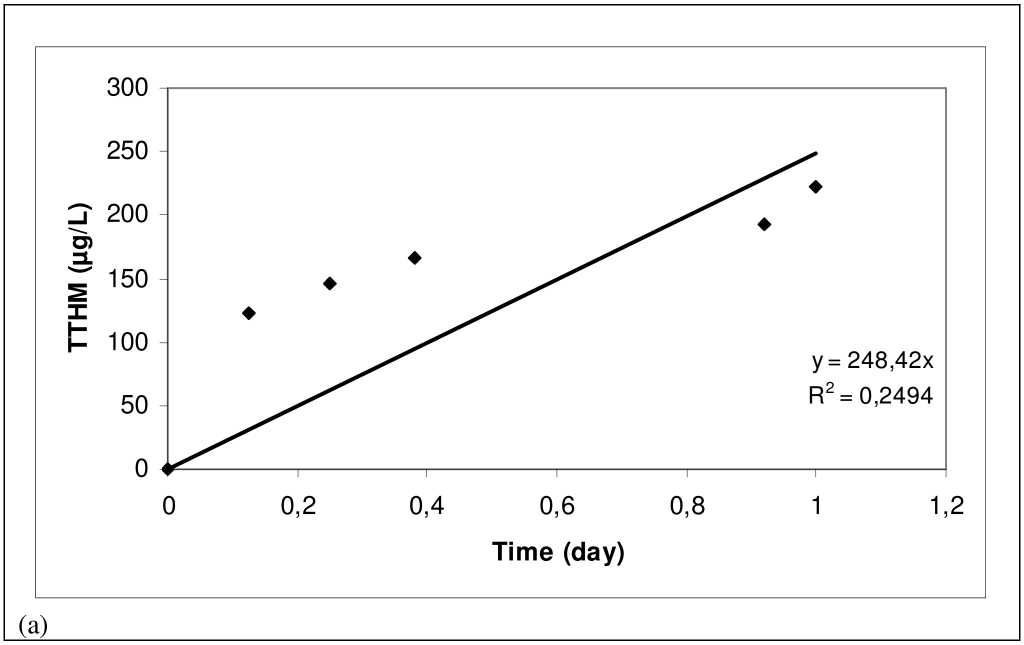


Figure 4.32 TTHM Formation Rate for High NPOC Humic Acid at Low Chlorine Dose (a) for the First 24 hr (b) between 1st day-Completion of THM formation



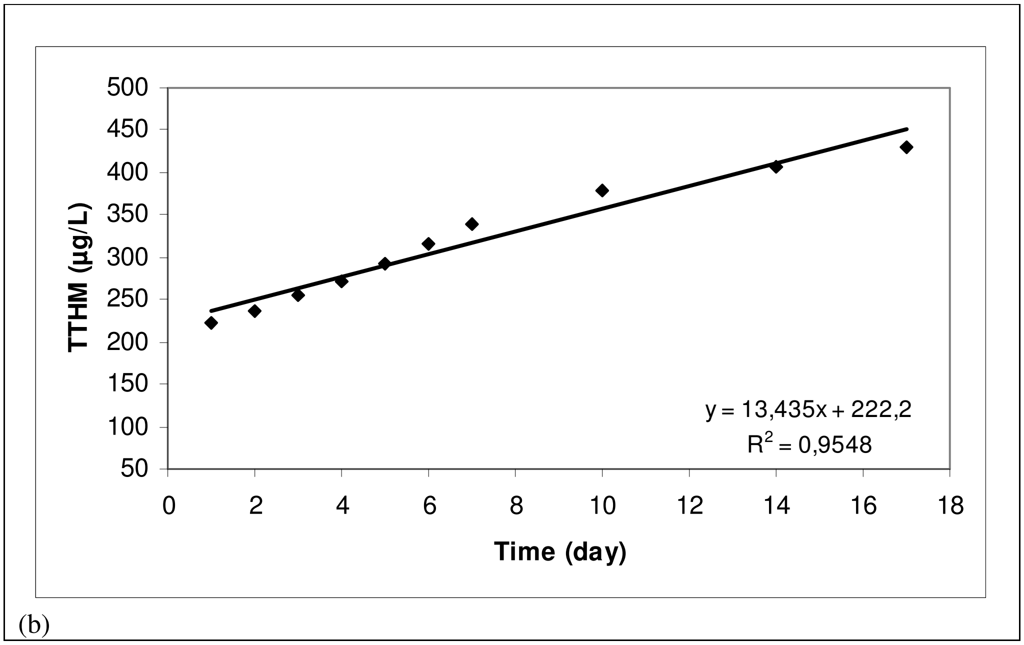


Figure 4.33. TTHM Formation Rate for High NPOC Humic Acid at High Chlorine Dose (a) for the First 24 hr (b) between 1st day-Completion of THM formation

Table 4.4. Comparison of the Rate Constants and r^2 Values for Atatürk Reservoir

Date	**Dose**	**First 24 hr**		**1st day-Completion**	
		k (µg/L.day)	**r^2**	**k (µg/L.day)**	**r^2**
May 2003	Low dose	35.795	0.7567	1.6660	0.9519
	High dose	37.543	0.4714	3.5805	0.9822
June 2003	Low dose	36.124	0.6137	2.5178	0.9596
	High dose	48.725	0.1276	4.0654	0.8924
July 2003	Low dose	52.381	0.5917	4.6376	0.9653
	High dose	60.471	0.3399	5.6939	0.9609
September 2003	Low dose	38.159	0.632	2.3968	0.9672
	High dose	33.888	0.6516	4.4088	0.9478
February 2004	Low dose	64.027	0.1759	3.9500	0.8908
	High dose	66.317	0.4578	6.3400	0.8960

Table 4.5. Comparison of the Rate Constants and r^2 Values for Devegeçidi Reservoir

Date	**Dose**	**First 24 hr**		**1st day-Completion**	
		k (µg/L.day)	**r^2**	**k (µg/L.day)**	**r^2**
May 2003	Low dose	80.599	0.7895	7.7422	0.8591
	High dose	134.630	0.9089	10.860	0.8644
June 2003	Low dose	98.477	0.8099	8.5077	0.8739
	High dose	135.590	0.9381	13.230	0.8943
July 2003	Low dose	136.020	0.3912	7.2192	0.8731
	High dose	148.610	0.5751	14.1450	0.9450
September 2003	Low dose	137.340	0.3341	8.8719	0.9124
	High dose	157.270	0.5006	14.9290	0.9575
February 2004	Low dose	167.010	0.6349	8.5026	0.8937
	High dose	154.630	0.6527	15.851	0.9111

Table 4.6. Comparison of the Rate Constants and r^2 Values for The Humic Acid

Solution	**Dose**	**First 24 hr**		**1st day-Completion**	
		k (µg/L.day)	**r^2**	**k (µg/L.day)**	**r^2**
Low NPOC	Low dose	85.394	0.0216	2.4846	0.8517
	High dose	105.410	0.4326	5.0963	0.9671
High NPOC	Low dose	229.120	0.0428	6.2400	0.9151
	High dose	248.420	0.2494	13.4350	0.9548

When the THM formation rate constants of humic acid solutions and the reservoir water samples are compared, it can be stated that although the constants of low and high NPOC humic acid solutions are higher than the ones observed in both reservoirs, constants of low NPOC humic acid and Atatürk Reservoir waters are similar which is also seen between the high NPOC humic acid solution and Devegeçidi Reservoir waters.

In addition, in our study, THM formation rates at high chlorine doses were generaaly higher than the ones observed for the low chlorine dosed samples due to the fact that initial chlorine concentration is an important factor affecting the amount and rate of THM formation (higher values of initial chlorine also results in higher reaction rates) as well as the time of completion of the reaction (Table 4.4-Table 4.6).

As seen in Table 4.4 through Table 4.6, THM formation is very rapid during the first 24 hr (THM formation rates ranging between 35 µg/L.day to 66 µg/L.day for Atatürk Reservoir waters, between 80 µg/L.day to 167 µg/L.day for Devegeçidi Reservoir waters and between 85 µg/L.day to 248 µg/L.day for humic acid solutions) followed by a more gradual formation (THM formation rates ranging between 2 µg/L.day to 6 µg/L.day for Atatürk Reservoir waters, between 7 µg/L.day to 16 µg/L.day for Devegeçidi Reservoir waters and between 3 µg/L.day to 14 µg/L.day for humic acid solutions) after 24 hr similar to the results obtained by various researchers (Gang, et al., 2003; Gallard and von Gunten, 2002; Boccelli, et al., 2003; Urano et al., 1983). However, Nikolaou et al. (2004) investigated the kinetics of the formation of different species of DBPs including THMs in the three river (Evergetoulas, Mylopotamos, Tsiknias) samples of Greece and observed that the formation of THMs were completed within 24 hr reaction time in all chlorinated waters. For $CHCl_3$, $CHCl_2Br$ and $CHClBr_2$ in chlorinated water from river Evergetoulas the formation rates were highest during the first hours of the reaction and then decreased which are similar to our findings. However, on the contrary, for waters from rivers Mylopotamos and Tsiknias the opposite behavior was observed, with the formation rates increasing after the first hours of the reaction. These dissimilarities may be explained by the differences in organic nature characteristics which affects the behaviours and rates of THM species.

Low r^2 values observed in the first 24 hr, especially in Atatürk Reservoir waters and humic acid solutions can be explained by the forcing trendlines to setting the intercept values at zero. However, as seen between Figure 4.24 – Figure 4.27, initial rates (at the first 3 hours) are very high in both reservoir waters and the humic acid solutions (Table 4.7 and Table 4.8).

Therefore, the initial rates were investigated and found that they change etween 104-205 µg/L.day in the Atatürk Reservoir waters and between 245-505 µg/L.day in the Devegeçidi Reservoir waters at the sampled months. Also, the initial rates at low NPOC and high NPOC humic solutions were 370 µg/L.day and 996 µg/L.day, respectively.

Table 4.7. Initial THM Formation Rates for Atatürk and Devegeçidi Reservoir Waters

Date	**Dose**	**Atatürk**	**Devegeçidi**
		k (µg/L.day)	**k (µg/L.day)**
May 2003	Low Dose	104.0	244.8
	High dose	132.5	263.7
June 2003	Low dose	115.8	266.9
	High dose	217.2	288.9
July 2003	Low dose	177.2	473.3
	High dose	202.0	461.7
September 2003	Low dose	120.9	497.3
	High dose	106.8	549.3
February 2004	Low dose	274.0	497.3
	High dose	232.9	505.2

Table 4.8. Initial THM Formation Rates for Humic Acid Solutions

Solution	**Dose**	**k (µg/L.day)**
Low NPOC	Low Dose	358.2
	High dose	280.0
High NPOC	Low dose	1013.2
	High dose	978.1

4.3. Chlorine Decay Analysis

Several chlorine decay models have been investigated by different researchers. Haas and Karra (1984) investigated first-order decay, power-order decay, first-order decay with stable component, power law decay with stable component and parallel first-order decay. They found that the parallel first-order decay model, which assumes parallel decay of two components of chlorine residual (one decaying more rapidly than the other), provided the best results. The Water Treatment Plant model used three models in sequence to describe chlorine decay: zero-order from t=0 to t=5 min, second order from t= 5 min to 5 h, and first order for t>5 h (USEPA, 1992). Clark (1998) investigated the reliability and performance of second-order decay. He found that in all cases he examined second-order model provided higher correlation (r^2 values between 0.90-0.99) than the first-order model. In this study, first and second-order decay models were investigated and the results obtained were presented in Figure 4.34 and Figure 4.35 for Atatürk Reservoir (May 2003), in Figure 4.36 and Figure 4.37 for the Devegeçidi Reservoir (May 2003) and between Figure 4.38 and Figure 4.41 for the humic acid solution.

Chlorine decay in bulk phase is characterized by a first-order kinetic model as follows:

$$dC/dt = -kC \qquad \text{(Eq. 4.1)}$$

where;

C: chlorine concentration (mg/L),
k: first-order decay constant (day^{-1}),
t: time (day).

Integrating Eq 4.1 yields;

$C_t = C_o\, e^{-kt}$ (Eq. 4.2)

where;

C_t: chlorine concentration (mg/L) at time t,
C_o: initial chlorine concentration (mg/L),
t: time of reaction

Second-order kinetic model is characterized as follows:

$dC/dt = -kC^2$ (Eq. 4.3)

where;

C: chlorine concentration (mg/L),
k: second-order decay constant (L/mg.day),
t: time (day).

