SEASONAL VARIATION IN DISINFECTION BY-PRODUCT CONCENTRATIONS IN İZMİR DRINKING WATER

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ABSTRACT

SEASONAL VARIATION IN DISINFECTION BY-PRODUCT CONCENTRATIONS IN İZMİR DRINKING WATER

The goal of this study was to investigate the seasonal variation in disinfection by-product (DBP) concentrations in drinking water İzmir. In accordance with this aim, drinking water samples were collected from tap water of five sampling points in the distribution system of three different water sources (Tahtalı Reservoir, Balçova Reservoir and ground water) during a 10 month period, from June 2006 to April 2007. The samples were analyzed by GC-ECD according to EPA Method 551.1. In addition, while the organic matter content (measured as NPOC) and bromide ion concentration were measured in samples from Tahtalı and Balçova Water Treatment Plants, other parameters including pH, temperature and chlorine dose were obtained from the treatment plants. These parameters were used as explanatory variables in the multivariate regression analysis to construct statistical models for DBPs.

Trihalomethanes were the most abundant DBPs in all samples, followed by haloacetonitriles, chloropicrin and halogenated ketones. The mean total trihalomethanes (TTHMs) concentration of Balçova, Narlıdere and Güzelbahçe was 20.78 ppb while it was 94.71 ppb at Hatay. Concentrations of DBPs in all sampling locations were found to be the highest in spring and lowest in summer and fall. Although TTHM levels in all samples were found to be in accordance with the current drinking water regulations of Turkey, 41 % of the samples from Hatay exceeded the level that will be come into effect in 2012.

Multivariate regression analysis suggested that water temperature and total chlorine dose were the most effective parameters for DBPs. In addition, simple regression analysis between total haloacetonitriles and TTHMs revealed a very high correlation (R^2=0.83). Logistic regression models were able to predict the probability of exceedance of the selected TTHM thresholds with 76 % efficiency.

ÖZET

İZMİR İÇME SUYUNDAKİ DEZENFEKSİYON YAN ÜRÜNLERİ DERİŞİMLERİNİN MEVSİMSEL DEĞİŞİMİ

Bu çalışma İzmir içme suyundaki dezenfeksiyon yan ürünü (DYÜ) derişimlerinin mevsimsel değişimini incelemek amacıyla gerçekleştirilmiştir. Çalışma kapsamında, Haziran 2006 ve Temmuz 2007 tarihleri arasında, üç farklı su kaynağından (Tahtalı Barajı, Balçova Barajı ve Yeraltı suyu) su sağlanmakta olan beş örnekleme noktasından içme suyu örnekleri toplanmıştır. Toplanan bu örnekler elektron detektörü olan bir gaz kromatografi cihazı kullanılarak EPA metod 551.1' e göre analiz yapılmıştır. Ayrıca, Tahtalı ve Balçova İçme Suyu Arıtma Tesisleri'nden alınan örneklerdeki organik madde içeriği ve brom iyonu konsantrasyonu da ölçülmüştür. Sıcaklık, pH ve klor dozu verileri ise tesislerin kendi ölçümlerinden elde edilmiştir. Bu parametreler, DYÜ derişimleri için oluşturulan çoklu regresyon modellerinde bağımsız değişken olarak kullanılmıştır.

Tüm içme suyu örneklerinde en çok bulunan DYÜ'leri sırasıyla trihalometanlar, haloasetonitriller, kloropikrin ve halojenli ketonlardır. Balçova, Narlıdere ve Güzelbahçe ilçeleri için ortalama toplam trihalometan (TTHM) derişimi 20.78 ppb iken bu değer Hatay semtinden alınan içme suyu örnekleri için 94.71 ppb olarak bulunmuştur. Tüm örnekleme noktalarında en yüksek DYÜ derişimleri baharda, en düşük ise yaz ve sonbahar dönemlerinde ölçülmüştür. Tüm örneklerdeki toplam trihalometan derişimi Türkiye içme suyu standartlarına uygun olmakla birlikte Hatay semtinden alınan örneklerin % 41 2012'de yürürlüğe girecek olan sınır değeri aşmıştır.

Çoklu regresyon analizi sonuçlarına göre sıcaklık ve toplam klor dozu DYÜ derişimlerini en çok etkileyen parametrelerdir. Ayrıca, basit regresyon analizi uygulanarak toplam trihalometanlar ile toplam haloasetonitriller arasında oldukça yüksek bir korelasyon olduğu bulunmuştur (R^2= 0.83). Lojistik regresyon analizi ile elde edilen modeller ise belirlenen TTHM eşik değerlerini aşma olasılığını % 76 verimle tahmin edebilmektedir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

Disinfection is applied as a drinking water treatment process to provide inactivation of pathogenic microorganisms, and to prevent microbial recontamination throughout the distribution system. Chlorine is the most widely used disinfectant since it is effective against a broad range of pathogens, and provides residual in the distribution system to prevent microbial re-growth. However, chlorination of drinking water leads to formation of disinfection by-products (DBPs) which may create adverse health effects on human beings.

The major groups of DBPs are trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), and halogenated ketones (HKs). The epidemiological studies have suggested that exposure to these by-products increases the risk of bladder, colon-rectum, leukemia, stomach and rectal cancers as well as abortion, low birth weight, and birth defects (IARC 1991, Calderon 2000, Gallard and Gunten 2002, Villanueva et al. 2004).

The DBPs are formed as a result of reactions between the precursor materials (natural organic matter and bromide ion) and aqueous forms of the disinfectants. THMs include mainly four species; chloroform, bromodichloromethane, dibromochloromethane and bromoform. Among all, chloroform is the most frequently detected compound with a concentration range of 2-228 µg/L (Rodriguez et al. 2003). However, depending on the bromide content of raw water, the concentration of bromoform may be greater than chloroform (Westerhoff et al. 2004). Other groups of DBPs are generally detected at lower concentrations than THMs.

The formation of DBPs is affected by several factors including water temperature and pH, nature and concentration of the natural organic matter (NOM), concentration of bromide ion, disinfectant type and dose, residence time of water in the distribution system. The concentration of NOM is the most significant parameter affecting DBP formation (Liang and Singer 2003, Ates et al. 2006). The temperature and pH also affect the reaction rates of chlorine depletion in water, and aqueous stability of DBPs (Villanova et al. 1998, Glezer et al. 1998, Kim et al. 2002). In addition, increase in the bromide ion concentration shifts the type of DBPs from chlorinated

compounds to brominated ones (Heller and Grossman, 1993, Kampioti et al. 2000, Duong et al. 2003).

Many studies on seasonal variation of THMs suggested that these compounds tend to be higher in summer since organic matter content of water source increases with temperature (Williams et al. 1993, Rodriguez et al. 2004). The highest THM concentrations were also detected in water samples taken near the end of the drinking water distribution systems since the reaction between free residual chlorine and natural organic matter continues throughout the distribution system and chlorine is dosed at certain intervals as a protection against waterborne diseases (LeBel et al. 1997, Golfinopoulos 2000).

In Turkey, seasonal and spatial variations of THMs were studied by several researchers (Tokmak et al. 2004, Toroz and Uyak 2005, Ates et al. 2006). However, there is no study on seasonal and spatial variation in HAN levels, which are found to be more toxic than regulated carbon based DBPs such as the HAAs (Muellner 2007). In a recent study, which was conducted to investigate VOC levels in drinking water of İzmir, carcinogenic risk levels were found to be greater than the acceptable level for brominated THMs even at concentrations that were in attainment of drinking water standards (Kavcar et al. 2006). Although the study gathered information about THM concentrations in drinking water samples across the metropolitan area of Izmir, seasonal variation was not investigated. A study on the seasonal variation of DBPs levels would be useful to enhance the estimated risk levels. Furthermore, there is an increasing trend in investigating locational and temporal variations of DBPs since the proposed standards for TTHMs will take seasonal average of THM concentrations into account.

The main goal of this study was to investigate seasonal and spatial variations in concentrations of THMs, HANs and HKs in drinking water of İzmir. In addition, effects of water quality and operational parameters on DBP formation will be determined by developing statistical models. In the following chapters, information regarding the disinfection process, DBP groups and factors affecting their formation, concentration of DBPs reported in the literature, previous modeling studies on DBP formation (Chapter 2), and materials and methods employed in this study (Chapter 3) are presented. The results and discussion (Chapter 4) is followed by conclusions (Chapter 5).

CHAPTER 2

LITERATURE REVIEW

2.1. Drinking Water Disinfection

Disinfection, the most important step in drinking water treatment, is applied to drinking water to inactivate the pathogenic (disease-causing) microorganisms exist in water supply. The first introduction of disinfection at water treatment plants was the use of chlorination as a continuous water treatment process in Belgium in early 1900s. In addition to chlorine, other chemical disinfectants such as ozone, chloramines and chlorine dioxide are also used for water disinfection.

2.1.1. Chlorine

Chlorine is the most widely used disinfectant since it is considered as an ideal disinfectant based on its proven characteristics: (1) it is effective against a broad range of pathogens such as bacteria, viruses and protozoa, (2) it provides residual to prevent microbial re-growth and protect treated water throughout the distribution system, (3) it is suitable for a broad range of water quality conditions, (4) it can be easily monitored and controlled, and (5) it is relatively inexpensive. The chlorine can be applied to drinking water either as primary or secondary disinfectant. The objective of the pre-chlorination is to achieve the necessary microbial inactivation while post chlorination is applied to provide detectable levels of residual chlorine at the extremities of the distribution system.

Chlorine can be typically used in one of the three forms: elemental chlorine (chlorine gas; Cl_2), sodium hypochlorite (NaOCl) or calcium hypochlorite ($Ca(OCl)_2$). When chlorine gas is applied to water it hydrolyzes very rapidly to form hypochlorous acid (HOCl) and hydrochloric acid (HCl) according to following reaction (Larson and Weber 1994):

$$Cl_{2(g)} + H_2O \Rightarrow HOCl + H^+ + Cl^- \tag{2.1}$$
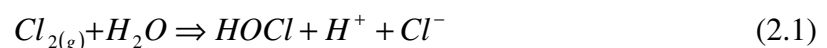
Addition of chlorine to water reduces the pH of the water due to the production of hydrogen ion. Hypochlorous acid is a weak acid (pKa of about 7.5), that dissociates slightly into hydrogen and hypochlorite ions as given in the following reaction:

$$HOCl \Leftrightarrow H^+ + OCl^- \qquad (2.2)$$

The relative abundance of HOCl and OCl⁻ strongly depend on the pH level of water. When the pH is between 2 and 7, the equilibrium is in favor of HOCl. At a pH of 7.4, HOCl and OCl⁻ are about equal, and as the pH goes above 7.4, increasing proportions of OCl⁻ are present.

In addition to gaseous form, chlorine is also applied to drinking water in hypochlorite form as aqueous solution of sodium hypochlorite (NaOCl) or as dry solid calcium hypochlorite, $Ca(OCl)_2$. Similar to chlorine gas, both form of the chlorine reacts with water to form hypochlorous acid according to following reactions (USEPA 1999).

$$NaOCl + H_2O \Rightarrow HOCl + Na^+ + OH^- \qquad (2.3)$$

$$Ca(OCl)_2 + 2H_2O \Rightarrow 2HOCl + Ca^{++} + 2OH^- \qquad (2.4)$$
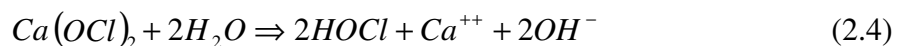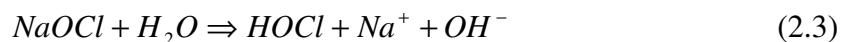
The sum of the concentrations of HOCl and OCl⁻ is defined as "free residual chlorine" and it prevents the re-growth of microorganisms in the distribution system before the water reaches the consumer's tap. HOCl, which is an electrically neutral ion, can more readily penetrate to the surface of the microorganisms than OCl⁻ since the surface of pathogens carry a natural negative electrical charge (Conell, 1996). The pathogenic inactivation can be carried out by several mechanisms. These mechanisms are the destruction or impairment of cellular structural organization, interference with energy-yielding metabolism or biosynthesis and growth (USEPA, 1999a).

The germicidal efficiency of any disinfectant is characterized by using the CT factor, a version of the Chick-Watson law. The C*T factor is the product of the residual disinfectant, C, in milligrams per liter (mg/L), and the contact time, T, in minutes. This factor implies that an equivalent level of disinfection can be achieved by different

combinations of disinfectant concentrations and contact times. CT factors are typically determined for different levels of pathogen inactivation.

2.1.2. Alternative Disinfectants

Chemical disinfectants such as ozone (O_3), chloramines, and chlorine dioxide (ClO_2) have been used as alternatives to chlorine since the discovery of the formation of potentially harmful by-products as a result of drinking water chlorination. Some of these alternative disinfectants, however, lead to formation of different types of disinfection by-products. In the following sections, the aqueous chemistry as well as the advantages and disadvantages of the different disinfectants will be discussed.

2.1.2.1. Ozone

Ozone gas is a more powerful oxidant than all other disinfectants and it is able to achieve the disinfection with less contact time and concentration. However, ozone can not serve as a secondary disinfectant since it cannot provide a residual in the distribution system. Ozonation of drinking water produces non-halogenated by-products including aldehytes, hydrogen peroxide, formic acid and acetic acid. Brominated by-products which include bromate ion, bromoform, the brominated acetic acids and acetonitriles, bromopicrin, and cyanogen bromide (if ammonia is present) are formed in the presence of bromide ion in water. Bromate (BrO^-) and iodate ions are formed by the reaction of ozone with hypobromite (OBr^-) or iodide ions, respectively (Von Gunten 2003). Bromate is considered as a probable human carcinogen by the USEPA and maximum contaminant level goal (MCLG) and maximum contaminant level (MCL) are proposed as 0.0 and 0.01 mg/L, respectively (USEPA 2006).

2.1.2.2. Chloramines

Chloramines are generated by the reaction of ammonia with aqueous chlorine (i.e., HOCl). The main advantage of chloramines is to reduce the formation of DBPs since they are not as reactive with precursor materials as free chlorine. They are also more stable than free chlorine and removes taste and odor more efficiently. The

following reactions show the simplified stoichometry of the chlorine-ammonia reactions which result in the formation of monochloramine (NH_2Cl), dichloramine ($NHCl_2$) and nitrogen trichloride (NCl_3). Total amount of the chloramines are defined as *total combined chlorine.*

$$NH_3 + HOCl = NH_2Cl + H_2O \qquad (2.5)$$

$$NH_2Cl + HOCl = NCl_2 + H_2O \qquad (2.6)$$

$$NHCl_2 + HOCl = NCl_3 + H_2O \qquad (2.7)$$
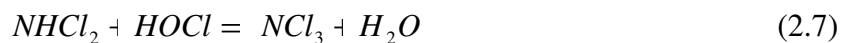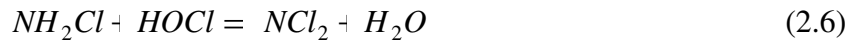
These formation reactions are affected by pH, temperature, contact time and chlorine to ammonia nitrogen (Cl_2:N) ratio. The Cl_2:N ratio is the most important parameter for the formation of chloramines. If the Cl_2:N ratio increases from 5:1 to 7.6:1 breakpoint reaction occurs, reducing the residual chlorine to a minimum level. At Cl_2:N ratios higher than 7.6:1, free chlorine and nitrogen trichloride are present (Figure 2.1). To avoid the breakpoint reactions Cl_2:N ratio between 3 and 5 should be maintained by the utilities (USEPA 1999).
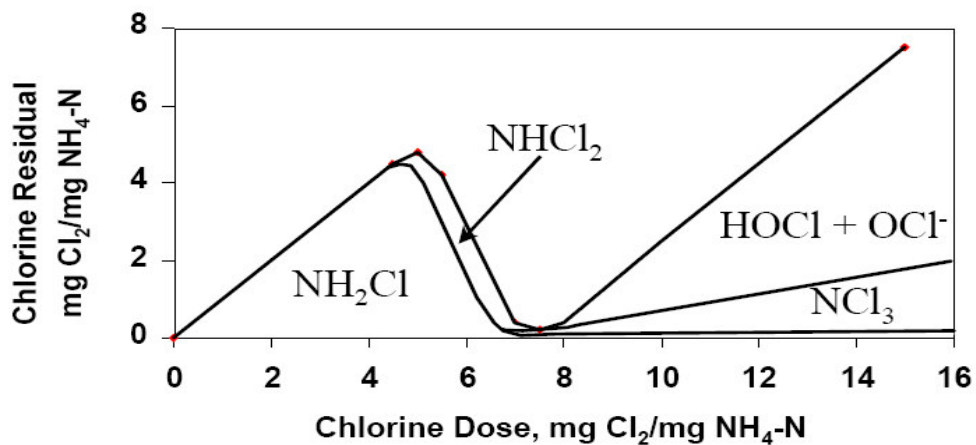
Figure 2.1. Theoretical breakpoint curve
(Source: USEPA 1999)

The use of chloramines as secondary disinfectant at lower chlorine to ammonia ratios may result in nitrification. The Equations 2.8 and 2.9 depict the nitrification, which is a microbial process by which reduced nitrogen compounds are sequentially oxidized to nitrite and nitrate.

$$NH_3 + O_2 \Rightarrow NO_2^- + 3H^+ + 2e^- \tag{2.8}$$

$$NO_2^- + H_2O \Rightarrow NO_3^- + 2H^+ + 2e^- \tag{2.9}$$
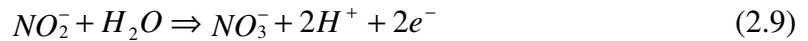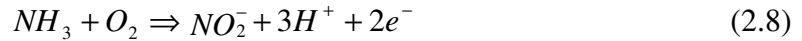
Nitrification can lower pH of the water due to hydrogen ion production as shown in equations 2.8 and 2.9. Water with low pH levels has corrosive effects on pipe surfaces and consequently results in lead (Pb) and copper (Cu) release into drinking water. Nitrification could be controlled by reducing the detention time, keeping water temperatures low, increasing the chlorine to ammonia ratio, checking the ammonia concentration, and maintaining chloramine residuals > 2 mg/L (USEPA 1999a). Switzer et al. (2006) investigated the effect of monochloramine and $HOCl/OCl^-$ on the dissolution of Pb films. A 0.5 µm thick Pb film nearly completely dissolved in a NH_2Cl, but it was passivity in a $HOCl/OCl^-$ solution. The results of the X-Ray diffraction showed that the NH_2Cl oxidized the Pb to Pb(III) species such as $Pb_3(OH)_2(CO3)_2$ which has a high solubility in water. The $HOCl/OCl^-$ solution resulted in the formation of PbO_2 which is a less soluble compound than $Pb_3(OH)_2(CO_3)_2$. The concentrations of Pb in the solutions of two disinfectants were measured by atomic absorption spectroscopy. The solution of $HOCl/OCl^-$ resulted in a 0.2 ppm Pb concentration whereas the NH_2Cl solution resulted in 1.7 ppm Pb concentration.

2.1.2.3. Chlorine Dioxide

Chlorine dioxide has high solubility in water and it remains in its molecular form in the pH range of natural waters. It also functions as a selective oxidant due to its unique, one-electron transfer mechanism where it is reduced to chlorite (ClO_2^-). In drinking water, chlorite is the predominant reaction end-product, with approximately 50 to 70 percent of the chlorine dioxide converted to chlorite and 30 percent to chlorate (ClO_3^-) and chloride (Cl^-). Chlorine dioxide is more effective disinfectant than chlorine

but is less effective than ozone. It is also effective in destroying taste and odor producing phenolic compounds. Chlorite and chlorate are the specific by-products of chlorine dioxide.

2.2. Disinfection By-Products (DBPs)

Disinfection by-products are formed as a result of chemical reactions between disinfection agents used for drinking water treatment and precursor materials present in the raw water. The precursor materials for DBPs are bromide ion (inorganic precursor) and the natural organic matter (organic precursor). At the pH levels of drinking water, disinfectants occur as acids (e.g., HOCl, HOBr) or as anions (e.g., OCl^-, OBr^-) which react with the NOM to produce halogenated DBPs. The major by-products of water chlorination are trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), halogenated ketones (HKs), chloral hydrate (CHY) and chloropicrin (CP). The physical and chemical properties of DBPs are given in Table 2.1.

2.2.1 Trihalomethanes

THMs are the first category of disinfection by-products detected in drinking water (Rook 1974, Bellar et al. 1974). The THMs are named as derivatives of the compound methane. They are formed when three of the four hydrogen atoms attached to carbon atom in the methane compound are replaced with atoms of chlorine, bromine and/ or iodine. The THMs include four species; chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) (Figure 2.2). The total concentration of these four compounds is referred to as Total Trihalomethanes (TTHMs) in drinking water.