Integrating Eq 4.3 yields;

$[1/C_t] - (1/C_o) = kt$ (Eq. 4.4)

where;

C_t: chlorine concentration (mg/L) at time t,
C_o: initial chlorine concentration (mg/L),
t: time of reaction

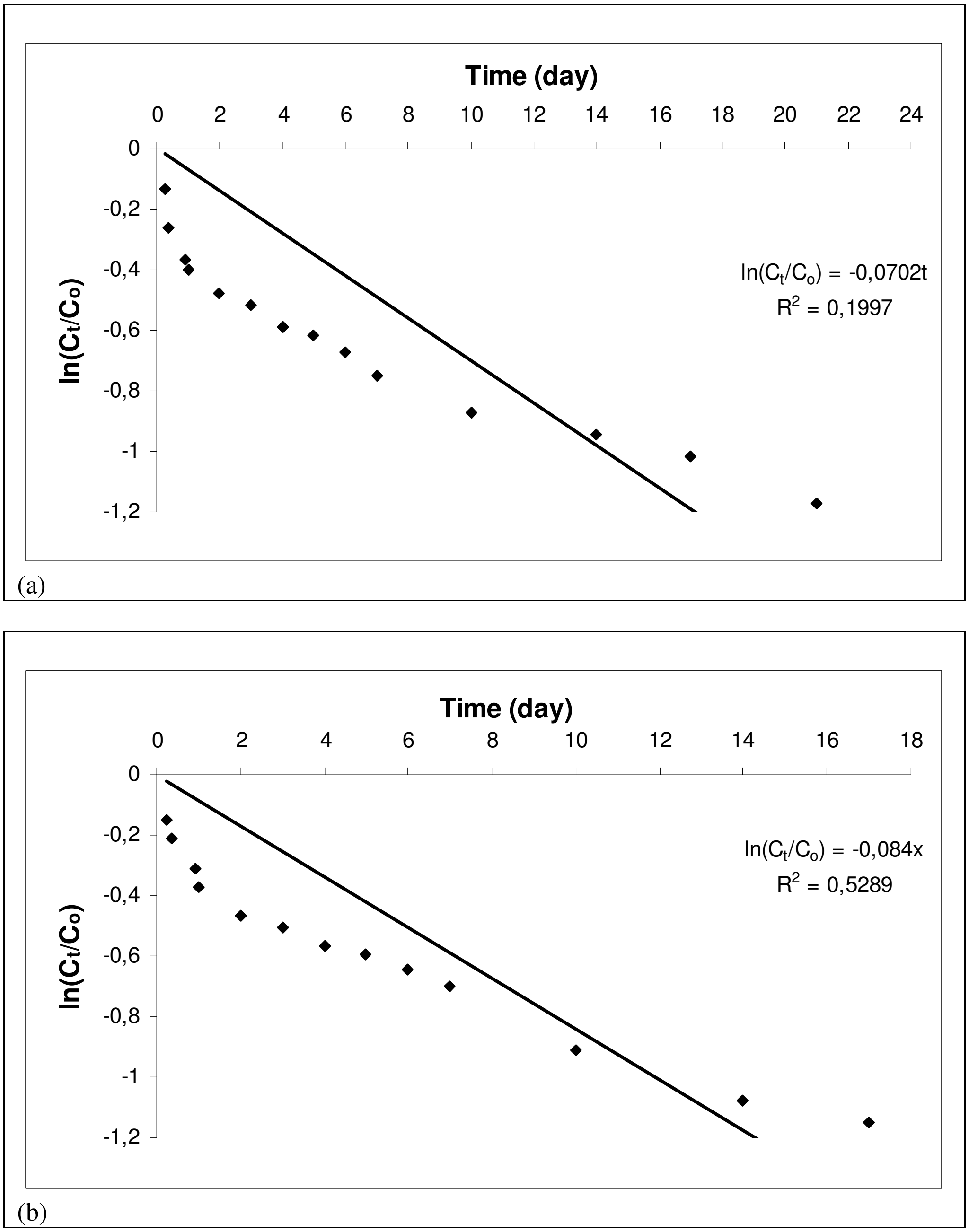


Figure 4.34. First-order Chlorine Decay Rates in Atatürk Reservoir in May 2003 (a) for Low Dose (b) for High Dose

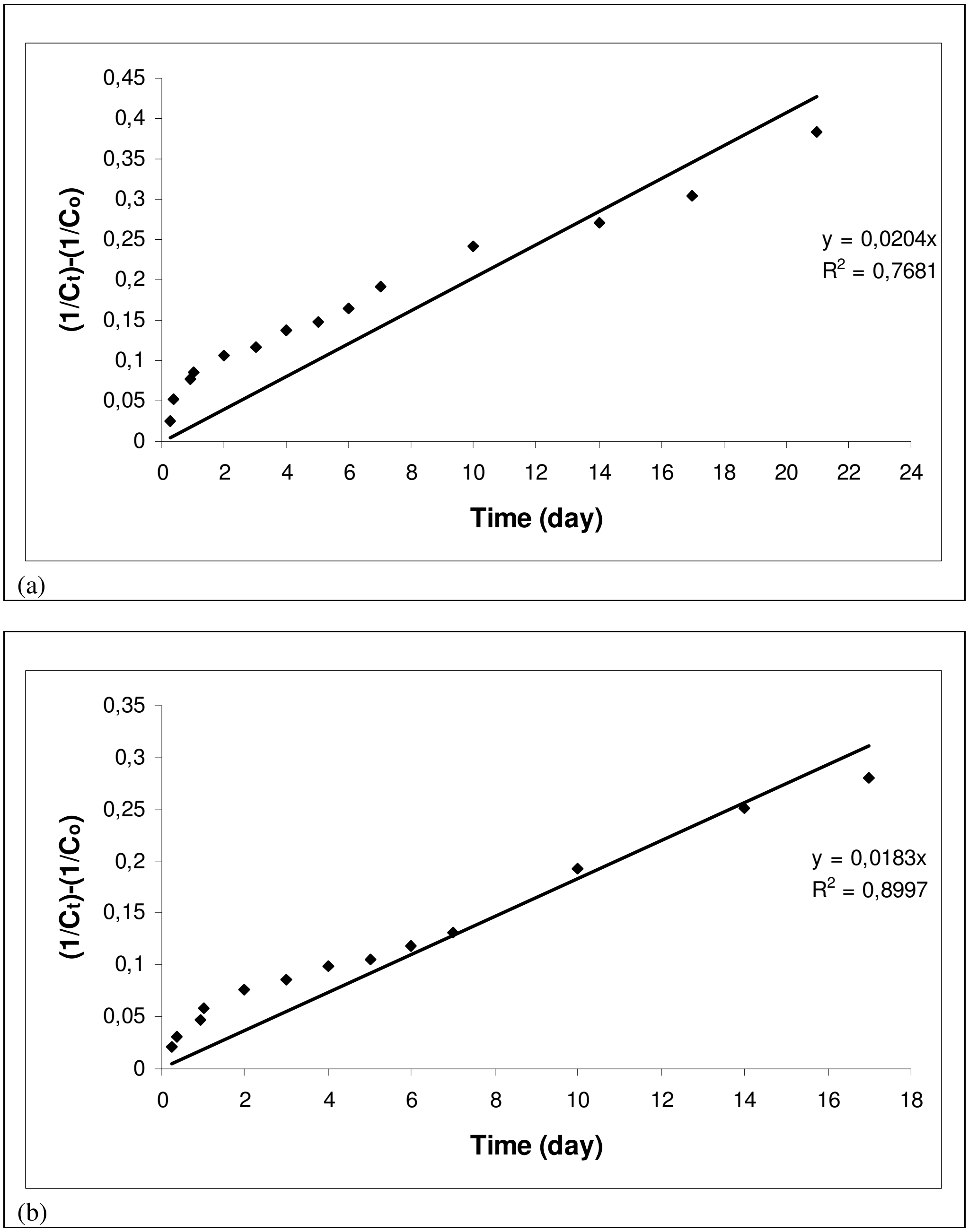
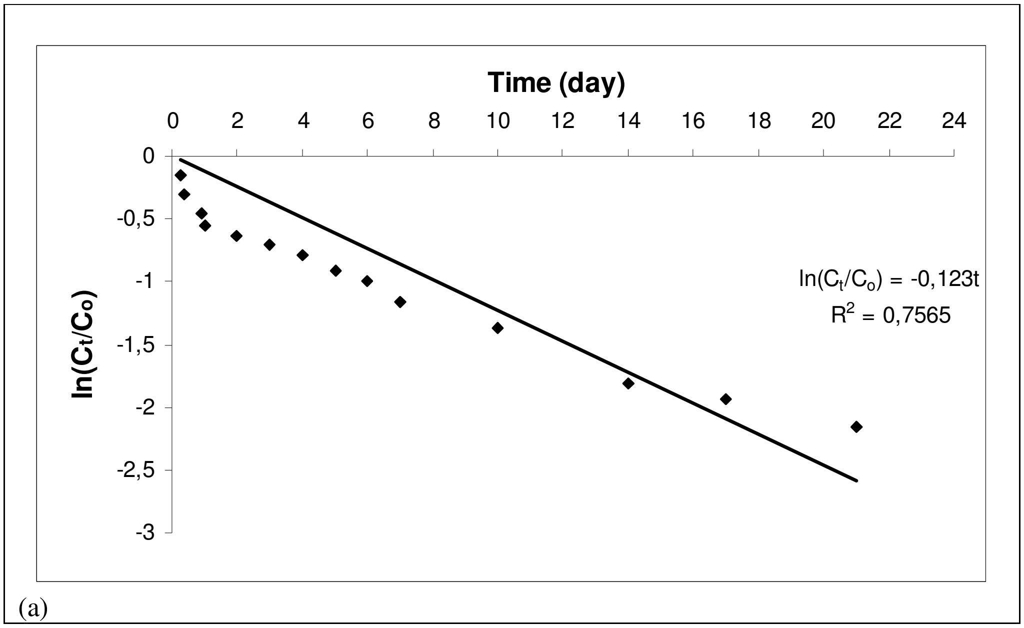


Figure 4.35. Second-order Chlorine Decay Rates in Atatürk Reservoir in May 2003 (a) for Low Dose (b) for High Dose

The results obtained with Atatürk Reservoir waters showed that second-order in terms of chlorine decay model provided better correlation (r^2 values between 0.62 and 0.87 for the low dose and between 0.78 and 0.90 for the high dose) than the first-order decay model which is similar to the findings of the work of Clark (1998). Comparison of the decay rate constants and r^2 values for first-order and second-order models are presented in Table 4.9.

Table 4.9. Comparison of the Decay Rate Constants and r^2 Values for First Order and Second Order Models for Atatürk Reservoir

Date	**Dose**	**First-order Decay**		**Second-order Decay**	
		k (day^{-1})	**r^2**	**k (L/mg.day)**	**r^2**
May 2003	Low dose	0.0702	0.20	0.0204	0.77
	High dose	0.0840	0.53	0.0183	0.90
June 2003	Low dose	0.0834	0.20	0.0225	0.77
	High dose	0.1175	0.36	0.0284	0.83
July 2003	Low dose	0.1002	0.40	0.0254	0.87
	High dose	0.0870	0.20	0.0130	0.78
September 2003	Low dose	0.0823	0.28	0.0231	0.78
	High dose	0.0962	0.43	0.0201	0.81
February 2004	Low dose	0.0782	0.10	0.0174	0.62
	High dose	0.0664	0.38	0.0076	0.79



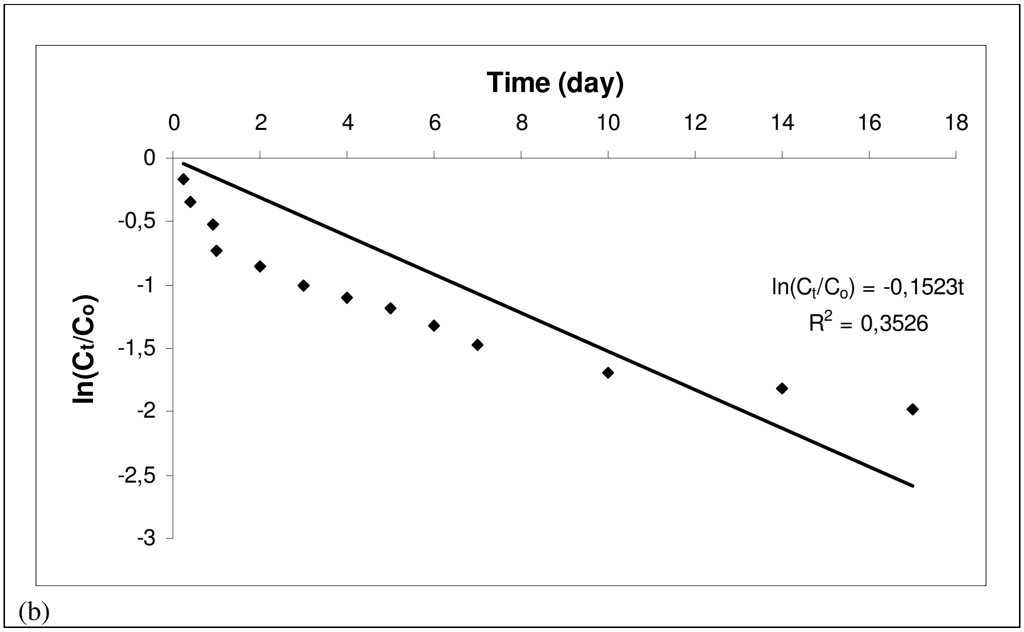
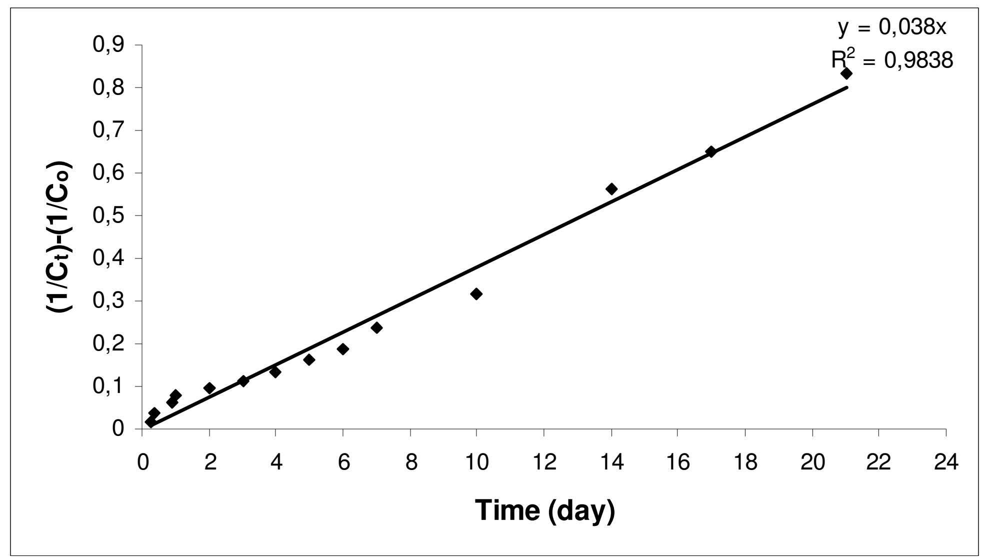
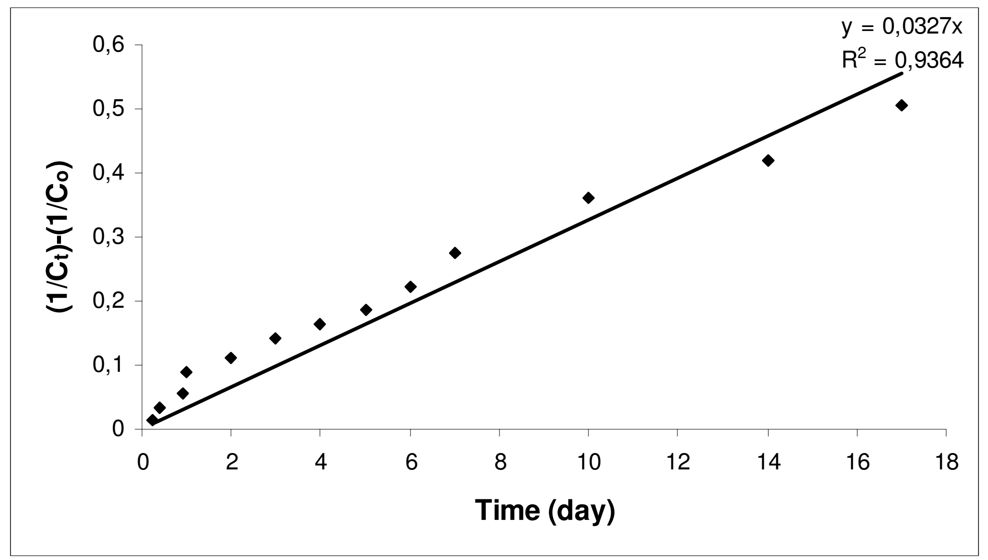


Figure 4.36. First-order Chlorine Decay Rates in Devegeçidi Reservoir in May 2003 (a) for Low Dose (b) for High Dose



(a)



(b)

Figure 4.37. Second-order Chlorine Decay Rates in Devegeçidi Reservoir in May 2003 (a) for Low Dose (b) for High Dose

The results with Devegeçidi Reservoir waters showed that second-order decay model provided better correlation (r^2 values between 0.89 and 0.98 for the low dose and between 0.88 and 0.97 for the high dose) than the first-order decay model (r^2 values between 0.32 and 0.76 for the low dose and between 0.35 and 0.76 for the high dose) which is similar to our findings of Atatürk Reservoir and the work of Clark (1998). Comparison of the decay rate constants and r^2 values for first-order and second-order models are presented in Table 4.10.