Table 2.1. Physical and chemical properties of DBPs

Compound	Abbreviation	Molecular Weight (g/mole)	Melting Point (^{0}C)	Boiling Point (^{0}C)	Density at 20^0 C (g/mL)	Water Solubility at 25 ^{0}C (mg/L)	Vapor pressure at 20 ^{0}C (mmHg)	Henry's Law constant 25 ^{0}C (atm.L/mole)
Chloroform	CF	119.38	-64[a]	62[a]	1.485[a]	$7.43*10^{3a}$	160[a]	$3*10^{-3a}$
Bromodichloromethane	BDCM	163.83	-57.1[b]	90[b]	1.98[b]	4500[b]	50[b]	$2.41*10^{-3\,b}$
Dibromochloromethane	DBCM	208.28	-20[c]	120[c]	2.451[c]	$2.7*10^{3c}$	76[c]	$9.9*10^{-4c}$
Bromoform	BF	252.73	8[c]	149.1[c]	2.899[c]	$3.1*10^{3c}$	5[c]	$5.6*10^{-4c}$
Trichloroacetonitrile	TCAN	144.39	-42[c]	84.6[d]	1.44[d]	-	-	-
Dichloroacetonitrile	DCAN	109.94	112[c]	112.5[d]	1.37[d]	-	-	-
Bromochloroacetonitrile	BCAN	119.95	-	125-130[e]	1.68[e]	-	-	-
Dibromoacetonitrile	DBAN	198.84	-	67-69[e]	2.30[e]	-	-	-
1,1-dichloro-2-propanone	1,2-DCP	164.39[f]	-	88.1[e]	1321[e]	2700 [f] at 20 ^{0}C	68.3 [e]	-
1,1,1-trichloropropanone	1,1,1-TCP	-	-	-	-	-	-	-
Chloropicrin	CP	164.5[†]	-64[†]	112[†]	1.65[†]	1621[†]	23.8[e]	-

[a] ATSDR (1997)   [d] Nikolaou et al. (1999)

[b] ATSDR (1989)   [e] WHO (2004)

[c] ATSDR (2005)   [f] WHO(2003)
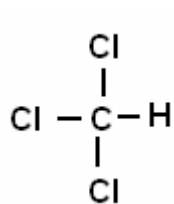
Chloroform
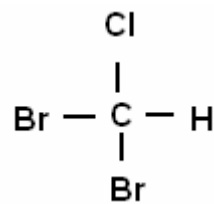
Dibromochloromethane
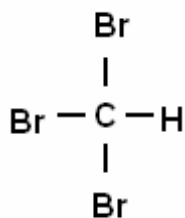
Bromoform
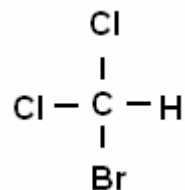
Dichlorobromomethane

Figure 2.2. Molecular structure of THMs

The formation of trihalomethanes may occur through many different reaction mechanisms. One of the most widely discussed is the haloform reaction (Figure 2.3). This involves the stepwise chlorine substitution of the enolate form of a methyl ketone. The resulting trichloroacetyl compound undergoes base hydrolysis liberating chloroform and a carboxylic acid. This mechanism indicates that THM formation is base catalyzed and therefore concentration of THMs increases with the pH level of water (Larson and Weber 1994). In the reaction THM formation, halogens (e.g. aqueous chlorine, bromine, and iodine) react with NOM via oxidation (i.e., cleaving carbon-carbon double bonds) and/or substitution (i.e. replacement of functional groups) by a halogen molecule.

Since the discovery of the THMs, numerous toxicological (studies of harmful effects of chemicals on living organisms) and epidemiological (medical studies that deal with the incidence, distribution and control of disease in a population) studies have been conducted to determine possible health effects of DBPs. The results of epidemiological studies showed that exposure to chlorination by-products increased the risk of bladder, colon-rectum, brain, leukemia, stomach, large intestine, and rectal cancer as well as abortion, low birth weight, and birth defects (IARC 1991, Calderon R.L. 2000, Gallard and Gunten 2002, Villanueva et al. 2004).
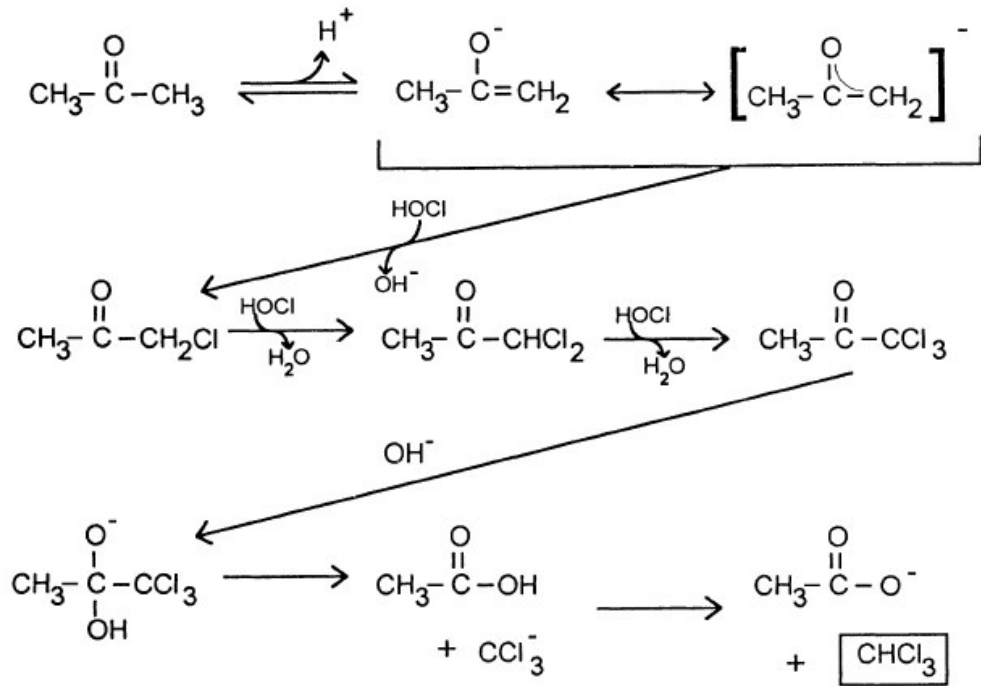
Figure 2.3. Haloform reaction

(Source: Singer and Reckhow 1999)

Inhalation is one of the exposure routes of the THMs since these compounds are very volatile. To investigate the respiratory uptake of haloketones and chloroform (as a reference compound) during showering, Xu et al. conducted a controlled human study. They measured breath and air concentrations of the haloketones and chloroform by using GC-electron capture detection (ECD) during and following the inhalation exposures. A lower percentage of the haloketones (10%) was released from shower water to air than was chloroform (56%), which is more volatile. The breath concentrations were elevated during the inhalation exposure, but declined rapidly afterwards. Approximately 85-90% of the inhaled haloketones were absorbed, as compared to only 70% of the chloroform (Xu et al. 2005).

The human health risk assessment studies have focused on trihalomethanes due to their high occurrence in chlorinated water supplies and their carcinogenic characteristics. Hsu et al. estimated the lifetime cancer risks for trihalomethanes in the tap water of Taiwan. Since CF was detected in highest concentrations, the highest lifetime cancer risks (range 87.5%-92.5%) attributed by this compound. The lifetime

cancer risks for CF, BDCM, DBCM and BF from consuming tap water were higher than 10^{-6}. The sum of the total lifetime cancer risk for total trihalomethanes was found to be 1.94×10^{-4} (Hsu et al. 2001).

In another risk assessment study conducted by Uyak (2006), the lifetime cancer risk of THMs through oral ingestion, dermal absorption, and inhalation exposure from tap of Istanbul were estimated. The lifetime cancer risk of chloroform was higher than 10^{-6}, the negligible risk level defined by the USEPA. The study also showed that approximately 5 of the 8 million Istanbul residents could get cancer from the daily intake of tap water. However, the study did not consider the variation in type of water drunk, drinking water consumption rate, and body weight in the population. In addition, the slope factor for chloroform was withdrawn by USEPA concluding that oral RfD is sufficiently protective. Therefore cancer risk estimates that consider chloroform are overestimations. These studies were criticized for including chloroform in the cancer risk assessment with detailed reasoning (Butterworth 2005).

According to USEPA's Integrated Risk Information System (IRIS) (WEB_2 2007), chloroform, bromodichloromethane and bromoform are classified in group B2, meaning that they are probable human carcinogens based on limited evidence from epidemiological studies and/or sufficient evidence from animal studies. However, the dibromochloromethane is classified in group C, meaning that it is a possible human carcinogen based on limited evidence from animal studies and inadequate or no data in humans. The IRIS has also reported that chloroform is likely to be carcinogenic to humans by all routes of exposure conditions that lead to cytotoxicity and regenerative hyperplasia in susceptible tissues.

2.2.2 Haloacetic acids

HAAs includes nine compounds which are monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoaceticacid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and dibromochlorocacetic acid (DBCAA). Among the HAAs, DCAA and TCAA are the most frequently detected compounds in drinking water. Other HAAs, which are generally detected at lower levels, are BCAA, DBAA, MCAA and MBAA. The total of the concentration of

DCAA, TCAA, DBAA, MCAA and MBAA is denoted as HAA5.

The epidemiology studies also investigated the health effects of HAAs. For example, TCAA was found to be hepatocarcinogen in mice causing adenomas and carcinomas in both genders. The target organ of tumorigenesis of the HAA was liver (Komulainen 2004). The DCAA was also reported to be hepatocarcinogen in male and female mice. At high repeated doses, it caused kidney damage and neuro toxicity in rats (IARC 1995). According to USEPA's Integrated Risk Information System the DCAA and TCAA are Group 2B and Group C carcinogens, respectively. The USEPA has also proposed maximum contaminant level goals (MCLGs) for MCAA, DCAA and TCAA as 70, 0 and 20 µg/l, respectively (USEPA 2006).

2.2.3. Haloacetonitriles

HANs frequently detected in drinking water, are trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN). DCAN has reported to be most predominant HAN species detected in drinking-water from sources with bromide level of 20 µg/L or less (Kim et al. 2002, Kawamoto and Makihata 2004).

The concentrations of HANs were found to be much lower than THMs due to the fact that these compounds undergo hydrolysis reaction during the transport of drinking water in distribution system. It has been reported that the concentration of dibromoacetonitrile in tap water was generally 20–50% of that at the treatment plants, indicating that hydrolysis occurred during transport (Peters et al. 1999).

2.2.4. Other DBPs

Halogenated Ketones (HKs) are volatile DBPs and comprise two main species 1,2-dichloro-2-propanone and 1,1,1-trichloropropane. They have been detected at concentrations of an order of magnitude lower than THMs and HANs (Golfinopoulus and Nikolaou 2005).

Chloropicrin is formed in water by the reaction of chlorine with humic acids, amino acids, and nitrophenols. The presence of nitrates increases the amount formed and this compound is reduced to chloroform when reducing agents are added into water

to remove excess chlorine (WHO, 2003). Xu et al. investigated the permeabilities of DBPs by using *in vitro* methods. The results showed that dichloropicrin and chloropicrin can penetrate to human skin within a few minutes and therefore the dermal exposure route is important for these two compounds (Xu et al. 2002).

2.3. Factors Affecting the DBP Formation

The formation and speciation of DBPs may depend on several factors including the concentration and properties of organic matter, concentration of bromide ion, temperature and pH level of water. The effect of these parameters on DBPs should be well understood in order to control the formation of DBPs. In general, increase in chlorine dose applied to drinking water and the concentration of natural organic matter results in higher DBP formation. In addition, the presence of bromide ion shifts the speciation of DBPs to more brominated analogues. Increased pH level of the water enhances THM formation while it inhibits formation of HANs and HKs (Nikolaou et al. 2004a).

2.3.1. Natural Organic Matter (NOM)

2.3.1.1. Source and Characteristics of NOM

The aquatic natural organic matter (NOM) results from the degradation and leaching of the organic materials within the watershed or human activities such as agriculture. Its major components are humic substances, hydrophilic acids, protein, lipids, carbohydrates, carboxylic acid, amino acid, and hydrocarbons (Kitiş et al. 2001). The presence of NOM in water supplies may lead to many problems in water treatment plants and water distribution systems. For example, NOM increases the biological growth by serving as substrate and therefore results in higher oxygen demand. It also affects the water quality (taste and odor) and performance of the unit processes of the water treatment (i.e. oxidation, coagulation and adsorption). In addition, it binds the regulated metals (e.g., lead, copper, cadmium), transports them through the treatment plant and distribution system, and increases the coagulant and disinfectant/oxidant demands (Matilainen et al. 2002).

NOM can be divided into two main fractions, which are named as humic and non-humic fractions. The humic fraction is more hydrophobic and comprises humic and fulvic acids having carboxylic and phenolic moieties. On the other hand, the non-humic fraction is more hydrophilic and contains compounds such as proteins, amino acid and carbohydrates (Figure 2.4). The humic and fulvic acids constitute major components of NOM by contributing to 60-80% of the total mass of the NOM (Singer et al. 1999).
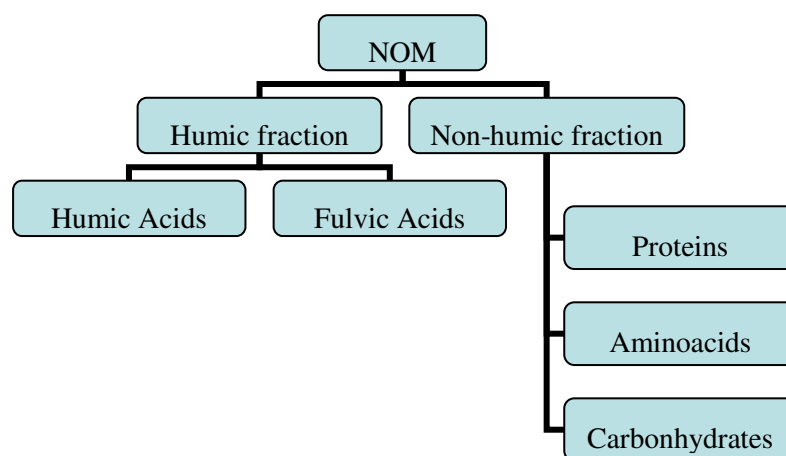
Figure 2.4. Fractions of natural organic matter

The major functional groups which are included in humic and fulvic acids are carboxy (-COOH), phenolic OH^-, aliphatic OH^-, C=O, OCH_3. The molecular structure of the humic acid contains free and bound phenolic OH groups, quinine structures, nitrogen and oxygen as bridge units and COOH groups variously placed on aromatic rings (Figure 2.5). Humic acid has more aromatic structure and larger molecular size as compared to fulvic acid and this provides more active sites for halogen substitution or addition. For this reason, humic acid acts as a major precursor material for DBP formation (Kampioti and Stephanou 2002, Liang and Singer 2003).
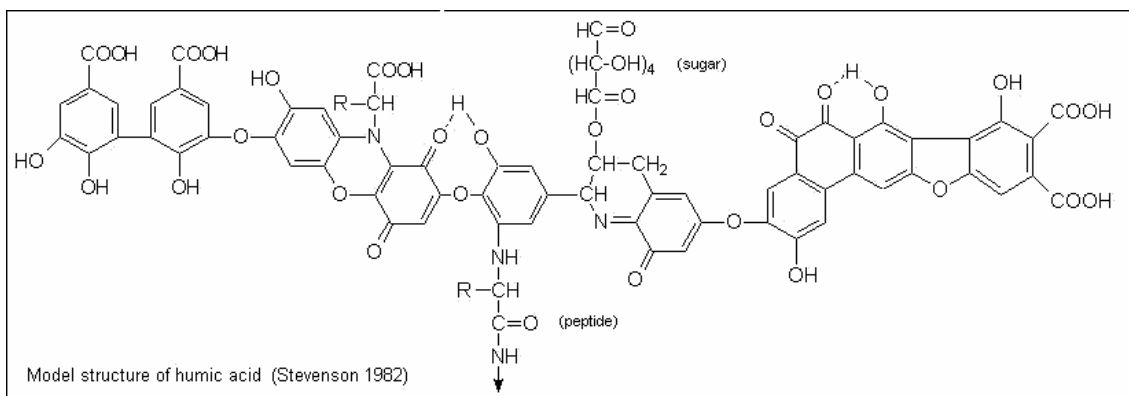
Figure 2.5. Molecular structure of humic acid

The fulvic acid contains more functional groups of acidic nature, particularly COOH. The oxygen in fulvic acids can be accounted for largely in functional groups such as COOH, OH, C=O while a high portion of the oxygen in humic acid seems to occur as a structural component of the nucleus. The model structure of the fulvic acid contains both aromatic and aliphatic structures, extensively substituted with oxygen containing functional groups (Figure 2.6)
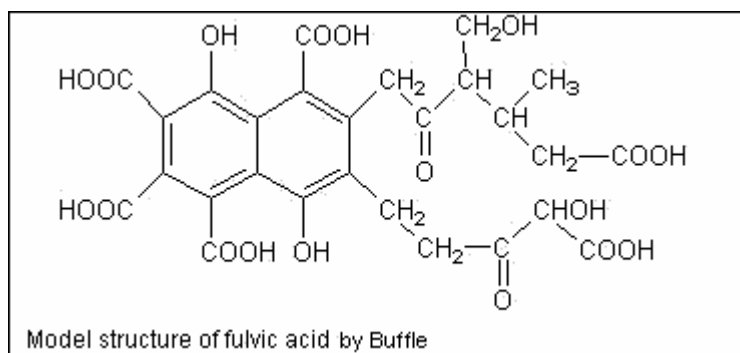
Figure 2.6. Molecular structure of fulvic acid

The surrogate parameters such as total organic carbon (TOC) or dissolved organic carbon (DOC) are used to quantify the organic matter content of drinking water. DOC, which represents the 80-90% of the TOC, is the fraction that passes through a 0.45-um pore diameter filter. The fraction retained by the 0.45-µm filter is also named as particulate organic carbon (POC). The most commonly used parameter is TOC and it measures the amount of organically bound carbon in water sample. The level of TOC in natural waters can range from 1 to 40 mg/L depending on the source and climate (Kitis

16

et al. 2001). In general, surface waters have higher TOC concentration than ground water since surface waters receive run-off water that contains humic substances from decaying vegetation.

2.3.1.2. The Effect of NOM on DBP Formation

Since NOM is known as the major precursor material for DBP formation, many studies were conducted to investigate the effects of the concentration and characteristics of NOM on DBP formation.

Singer et al. 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, was 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 activated aromatic carbon content of the various humic and fulvic acids (Singer et al. 1999).

In a study conducted by Liang and Singer, raw water samples were fractionated into hydrophilic and hydrophobic fractions, and then chlorinated at pH 6 and 8. After waiting at 20 ^{o}C for various contact times, the samples were analyzed for THMs and HAAs. The hydrophobic fraction resulted in higher DBP formation than the corresponding hydrophilic fraction because the hydrophobic fraction contains more aromatic carbon and higher molecular weight material than hydrophilic fraction. Bromine incorporation into these two fractions was also different. Bromine was found to be more reactive with the hydrophobic fraction than with the hydrophilic fraction at the equal conditions (chlorine dose, contact time, pH, temperature, initial Br/Cl_2 ratio) (Liang and Singer 2003).

Panyapinyapol et al. conducted a study to characterize raw water of a drinking water treatment plant in Bangkok, Thailand. By using resin adsorption techniques, the dissolved organic matter in the water was fractionated into six fractions, including hydrophilic acidic, hydrophilic basic, hydrophilic neutral, hydrophobic acidic, hydrophobic basic and hydrophobic neutral. The trihalomethane formation potential (THMFP) of each fraction was determined by THMFP test which is an index of the potential extent of THM formation after the application of chlorine. According to

Standard Methods (1995) 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. The highest THMFP was obtained from the hydrophilic neutral and hydrophobic acidic fractions with 32% and 21% by weight of THMFP, respectively. The higher THMFP from hydrophilic neutral and hydrophobic acidic fractions was mainly due to highest occurrence (79 % of the TOC) of these two fractions (Panyapinyapol et al. 2005).

In a study conducted by Ates et al. raw water samples collected from 29 different surface waters from different regions in Turkey, were analyzed for THMs and HAAs after chlorination in laboratory conditions. They reported that both THM and HAA concentrations increase exponentially with the DOC level of the raw water. The correlation coefficients (r) between the THM-DOC and HAA-DOC were also very high (0.92 and 0.88, respectively). In addition, the DOC levels of the water samples were very low, ranging between 0.91 to 4.41 mg/L. The annual average DOC concentration for Tahtalı and Balçova Dams were 3.06 and 1.8 mg/L. The annual average concentrations of TTHMs in chlorinated samples collected from Tahtalı and Balçova Dams and chlorinated at laboratory were approximately 88 and 64 µg/L, respectively (Ates et al. 2006).

As stated in literature, DBP formation increases with the concentration of aquatic natural organic matter. The characteristic of the NOM also plays an important role for DBP formation and speciation. For example, humic acid fraction of NOM results in higher DBP formation than the corresponding fulvic acid fraction. In addition, the bromide ion is more reactive with the hydrophilic fraction.