Table 4.10. Comparison of the Decay Rate Constants and r^2 Values for First Order and Second Order Rates for Devegeçidi Reservoir

Date	**Dose**	**First-order Decay**		**Second-order Decay**	
		k (day^{-1})	**r^2**	**k (L/mg.day)**	**r^2**
May 2003	Low dose	0.1230	0.76	0.0380	0.98
	High dose	0.1523	0.35	0.0327	0.94
June 2003	Low dose	0.0984	0.37	0.0170	0.90
	High dose	0.0781	0.76	0.0075	0.96
July 2003	Low dose	0.0836	0.36	0.0114	0.89
	High dose	0.1032	0.70	0.0095	0.97
September 2003	Low dose	0.1204	0.46	0.0201	0.95
	High dose	0.1034	0.61	0.0094	0.92
February 2004	Low dose	0.1049	0.32	0.0151	0.91
	High dose	0.0986	0.57	0.0089	0.88

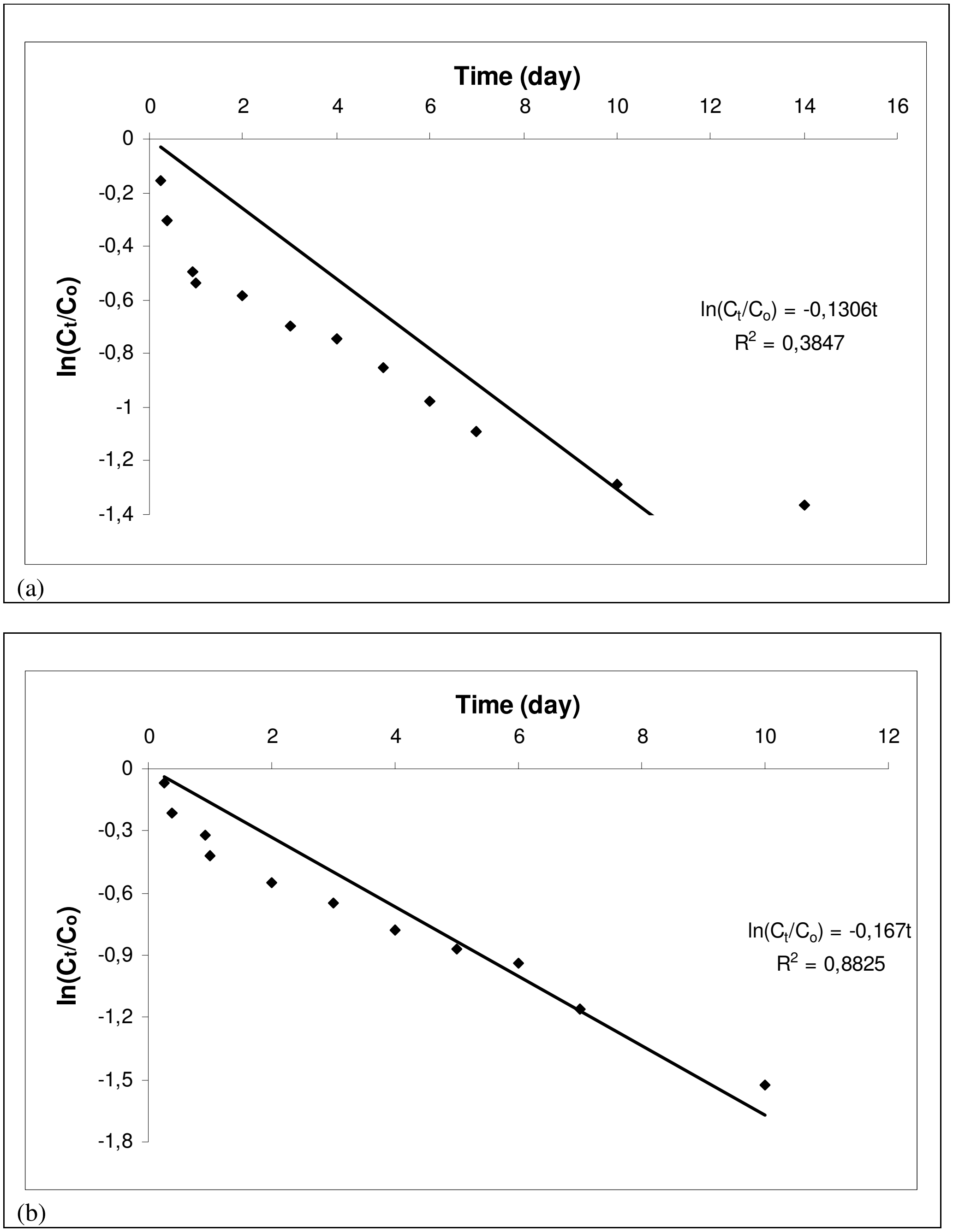
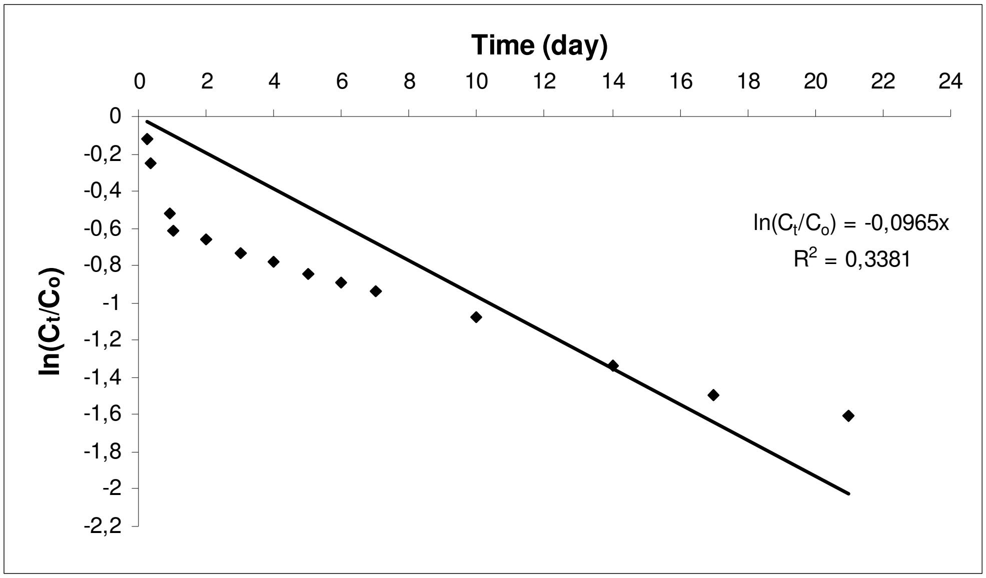
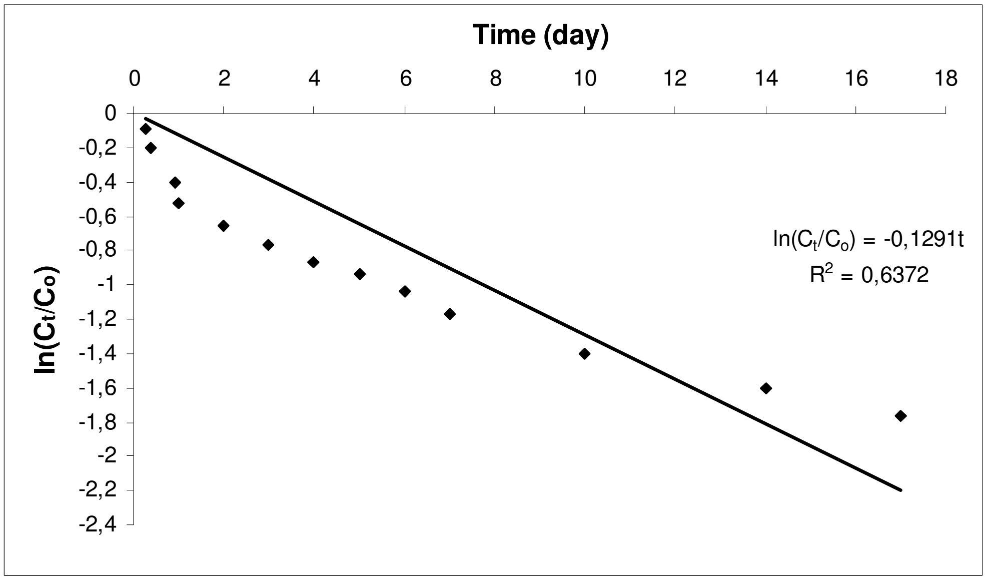


Figure 4.38. First-order Chlorine Decay Rates for Low NPOC Humic Acid (a) for Low Dose (b) for High Dose



(a)



(b)

Figure 4.39. First-order Chlorine Decay Rates for High NPOC Humic Acid (a) for Low Dose (b) for High Dose

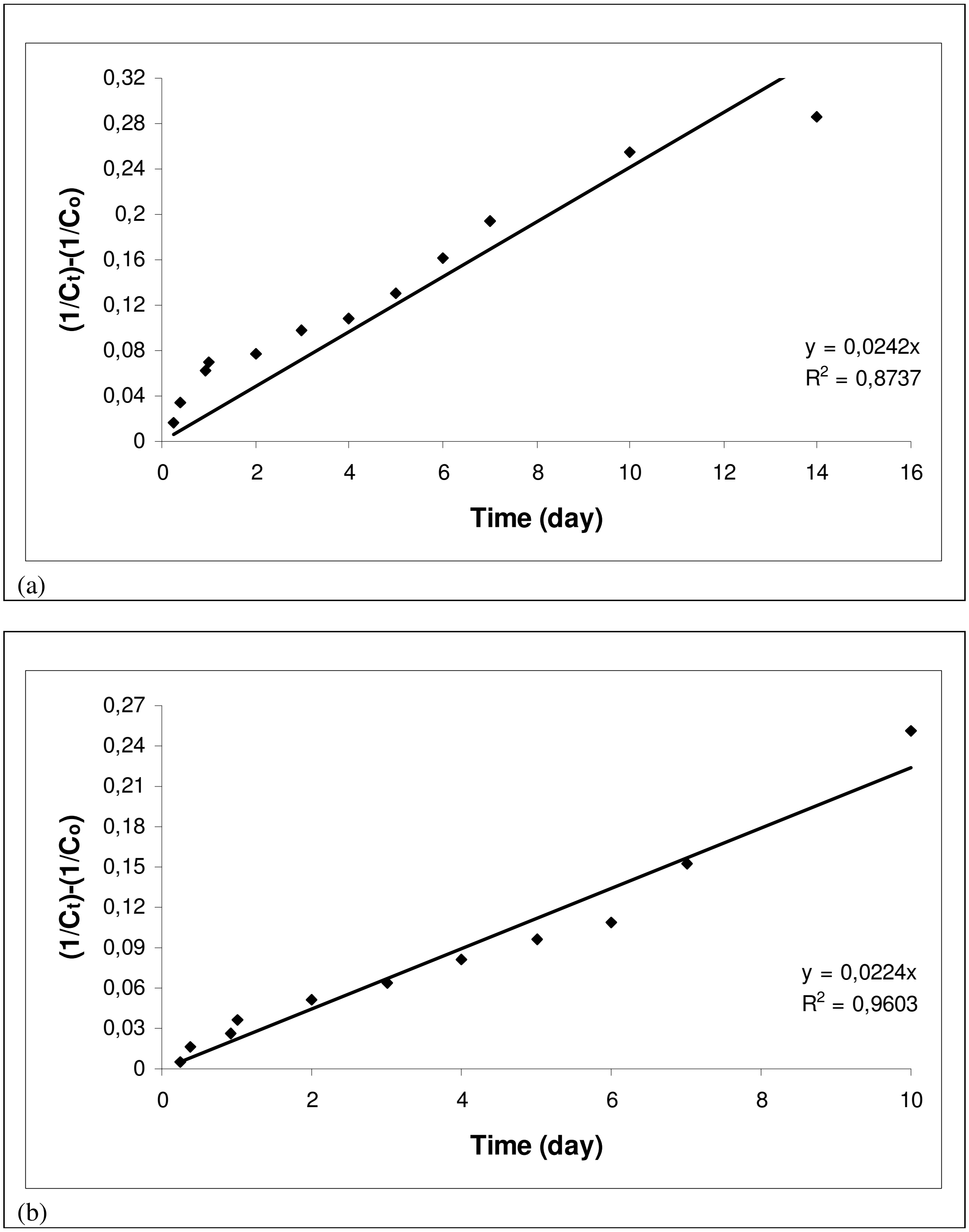
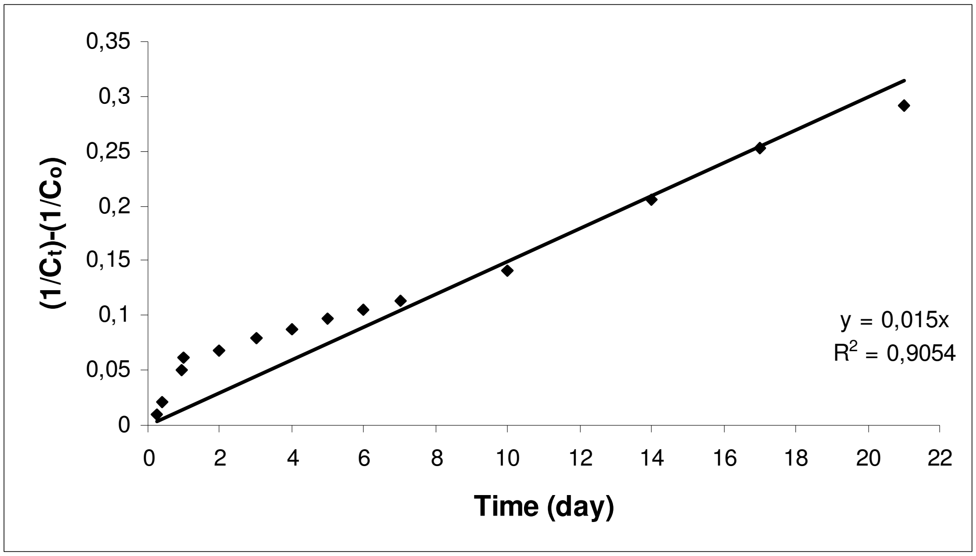
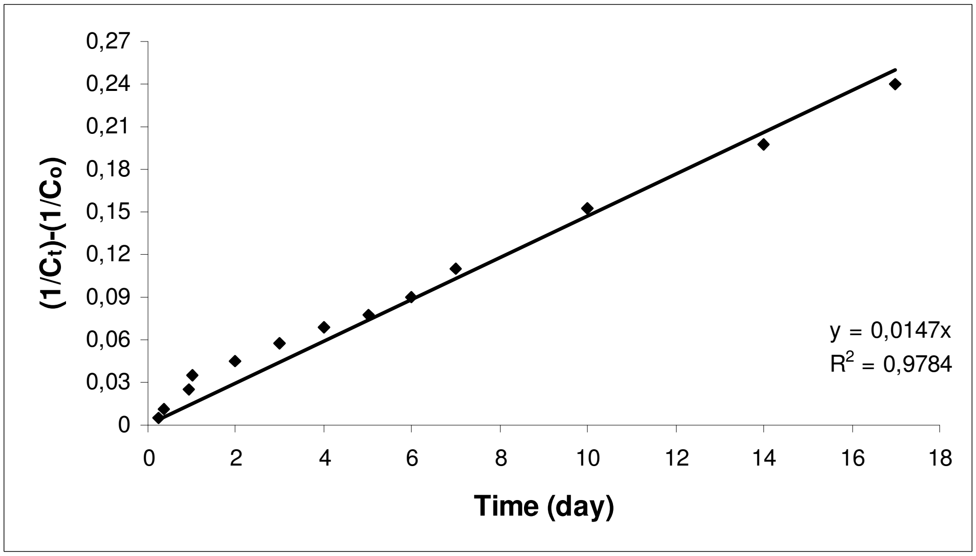