2.3.2. Bromide Ion

Bromide ion, regarded as inorganic precursor for DBP formation, is naturally present in the ground water of coastal areas as a result of seawater intrusion. In the presence of bromide ion in chlorinated drinking water, it is oxidized by hypochlorous acid to form hypobromous acid (HOBr) which subsequently reacts with NOM to form brominated DBPs (Equations 2.10 and 2.11).

$$HOCl + Br^- \rightarrow HOBr + Cl^-\qquad\qquad(2.10)$$

$$HOBr + NOM \rightarrow \text{Brominated DBPs}\qquad\qquad(2.11)$$

In many studies, it was proved that the simultaneous presence of bromide and chlorine in water source used for drinking purposes can significantly contribute to the formation of brominated and mixed bromo/chloro DBPs during chlorination process (Pourmoghaddas and Stevens 1995, Chang et al. 2001, Kawamoto and Makihata 2004).

Formation of brominated THMs were investigated by chlorinating the raw water samples collected from the Lake Kinneret in Israel, which contained an extremely high bromide concentration (1.9 mg/L) compared to the bromide levels commonly found in surface waters around the world (0.04-1.0 mg/L). The results of this study showed that brominated species constituted over 85 % of the THMs. It was also stated that HOBr reacts faster with precursor material having a weak aromatic character in contrast to HOCl which reacts faster with the precursor of strong aromatic character (Heller and Grossman 1993).

Duong et al. investigated the occurrence and the fate of trihalomethanes (THMs) in the water supply system of Hanoi City, Vietnam from 1998 to 2001. They evaluated high bromide and low bromide containing groundwater resources for THM formation. The results of the study showed that THM speciation occurred as 80% bromo-THMs in high bromide containing water due to the noticeable high bromide level (50-140 μg/L) (Duong et al. 2003).

In 2004 Westerhoff et al. conducted a study to investigate the reactivity of aqueous chlorine and aqueous bromine with NOM. In order to determine the selectivity of the reaction of these two oxidants, they added bromine and chlorine separately into the solutions of model organic compounds such maleic acid, phenol, aniline and recorcinol. They found out that the haloform substitution efficiency (CHX_3 produced per mole X_2 consumed) for bromine was always greater than chlorine. The higher substitution reaction of bromide was related to its higher electron density and smaller bond strength relative to chlorine atom. The consumption of bromine or chlorine by the model compounds was primarily affected by the characteristics of the model compounds (Westerhoff et al. 2004).

Generally stronger electron donating functional groups (e.g. hydroxyl; -OH) increased the rate of reaction. The researchers also found out that chlorination resulted a

50 % change in UVA at 260 nm (indicator for existence of unsaturated bonded organic compounds) whereas bromine resulted only an 8 % change. This was explained as chlorine may have cleaved to aromatic ring, producing both chlorinated and oxygenated by-products whereas bromine may have substituted into the ring structures without cleavage. In addition, the second order rate constant (k) for bromine was approximately 10 times higher than chlorine.

The bromine incorporation factor n(Br), which is a dimensionless factor used to evaluate THM speciation, is first introduced by Gould et al. (1983). The n(Br) for THMs is given by the following equation:

$$n(Br) = \frac{CHBrCl_2 + 2CHClBr_2 + 3CHBr_3}{TTHMs} \qquad (0 \le n \le 3) \qquad (2.12)$$

Where, the $CHBrCl_2 + 2CHClBr_2 + 3CHBr_3$ (µmole/L) is the molar amount of bromine in the THMs and the TTHMs (µmole/L) is the sum of four THMs.

The value of n(Br) varies between 0 and 3, with 0 corresponding to the formation only $CHCl_3$ and 3 to that of $CHBr_3$. In the study of Kawamoto and Makihata the bromine incorporation factor was calculated for tap water samples derived from different water sources such as lake, river, well and river bed. The highest n(Br) values were reported for tap water derived from ground water (0.58-1.18, 0.86), whereas the lowest values were obtained for the tap water samples derived from river water (0.66-0.73, 0.69). For the tap water samples from the surface water, moderate n(Br) levels were obtained ranging between 0.09-0.56 with a mean value of 0.40 (Kawamoto and Makihata 2004).

Kampioti et al. also investigated the impact of bromide on DBP formation and speciation in drinking water for 15 cities in Greece. They measured the DBP concentrations in tap water samples and levels of surrogate parameters such as bromide concentration and TOC in the raw waters before disinfection. For the City of Heraclion, which is located in a coastal area, the bromide ion levels in the raw water were very high (0.04-4.02 mg/L) and therefore the brominated species of THMs dominated over the chlorinated species. For example, BF contributed 75.58% to the total THMs, whereas the CF contributed only 2.71 %. The n(Br) values were also very high (1.57 to 2.94) due to high bromide content of the Heraclion raw water (Kampioti et al. 2002).

In conclusion, the presence of bromide ion in the water being chlorinated results in simultaneously formation of brominated and chlorinated species. Bromide ion is more active than chlorine in reacting with the NOM. In addition, the reaction of bromide with the NOM occurs by substitution whereas chlorine was reacts by addition reaction.

2.3.3. Temperature

When the water temperature is high, disinfectant residuals deplete rapidly, therefore it is difficult to maintain the minimum residual level in the large distribution systems. For this reason, during warm months higher disinfectant doses are applied to maintain the adequate residual (Villanova et al. 1997; Rodriguez and Serodes 2001).

Villanova et al. investigated the effect of various parameters including the chlorine dose, residence time, residual free chlorine and total chlorine, TOC, pH and temperature on the formation of chloroform. The results of this study indicated that pH and temperature are the most significant parameters for THM formation. A predictive model (R=0.995, p<0.0001) was also developed for chloroform formation as a function of pH and temperature. This model showed that increasing the levels of pH and temperature, increased the concentration of chloroform up to a critical temperature (17.30 ^{o}C) after which a sharp decrease occurred. At the critical temperature removal rate of THM was possibly higher than their formation due to their high volatility (Villanova et al. 1997).

In a study conducted by Rodriguez and Serodes, a 25-week intensive sampling program was performed to investigate the seasonal and spatial variation of THMs in the three distribution systems (Sainte-Foy, Levis and Charlesbourg) of Quebec (Canada). When the water temperatures were below 15 ^{o}C, total THM concentrations in Sainte-Foy, Levis and Charlesbourg were 34.2, 35.5 and 35.7 µg/L, respectively. However, when the water temperature exceeded 15 ^{o}C, the concentrations were 64.2, 40.6 and 60.8 µg/l, respectively (Rodriguez and Serodes 2001).

2.3.4. pH

Many studies have been conducted to investigate the effect of pH on the formation and speciation of DBPs. Generally, the concentrations of THMs increased with pH whereas HANs decreased with pH.

Glezer et al. conducted a study to investigate the hydrolysis rates of HANs in aqueous buffer solutions at pH levels of 5.4, 7.2 and 8.7. The optimal stability for trihaloacetonitriles were observed at pH 5.4, suggesting that HANs should be preserved in weakly acid solutions between sampling and analysis. They reported that the hydrolysis rate of HANs increased with increasing pH and with the number of halogen atoms in the molecule. Therefore, the monochloroaceonitrile was the most stable and less affected by the pH changes, while the TCAN was the least stable and most sensitive to pH changes. In addition, the number of bromine atoms in a specific HAN molecule, was also found to be an important factor that increase the stability of the molecule (Glezer et al. 1998).

In a study conducted by Kim et al., raw water samples from different water sources were chlorinated at different pH levels to investigate the impact of pH on DBP formation. They measured the DBP formation potential for THMs, HAAs, HANs and HKs. The THMFP showed an increasing trend as the pH level is increased whereas the HAAFP and HANFP decreased with the pH. The THMFP levels at pH 5.5, 7.0 and 7.9 were measured as 9.7, 20.7 and 41.6 μg/L, respectively (Kim et al. 2002).

Liang and Singer studied the effect of various water quality and treatment characteristics on the formation and distribution of disinfection by-products. For this purpose, researchers collected raw water samples from different utilities and chlorinated in laboratory conditions at pH 6 and 8. The results of this study indicated that, THM formation at pH level of 8 was higher than at pH 6, due to fact that at high pH levels the concentration of the HOCl, which is a more reactive oxidant, was greater than that of OCl$^-$ (Liang and Singer 2003).

2.3.5. Disinfectant Type and Dose

The type and dose of the disinfectant applied to water are two important factors that affect the DBP formation and speciation. In general, increase in the chlorine dose

results higher free residual chlorine and higher DBP formation in drinking water (Heller and Grossman 1999).

Simpson and Hayes collected chlorinated and chloraminated drinking water samples from different locations across Australia and analyzed for DBPs. In chloraminated water samples, the overall DBP formation was lower due to the weaker oxidation properties of this disinfectant. In addition, THMs contributed 24% for overall DBPs in chloraminated water samples whereas 46 % for chlorinated samples (Simpson and Hayes 1998).

In a recent study, raw water samples collected from different Italian drinking water sources were dosed with different disinfectants such as chlorine, chlorine dioxide and ozone. The results of this study indicated that THM formation increases with increasing the chlorine dose and for the doses higher than 1.3-1.5 mg/L, concentrations of THMs were measured over the Italian MCL (30 µg/L). In addition, the use of chlorine dioxide and ozone resulted in nearly 98 % decrease in the TTHM concentrations. TTHMs levels during chlorine dioxide and ozone oxidation were in the range of 0-15 µg/L with a mean value of 2 µg/L (Sorlini and Collivignarelli 2005).

Guay et al. conducted a study to investigate the use of alternative disinfection strategies to reduce the DBP formation. They evaluated the formation of THMs and HAAs in real and laboratory-scale distribution systems. In the water treatment plant under study, chlorine was used as primary disinfectant after slow sand filtration and as post disinfectant following the water storage. In laboratory scale studies the researchers used different disinfection scenarios. In the first scenario, the use of ozone as primary disinfectant resulted in an average reduction of 44% and 37 % for THMs and HAAs, respectively. In another scenario, in which ozone was used as primary disinfectant and chloramine for post disinfection, the average reductions in the THMs and HAAs were 98 % and 93 %, respectively. The results of the study implicated that the use of ozonation prior to sand filtration decreases the formation THMs and HAAs significantly as compared with the chlorine disinfection alone (Guay et al. 2005).

2.3.6. Residence Time of Water in the Distribution System

Residence time of water is the travel time or in other words the hydraulic retention time of the water between the point representing the water leaving the plant

and sampling point in the distribution system. Residence time has a considerable impact on DBP evolution since the formation reactions of THMs not only occur at the treatment plant after chlorination but also continue in the distribution system leading to depletion of free residual chlorine.

Lebel et al. measured concentrations of THMs, HAAs, HANs, halogenated ketones (HKs), chloral hydrate (CH) and CP in drinking water samples collected along the distribution system of a conventional water treatment system that used chlorine for primary and secondary disinfection processes. TTHMs showed an increasing trend with the residence time and the THM concentrations at the raw water and three sampling points at an increasing distance from the treatment plant were measured as 24.8, 37.5, 48.4 and, 61.4 μg/L, respectively (Lebel et al. 1997).

Rodriguez and Serodes performed a study to evaluate the spatial and temporal evolution of the THM concentrations in three distribution systems of the Quebec City in Canada. They collected water samples along the distribution system between the treatment plant and the system extremities for 25 weeks. The results of the study indicated that the concentrations of THMs increased from 1.5 to 2 times between the finished water and the system extremity depending on the utility (Rodriguez and Serodes 2000).

Nikolaou et al. investigated the kinetics of formation of chlorination by-products by chlorinating the surface water samples in laboratory conditions. They used two different chlorine doses (2 and 4 mg/L) and different reaction times between 0 and 72 h. The concentration of chloroform, after a 72 h contact time, was 6 times higher than its initial concentration. Other DBPs such as HKs, BCAA and DCAA generally decomposed after a initial formation step (Nikolaou et al. 2004).

As stated in the literature, generally the DBP concentrations increase with the residence time of water in the distribution system. This results in higher risk for the consumers living at the extremity of the water distribution system. The concentrations of THMs generally increase with the residence time while the concentrations of HKs, HANs and HAAs decrease due to a possible hydrolysis reaction.

2.4. DBPs in Drinking Water

2.4.1. Drinking Water Regulations for DBPs and Disinfectant Residuals

In 1979, EPA set the first regulatory standard for annual average of total trihalomethanes (TTHMs) under the Safe Drinking Water Act (SDWA) as an interim maximum contaminant level (MCL) of 100µg/L. This standard was applicable to all community water systems that use chlorine compounds for disinfection and serve at least 10,000 people. In 1986, as a part of the safe Drinking Water Act Amendments (SDWAA), the USEPA proposed two-stage Disinfectants and Disinfection By-products Rule (D/DBPs). The Stage 1 D/DBPs Rule established maximum contaminant levels MCLs of 80 µg/L for TTHM and 60 µg/L for HAA5, based on running annual averages (RAA) of all samples collected in a utility's distribution system over a one-year period (USEPA,1998). RAA is calculated by averaging the quarterly averages of the each location. Stage 1 D/DBPs Rule also contains non-enforceable MCLGs, the level at which no known or anticipated adverse health effects occur, for BDCM, BF and DBCM, DCAA, TCAA and chlorite. The Stage 2 D/DBPs Rule was designed to address spatial variations in DBP locational running annual average (LRAA) for the same MCLs proposed by the Stage 1 DBPR. LRAA is defined as the average of sample analytical results for samples taken at a particular monitoring location during the previous four calendar quarters (USEPA, 2006). World Health Organization published drinking water guidelines for a few DBPs including THMs, HAAs, HANs (WHO 2006) In addition to individual THM guidelines, WHO has also suggested that the sum of the ratios of the THM levels should not exceed 1 (Table 2.2). The WHO also proposed provisional guideline levels of 20µg/L and 70 µg/L for DCAN and DBAN, respectively.

Drinking water guidelines and standards for DBPs has also promulgated by other authorities around the world in order to minimize the associated risks for the water consumers' health. The drinking water standards of Health Canada, European Union and Turkish Ministry of Health are also summarized in Table 2.2 for comparison.

Table 2.2. Drinking water regulations/guidelines for DBPs

Compound	Health Canada[a]	WHO[b]	EC[c]	Turkey[d]	EPA[e] MCLG	MCL
CF	-	300	-	-	70	
BDCM	-	60	-	-	0	
DBCM	16	100	-	-	60	-
BF	-	100	-	-	0	
TTHM	100	$\sum_{i=1}^{4} \dfrac{THM}{WHO} \le 1^{**}$	$150^{\dagger}$	$150^{\ddagger}$	-	80
DCAN	-	20	-		-	-
DBAN	-	70	-		-	-

- not included in regulations
** sum of the concentration of each
 THM to its respective guideline value
 should not exceed 1
‡ 100 µg/L must be met by the 2012
† 100 µg/L must be met by the 2008

[a] WEB_1 (2006)
[b] World Health Organization (2006)
[c] European Community (1998)
[d] Ministry of Health (2005)
[e] USEPA (2006)

The USEPA has also regulated disinfectant residuals by setting maximum residual disinfectant level goals (MRDLGs) and maximum residual disinfectants levels (MRDLs) for different disinfectants (Table 2.3).

Table 2.3. Drinking water regulations for residual disinfectants[‡]

Disinfectant	MRDLG	MRDL
Chlorine[*]	4 (as Cl_2)	4(as Cl_2)
Chloramine[†]	4(as Cl_2)	4(as Cl_2)
Chlorine Dioxide	0.8(as ClO_2)	0.8(as ClO_2)

Concentrations are in mg/L   [‡] (USEPA, 1998)
[*] Measured as free chlorine
[†] Measured as total Chlorine

2.4.2. DBP Concentrations in Drinking Water

Many studies have been conducted to investigate the occurrence of DBPs in drinking water. In these studies, DBP concentrations were measured in drinking water samples either collected from drinking water treatment plants or distribution system. In tap water samples, THMs were the most abundant disinfection by-product. The data obtained from these studies were either used as input data for statistical models, which are constructed to predict the DBPs based on raw water quality parameters, or used for exposure assessment in the epidemiological and health risk assessment studies.

Rodriguez et al. conducted a 16-month study to investigate concentrations of THMs in the distribution system of the five major drinking water utilities of Quebec, Canada. They found that CF is the most abundant THM in water samples with a concentration range of 2-228 µg/L. The maximum concentrations for BDCM and DBCM were measured as 15 µg/L and 8 µg/L, respectively (Rodriguez et al. 2003).

Nikolaou et al. monitored the DBP concentrations in tap water samples collected from distribution system of two water treatment plants in Greece. Among the DBPs, CF, DCBM and DBCM were the most frequently detected compounds. The total THM concentrations ranged from 5.1 to 24.6 µg/L and total HAAs ranged form 8.56 to 107.38 µg/L. Concentrations of other DBPs, such as HKs and CH, were found to be below 1 µg/L (Nikolaou et al. 2004)

A study was conducted by Golfinopoulos and Nikolaou to investigate the occurrence of DBPs in drinking water samples collected from Athens, Greece. The researchers collected drinking water samples from different sampling points in the treatment plant and the distribution system. In the water samples collected from the plant, CF was the most abundant THM compound with a concentration range of 4.2-70.4 µg/L, while the DCBM concentrations ranged from 2.4 to 21 µg/L. The lower formation of brominated DBPs was related to low bromide ion concentration (0.05-0.08 mg/L) in the raw water (Golfinopoulos and Nikolaou 2005).

Tokmak et al. also measured THM concentrations in tap water samples from the 22 different districts in Ankara, Turkey. The total THM concentration of the water leaving the plant was measured as 35 µg/L. TTHM level at the Konutkent district, one of the distant sampling point from the treatment plant, was 110 µg/L. CF was the major compound (90-95% of the total THM) in all of the samples (Tokmak et al. 2004).

Toroz and Uyak measured TTHM concentrations in European side of Istanbul, Turkey. The annual average concentrations of CF, DBCM, BDCM, BF and TTHM in Istanbul drinking water were measured as 24 µg/L, 28 µg/L, 32 µg/L, 10 µg/L and 94 µg/L, respectively. The higher occurrence of brominated THMs was due to medium level of the bromide ion content of water source (Büyükçekmece Lake) which is measured as 255 µg/L (Toroz and Uyak 2005).

Kavcar et al. measured VOC concentrations in drinking water collected from 9 districts of İzmir. The mean concentrations of CF, BDCM, DBCM and BF were 4.41, 3.73, 2.61 and 0.62 µg/L. These concentrations are low compared to İstanbul and Ankara possibly due to differences in raw water quality of the cities such as concentration and aromatic character of natural organic matter as suggested by Ates at al. (2006) and the residual goal of 0.5-0.7 ppm set by the water authority of the city of İzmir (Kavcar et al. 2005).

2.4.3. Seasonal Variation in DBP Concentrations

Concentrations of DBPs vary seasonally depending upon changes in water temperature, chlorine demand and concentration of natural organic mater. During warm months of the year, the organic matter content of the surface waters increases due to rapid decay of vegetation. In addition, rain and snow melting also leads to organic matter leaching into the water source. Depending on the level of increase in the temperature and the organic matter level the chlorine demand also increases, resulting in the higher DBPs formation (Willimas et al. 1998, Rodriguez et al. 2004).

Williams et al. collected drinking water samples from 53 water treatment utilities in Canada. The samples were taken in winter and summer from raw water, treatment plant, and water leaving the plant and midpoint in the distribution system. The compounds CF, DCAA and TCAA were detected in highest levels. TTHM levels during winter and summer were measured as 33.4 µg/L and 62.5 µg/L, respectively (Williams et al. 1993).

Rodriguez et al. conducted a 14-month intensive sampling program in Quebec City, Canada, to investigate the seasonal variations in THM concentrations. They detected highest THM3 (total concentration of CF, BDCM and DBCM) concentrations during summer (101 µg/L) and fall (106 µg/L). The highest formation of

trihalomethanes in the fall was related to high TOC levels (3.77 mg/L) which resulted from the frequent rains and relatively rapid decay of vegetation. During the summer period second highest THM3 levels were measured due to high water temperature and high chlorine doses. In winter, the existence of an ice layer on the watersheds of the region, which protects the water source from pollution, resulted in lower THM3 concentration (5.1 µg/L) than all other seasons (Rodriguez et al. 2004).

Toroz and Uyak monitored the THM concentrations within the distribution system of the Büyükçekmece Water Treatment Plant in İstanbul based on an 30-week intensive sampling program. In the study, highest TTHM levels were reported during summer (117 µg/L) and lowest during spring (75 µg/L). The high DBP formation in summer was due to high chlorine doses, 1.2-2 times higher than spring, applied to drinking water to maintain sufficient residual. The low levels of DBPs in spring were related to relatively lower water temperature (Toroz and Uyak 2004).

2.5. Literature Review on Predictive Models of DBP Formation

Multivariate statistical models are developed in order to predict the DBP concentrations by using various combinations of explanatory variables including water quality (TOC, bromide ion concentration, pH, etc.) and operational parameters (disinfectant dose, residence time, etc.). In some cases, modeling is aimed at identifying the significance of diverse operational and water quality parameters controlling the formation of the DBPs or at investigating the kinetics for their formation. In other cases, they are developed with predictive purposes as an alternative to monitoring in the field. Generally, the statistical models in the literature were multivariate regression models which use different input variables (Table 2.4).