Figure 4.40. Second-order Chlorine Decay Rates for Low NPOC Humic Acid (a) for Low Dose (b) for High Dose



(a)



(b)

Figure 4.41. Second-order Chlorine Decay Rates for High NPOC Humic Acid (a) for Low Dose (b) for High Dose

The results (Figure 4.38 - Figure 4.41) showed that second-order decay model provided high correlation both in low NPOC (r^2 values of 0.87 for the low dose and 0.96 for the high dose) and high NPOC (r^2 values of 0.91 for the low dose and 0.98 for the high dose) containing humic acid solution. However, first-order decay model provided low r^2 values ranging between 0.34 and 0.88 for the low and high NPOC humic acid solutions. Comparison of the decay rate constants and r^2 values for first-order and second-order models are presented in Table 4.11.

Table 4.11. Comparison of the Decay Rate Constants and r^2 Values for First Order and Second Order Models for The Humic Acid

Solution	**Dose**	**First-order Decay**		**Second-order Decay**	
		k (day^{-1})	**r^2**	**k (L/mg.day)**	**r^2**
Low NPOC	Low dose	0.1306	0.39	0.0242	0.87
	High dose	0.1670	0.88	0.0224	0.96
High NPOC	Low dose	0.0965	0.34	0.0150	0.91
	High dose	0.1291	0.64	0.0147	0.98

Chlorine consumption were very rapid during the first hours of the reaction followed by a more gradual decay after 24 hr similar to the results obtained by various researchers (Gang, et al., 2003; Gallard and von Gunten, 2002; Boccelli, et al., 2003; Urano et al., 1983). The decay rate constants obtained with the reservoir samples (ranging between 0.0664-0.1175 day^{-1} for the first-order decay and between 0.0076-0.0284 L/mg.day for the second-order decay in the Atatürk Reservoir waters and ranging between 0.0781-0.1523 day^{-1} for the first-order decay and between 0.0075-0.0380 L/mg.day for the second-order decay in the Devegeçidi Reservoir waters) are close to the values obtained by the humic acid solutions (ranging between 0.0965-0.1670 day^{-1} for the first-order decay and between 0.0147-0.0242 L/mg.day for the second-order decay).

4.4. Prediction of THM Values by USEPA Simulation Model

The actual levels of THMs in drinking water vary greatly depending on temperature, organic matter nature and concentration, applied chlorine dose, pH, reaction time and inorganic ions like bromide. By including all these factors, USEPA developed a simulation model for predicting THM concentrations and the following equations are used to compute the TTHM levels (Hutton, 1993):

$$\text{TTHM} = 0.00309\ [(\text{TOC})(\text{UVA}_{254\text{nm}})]^{0.44}\ (\text{Cl}_2)^{0.409}\ (t)^{0.265}\ (T)^{1.06}\ (\text{pH}-2.6)^{0.715}\ (\text{Br})^{0.036} \quad \text{(Eq. 4.5)}$$

$$\text{AWM} = 105(\text{UVA})^{-0,089}\,(\text{Br}+1)^{0.48} \quad \text{(Eq. 4.6)}$$

where;

TTHM: total trihalomethane concentration (µmole/L),
TOC: total organic carbon concentration (mg/L),
$UV(A)_{254nm}$: ultraviolet absorbance at 254 nm,
Cl_2: chlorine dose (mg/L),
t: reaction time (hr),
T: temperature (^{o}C),
Br: bromide ion concentration (mg/L)
AWM: apparent molecular weight (µg/µmole).

Observed TTHM concentrations during the experiments were compared with the predicted values by the USEPA model and shown between Figure 4.42 and Figure 4.46 for the Atatürk Reservoir, between Figure 4.47 and Figure 4.51 for the Devegeçidi Reservoir and in Figure 4.52 and Figure 4.53 for the humic acid solutions, respectively.

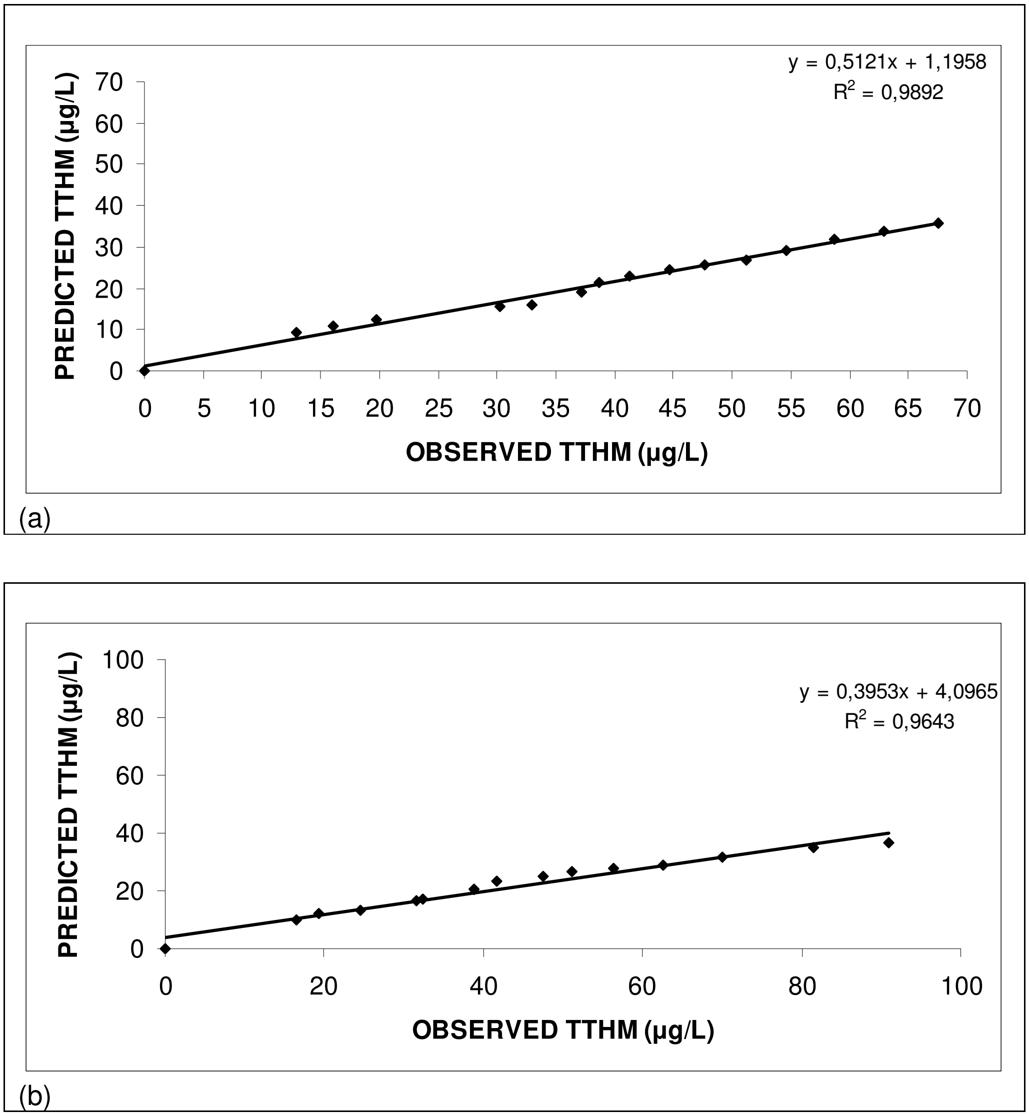


Figure 4.42. Comparison of Observed and Predicted TTHM Values in Atatürk Reservoir in May 2003 (a) for Low Dose (b) for High Dose

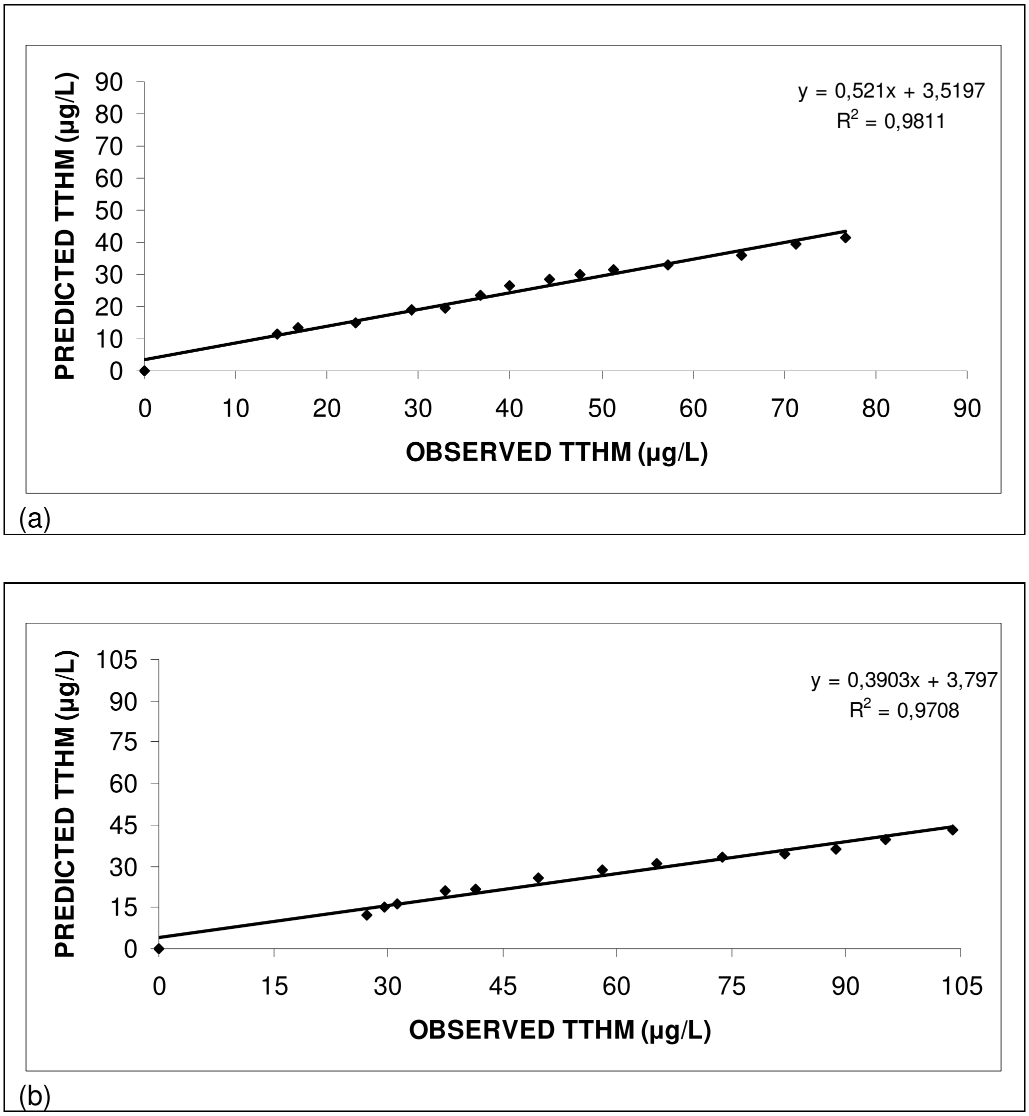


Figure 4.43. Comparison of Observed and Predicted TTHM Values in Atatürk Reservoir in June 2003 (a) for Low Dose (b) for High Dose