A multiple regression model was generated for predicting THM levels in the finished water leaving the plant using the field sampling of Galatsi Treatment Plant in Athens with respect to temperature, pH, chlorine dose, bromide and chlorophyll (chla) (Golfinopoulus et. al. 1998). The THM concentrations were measured in finished water while pH, temperature, bromide and chla were measured for raw water. The sum of the pre chlorination and post chlorination were used as chlorine dose. Season was included as a dummy variable in the model, which was statistically significant variable at $\alpha=0.05$. The coefficient of the determination was also very high (0.98). The validation the model

showed that the 82% of the predicted values were within ± 20% of the measured values.

In the study of Rodriguez and Serodes samples were collected at the treatment plant of Levis City and Sainte-Foy in Canada after and before final chlorination and at least two points in the distribution system in order to represent water with moderate and high residence time. The model developed for Levis City also included the THM concentration following pre-chlorination as input variable. In addition, temperature, pH and flow rate was found to be statistically significant. The model was very good at predicting the THM concentration with a correlation coefficient of 0.92 (Rodriguez and Serodes 2001).

Golfinopoulos and Arhonditsis constructed multivariate regression models for prediction of THM concentrations in the finished water of the Menidi Water Treatment Plant of Athens, Greece. The input variables were the parameters measured in raw water including temperature, pH, bromide, chlorophyll a and chlorine dose (sum of the pre and post chlorine doses). In addition, dummy variables for the seasons (spring, summer and winter) were also included in the model. After testing the normality of the input variables the relationship between them were examined by simple correlation. Three models were obtained for the prediction of TTHM, CF and BDCM concentrations and the corresponding R^2 values for these models were calculated as, 0.52, 0.51 and 0.62, respectively (Golfinopoulos and Arhonditsis, 2002).

Table 2.4. Summary of predictive models for DBPs

Author	N	r^2	Output	Predictive Models
Golfinopoulus et. al. (1998)	88	0.98	TTHM	$TTHM = 13.54\ln[chla] - 14.47pH + 230.25[Br] - 139.62[Br]^2 - 25.28S + 110.55Sp - 6.59(T \times Sp) + 1.48(T \times [Cl])$
Rodriguez and Serodes (2001)	14	0.92	THM	$THM_{ave} = 0.68(THM_{pc}) + 0.031 \times (T_t)^2 - 34.8(pH_t) - 0.0015(Q_t) + 298.2$
Golfinopoulos and Arhonditsis (2002)	126	0.62	CHCl$_3$	$CHCl_3 = -0.32chla + 0.68pH + 2.51[Cl] + 1.93Sp - 22.07S + 1.38T \times S - 0.12T \times Cl$
Rodriguez et al. (2004)	63	0.77	THM3	$THM = 134 + 1.471(CDBP_0) - 17.42(pH_0) - 734.4(UV_0) + 0.748(t_r)$
		0.70	THM3	$THM = 286.9(CDBP_0)^{0.745}(t_r)^{0.298}$
Uyak et al., (2005)	120	0.986	TTHMs	$THMs = 7.07 \times 10^{-2}(TOC + 3.2)^{1.314}(pH - 4)^{1.496}(dose - 2.5)^{-0.197}(temp + 10)^{0.724}$
Toroz and Uyak (2005)	30	0.827	TTHMs	$THM = 11.967(TOC)^{0.398}(Temp)^{0.158}(Cl)^{0.702}$

Note: All DBP concentrations are in µg/L *Nomenclature:* N: sample size, r^2: Coefficient of determination for regression analysis, chla : chlorophyll (mg/m^3)
Br: Bromide ion (mg/L) , S: Dummy variable (summer) , Sp:Dummy variable (spring) ,T: Temperature C , Cl and D : Chlorine dose (mg/L) Sd2: Extremity point in distribution system, Sc2: Treated water at the plant , CDBP$_0$, pH$_0$ and UV$_0$ water quality parameters before post chlorination , tr: Residence time (h), THM$_{pc}$: THM concentration followed pre-chlorination, THM3 : Total concentration of CF, BDCM and DBCM

Linear and non-linear models were developed for THM formation in drinking water of the Quebec City in Canada (Rodriguez et al., 2004). Drinking water samples were collected for an intensive sampling period of 14 months. The models obtained in this study were based on the initial THM concentration and water quality parameters such as TOC, UV-254, and residence time monitored in water samples collected before post-chlorination. The linear model was proved to be moderately more useful for THM formation according to R^2 values. For both models, the initial THM formation is the most significant parameter for THM formation.

Linear multivariate regression model was developed based on raw water characteristics e.g. TOC, pH, temperature, and the sum of the applied pre and final chlorine doses, to predict the THMs in the processed water of the Kağıthane Çelebi Mehmet Han water treatment plant in İstanbul (Uyak et al., 2005). In the study, pH and temperature were found to be statistically most significant parameters for THM formation. The coefficient of determination for the regression model was calculated as 0.986. The model was also validated by using another data set obtained from Büyükçekmece Water Treatment Plant which has different water quality characteristics.

Toroz and Uyak collected drinking water samples from the distribution system of the Büyükçekmece Water Treatment Plant in order to monitor the THMs and other water quality parameters. After a 30-week intensive sampling program, multiple linear regression analysis was conducted to predict the THM formation from the TOC, temperature and chlorine dose parameters. The determination coefficient of the model was very high (0.827) and model was useful to determine the seasonal variation in THM concentrations since it included both the TOC and temperature as explanatory variables (Toroz and Uyak 2005).

Milot et al. developed a logistic regression model to investigate the susceptibility of drinking water utilities to form high concentrations of THMs in Quebec City, Canada. The probability to exceed the established THM thresholds, based on general utility characteristics like type of water source (lake=1 or river=0), type of water treatment (chlorination alone=1 or other=0), geographical location (region I=1, region II=0), the season (summer=1 or other=0) were estimated by using logistic regression analysis. The model obtained for the TTHM threshold of 80µg/l is given below (Milot et al. 2000).

$$P = \frac{e^{0.706(treatment) + 1.138(region) + 0.181(season) + 0.653(source) - 1.522}}{1 + e^{0.706(treatment) + 1.138(region) + 0.181(season) + 0.653(source) - 1.522}}$$

The predictive models can be used by different authorities for different purposes. For example, water utility managers can use the models for operational control during the treatment process like adjustment of pH and disinfectant dose or for controlling the hydraulic residence time in reservoirs to minimize the DBP formation. Regulatory agencies also use the predictive models for updating the regulations and standards by evaluating the required reduction in precursors, which allow compliance DBP standards, and thus estimate the infrastructure needs for upgrading of treatment facilities. In addition, the predictive models can be used in environmental epidemiological studies and human health risk assessment in order to estimate the human exposure to DBPs at desired location in the water distribution system.

CHAPTER 3

MATERIALS AND METHODS

3.1. Sampling Procedure

Drinking water samples for DBP analysis were collected from tap waters of Konak (Hatay), Balçova, Narlıdere, Güzelbahçe and Urla districts (Figure 3.1). Samples were collected between July 2006 and April 2007 from tap water at one sampling point in each district every six days. Among sampling locations, Urla represented the non-urban area whereas Konak, Balçova, Narlıdere and Güzelbahçe represented urban and sub-urban area. In the urban area there were two different drinking water sources: Tahtalı and Balçova Reservoirs. Konak district supplied drinking water from Tahtalı Reservoir, whereas Balçova, Narlıdere, and Güzelbahçe districts supplied from Balçova Reservoir.
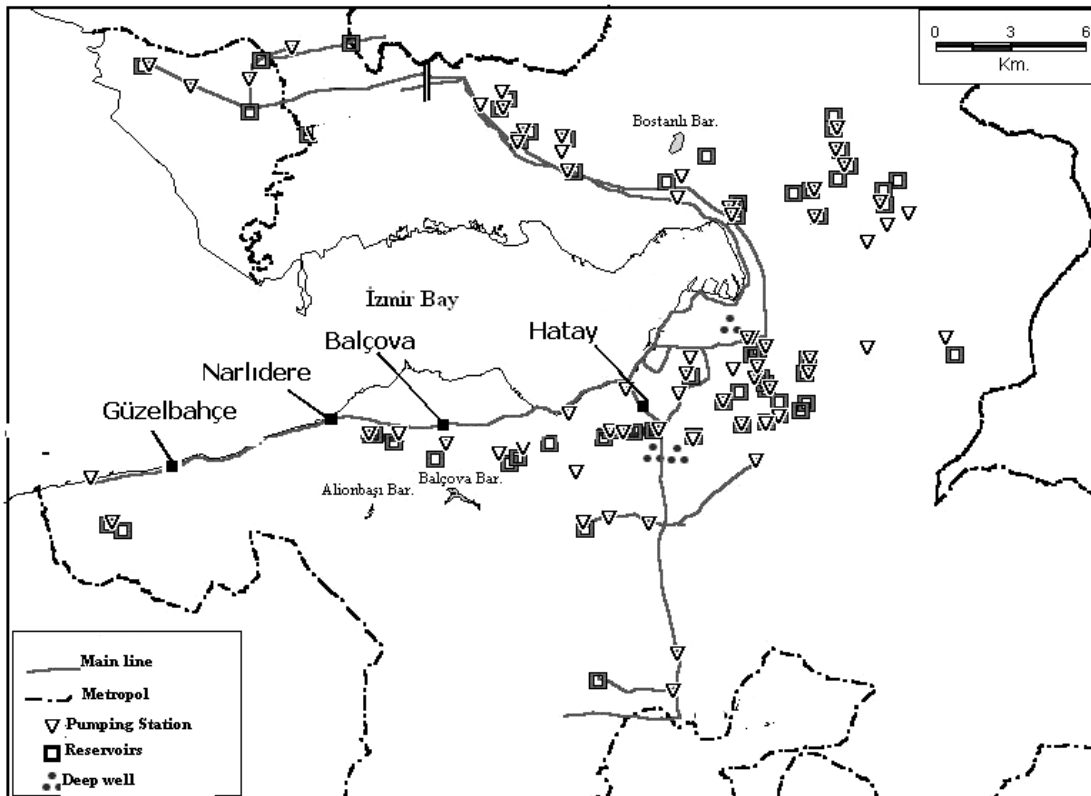

Figure 3.1. Map of İzmir city and distribution system area

The drinking water supplied from Tahtalı Reservoir is treated in Tahtalı Drinking Water Treatment Plant (TDWTP) and distributed to Hatay, Buca, Karabağlar, and Yeşilyurt regions. TDWTP has a capacity of 520,000 m^3/day and contains aeration, coagulation, flocculation-sedimentation, filtration, chlorination and filter press units. Pre-chlorination is applied to aerated water and final chlorination is applied to water before leaving the plant. The drinking water of Balçova Dam is treated in Balçova Drinking Water Ttreatment Plant (BDWTP) which has a capacity of 70,000 m^3/day. The plant has aeration, pre-chlorination, rapid-sand filters and final chlorination units. The drinking water source of the Urla district is ground water. Balçova, Narlıdere and Güzelbahçe districts are on the same main line of the BDWTP distribution system.

A total of 44 samples were collected at each sampling point. These samples were analyzed for THMs (CF, DBCM, BDCM and BF), HANs, HKs and CP. In addition, samples collected at sampling points in Urla and Tahtalı raw water were analyzed for bromide ion. Samples were also collected from inlet and outlet of the Tahtalı Drinking Water Treatment Plant (TDWTP), and analyzed for Non-Purgeable Organic Carbon (NPOC). Sampling at the TDWTP was carried out by IZSU and than the samples were send to IYTE for analysis of NPOC and bromide ion. For BDWTP all parameters were obtained from IZSU.

Sampling in the distribution system was performed in public buildings using the faucet of the washroom nearest to the street. Before collecting the samples, the system was flushed for about 3 min to ensure that water was coming directly from the public distribution system instead of plumbing system of the building. For DBP analysis samples were collected in 40 ml pre-cleaned screw cap amber glass vials with polypropylene cap and silicone septa (Supelco). Vials were washed with detergent and rinsed with tap water and ultra pure chemical free MilliQ (Millipore Elix 5) water, and than placed in an oven at 105 ^{o}C for 1 hour. Before sampling 0.8 g of the mixture of 1 % sodium phosphate monobasic (NA_2HPO_4) and 99 % potassium phosphate monobasic (KH_2PO_4) by weight was added to vials to lower the sample pH to 4.8 and 5.5 in order tto inhibit base catalyzed degradation of the HANs and to standardize the pH of the samples. Then, 0.004 g of the ammonium chloride NH_4Cl (Merck) was added to provide 100 mg/l in each vial to eliminate any remaining residual chlorine to stop further DBP formation. Once collected, samples were stored in the dark at 4 ^{o}C and carried to laboratory for analytical procedures. At each time, free residual chlorine was measured in the field by using DPD test kit (Lovibond, PC Checkit 60684). For NPOC

analysis samples were also collected in 40 ml amber glass vials with screw cap and acidified with 2 ml 98% H_2SO_4. Samples for bromide analysis were collected in 60 ml HDPE bottles (Nalgene). The water quality and operational parameters such as pH, temperature and chlorine dose were obtained from the routine measurements of the treatment plants.

3.2. Analytical Methods

3.2.1. Analysis of Disinfection By-Products

In this study USEPA method 551.1 was followed for the analysis of trihalomethanes, (THMs), haloacetonitriles (HANs), halogenated ketons (HKs) and chloropicrin (CP) (USEPA 1995). After the liquid-liquid extraction, analysis of DBPs were made by using gas chromatography (GC) equipped with electron capture detector (ECD). For the extraction of water samples, first 10 mL of the 40 mL sample was discarded with a glass pipettes using an automatic pipette aider. Immediately after, 2 mL of methyl-tert butyl ether (Merck) as an organic solvent phase was added to the vial very gently, just above the surface of the water. After gently inverting the vial once, 8 g of the reagent grade sodium sulfate (NA_2SO_4) (Merck ACS grade) was added to the extraction vial to increase the ionic strength of the aqueous phase, by increasing the partitioning of DBPs to MTBE phase and decreasing the solubility of MTBE. Then, the extraction vials were closed and shaken by hand for 2 minutes. The phase separation took place within 6 minutes. Using disposable pasteur pipettes about 1 mL of the MTBE phase was transferred to the 2-mL clear glass GC vials (Supelco) and sealed with aluminum crimp caps with teflon faced septa (Supelco), and subsequently analyzed with GC-ECD (Agilent 6890N) equipped with an auto sampler (Agilent 7893). Operating conditions for GC are given in Table 3.1.

Table 3.1. Operating conditions for GC-ECD

Instrument / Condition	Description
Gas Chromatography	Agilent 6890N
Column	HP-5 5 % phenyl Methyl Siloxane, film thickness: 0.25 um, diameter: 320 um.
Carrier gas and flow rate	Helium at 1.3 mL/min
Injection Mode	Splitless
Injection Volume	2 μL
Inlet Temperature	175 ^{o}C
Detector Temperature	310 ^{o}C
Temperature Program	10 min at 35 ^{o}C 35 ^{o}C to 50 ^{o}C at 1 ^{o}C per min. 50 ^{o}C to 75 ^{o}C at 4 ^{o}C per min.

THM calibration mix (Supelco) was purchased as 2000 µg/L in acetone whereas halogenated volatiles mix (HANs, HKs and CP) (Supelco) was 2000 µg/L in methanol. Primary dilution standards were prepared at concentrations which could be easily diluted to prepare aqueous calibration solutions that would bracket the working concentration range. These standards were prepared in acetone in 2-mL crimp capped vials to achieve minimum headspace and stored in the dark in a freezer at -27°C. Procedural calibration standards were prepared and extracted in exactly the same manner as a sample to compensate for any inefficiencies in the processing procedure. The calibration standards were 2, 10, 20, 50 and 100 µg/L for THMs and 0.25, 1, 5, 10, 25 µg/L for HANs, HKs and CP. The R^2 values for the linearized calibration curves were between 0.979 and 0.999 for all DBPs.

3.2.2. Analysis of Non-Purgeable Organic Carbon

Non-purgeable organic carbon (NPOC) measurements were carried out by a Shimadzu TOC-V$_{CPH}$ analyzer with OCT-1 Shimadzu sampler. In order to obtain the calibration curves, the stock standard solution for total carbon was prepared by dissolving 2.125 g potassium hydrogen phthalate ($C_8H_5KO_4$) in 1000 mL organic free

distilled water. Then the stock solution was diluted in appropriate amounts with de-ionized water with concentrations 1, 5, 10, 20, 50 mg/L.

3.2.3. Analysis of Bromide Ion

The concentration of bromide ion was measured according to EPA method 300 employing an ion chromatography system (Dionex), which included an electrochemical detector (ED 50), a pump (GP 50 gradient), an analytical column (AS9-HC, Ionpac). Eluent composition was 10 mM Na_2CO_3 with a flow rate of 1 mL/min. External bromide standards with concentrations 0.5, 2.5, 5, 10, and 20 mg/L were prepared from a standard that included 100 mg/L bromide ion (Dionex). The detection limit of the method was 0.15 µg/L.

3.3. Quality Assurance/Quality Control Procedure (QA/QC)

Laboratory requirements included, initial demonstration of laboratory capability, determination of method detection limit, analysis of laboratory reagent blanks, field reagent blank, field duplicates and calibration check standards (USEPA 1995).

For the initial demonstration of the laboratory capability, the observed chromatographic peaks, obtained by running a standard solution method analytes were identified by comparing the retention times with those given in the EPA method 551. Then, oven temperature program were modified according to retention time of the last peak of the method analyte. To obtain a smooth baseline, a non-polar organic solvent (hexane) was run before analysis of the each batch of samples. Before each run, GC syringe was also rinsed three times with ultra pure water and acetone, respectively.

The field reagent blanks were collected to determine if any interference was present in the field environment. Laboratory reagent blanks were analyzed to determine if method analytes or other interferences were present in the laboratory environment, the reagents, or the apparatus. On the other hand, the precision of the measurements was provided by field duplicates (FD), two separate samples collected at the same time and place under identical circumstances throughout field and laboratory procedures. The relative percent difference between two parallel samples was calculated according to Equation 3.1. The average RPDs for TTHMs, total HANs, HKs and CP were calculated

as 13.687, 28.119, 25.340, 26.299, respectively. The RPDs for HANs, HKs and CP were found to be higher than 20 %. Even though these RPDs were higher than the literature values, these compounds were detected at very low concentrations (i.e., detection limit of instrument).

$$RPD(\%) = \frac{(FD1 - FD2)}{1/2(FD1 + FD2)} * 100 \qquad (3.1)$$

The method detection limits (Table 3.2) were calculated for each compound according to following equation by analyzing seven replicates of standard solution at a concentration of 0.05 µg/L for HANs, HKs, CP and 0.25 µg/L for THMs.

$$MDL = SD * t_{\alpha/2, n-1} \qquad (3.2)$$

where; SD is the standard deviation of the mean for seven replicate samples and t-value is the student's t value for 99 % confidence level and n-1 degrees of freedom.

Table 3.2. Method detection limits and recoveries for DBPs

Compound	MDL (µg/L)	Recovery (%)
CF	0.030	99
TCAN	0.009	50
DCAN	0.002	108
BDCM	0.057	87
DCP	0.026	135
CP	0.015	74
DBCM	0.014	103
BCAN	0.018	76
TCP	0.009	109
BF	0.044	139
DBAN	0.073	62

Continuing calibration checks were performed every 20 samples. If the relative percent difference between response of the initial calibration and the calibration check

standard was higher than 20 %, the instrument was considered out of calibration and recalibrated.

3.4. Statistical Methods

Statistical analyses of descriptive statistics, hypothesis tests and multivariate and logistic regression analyses were performed using SPSS 7.0.

3.4.1. Goodness-of-Fit Tests

Goodness-of-fit tests are formal statistical tests of the hypothesis that the set of sampled observations are an independent sample from the assumed distribution. The null hypothesis is that the randomly sampled sets of observations are independent, identically distributed random variables with distribution function F. The commonly used goodness-of-fit tests include the chi-square test, Kolmogorov-Smirnov test, and Anderson- Darling test. The chi-square test is based on the difference between the square of the observed and expected frequencies. It is highly dependent on the width and number of intervals chosen and is considered to have low power. It is best used to reject poor fits. The Kolmogorov-Smirnov Test is a non-parametric test based on the maximum absolute difference between the theoretical and sample Cumulative Distribution Functions (CDFs). The Kolmogorov-Smirnov test is most sensitive around the median and less sensitive in the tails and is best at detecting shifts in the empirical CDF relative to the known CDF. It is less proficient at detecting spread but is considered to be more powerful than the chi-square test. The Anderson-Darling test is designed to test goodness-of-fit in the tails of a Probability Density Function (PDF) based on a weighted-average of the squared difference between the observed and expected cumulative densities (USEPA 1997). This test is more powerful at the tails.

3.4.2. Non-Parametric and Parametric Tests

Non-parametric statistical tests such as, Mann-Whitney and Kruskal-Wallis, were used to investigate whether the concentrations of DBPs differed depending upon water source and seasons. Mann-Whitney test, which is non-parametric equivalent to

two sample t-test, was used to test whether two independent samples are from the same population. Kruskal-Wallis Test compares several populations on the basis of independent random samples from each population. The null hypothesis for the Kruskal-Wallis test is that the distribution of the response variable is the same in all the populations. The alternative hypothesis is that responses are systematically different in some populations than in others. Kruskal-Wallis test is also alternative to one way analysis of variance F-test (Montgomery 2007).

Two sample t-test is a parametric test which is used to determine whether the two population means are equal. A common application of this is to test if a new process or treatment is superior to a current process or treatment (WEB_3 2007).

The p-values, the probability of error in accepting the observed result as valid, obtained by non-parametric tests are compared with the chosen α value (0.05). The p-values smaller than 0.05, which is equivalent to say the medians were different with a probability of 95 %, showed a statistical significant difference between compared samples.

3.4.3. Multivariate Regression Analysis

Multiple regression model, which is a direct extension of a polynomial regression model in one independent variable, relates a dependent variable Y to a set of quantitative independent variables (x_i). The general structure of the multiple linear model is given by equation 3.3 (Ott 2001);

$$Y = \beta_0 + \beta_1 x_{i1} + \beta_2 x_{i2} + \cdots + \beta_k x_{ik} + \varepsilon_i \qquad (i = 1,2,......,n; n > k) \qquad (3.3)$$

where, β_i denotes the regression coefficients and ε_i denotes the random error.

Any of the independent variables may be the powers of the other independent variables (e.g, $x_2 = x_1^2$), cross product of the other terms (e.g, $x_3 = x_2 x_1$) or logarithm of another term ($x_4 = \log x_1$). The only restriction is that no x is perfect linear function of any other x. The multivariate regression models can also be logarithmic or polynomial. The logarithmic models are developed by transforming all variables using the nth logarithmic

function and then linear regression is applied. In the case of polynomial regression model, explanatory variables are expressed by their n^{th} order terms, and then a linear regression is applied (Rodriguez et al. 2003). The following equations depict the structure of the logarithmic and polynomial regression models.

$$y = K(x)^a (z)^b \cdots (m)^n \qquad (3.4)$$

$$y = K + a(x)^1 + \cdots b(x)^4 + c(z)^1 + \cdots d(z)^4 + \cdots n(m)^4 \qquad (3.5)$$

The regression analysis was carried out by using the *stepwise* procedure of the statistical software SPSS, the method consists of first classifying the predictor variables according to their statistical significance (p) and then including one variable at a time different steps. The criterion used to judge whether or not to consider selected variables in the models during the regression stepwise procedure was a significance level of 5% ($p<0.05$). After each variable was included in model, also examined for removal according to the removal criterion ($P_{out} = 0.10$).

3.4.4. Logistic Regression Analysis

Logistic regression analysis makes it possible to predict the probability of an event taking place based on a set of independent variables that may be continuous, categorical or dichotomous. The variable to predict must be dichotomous and binary coded, 0 and 1 (for example, 1 when the event takes place, and 0 when the event does not). In the logistic regression, the probability P, that an event will take place may be associated with a series of independent variables in a model as follows:

$$\log\left[\frac{P}{1-P}\right] = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \cdots + \beta_n X_n \qquad (3.6)$$

where, β_is are regression coefficients of the equation and estimated by using the method of maximum likelihood.

The transformed form of the regression equation is given as follows;

$$P = \frac{e^{b_0 + b_1 x_1 + b_2 x_2 + \ldots + b_n x_n}}{1 + e^{b_0 + b_1 x_1 + b_2 x_2 + \ldots + b_n x_n}} \qquad (3.6)$$

In order to check the model performance χ^2 values were used. χ^2 measured the ability of the model to adapt and adjust to available observations. It represents the difference in efficiency between a model characterized solely by the constant b_0 (in which the terms b_1 to b_n of Equation 3.6 all equal 0) and the model in question here which posses one or more explanatory variables. The higher the χ^2, the more the model is statistically significant. Another criterion for the model performance is the percent correct prediction.

CHAPTER 4

RESULTS AND DISCUSSION

The results of this study are given under three main sections. The first section includes evaluation of operational and drinking water quality parameters. In the second section, level of DBP concentrations as well as variation by source, season and location are discussed. Multivariate regression analysis and logistic regression for prediction of DBP concentrations are presented in the last section

4.1. Operational and Drinking Water Quality Parameters

In order to evaluate the relationship between DBP occurrence with operational and drinking water quality parameters, the concentration of non-purgeable organic carbon (NPOC), pH and temperature were measured in raw and treated water of both Tahtalı and Balçova water treatment plants. As presented in Table 4.1, the organic matter content (measured as NPOC concentration) of the raw water of both Tahtalı and Balçova Treatment plants were below 5 mg/L, which is typical for unpolluted fresh-surface waters. The number of samples from BDWTP was less because the plant supplied water to the system only five months of the sampling period.

Table 4.1. Descriptive statistics for operational and drinking water quality parameters

Parameter	TDWTP						BDWTP					
	N	Mean	Med.‡	SD	Min	Max	N	Mean	Med.‡	SD	Min	Max
NPOC*	43	3.76	3.76	0.46	3.05	5.06	9	3.55	3.56	0.48	2.85	4.31
NPOC**	42	3.20	3.18	0.46	2.45	4.60	9	3.50	3.36	0.85	2.62	4.89
Temperature*	43	16.91	16.9	5.14	9.60	24.4	16	10.9	10.3	1.97	7.70	14.2
pH*	43	7.87	7.87	0.27	7.50	8.70	16	8.13	8.13	0.38	7.52	8.64
PreCl$_2$ dose	48	3.34	3.34	1.36	2.00	6.01	23	0.75	0.75	1.11	0.36	5.50
FinalCl$_2$ dose	48	1.02	1.02	0.16	0.83	1.74	23	0.29	0.29	0.10	0.16	0.70

*Values are for raw water, ** Values are for treated water, ‡Median
N: Sample size, SD: Standard deviation, NPOC concentrations and chlorine doses are in mg/L

However, annual average concentration of NPOC in raw water of TDWTP was found to be slightly higher than that was measured in the raw water of BDWTP. Also, it should be noted that, mean NPOC concentration for BDWTP raw water represented only winter months (December, January and February) since the data for other months were not available. In addition, if we compare the mean winter NPOC concentrations of TDWTP and BDWTP, we can say that the difference between the mean concentrations is not significant (p=0.51). Moreover, mean concentrations of pre- and final chlorine doses applied TDWTP were about 3 times higher than that of BDWTP for overall and five months period in which both plants were in operation. Bromide ion concentrations were also measured in raw water of TDWTP. Annual average concentration was found to be 0.26 mg/L. The annual average concentration of DOC levels in raw water of TDWTP and BDWTP were reported as 3.06 and 1.80 mg/L, respectively, for the year 2004. Although, bromide ion concentration was not measured for BDWTP, it was reported to be lower than 0.02 mg/L (Ates et al. 2006).

Because of relatively higher organic matter content of the raw and treated water of TDWTP and high chlorine doses applied at this plant we can conclude that TDWTP has higher DBP formation potential compared to BDWTP. THM formation potential of TDWTP and BDWTP were also reported to be 87 µg/L and 63 µg/L, respectively (Ates et al 2006).

4.1.1.Seasonal Variation in Operational and Water Quality Parameters

Seasonal variation in surface water quality is mainly related to changes in climatic parameters like temperature and rainfall. During warm months of the year, organic matter content increases due to rapid decay of vegetation. Rains also increase the organic matter content by leaching of organic matter into the watersheds. Seasonal variation in NPOC concentration in TDWTP raw water is presented in Figure 4.1.

Although, the mean concentration of NPOC in summer, fall and winter were comparable, the highest NPOC levels were measured in summer (5.06 mg/L) and fall (4.03 mg/L). The differences in mean NPOC concentrations in spring and the remaining seasons were not significant (p>0.19). The reason for the stable NPOC level in raw water was possibly climatic conditions during the study period which resulted in unusual relatively high temperatures in winter and low precipitation throughout Turkey.
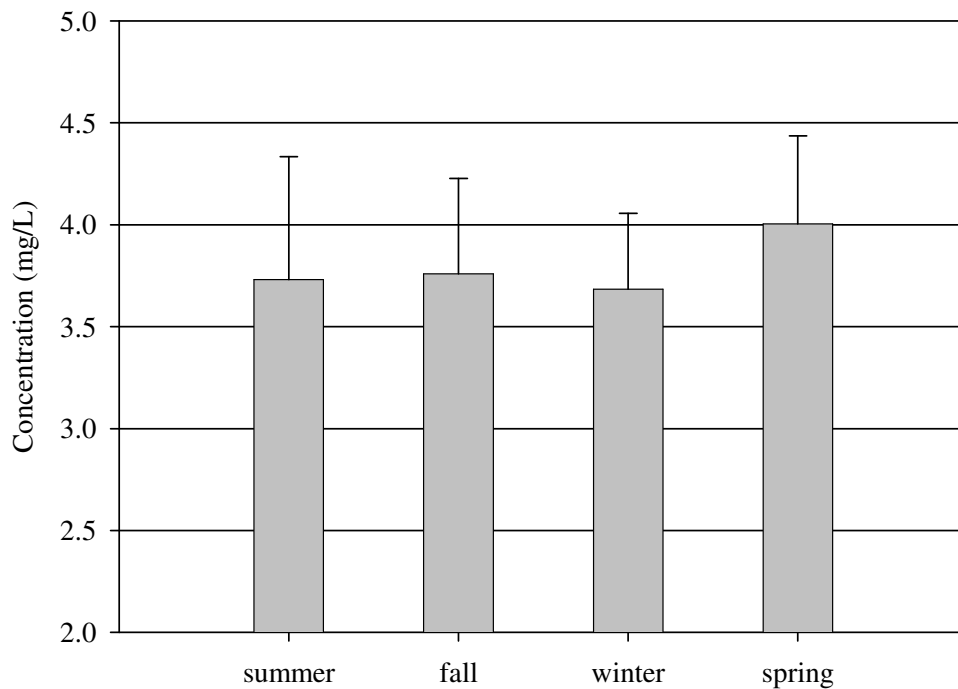
Figure 4.1.   Seasonal variation in NPOC concentration in raw water of TDWTP (Error bars show one standard deviation)

For TDWTP, the seasonal variation in raw water temperature and total chlorine dose are presented in Figure 4.2. Similar trends were observed for chlorine dose and temperature in terms of seasonal variation, increasing in summer months and decreasing in winter. The relationship between chlorine dose and temperature was explained as, the rates for chlorine decay are higher at high water temperature, and therefore plant operators should apply higher chlorine doses at the pre- and post-chlorination stages to ensure acceptable levels of residual chlorine in the distribution system (Rodriguez and Serodes 2001). For BDWTP, there were no available data for spring and fall seasons, therefore the seasonal variation in these parameters can not be evaluated for this plant.
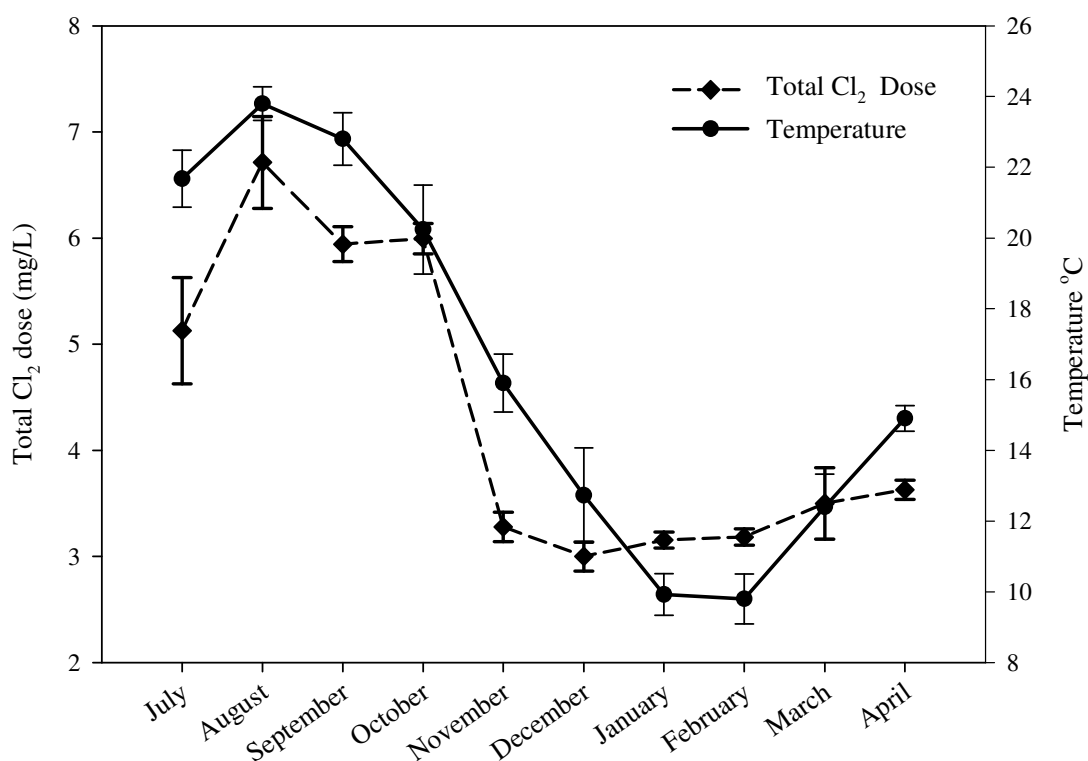
Figure 4.2.   Seasonal variation of Total Cl$_2$ (pre + final chlorine) Dose and temperature at TDWTP (Error bars show one standard deviation)

Concentrations of bromide ion in chlorinated waters significantly affect DBP formation and speciation since it is considered as inorganic precursor for DBPs. In order to evaluate this effect, bromide ion concentrations in raw water of TDWTP and in tap water of Urla was monitored over the sampling period. Mean concentration of bromide ion in raw water of TDWTP was 0.24 mg/L, which is in the typical range (0.04-1 mg/L) for surface waters, whereas it was 1.9 mg/L in tap water of Urla. The high occurrence of bromide ion in Urla may be related to intrusion of sea water to the ground water since this district is located on the coast.

Seasonal variation in bromide ion concentrations for both TDWTP and Urla is presented in Figure 4.3. For TDWTP seasonal trend for bromide concentration was not notable. However, in Urla, mean concentration of bromide ion winter and spring was about 1.8 times higher than summer and fall. Seasonal difference in bromide ion level may be due to increase in the seawater intrusion with decreasing ground water table which resulted from lower amount of rainfall during the sampling period
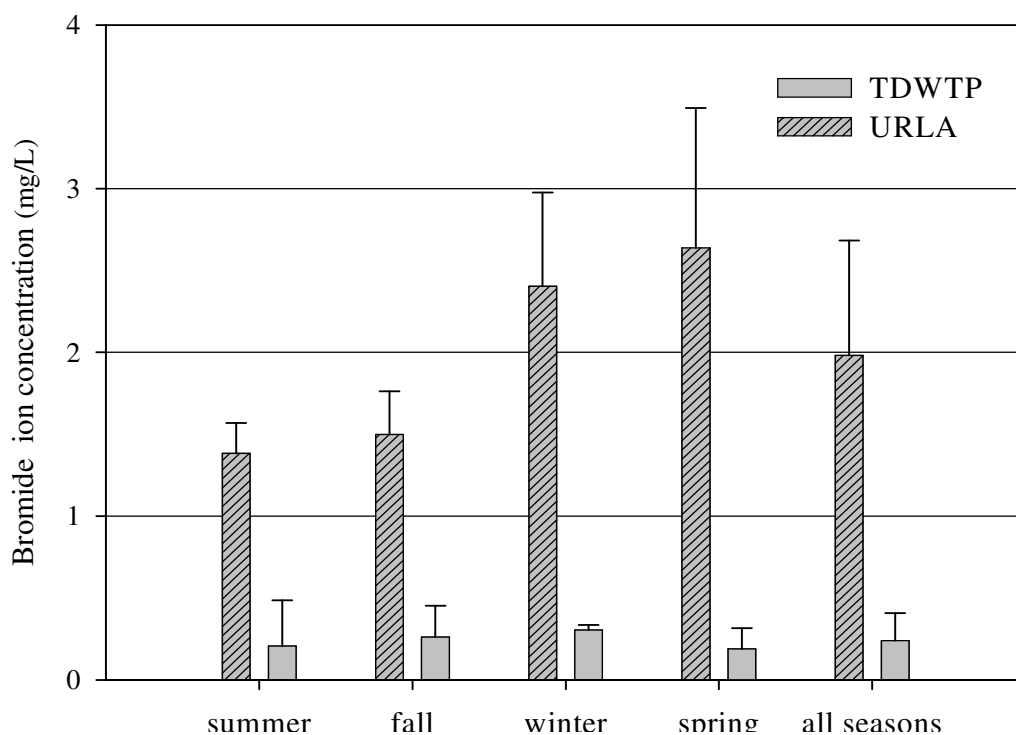
Figure 4.3. Seasonal variation in bromide ion concentration (Error bars show one standard deviation)

4.2. Concentrations of Disinfection By-Products

Concentrations of disinfection by-products, which include four THM species (CF, BDCM, DBCM and BF), four HAN species (DCAN, TCAN, BCAN and DBAN), HKs (1,2-DCP, 1,1,1-TCP), and CP were measured in samples from tap water at five sampling points for ten months between June 2006 and April 2007. A total of 88 samples were collected in duplicate at each point.

Detection frequencies for DBPs, which take into account all seasons and all sampling locations, are listed in Table 4.2. All frequencies were found to be higher than 75 % except for TCAN and CP, since these compounds were not detected in any of the

Urla samples. DBCM, CF, BF and DCAN were the compounds with the highest detection frequencies (>99%). The detection frequencies for each sampling location are discussed in Section 4.2.1.

Table 4.2. Detection frequencies of DBPs

THMs	Freq.(%)[*]	HANs	Freq. (%)[*]	Other DBPs	Freq.(%)[*]
CF	99	TCAN	67	1,1,1-TCP	80
BDCM	83	DCAN	99	1,2-DCP	81
DBCM	100	BCAN	95	CP	70
BF	99	DBAN	95		

*Frequency

Outliers are defined as the measurements that are extremely large or small relative to the rest of the data and, therefore are suspected of misrepresenting the population from which they were collected (USEPA 2000). Box and Whisker plots were constructed for THMs and HANs to identify potential outliers and are presented in Figures 4.4 and 4.5, respectively. The concentration values marked by an asterisk (*) indicate *mild outliers,* where the plus sign (+) represents *extreme outliers.* Extreme outliers were the case for only TCAN in Urla which can be attributed to very low concentrations close to the detection limit. Therefore, all the mild and extreme outliers were included in statistical calculations since the precision of the measurement for corresponding concentrations was proved to be high (RPD < 20%).
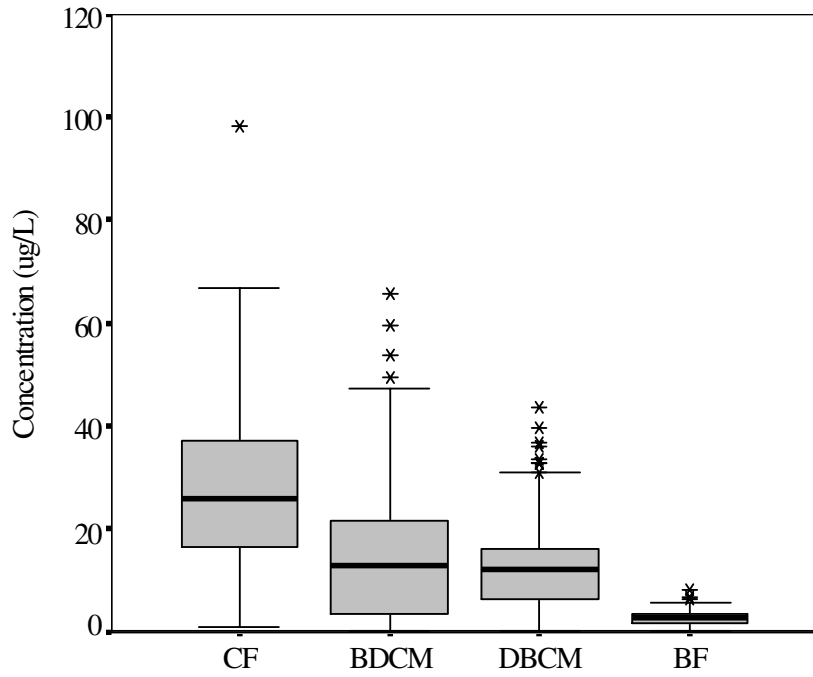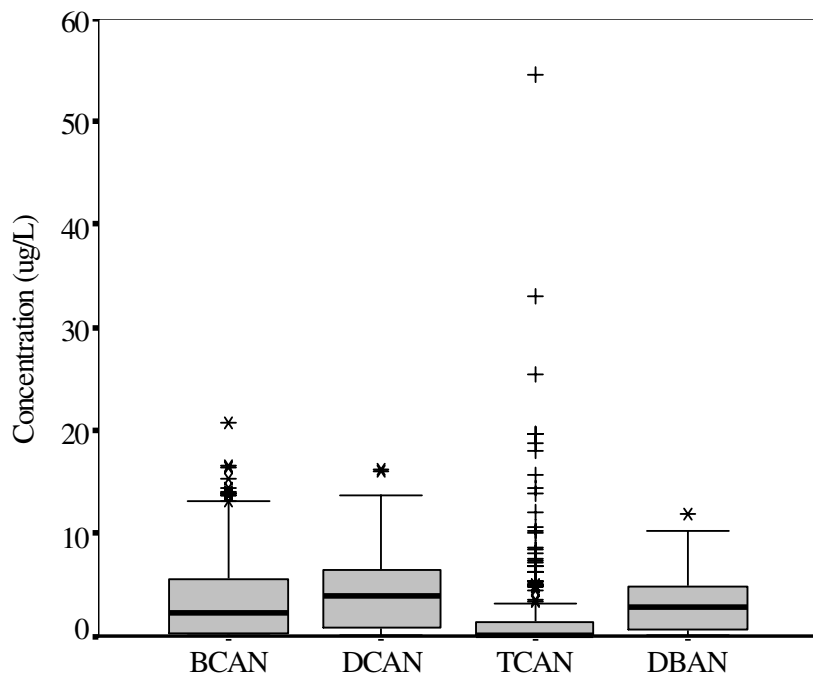
Figure 4.4. Box and Whisker Plots for THMs

Figure 4.5. Box and Whisker Plots for HANs

The descriptive statistics (mean, median, standard deviation) as well as minimum, maximum, 90th and 95th values for DBP concentrations, which included all sampling locations and all seasons, are listed in Table 4.3. For all compounds, variability, the difference between minimum and maximum observations, was found to be very high since the descriptive statistics include low DBP levels from Urla district. Among all DBPs, CF was the most abundant compound with a concentration range of 0.03-98.39 µg/L.