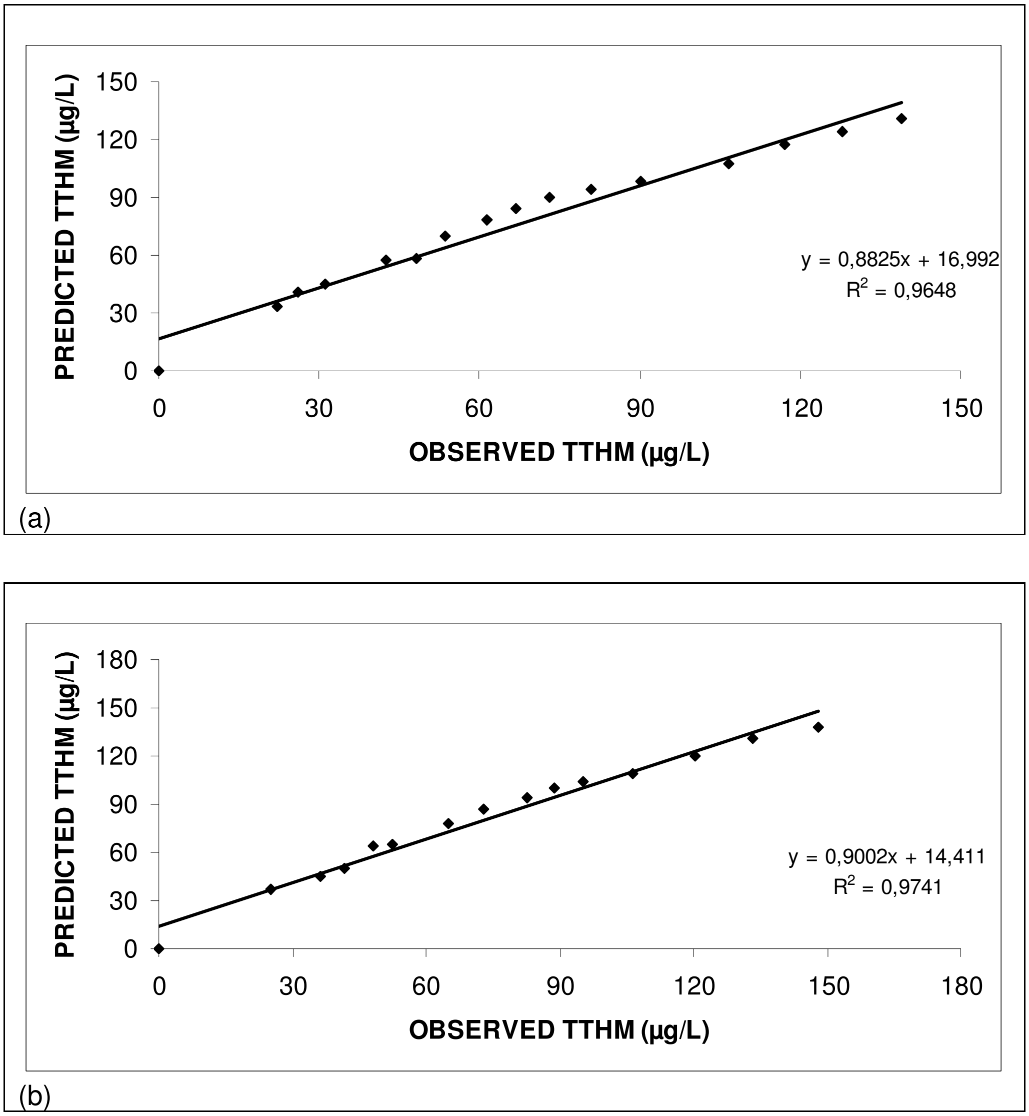
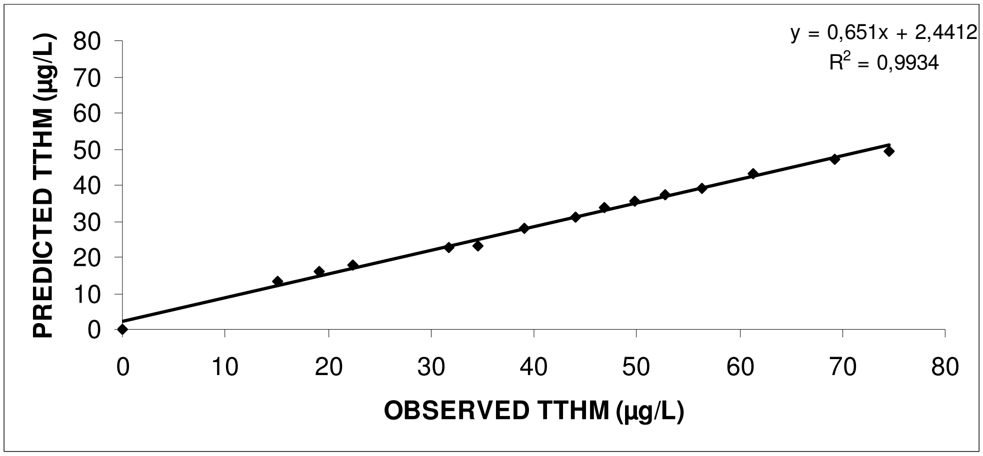
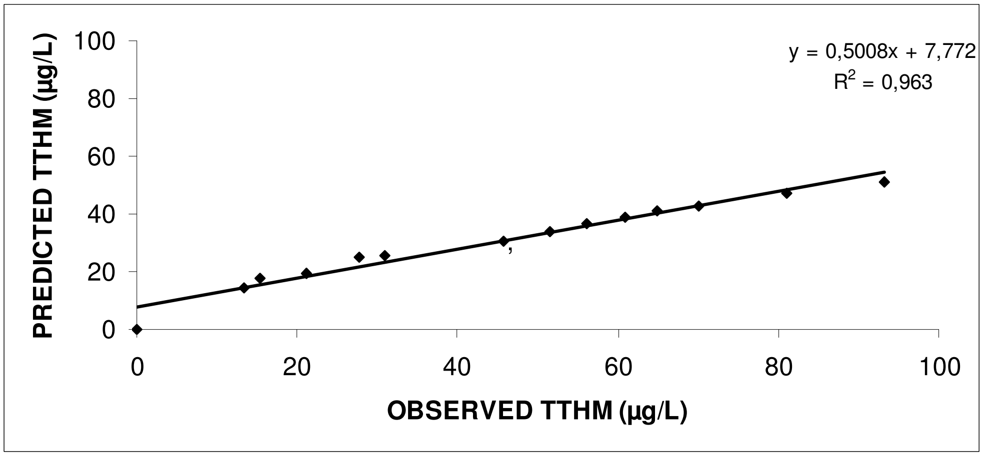


Figure 4.44. Comparison of Observed and Predicted TTHM Values in Atatürk Reservoir in July 2003 (a) for Low Dose (b) for High Dose



(a)



(b)

Figure 4.45. Comparison of Observed and Predicted TTHM Values in Atatürk Reservoir in September 2003 (a) for Low Dose (b) for High Dose

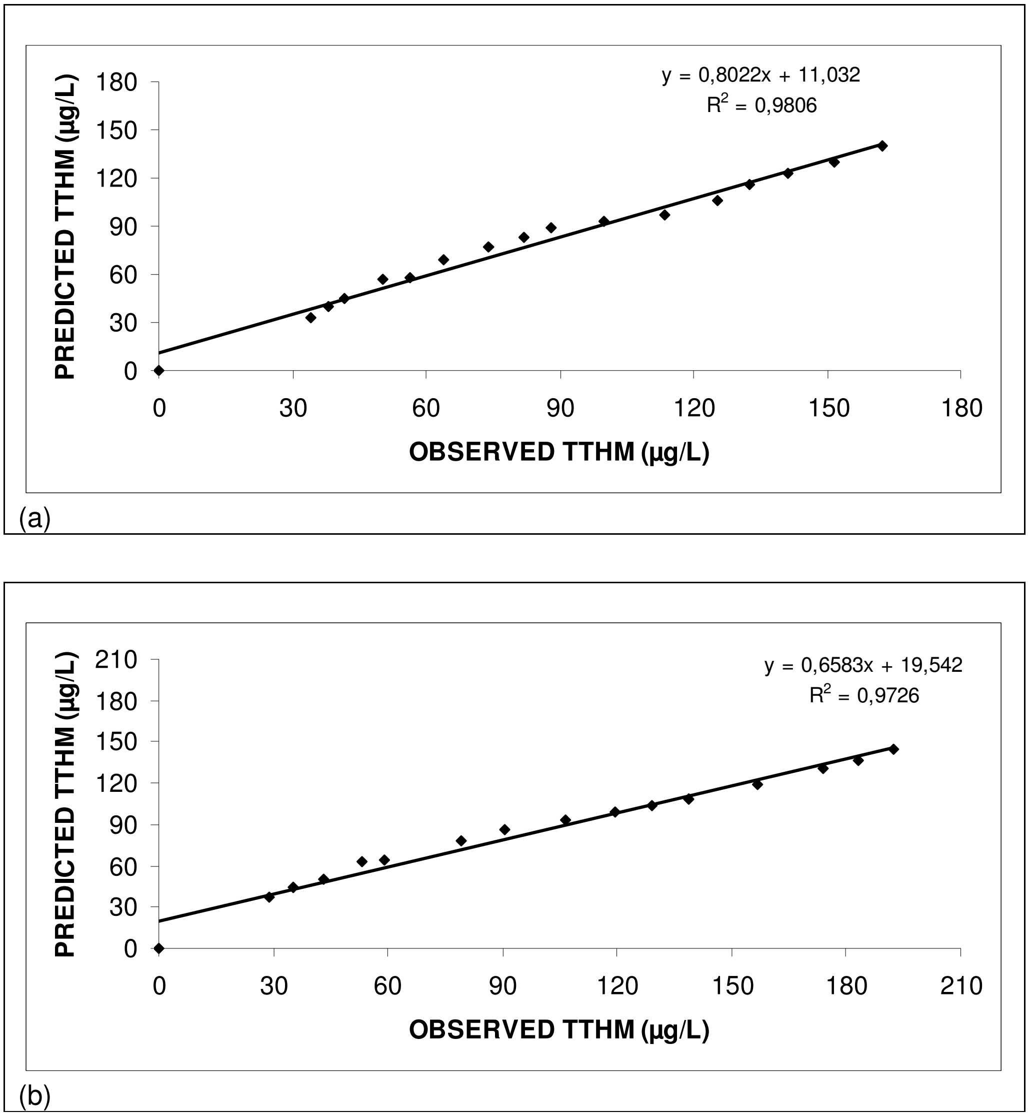


Figure 4.46. Comparison of Observed and Predicted TTHM Values in Atatürk Reservoir February 2004 (a) for Low Dose (b) for High Dose

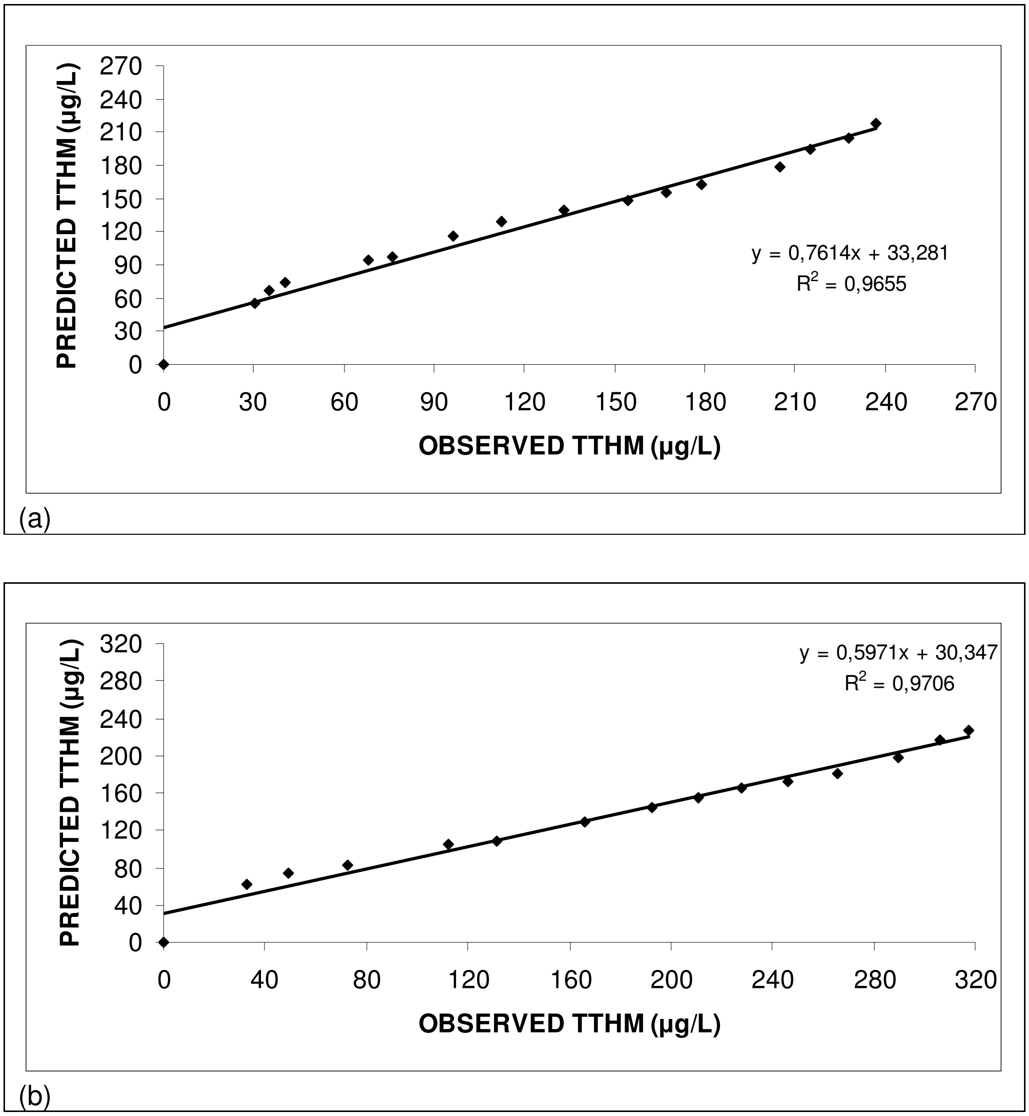
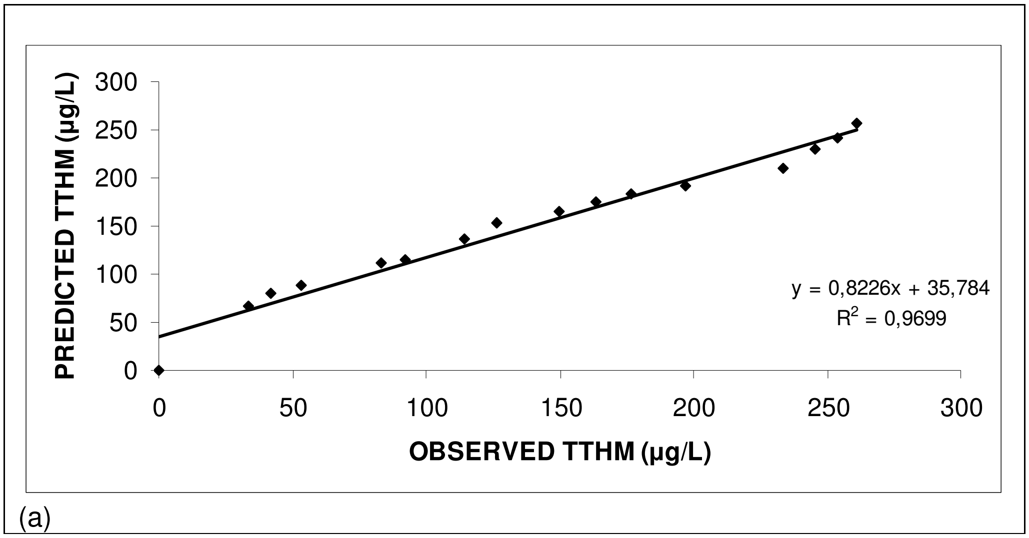


Figure 4.47. Comparison of Observed and Predicted TTHM Values in Devegeçidi Reservoir in May 2003 (a) for Low Dose (b) for High Dose



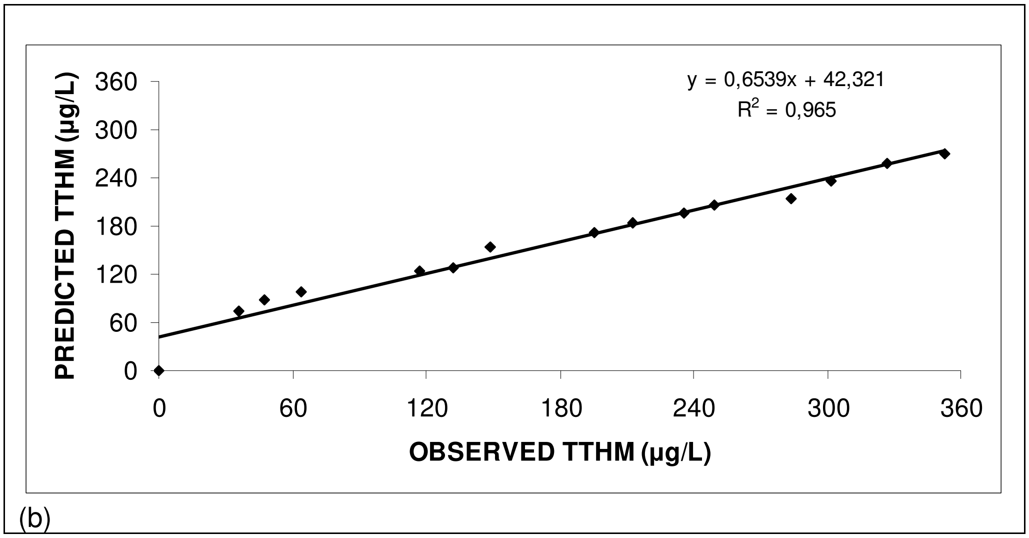


Figure 4.48. Comparison of Observed and Predicted TTHM Values in Devegeçidi Reservoir in June 2003 (a) for Low Dose (b) for High Dose

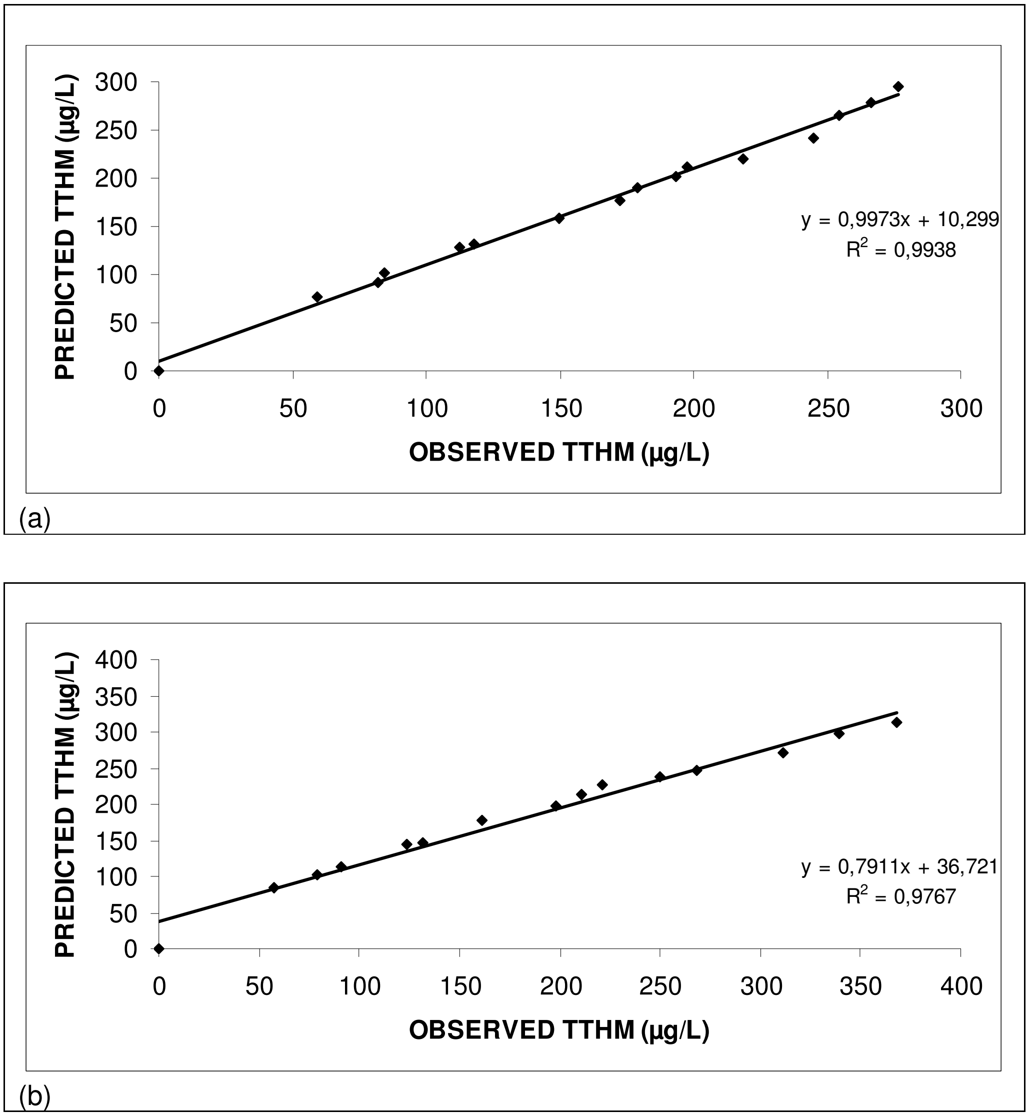


Figure 4.49. Comparison of Observed and Predicted TTHM Values in Devegeçidi Reservoir in July 2003 (a) for Low Dose (b) for High Dose

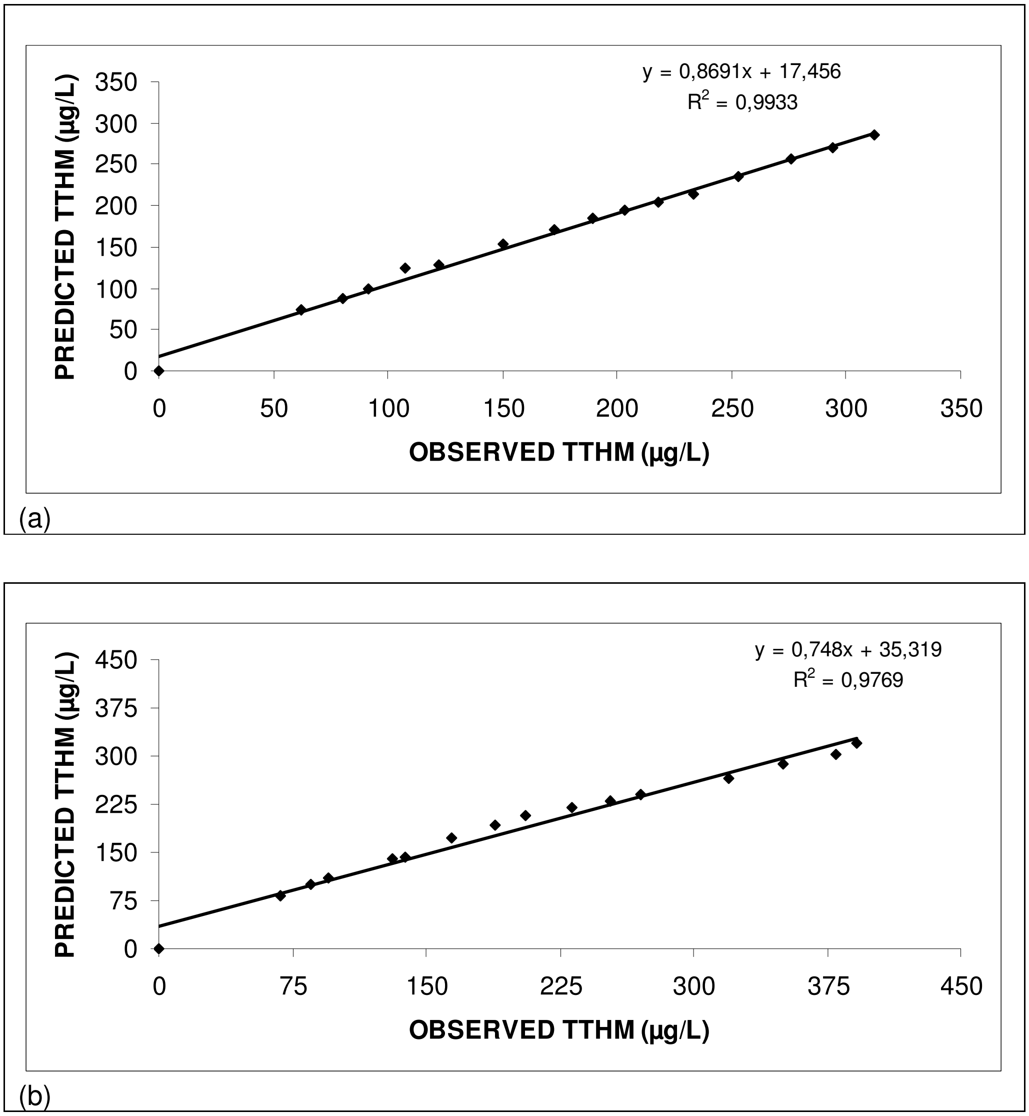
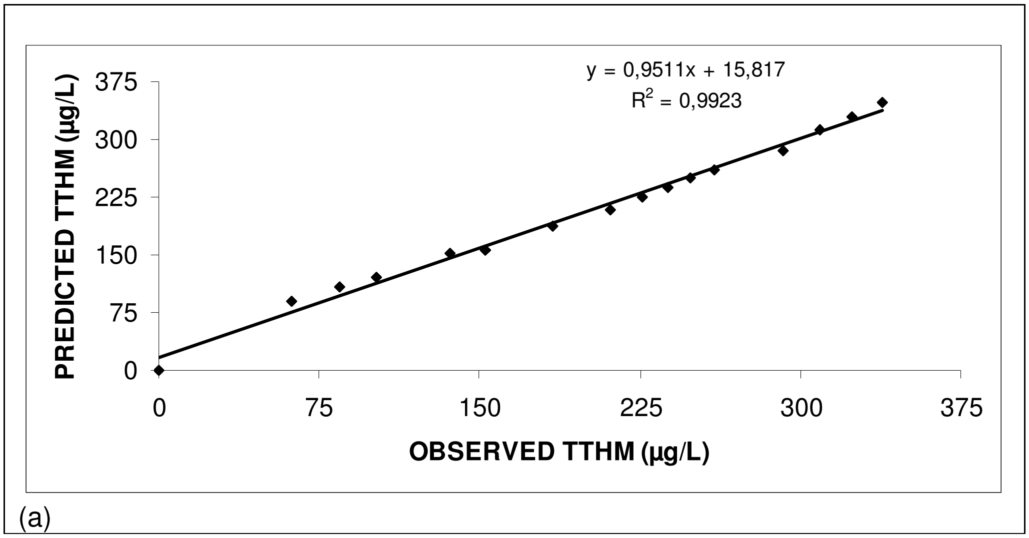


Figure 4.50. Comparison of Observed and Predicted TTHM Values in Devegeçidi Reservoir in September 2003 (a) for Low Dose (b) for High Dose