The concentrations of HANs were found to be much lower than THMs, which is in agreement with the data in the literature (Simpson and Hayes 1998, Kim et al. 2002). The mean THAN concentration of 13.09 µg/L was much higher than it was measured in Melbourne, Australia (Simpson and Hayes 1998), and in Hyogo Prefecture, Japan (Kawamoto and Makihata 2004). The mean concentrations of 1,2-DCP and 1,1,1-TCP were found to be lower than the other DBPs except for CP, as suggested by Golfinopoulos and Nikolaou (2005). No drinking water concentration levels were reported for HANs and HKs for Turkey in the literature.

Table 4.3. Descriptive statistics for DBP concentrations in İzmir drinking water

DBPs	N	Median	Mean	SD	Min	Max	90th %ile[*]	95th %ile[*]
CF	221	21.95	22.00	18.35	0.03	98.39	47.65	55.17
BDCM	177	13.00	10.27	9.019	0.01	43.82	22.28	28.91
DBCM	221	8.388	14.71	12.72	0.19	65.91	31.85	38.87
BF	221	2.768	4.453	4.334	0.04	19.13	12.23	14.24
TTHMs	221	46.28	48.52	35.83	2.86	183.0	99.49	124.8
DCAN	221	3.966	3.591	4.123	0.00	20.83	8.767	13.25
BCAN	221	2.261	3.197	2.735	0.01	11.97	7.415	8.238
DBAN	217	2.768	4.229	3.623	0.00	16.42	9.723	11.40
TCAN	178	0.045	2.489	6.348	0.00	54.63	7.691	14.57
THANs	217	10.05	13.09	10.76	0.25	88.40	27.40	33.62
1,2-DCP	177	0.452	0.599	0.751	0.01	7.823	1.163	1.594
1,1,1-TCP	177	1.613	1.882	1.498	0.01	7.806	3.655	4.660
HKs	177	2.065	2.481	2.249	0.02	15.629	4.818	6.254
CP	177	0.173	2.481	1.913	0.08	9.330	4.949	6.003

All values are in µg/L , N: Sample size, SD:Standard Deviation, *Percentile

In the case of THMs, mean TTHM level of 48.52 µg/L falls in the range of TTHM levels measured in Australia (Simpson and Hayes 1998) and in Mediterranean area (Alacant and Barcelona) of Spain (Villanueva et al. 2003). Comparisons with concentrations measured in Ankara and Istanbul will be made in the next section.

Kavcar et al. measured tap water THM concentrations in 100 grab samples collected from all over the Province of İzmir according to geographical population distribution through August to December, 2004, and estimated associated risk levels. The median TTHM concentration was about three times less than the overall median concentrations of the urban area measured in this study. Higher levels and larger range of concentrations measured in this study indicated that seasonal variation is an important factor in İzmir, therefore the estimated human health risk values should be revised taking the seasonal variation into account (Kavcar et al. 2006).

4.2.1. Variation in DBP Concentrations by Water Source

The five selected sampling points in this study represented three different water sources. While the Tahtalı and Balçova Resorvoirs are surface water, drinking water source of the Urla district is ground water. Detection frequencies of DBPs for each sampling location are given in Table 4.4. For all compounds detection frequencies were found to be the highest at Hatay where drinking water is supplied from TWTP. While CF was detected in all samples from all sampling locations, TCAN was detected with the lowest frequency, and it was not detected in any of the samples from Urla. All water samples from Hatay and Güzelbahçe contained all THM species.

Table 4.4. Detection frequencies (%) of DBPs at each sampling location

DBPs	Hatay	Balçova	Narlıdere	Güzelbahçe	Urla
CF	100	100	100	100	100
BDCM	100	100	100	100	14
DBCM	100	100	98	100	100
BF	100	98	98	100	100
TCAN	86	77	62	76	0
DCAN	100	100	100	100	98
BCAN	100	100	98	100	77
DBAN	98	93	91	100	100
1,1,1-DCP	98	98	96	96	7
1,2-TCP	100	96	96	100	2
CP	91	80	73	80	0

The descriptive statistics for each water source are listed in Table 4.5. All comparisons made for the variation by source consider the five months period in which two plants were in operation.

The highest concentrations of TTHMs, THANs and HKs were measured at Hatay, where drinking water is supplied from Tahtalı Reservoir. The lowest concentrations were measured in Urla. All DBPs concentrations in Urla were below 20 µg/L since the source of the water is ground water, which has much lower organic matter content compared to surface waters being naturally protected from run-off water. The mean, median and minimum concentrations of DBPs for Tahtalı Reservoir were found to be higher than those for Balçova Reservoir. The high occurrence of DBPs for Tahtalı reservoir may be related to relatively higher NPOC concentrations in raw water as well as high pre- and post-chlorine doses applied during drinking water treatment. These findings were also in agreement with the results of the study by Ates et al. (2006) which reported 87 µg/L and 63 µg/L annual average concentrations of TTHMs in water samples from Tahtalı and Balçova Reservoirs, respectively, chlorinated at the laboratory.

Table 4.5. Descriptive statistics for DBP concentrations across water sources

DBPs	S[a]	N	Mean	Median	SD	Min	Max	90th %ile[*]	95th %ile[*]
TTHMs	1	21	88.95	84.20	20.34	39.98	124.9	115.3	124
	2	21	45.84	44.35	16.75	19.94	87.36	68.59	85.64
	3	18	12.44	12.68	3.562	4.930	18.37	16.79	-
THANs	1	21	20.11	16.37	10.37	7.36	43.55	38.31	43.12
	2	21	12.66	11.60	9.159	2.853	41.19	21.92	39.29
	3	18	4.857	5.782	3.497	0.240	10.35	9.726	-
HKs	1	21	4.10	4.322	2.425	0.56	9.06	7.398	8.904
	2	21	2.725	2.963	1.594	0.330	5.460	4.911	3.855

All concentrations are in µg/L
N: Sample size, SD: Standard deviation
[a] Water source, *Percentile

(1): Tahtalı Reservoir
(2): Balçova Reservoir
(3): Ground Water

When we compared the TTHM levels with regulatory standards, one of the 45 samples from the distribution system of TDWTP exceeded the maximum contaminant level stated in Turkish drinking water regulations (150µg/L). However, 41 % of the samples were not in attainment of the maximum contaminant level (100 µg/L) which will come into effect by the year 2012. In addition, 61 % of the samples were found to exceed the maximum contaminant level of USEPA (80µg/L). In the case of BDWTP, while all TTHM concentrations comply with the Turkish drinking water regulations, one sample exceeded the EPA's limit.

The species distributions of THMs and HANs were also evaluated for each water source. As seen in Figure 4.6, CF was the most abundant THM compound followed by BDCM, DBCM and BF, for samples from Tahtalı and Balçova reservoirs, a result in agreement with Ates et al. (2006). The composition was similar for the two reservoirs with approximately 50%, 23%, 24% and 4%, for CF, BDCM, DBCM and BF, respectively. However, chloroform was found to be major THM species in drinking water of Ankara, being 90- 95 % of the TTHMs (Tokmak et al. 2004) probably due to low bromide ion level in raw water. When we compared the mean concentrations of four THM species with those reported for İstanbul tap water (Toroz and Uyak 2005), all concentrations were found to be lower in İzmir except for CF, although the annual average concentration of bromide ion in İzmir (0.26 mg/L) was higher than that of İstanbul (0.19 mg/L).
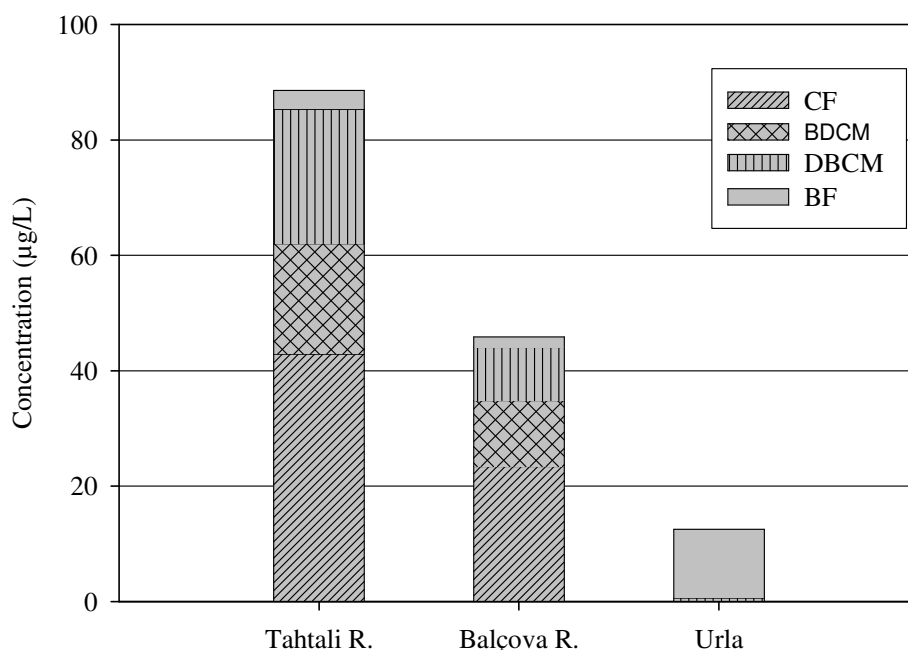
Figure 4.6. Species distribution of THMs across water sources

In Urla, because of extremely high bromide ion level (1.1-3.4 mg/L), concentration of BF contributed to about 95 % of total THMs. However, for Hatay samples, concentrations of BF accounted for only 3 % of TTHMs, which can be related to low bromide ion level (0.24 mg/L) in the raw water of TDWTP. The increase in brominated species in the presence of high bromide ion level in water being chlorinated can be attributed to higher reactivity and haloform substitution efficiency of bromide ion (Westerhoff et al. 2004).

Distribution of HAN species for tap water from Tahtalı and Balçova reservoirs along with Urla are shown in Figure 4.7. As in the case for THM speciation in Urla, brominated compounds, DBAN and BCAN, were found to be predominant species which constituted 97 % and 2 % of the THAN concentration, respectively. However, due to low bromide ion level (<0.25 mg/L) in both Tahtalı and Balçova reservoirs, DCAN was found to be the major HAN specie, as suggested by Kim et al. (2002). In addition, when we assessed the compliance of HANs to World Health Organization (WHO 2004), which proposed guideline values of 20 and 70 µg/L for DCAN and DBAN, respectively, the concentrations of these compounds in all samples were in attainment of the guideline values.
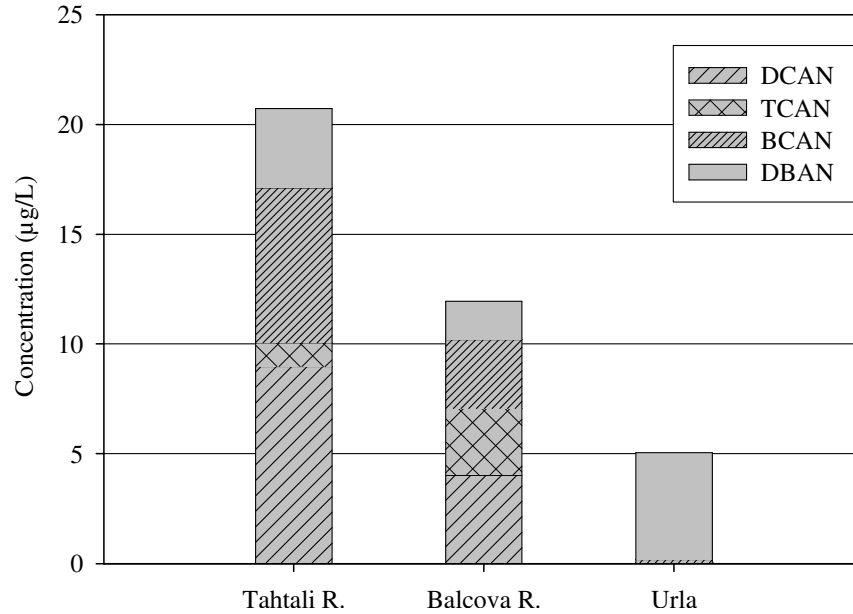
Figure 4.7. Species distribution of HANs across water sources

Bromine incorporation factor, n(Br), is the moles of bromine incorporated into a class of DBP species (e.g. THMs or HANs) per total moles of species formed and varies from 0 to 3 depending on the degree of bromine substitution on THMs. In order to evaluate the effect of bromide ion on THM and HAN speciation, n(Br) is calculated according to equation 2.12, for these DBP groups measured in tap water from each water source, and shown in Figure 4.8. n(Br) levels were found to be comparable for Tahtalı and Balçova reservoirs. However, the n(Br) for both THMs and HANs in Urla tap water was found to be about 3-4 times higher than those for the other sources, with the mean levels of 2.9 and 1.9 for THMs and HANs, respectively. Similarly, high n(Br) levels for THMs (2.01-2.30) were obtained for coastal cities while lower levels (0.54-1.11) were found for non-coastal cities in Greece (Kampioti and Stephanou 2002). In another study, n(Br) values of 0.69 and 0.35 were reported for tap water samples from ground water and surface water, respectively (Kawamoto and Makihata 2004).
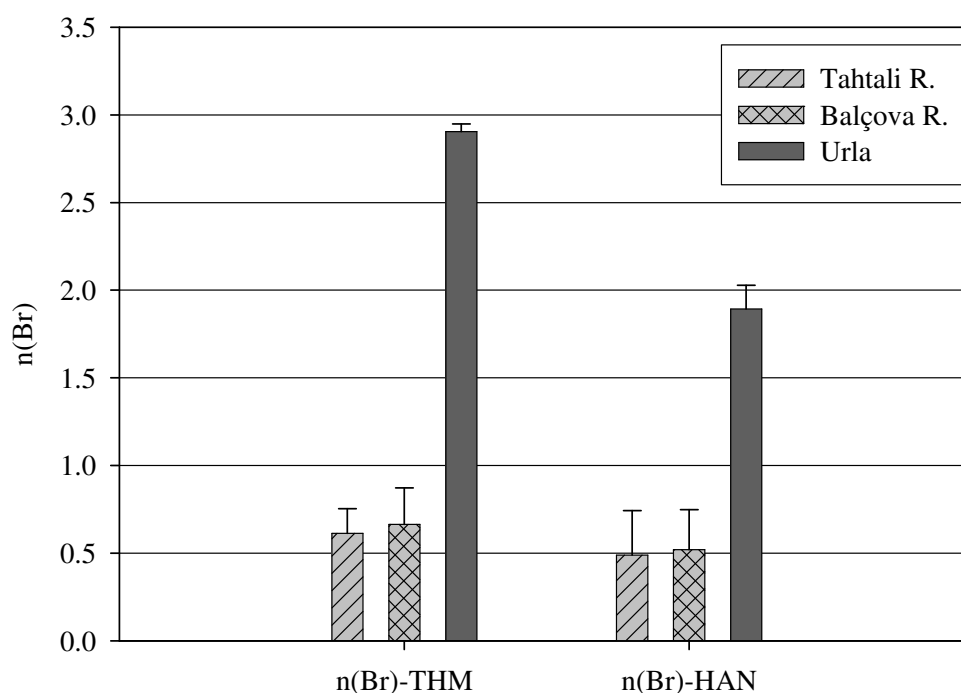
Figure 4.8. Bromine incorporation factors according to water sources (Error bars show one standard deviation)

Average concentrations of all DBPs for TDWTP were nearly identical for the whole sampling period and five months in which both plants were in operation. Therefore, in both cases all comparisons made by source reveal identical results.

4.2.2. Seasonal Variation in DBP Concentrations

In order to investigate the seasonal variation in DBP concentrations, tap water samples were collected during summer (July and August), fall (September, October, November), winter (December, January, February) and spring (March and April). The descriptive statistics, which were calculated as seasonal average concentrations of four of the five sampling locations (Hatay, Balçova, Narlıdere and Güzelbahçe) are listed in Table 4.6. Since the water source of Urla is ground water, which has a stable water quality in terms of seasonal variation, the concentrations from Urla was not included in the analysis. In addition, DBP concentrations which were measured in Balçova, Narlıdere and Güzelbahçe on the dates when the BDWTP was not in operation are not

included in the analysis.

While the highest DBP concentrations were measured in spring, lowest were detected during summer. The mean THM concentration in spring was significantly higher than fall (p=0.001). The difference between mean concentrations in spring and winter was also significant (p=0.016).

Table 4.6. Seasonal descriptive statistics for DBPs

Season	DBPs	N	Mean	Median	SD	90th %ile[*]	95th %ile[*]
Summer	TTHMs	15	56.94	59.35	27.60	19.94	94.56
	THANs	15	7.739	8.928	3.652	2.853	12.11
	HKs	15	1.444	0.818	2.148	0.338	9.058
Fall	TTHMs	13	78.74	72.47	20.06	57.11	128.8
	THANs	13	13.19	12.39	5.267	7.460	25.99
	HKs	13	2.680	2.756	1.135	0.716	4.468
Winter	TTHMs	26	73.88	70.30	26.32	39.96	125.0
	THANs	26	18.99	17.81	8.575	6.470	43.55
	HKs	26	4.426	4.236	1.264	2.610	7.520
Spring	TTHMs	11	121.0	126.1	38.66	30.41	183.0
	THANs	11	35.91	35.84	7.211	22.18	49.31
	HKs	11	5.059	4.833	2.053	1.607	9.330

All concentrations are in µg/L, N: Sample size, SD: Standard deviation, *Percentile

The seasonal variation in TTHM and THAN concentrations for the three water sources is illustrated in Figures 4.9a and 4.9b. The high TTHM concentrations were measured in spring (15.41 µg/L) whereas lowest were measured in summer and fall (mean; 9.99 µg/L and 11.78 µg/L, respectively) at Urla sampling point. Similar trend was observed for TDWTP, highest THM occurrence at Hatay in spring (134.86 µg/L) and lowest in summer (78.84 µg/L). The increase in THM formation during spring was mainly due to relatively high raw water NPOC concentration (4.00 mg/L) compared to other seasons (<3.76 mg/L). In addition, TTHM levels in winter were found to be higher than in summer, which is an unexpected situation since many studies reported maximum THM formation in summer (Williams et al. 1998, Rodriguez et al. 2004, Toroz and Uyak, 2005). High THM formation in winter was probably due to relatively

higher treated water NPOC concentrations (mean, 3.32 mg/L) in winter compared to summer (mean, 3.08 mg/L) among other possible factors. Supporting the result of this study, Ates et al. (2006) reported higher THM concentrations in water samples collected during winter from Balçova and Tahtalı reservoirs than in summer, chlorinated in laboratory conditions at constant temperature.

In the case of Balçova Reservoir, which generally supplies drinking water for only three seasons, the trend for seasonal variability of TTHMs was similar to the Tahtalı reservoir. BWTP served for only July, August, December, January and February months in the 10 month study period. The lower TTHM levels were measured in tap water supplied from Balçova reservoir, since both pre- and post-chlorination doses were much lower for BDWTP although the NPOC levels of raw and treated waters of these two plants were comparable.