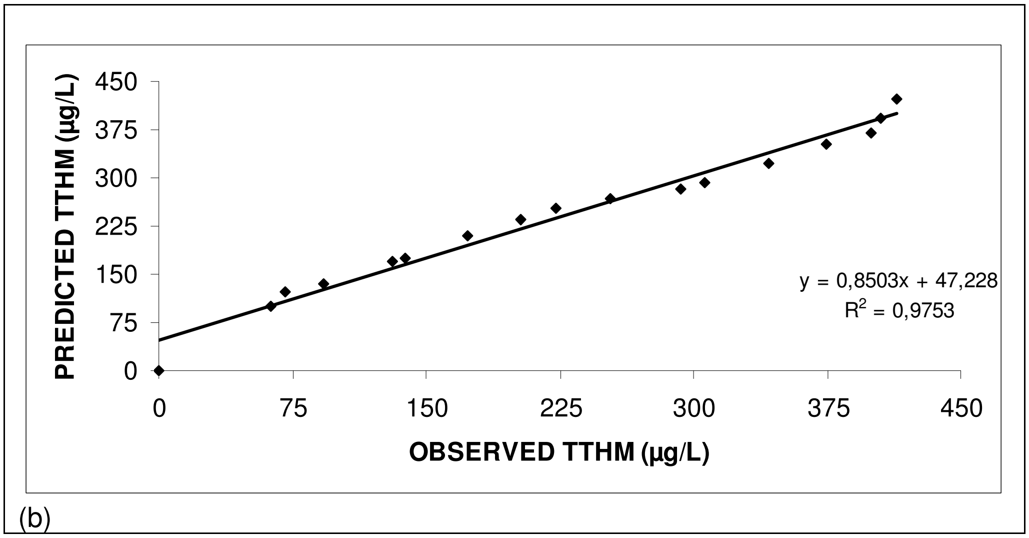
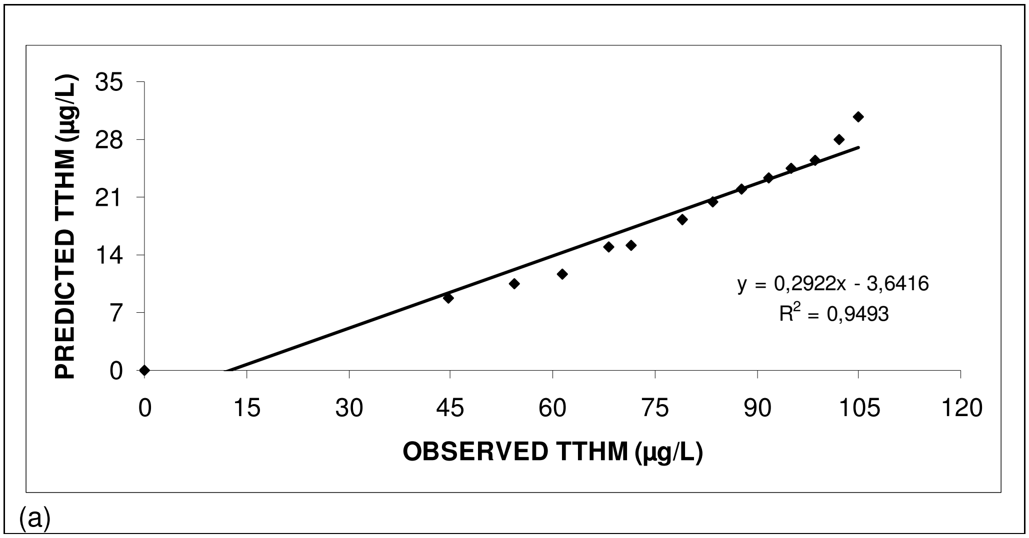


Figure 4.51. Comparison of Observed and Predicted TTHM Values in Devegeçidi Reservoir in February 2004 (a) for Low Dose (b) for High Dose



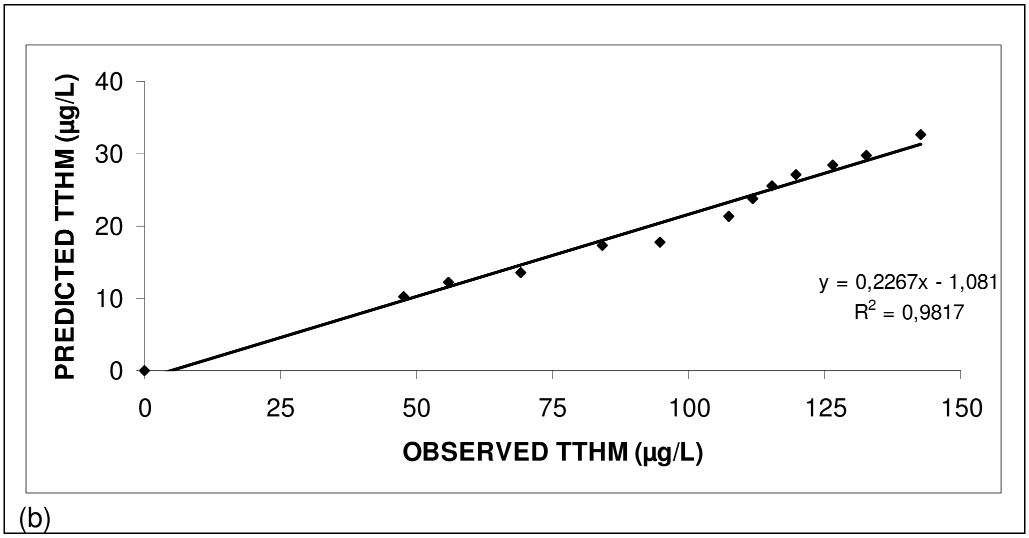


Figure 4.52. Comparison of Observed and Predicted TTHM Values for Low NPOC Humic Acid (a) for Low Dose (b) for High Dose

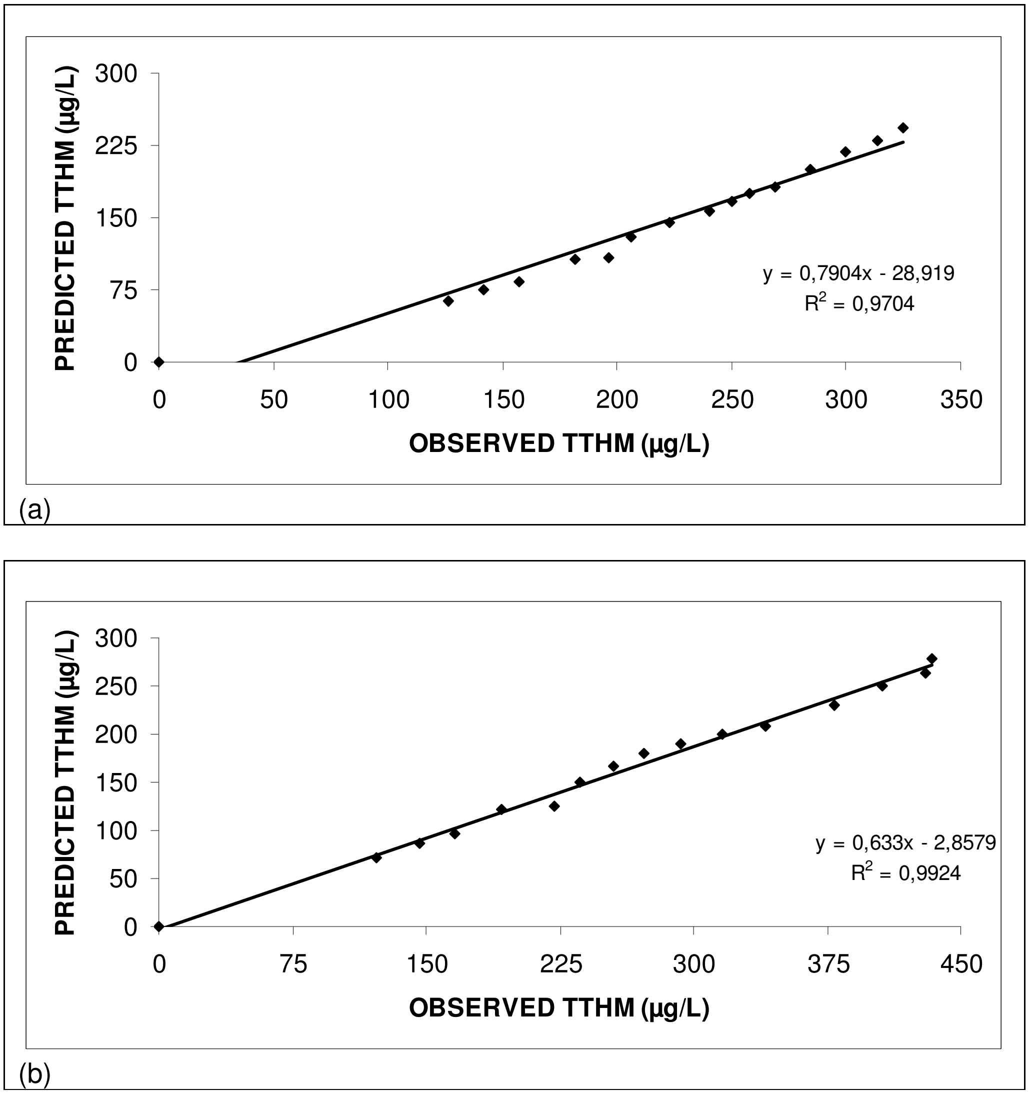


Figure 4.53. Comparison of Observed and Predicted TTHM Values for High NPOC Humic Acid (a) for Low Dose (b) for High Dose

As seen in the figures, the simulation model developed by USEPA shows quite high r^2 values. However, when the slope values are investigated, some values are not very close to 1 (observed TTHM values are much higher than the predicted ones) especially in the samples of Atatürk Reservoir waters. This observation and figures show that in some months there are under-predictions of the model. This confirms the idea that modeling of THM formation by surrogate parameters is difficult and complex. According to the predictive equation of USEPA (equation 4.5 and equation 4.6), the factors affecting THM formation are temperature, pH, $UV(A)_{254nm}$, Br concentration, applied chlorine dose and NPOC concentration. Moreover, several studies show that; chemical functional groups in the NOM play an important role in the formation of THMs. TOC and $UV(A)_{254nm}$ parameters cannot elucidate the functional groups that may either enhance or inhibit THM formation (Galapate et. al., 1999). Morris and Baum (1998) suggest that many types of organic chemical groups such as aliphatic carboxylic acids, hydroxobenzoic acids, phenolic compounds, pyrolle (nitrogen containing) derivatives are reactive substrates for chloroform production. For this reason, THM should be formulated taking all the listed factors as well as the organic nature/composition into consideration.

CHAPTER 5

CONCLUSIONS

This study examined the kinetics of THM formation in two reservoir waters (Atatürk and Devegeçidi) in Turkey and also in synthetic water prepared with the model compound, humic acid. Two different chlorine doses were applied in order to determine the effects of chlorine dose on THM formation.

Following conclusions were drawn based on the results of the experiments conducted with reservoir water samples of May 2003, June 2003, July 2003, September 2003, February 2004 and humic acid data:

- Organic matter content of Atatürk and Devegeçidi Reservoirs are below 5 mg/L, indicating that they are unpolluted fresh waters.

- SUVA values in Atatürk Reservoir waters are generally lower than 2 L/mg corresponding to hydrophilic carbon. In Devegeçidi Reservoir waters SUVA values are higher than the ones observed in Atatürk Reservoir waters, generally ranging between 2.0 and 2.7 L/mg, but showing also hydrophilic characteristics.

- Seasonal variation of $UV(A)_{254nm}$ values follow the same trend with the NPOC values, that is, $UV(A)_{254nm}$ values increased from spring to summer but reached their highest values in winter.

- Higher NPOC content of Devegeçidi Reservoir waters than the Atatürk reservoir waters resulted in higher chlorine demand and therefore higher THM formation in all the sampled months.

- Although the organic matter concentration of low NPOC is similar to the ones in Atatürk Reservoir waters and the same situation between high NPOC and Devegeçidi Reservoir waters, the ultimate TTHM concentration of low NPOC humic acid solutions were higher than the ones in Atatürk Reservoir waters as well as concentrations of high NPOC containing humic acid solutions were higher than the ones obtained with Devegeçidi Reservoir waters. This is an expected result since humic acids are the main precursors of THM formation.

- Chloroform was the dominant THM species observed after the chlorination of both reservoir waters in all of the sampled months as well as the model compound.

- THM concentration depended on the applied initial chlorine concentration. Although both low and high chlorine doses are higher than the chlorine demand of the water samples, as the chlorine dose was increased, more THMs formed. THM values measured at high chlorine doses were always higher than the ones measured at low chlorine doses in reservoir waters from all of the sampled months and the humic acid solutions.

- For a given initial chlorine dose, the formation of THMs and consumption of chlorine were both completed at the same reaction time, however, the time period required for the completion of THM formation varied with the applied chlorine dose and season. At high chlorine doses, THM formation was complete earlier than that for the low doses due to the fact that initial chlorine concentration is an important factor affecting the time of completion of the reaction as well as the amount and rate of THM formation (higher values of initial chlorine also results in higher reaction rates).

- THM formation did not complete in seven days in both reservoir waters and the humic acid solutions, and this, in turn, may result in underestimation of the ultimate potential of the water for producing trihalomethanes.

- Residual chlorine concentrations during the completion of THM formation, the overall yield values (total THM formed/total Chlorine consumed during the entire reaction periods) as well as the average yield values (µg TTHM formed/mg Chlorine consumed between two reaction times) differ through sampled months that may be attributed to the variations in the nature of organic matter which is also supported by the changes in SUVA values.

- The overall yield values obtained with Devegeçidi Reservoir waters (ranging between 18.99-23.36 µg TTHM formed/ mg Cl_2 consumed for the low chlorine doses and 20.00-25.10 µg TTHM formed/ mg Cl_2 consumed for the high doses) are higher than the ones obtained with Atatürk Reservoir waters (ranging between 12.35 - 15.50 µg TTHM formed/ mg Cl_2 consumed for the low dose and 13.70-16.14 µg TTHM formed/ mg Cl_2 consumed for the high doses) that can be attributed to the high organic content of Devegeçidi Reservoir waters which result in higher THM formation.

- In all months, the formation yields were highest during the first hours of reaction time and then decreased showing the rapid THM formation and chlorine decay. In addition, due to the excess chlorine concentrations in highly chlorine dosed water samples, the maximum yield values for low dose were always higher than the ones obtained for high dose.

- THM formation is very rapid during the first 24 hr (ranging between 35 µg/L.day to 66 µg/L.day for Atatürk Reservoir waters, between 80 µg/L.day to 167 µg/L.day for Devegeçidi Reservoir waters and between 85 µg/L.day to 248 µg/L.day for humic acid solutions) followed by a more gradual formation (THM formation rates ranging between 2 µg/L.day to 6 µg/L.day for Atatürk Reservoir waters, between 7 µg/L.day to 16 µg/L.day for Devegeçidi Reservoir waters and between 3 µg/L.day to 14 µg/L.day for humic acid solutions) after 24 hr.

- Initial THM formation rates (at the first 3 hours) were very high in both reservoir waters and the humic acid solutions. They change between 104-205 µg/L.day in the Atatürk Reservoir waters and between 245-505 µg/L.day in the Devegeçidi Reservoir waters at the sampled months. Also, the initial rates at low NPOC and high NPOC humic solutions were 370 µg/L.day and 996 µg/L.day, respectively.