Kruskal-Wallis test was used to determine whether the seasonal variation in concentrations of THMs is statistically significant. For TDWTP and BDWTP, p-values for all THMs were found to be lower than 0.05 which suggests significant variability with seasons. In the case of Urla, the p-values for all detected compounds were below 0.003 except for CF (p= 0.33), indicating that seasonal variation is not significant for only CF. As seen in the Figure 4.9b, the seasonal trend for THAN concentrations was similar to TTHMs, increasing from summer to spring. However, the seasonal differences in THAN concentrations were found to be higher than TTHMs. Kruskal-Wallis test also resulted in lower p-values for THANs (i.e, 10^{-6}, 0.001, and 10^{-5} for TDWTP, BDWTP, and Urla, respectively) indicating that the differences in THAN concentrations were more significant than TTHMs.
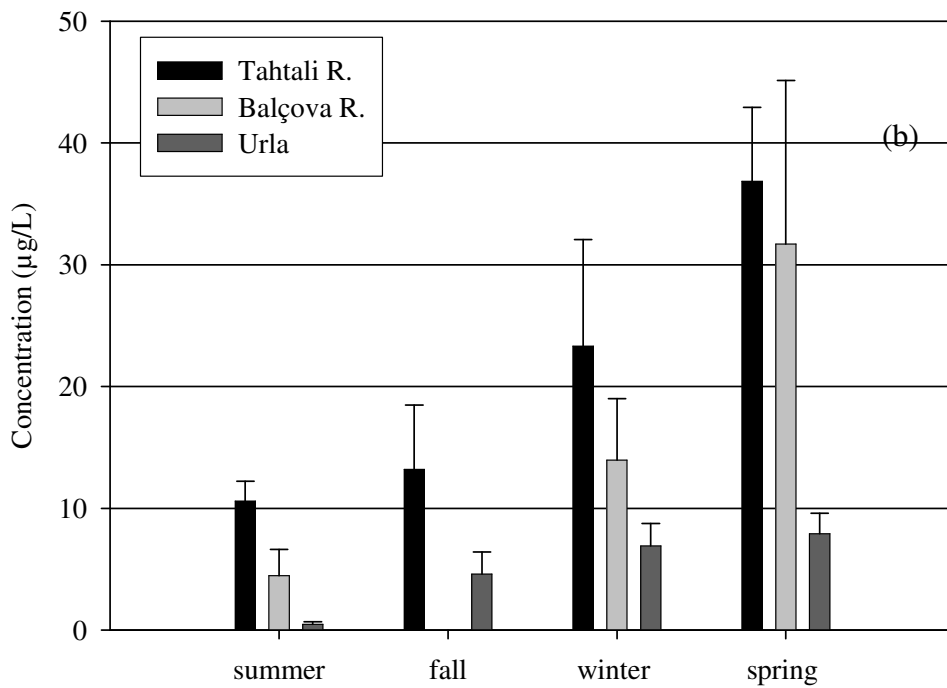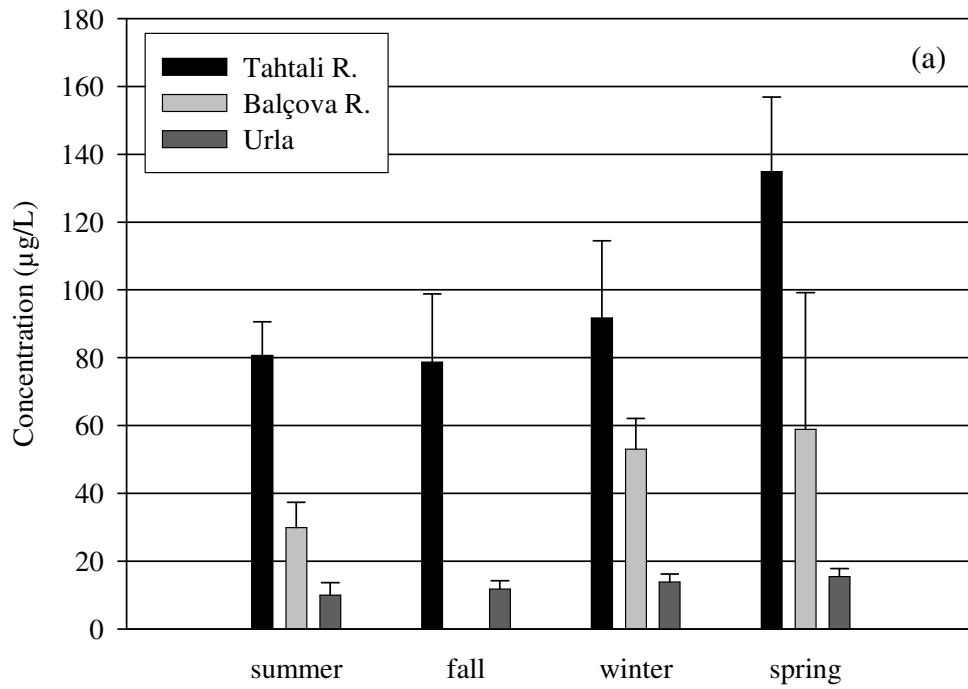
Figure 4.9.   Seasonal variation in (a) TTHM (b) THAN concentrations (Error bars show one standard deviation)

In addition to seasonal variations, the data collected during this study permitted the identification of relatively important intra-seasonal variations in DBP concentrations, since the water samples were collected weekly from each sampling point. Moving average graphs for the temporal variation in THM concentrations in tap water samples from the distribution system of TDWTP, BDWTP and Urla are presented in Figures 4.10a through 4.10c.

For THM concentrations from the distribution systems of TDWTP and Urla, an increasing trend was observed from July to April, although short-term fluctuations were also observed. In the case of BDWTP, the concentrations were found to be more variable throughout the sampling period since the system was supplied with drinking water from different water sources when the plant was not running. The intra-seasonal variation in DBP concentrations, as suggested by Rodriguez et al. (2004), was probably due to considerable changes in operational and water quality parameters which affect the formation and evolution of DBPs
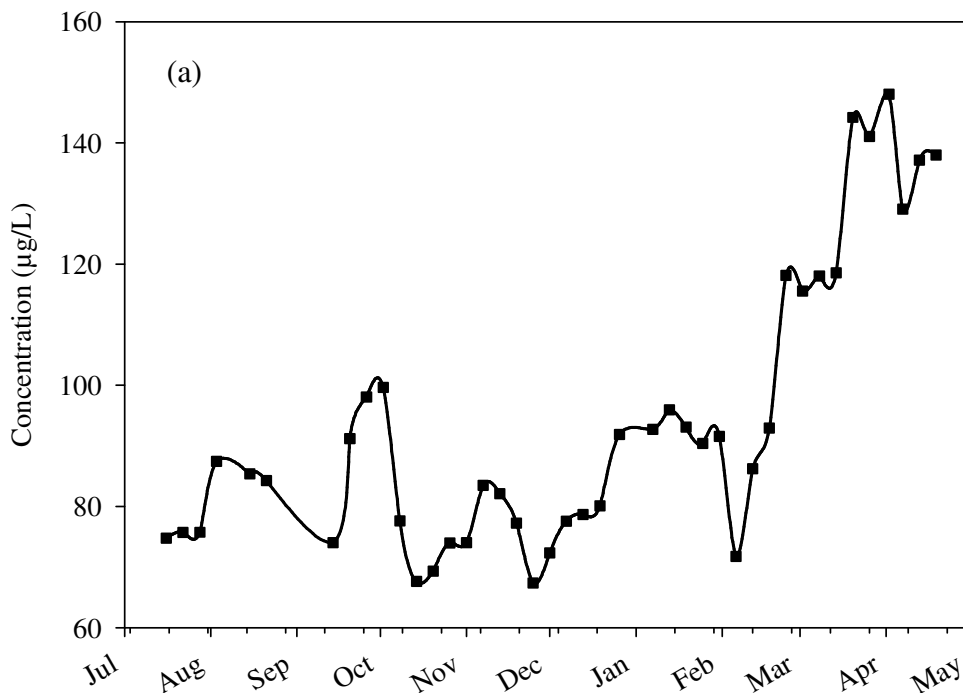

Figure 4.10. Temporal variation of TTHMs (a) in distribution system of TDWTP
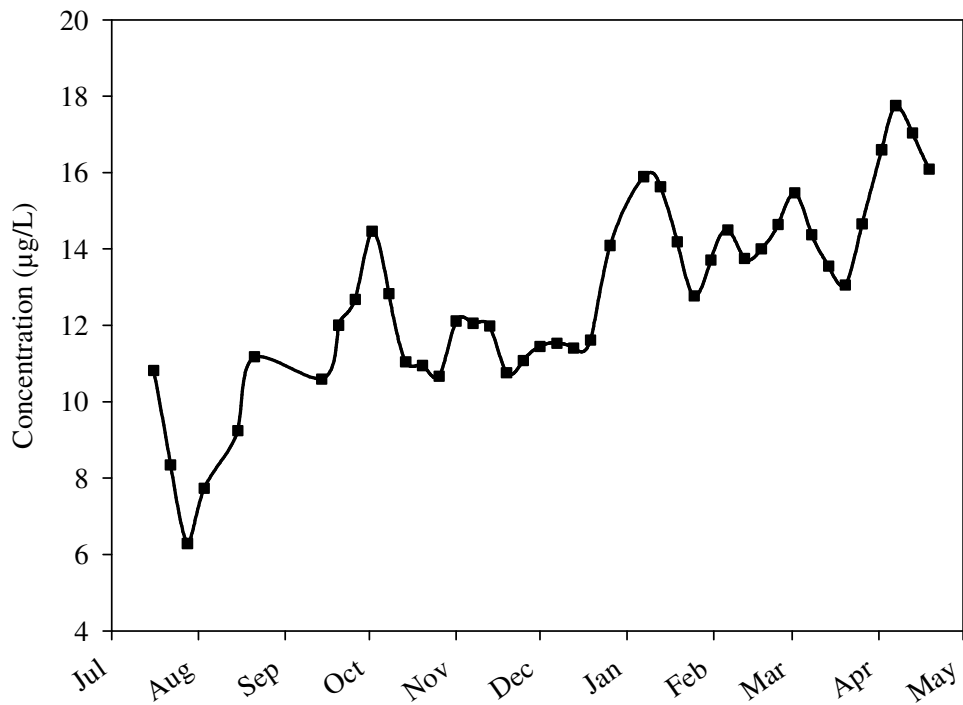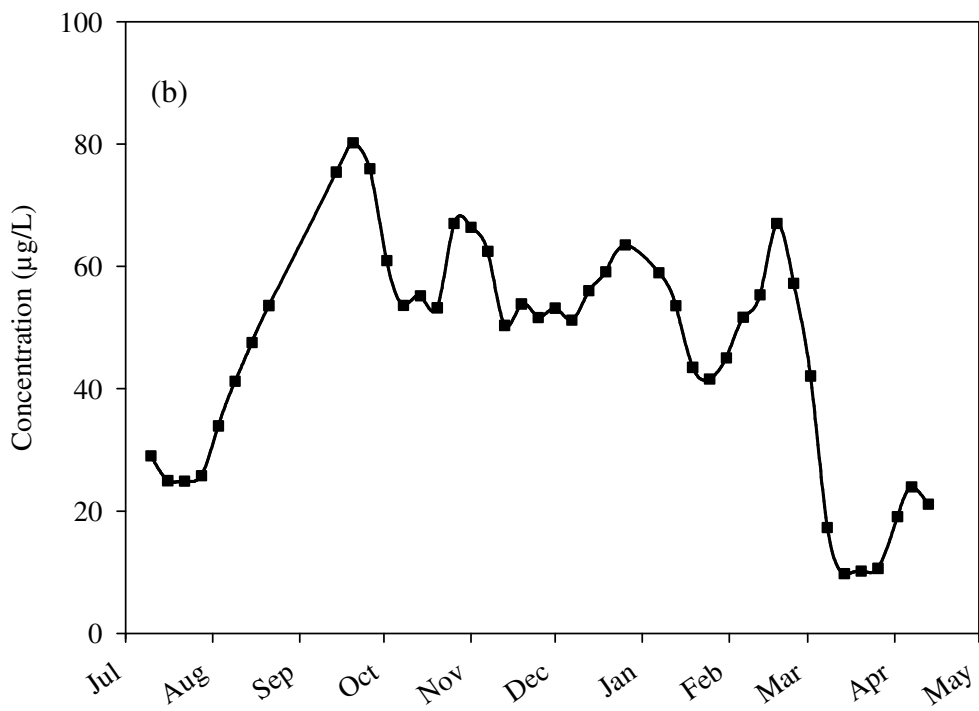
Figure 4.10. Temporal variation of TTHMs in (b) BDWTP (c) Urla

Water temperature is an important parameter affecting DBP formation and speciation since it influences formation reactions and volatility of DBP as well as the reactions of chlorine in drinking water. In this study, while the raw water temperature at TDWTP was above 17 $^{\circ}$C (the median value) during summer and the first half of the fall, it was below 17 $^{\circ}$C during second half of the fall, winter and spring. In addition, over the sampling period the difference between the minimum and maximum temperature was about 14.8 $^{\circ}$C. In order to determine the effect of temperature on DBP formation and speciation, mean DBP concentrations at both below and above 17 $^{\circ}$C was calculated for TDWTP and presented in Figures 4.11a and 4.11b.

As seen in the first graph, the concentrations of all THM species were lower at water temperatures above 17 $^{\circ}$C except for CF and the two sample t-test revealed that the difference in mean concentrations of all THMs were significant ($p<0.05$) except for TTHMs ($p=0.16$). Also, concentrations of brominated THMs decreased about 33 % when the temperature exceeded 17 $^{\circ}$C. These findings were not consistent with the literature since many studies reported increased levels of THMs with temperature (Villonava et al. 1997, Rodriguez et al. 2001).

In the case of HANs, concentrations of all compounds and total HANs were found to be lower at water temperatures above 17 $^{\circ}$C. The highest difference was observed in concentration of TCAN, which decreased about 97 % when the temperature exceeded 17 $^{\circ}$C. The percent difference between the total HAN levels, which is calculated as 47 %, was also high compared to TTHMs. The differences in mean HAN concentrations were found to be statistically significant except for DCAN ($p=0.65$).

The decrease in DBP levels with temperature may be associated with the volatility of these compounds since they are all volatile organic compounds, may be related to raw water quality and operational parameters, or could be due to the unusual climatic conditions during the sampling campaign.
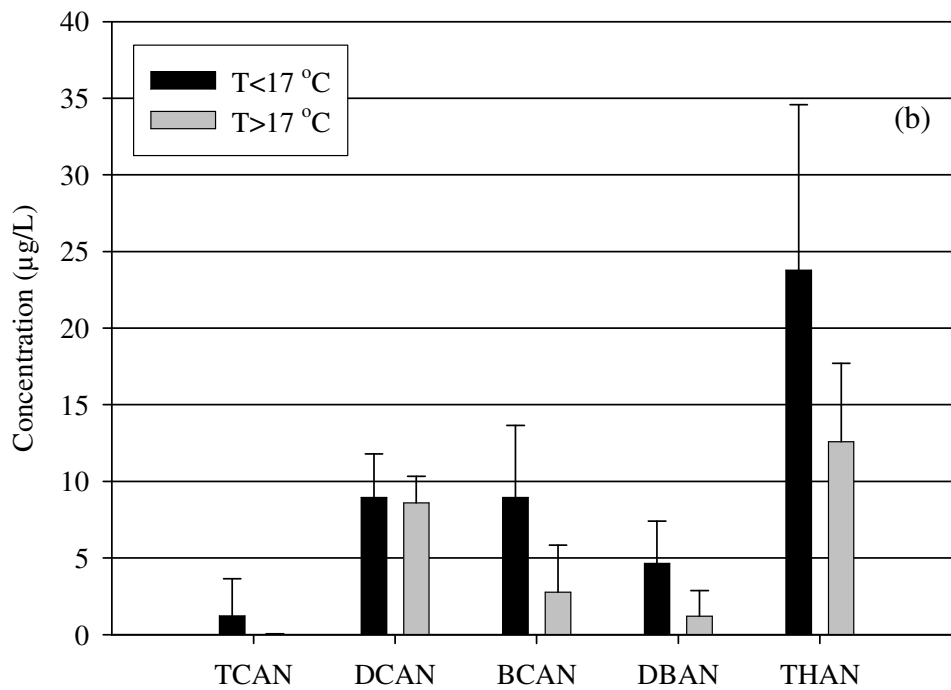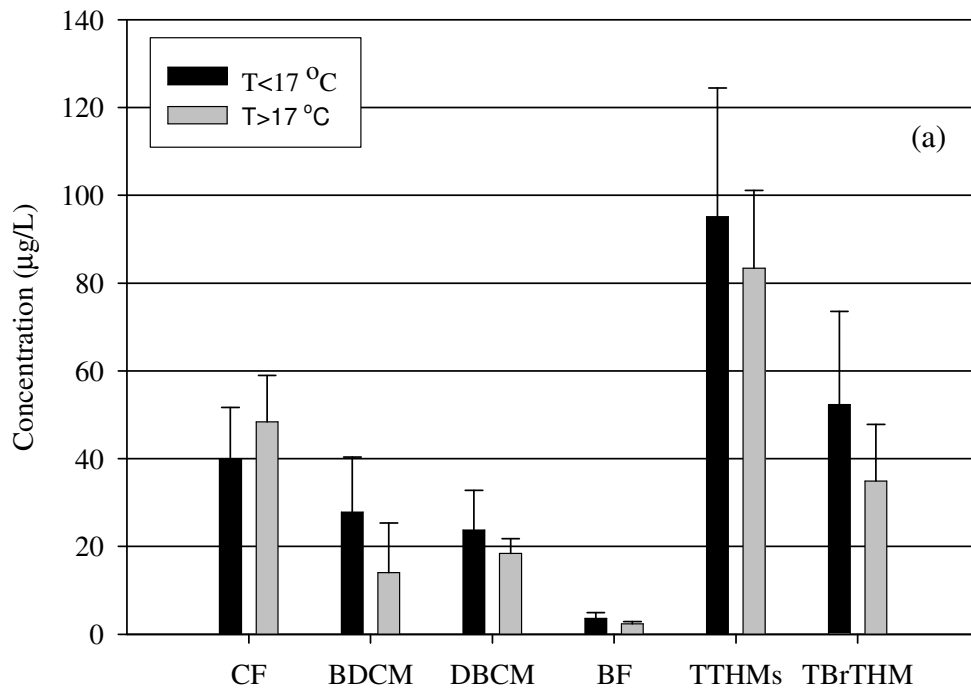
Figure 4.11. Effect of temperature on (a) THMs (b) HANs (Error bars show one standard deviation)

4.2.3. Spatial Variation in DBP Concentrations

In order to investigate spatial variation in DBP levels in the distribution system, tap water samples were collected from three sampling points (Balçova, Narlıdere, and Güzelbahçe) on the same main line with increasing residence times (see Figure 3.1). As illustrated in Figure 4.12, the highest concentration of THMs, HANs and HKs were measured in Güzelbahçe, which represents the system extremity. However, the results of the Kruskal-Wallis test indicated that the difference in all DBP concentrations with residence time were not significant except for DBCM and BF ($p<0.05$). In addition, two sample t-test was applied in order to compare the three sampling locations individually. The result of this test revealed that the difference in mean DBP concentrations between Balçova and Narlıdere, and Güzelbahçe and Narlıdere were not different, whereas mean HAN concentrations were found to be different in Balçova and Güzelbahçe ($p=0.037$). Also, the difference in mean THM concentrations was larger between Narlıdere and Güzelbahçe ($p=0.94$) than Balçova and Narlıdere ($p=0.87$), because of the booster chlorination applied between Narlıdere and Güzelbahçe districts. These findings were also in accordance with the other studies that reported increasing levels of DBPs with residence time (Lebel et al. 1997, Rodriguez and Serodes 2003).
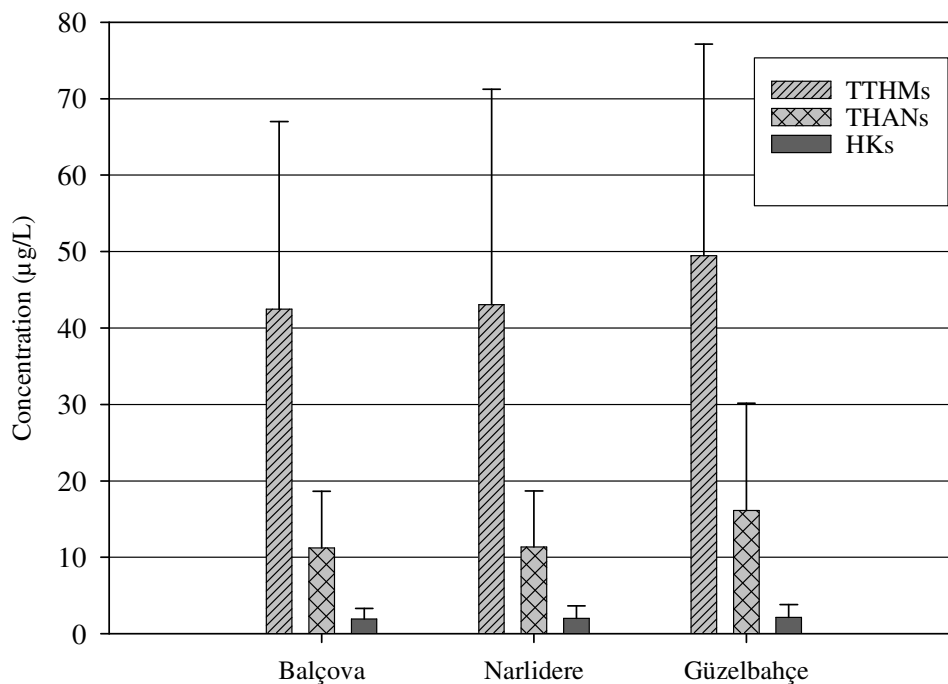