- Comparison of two different chlorine decay rates (first and second order) resulted in better correlation values obtained in second-order rate model both for the reservoir waters and humic acid solution (r^2 values between 0.62 and 0.90 for the Atatürk Reservoir, between 0.88 and 0.98 for the Devegeçidi Reservoir and between 0.87 and 0.98 for the humic acid solutions).

- In order to compare the kinetics of humic acid with the reservoir waters, NPOC values of the humic acid solutions were selected as similar values of Atatürk and Devegeçid Reservoir waters. The results showed that the trends and concentrations of THM formation and chlorine consumption in reservoir waters were similar with the ones observed in humic acid. Therefore, it may be stated that organic precursors responsible for THM formation in both reservoir waters show humic characteristics.

- A simulation model developed by USEPA for predicting THM concentrations was used for comparison of the observed and predicted values for both reservoirs and humic acid solution. The results showed quite high correlations between the observed and predicted values. Some under-predictions of the model observed especially in the Atatürk Reservoir and low NPOC containing humic acid solution can be attributed to the complex response of THM formation to various surrogate parameters as well as the differences in organic matter nature/characteristics.

CHAPTER 6

RECOMMENDED FUTURE WORK

- THM formation kinetics of both reservoirs should be studied for longer times (at least for all months in a year or preferably for more than one year) in order to better understand the seasonal changes and its effects on THM formation kinetics. In addition continuous monitoring of meteorological data (precipitation, temperature, etc.) to support the raw water quality data, is needed.

- In order to have a better insight on kinetics of THM formation, fractionation of natural organic matter (NOM) and its effects on THM should be studied.

- Molecular weight distribution of NOM in the raw waters should be studied in order to investigate its possible effect on kinetics of THM formation.

- Experiments should be conducted with waters from other reservoirs to determine the general trend in Turkey.

- Experiments should be conducted with different bromide contents to determine the effect of bromide ion concentration on formation kinetics of each THM compound.

- In order to observe the algal activity and its contribution to organic matter content, chlorophyll-A concentrations of the raw waters should be measured.

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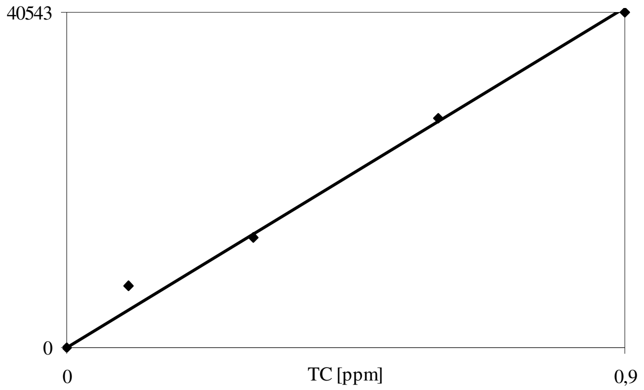
APPENDIX A

NPOC CALIBRATION CURVES



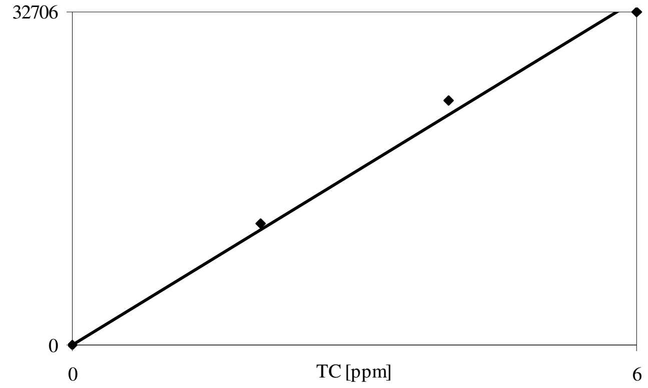
CAL CURVE F# 8
TC 4-POINT (SHIFT TO ORIGIN)
PROTECTED
LEAST SQUARES r=0.997

[CONDITIONS]
TC CATALYST : HIGH SENS
INJ VOL/SYRINGE SIZE : 88/250 µl
RANGE : X1
SPARGE TIME : 0 min
NO OF WASHES : 4
DATE : 12 (JUNE) – 06 – 2003

[DATA]

STD CONC	AREA	#INJ	SD	CV
0.9 ppm	40543	3	747	1.81%
0.6 ppm	27700	3	446	1.25%
0.3 ppm	13400	3	560	1,36%
0.1 ppm	7500	3	150	0.95%

Figure A.1. NPOC Calibration Curve (June 2003)



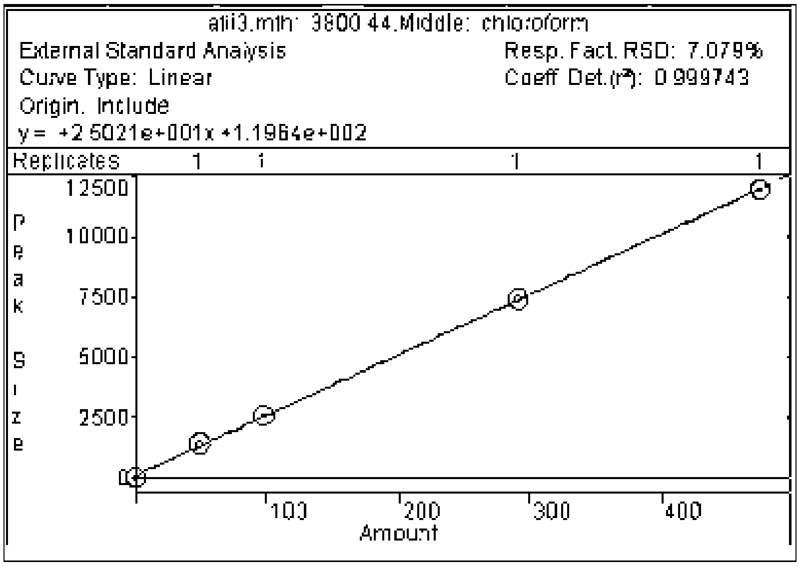
```
CAL CURVE F# 16
     TC 3-POINT (SHIFT TO ORIGIN)
     PROTECTED
     LEAST SQUARES r=0.996

[CONDITIONS]
     TC CATALYST                : HIGH SENS
     INJ VOL/SYRINGE SIZE       : 88/250 µl
     RANGE                      : X1
     SPARGE TIME                : 0 min
     NO OF WASHES               : 4
     DATE                       : 9 (FEBRUARY) – 02 – 2004
[DATA]
     STD CONC    AREA    #INJ    SD    CV
     6.0 ppm     32706     3     111   0.34%
     4.0 ppm     24021     3     266   1.10%
     2.0 ppm     11909     3     553   4.65%
```

Figure A.2. NPOC Calibration Curve (February 2004)

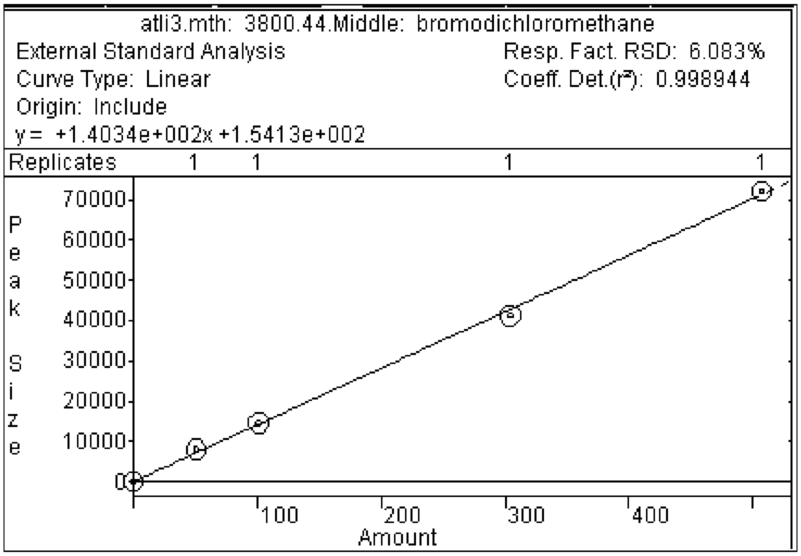
APPENDIX B

THM CALIBRATION CURVES



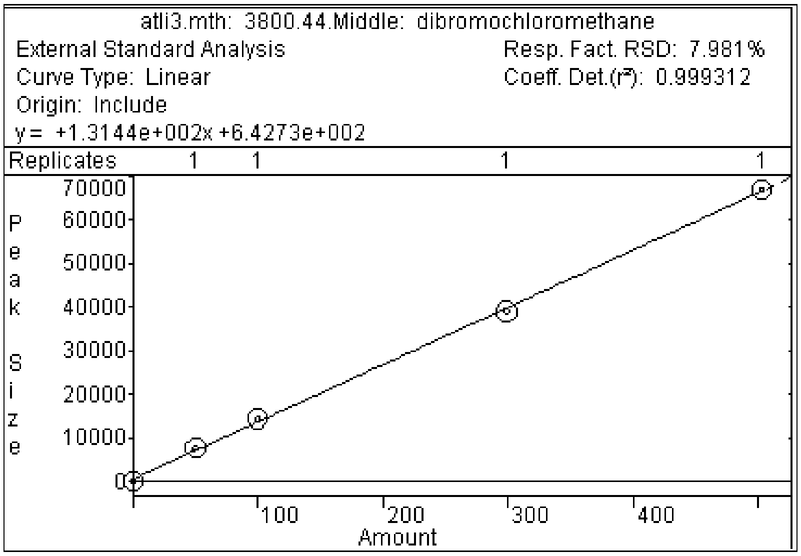
```
aiii3.mth: 3800 44.Middle: chloroform
External Standard Analysis                    Resp. Fact. RSD: 7.079%
Curve Type: Linear                            Coeff Det.(r²): 0.999743
Origin. Include
y = +2.5021e+001x +1.1964e+002
```

Figure B.1. Calibration Curve for Chloroform (July 2003)



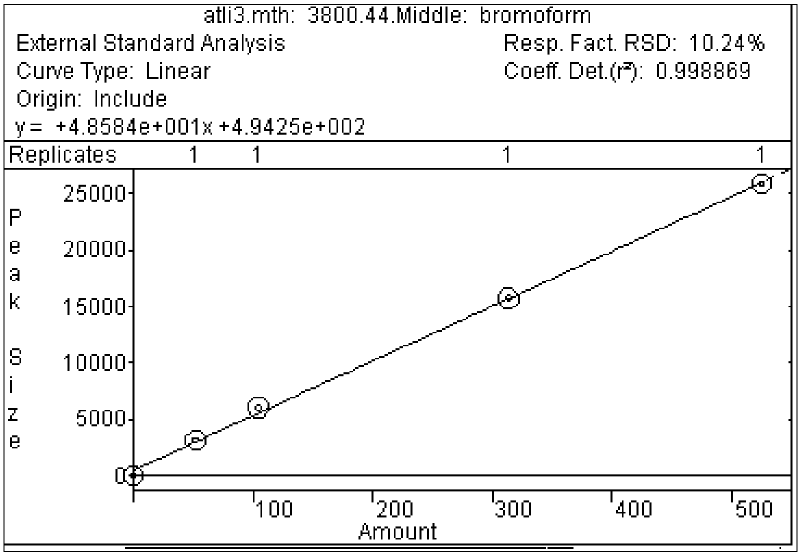
```
atli3.mth:  3800.44.Middle:  bromodichloromethane
External Standard Analysis                 Resp. Fact. RSD:  6.083%
Curve Type:  Linear                        Coeff. Det.(r²):  0.998944
Origin:  Include
y =  +1.4034e+002x +1.5413e+002
```

Figure B.2. Calibration Curve for Bromodichloromethane (July 2003)



```
atli3.mth:  3800.44.Middle:  dibromochloromethane
External Standard Analysis                 Resp. Fact. RSD:  7.981%
Curve Type:  Linear                        Coeff. Det.(r²):  0.999312
Origin:  Include
y =  +1.3144e+002x +6.4273e+002
```

Figure B.3. Calibration Curve for Dibromochloromethane (July 2003)


atli3.mth: 3800.44.Middle: bromoform

External Standard Analysis

Curve Type: Linear

Origin: Include

y = +4.8584e+001x +4.9425e+002

Resp. Fact. RSD: 10.24%

Coeff. Det.(r^2): 0.998869

Replicates	1	1	1	1

Figure B.4. Calibration Curve for Bromoform (July 2003)

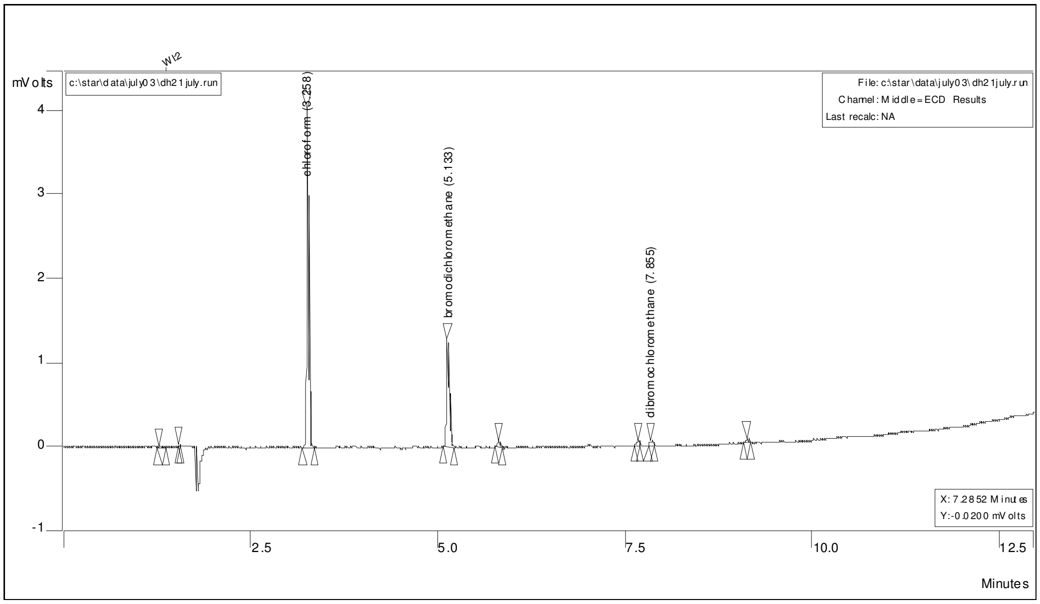


Figure B.5. Sample GC Output (July 2003)