Figure 4.12. Spatial variation of DBPs (Error bars show one standard deviation)

Throughout the sampling period, the concentration of free residual chlorine (FRC) was also measured at each sampling point. The variation in FRC concentrations across sampling locations is presented in Figure 4.13. In Hatay, the concentration of FRC was very low possibly due to high DBP formation which resulted in high chlorine consumption. The mean concentrations of FRC in Balçova, Narlıdere and Güzelbahçe were found to be higher than the sufficient level (0.2 mg/L) for microbial inactivation (USEPA, 2006a). In addition, a notable increase in the FRC concentration was observed in Güzelbahçe due to re-chlorination of drinking water before this sampling location.
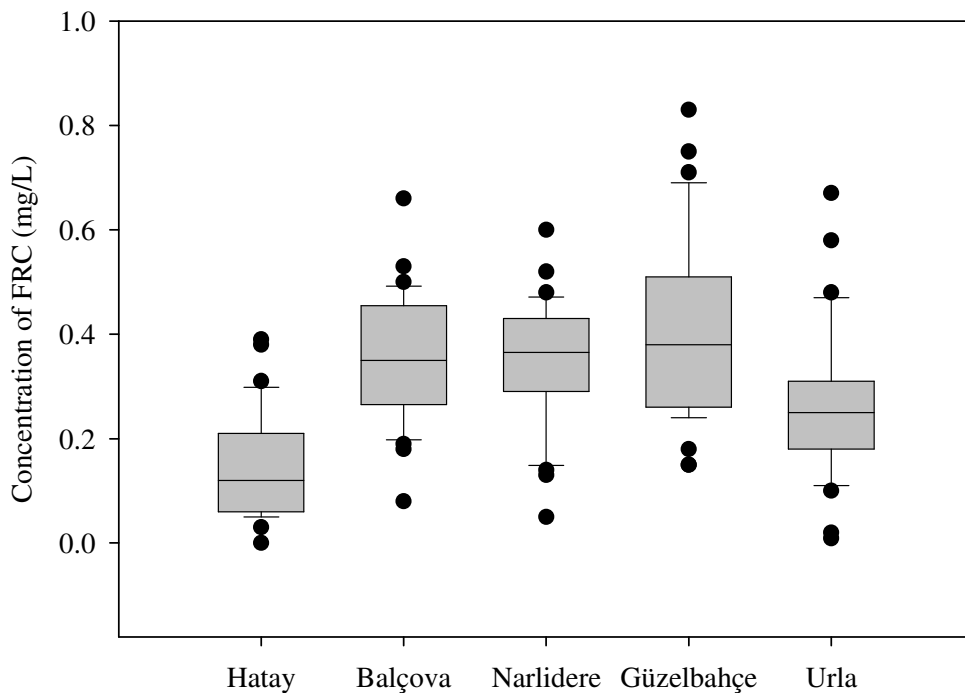
Figure 4.13. Variation in FRC concentration across sampling locations

4.3. Statistical Modeling of DBP Concentrations

The statistical modeling of DBPs was conducted to identify the most important parameters responsible for the variations of DBPs at the tap. In the following sections, results of the multivariate regression analysis and logistic regression are discussed. Diagnostics about the models followed the regression analyses.

4.3.1. Multivariate Regression Analysis

In this study, multivariate regression analysis was conducted to construct statistical models in which concentrations of DBP from Hatay were used as dependent variable while the parameters measured at TWTP, including pH, temperature, NPOC, chlorine dose and bromide ion concentration were used as independent (explanatory or predictor) variables. Before constructing the models, all dependent and independent variables were tested for normality by using one-sample Kolmogorov-Smirnov test and all p-values were found to be higher than 0.05, which does not provide enough evidence for rejecting the null hypothesis that the data follow normal distribution.

Before including the variables into a model a scatter plot matrix was constructed to visually identify the relationship between independent variables (NPOCo and NPOCi: Concentrations of Non-purgeable organic carbon in raw water and treated water, respectively; $preCl_2$ and $totCl_2$: Pre- and total chlorine doses). As seen in Figure 4.14, there is a positive correlation between temperature and chlorine doses (pre, final and total chlorine), which is possibly due to high chlorine doses are required at high water temperature as discussed in section 4.1.1.
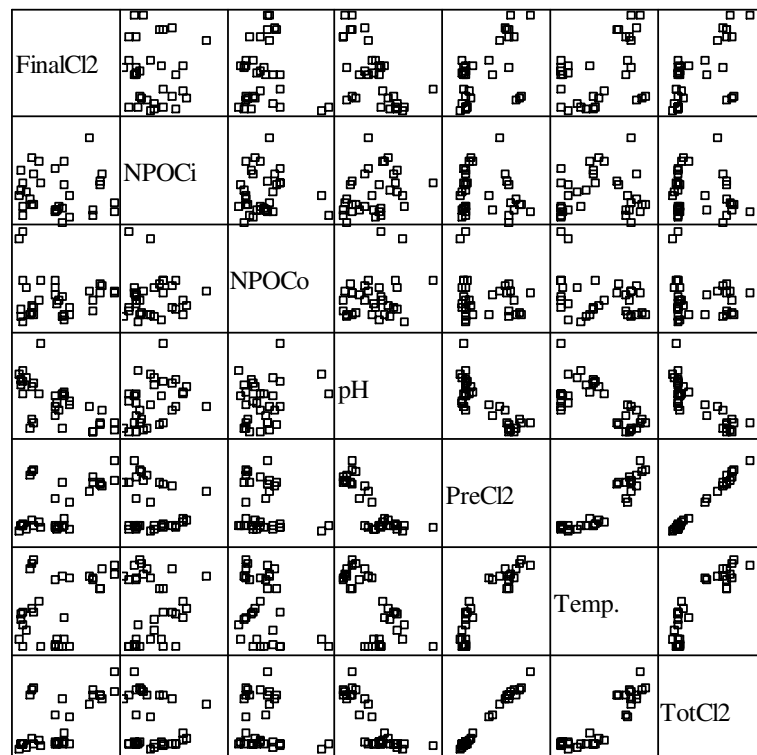

Figure 4.14. Scatter plot matrix for input variables

In contrast, pH level of the water was negatively correlated with both chlorine doses and temperature. The correlation matrix was also constructed in order to assess the strength of the relationship between all the variables and is presented in Table 4.7. Temperature was correlated with pH, pre-chlorine dose and total chlorine dose, whereas pH was correlated with pre-, final and total chlorine doses. Since these parameters do not appear statistically independent, it is difficult to identify their individual effect on DBP occurrence in the distribution system. Therefore, for the input variables highly correlated with each other, product terms (e.g., $temp*preCl_2$) were involved in the models in order to consider the interaction among independent variables.

The concentration of NPOC in both the raw and treated waters was poorly correlated (r<0.3) with DBP concentrations, which is an unexpected situation since the organic matter is the major precursor material for DBP formation. The water temperature, which is reported to be the most significant parameter for DBP formation (Golfinopoulos 1998, Golfinopuolos and Arhonditsis 2002), showed a positive corelation with only CF.

In contrast, the pH level of water showed a negative correlation with only CF, which is also unexpected situation since the THM formation is base catalyzed reaction. The chlorine dose was found to have a negative correlation with all DBPs except for CF. This result was not in agreement with the literature since many studies have suggested that THM concentrations increases with the chlorine dose (Sorlini and Collivignarelli 2005, Toroz and Uyak 2005). This may be due to covariation in operational parameters. The reason for the inconsistent situations with the expected ones for the relation of THM with water temperature, pH and chorine dose may be associated with the interaction of these parameters as discussed above. Although, the bromide ion was negatively correlated with all DBPs, it was found to be positively correlated with with BF, since this compound is formed in the presence of bromide ion.

In order to develop statistical models, linear and non-linear structures (Equations 3.1 and 3.2) were tested and the resulting models are presented in Table 4.7. Non-linear models were developed by transforming all variables using the natural logarithm (ln) function and then applying linear regression. The coefficients of the determination for regression equations obtained for CF, BF, BDCM and total brominated THMs, were not satisfactory (R^2<0.5), whereas relatively high R^2 values were obtained for HANs. In other words, the THM models described about 30 % while other models (except model 7) described about 50 % of the variation in DBP concentrations.

Table 4.7. Correlation matrix for water quality and operational parameters

	CF	BF	BDCM	TTHM	TBrTHM	THAN	NPOCi	NPOCo	TEMP	pH	PreCl$_2$	FinalCl$_2$	TotCl$_2$	Br
CF	1	0.230	-0.012	0.623[**]	0.166	0.161	0.049	0.218	0.407[*]	-0.296	0.440[*]	0.109	0.424[*]	-0.126
BF	0.230	1	0.602[**]	0.764[**]	0.820[**]	0.848[**]	-0.049	0.301	-0.568[**]	0.282	-0.476[**]	-0.313	-0.478[**]	0.045
BDCM	-0.012	0.602[**]	1	0.728[**]	0.925[**]	0.825[**]	0.079	-0.138	-0.519[**]	0.237	-0.482[**]	-0.235	-0.477[**]	-0.107
TTHM	0.623[**]	0.764[**]	0.728[**]	1	0.875	0.833[**]	0.048	0.120	-0.248	0.025	-0.162	-0.131	-0.166	-0.107
TBrTHM	0.166	0.820[**]	0.925[**]	0.875[**]	1	0.951[**]	0.031	0.017	-0.565[**]	0.215	-0.478[**]	-0.232	-0.472[*]	-0.056
THAN	0.161	0.848[**]	0.825[**]	0.833[**]	0.951[**]	1	-0.09	0.097	-0.623[**]	0.167	-0.5	-0.205	-0.490[**]	0
NPOCi	0.049	-0.049	0.079	0.048	0.031	-0.090	1	-0.002	0.014	0.331	-0.192	-0.062	-0.186	-0.092
NPOCo	0.218	0.301	-0.138	0.120	0.017	0.097	-0.002	1	-0.321	0.225	-0.218	-0.068	-0.211	0.3
TEMP	0.407[*]	-0.568[**]	-0.519[**]	-0.248	-0.565[**]	-0.623[**]	0.014	-0.321	1	-0.677[**]	0.912[**]	0.418[*]	0.899[**]	-0.153
pH	-0.296	0.282	0.237	0.025	0.215	0.167	0.331	0.225	-0.677[**]	1	-0.804[**]	-0.638[**]	-0.819[**]	-0.07
PreCl$_2$	0.440[*]	-0.476[**]	-0.482[**]	-0.162	-0.478[**]	-0.500[**]	-0.192	-0.218	0.912[**]	-0.804[**]	1	0.571[**]	0.997[**]	0.007
FinalCl$_2$	0.109	-0.313	-0.235	-0.131	-0.232	-0.205	-0.062	-0.068	0.418[*]	-0.638[**]	0.571[**]	1	0.637[**]	0.384[*]
TotCl$_2$	0.424[*]	-0.478[**]	-0.477[**]	-0.166	-0.472[**]	-0.490[*]	-0.186	-0.211	0.899[**]	-0.819[**]	0.997[**]	0.637[**]	1	0.045
Br	-0.126	0.045	-0.107	-0.107	-0.056	0.000	-0.092	0.300	-0.153	-0.070	0.007	0.384[*]	0.045	1

*Correlation is significant at the 0.01 level (two-tailed) ** Correlation is significant at the 0.05 level (two-tailed). *Nomenclature:* TBrTHM: Total brominated THMs; NPOCi: NPOC concentration in raw water; NPOCo: NPOC concentration in treated water; PreCl$_2$, FinalCl$_2$, TotCl$_2$: Pre-, final and post chlorine doses, respectively.

For the bromine incorporation factors, regression equations were also developed, which have the product term of the temperature and pH as independent variable. In addition, simple regression analysis revealed a high and statistically significant correlation (R^2=0.83) between total THM and total HAN (Figure 4.15). Therefore, this model may be useful for the estimation of HAN concentrations from THMs and may find applicability in environmental and toxicology studies for assessment of human health risk of DBPs for İzmir.

Although, all regression equations were found to be statistically significant (p<0.05), the DBP concentrations could not be adequately predicted by these models due to very low R^2 values (Table 4.8). The poor determination of these models may be attributed to the effect of other parameters on DBP formation, which are water residence time, characteristics of the organic matter as well as the THM concentration at the outlet of the treatment plant, not measured in this study.

Table 4.8. Summary of multivariate regression analysis for DBPs

Model #	Regression Models	R^2	Sig.[*]	S_E[**]
1	$CF = -1.318 + 0.159(temp*preCl_2) + 10.995(NPOC_o)$	0.325	0.003	9.99
2	$BF = 5.366 - 0.018(temp*pH)$	0.334	<0.001	0.99
3	$BDCM = 86.244 - 0.217(temp*pH) - 11.757(NPOC_o)$	0.384	0.001	10.5
4	$TBrTHMs = 82.208 - 0.289(Temp*pH)$	0.315	<0.001	15.7
5	$THAN = 145.609 - 0.221(Temp*pH) - 12.534(pH)$	0.503	<0.001	7.02
6	$TBrHAN = 481.545(Temp*preCl_2)^{-1.237}$	0.495	<0.001	5.58
7	$THAN = -11.485 + 0.335(TTHM)$	0.833	<0.001	5.41
8	$n(Br)THM = 0.905 - 0.0026(temp*pH)$	0.562	<0.001	0.09
9	$n(Br)HAN = 1.036 - 0.0049(temp*pH)$	0.555	<0.001	0.17

* p-value, ** Standard error of estimate, All DBPs are in µg/L, temperature in ^oC, NPOC and preCl$_2$ dose are in mg/L
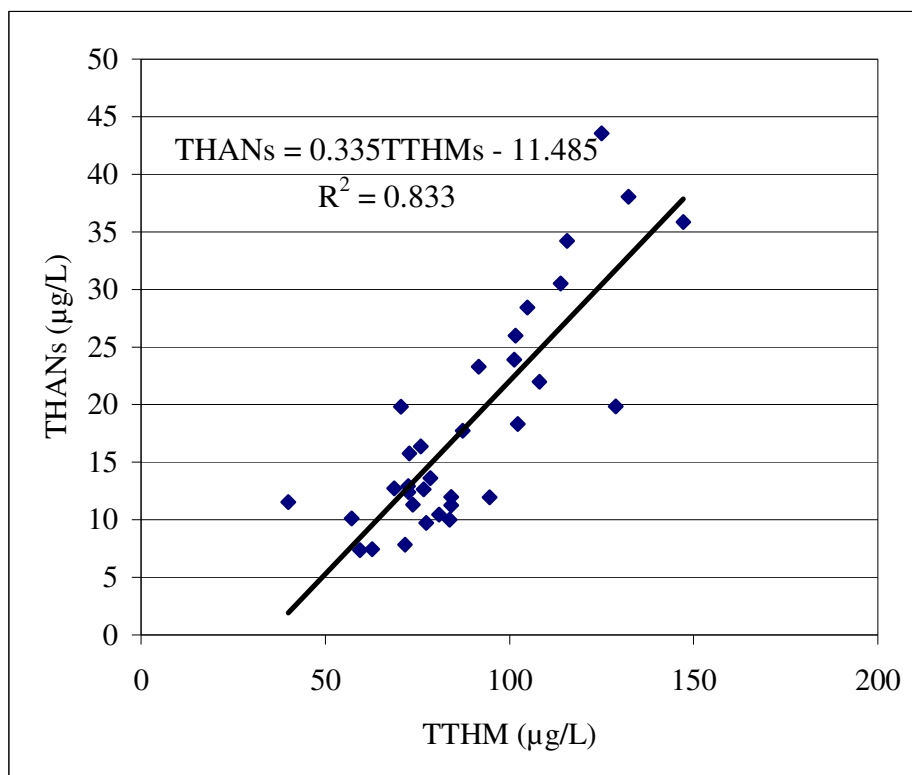
Figure 4.15. Correlation between THM and HAN levels

4.3.1.1. Residual Analysis

Residual analysis was performed in order to assess the appropriateness of the models according to behavior of the observed residuals. The residuals, which are the differences between observed and predicted values, should be independent, have zero mean, have a common variance, and follow a normal distribution (Ott 2001).

The normality of residuals from the models obtained in this study was assessed by constructing normal probability plots as illustrated in Figure 4.16. As seen in these graphs, the scatter of the points does not reflect any obvious deviation from normality. In addition, residuals were examined for homoscedasticty, as presented in Figure 4.17 and Figure 4.18, where residuals are plotted as a function of their standardized predicted Y values. As seen in these graphs, residuals have nearly constant variance and therefore the models are valid to describe the observed data.
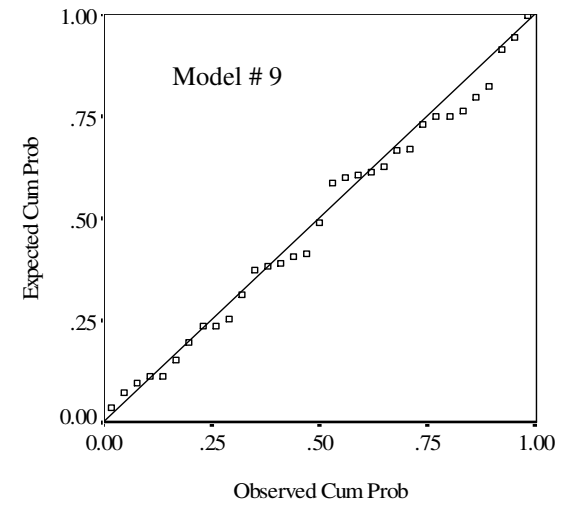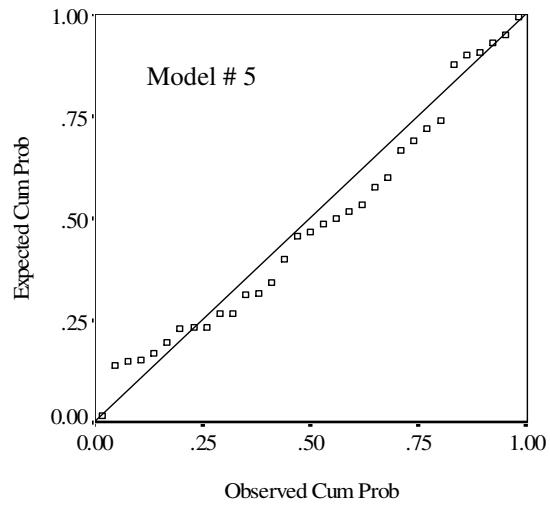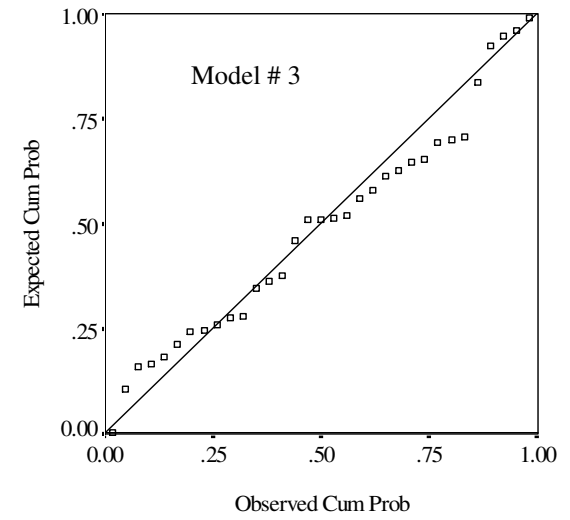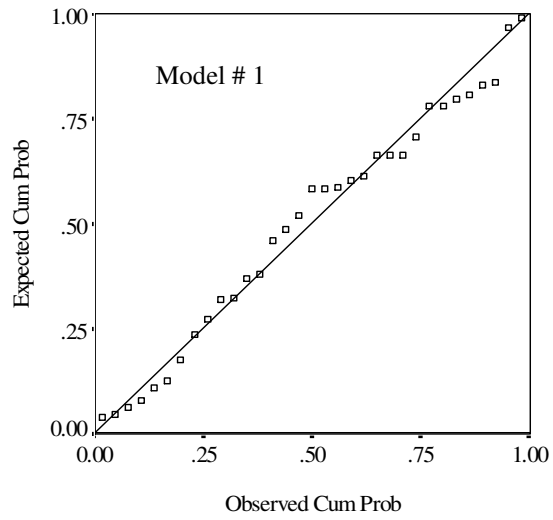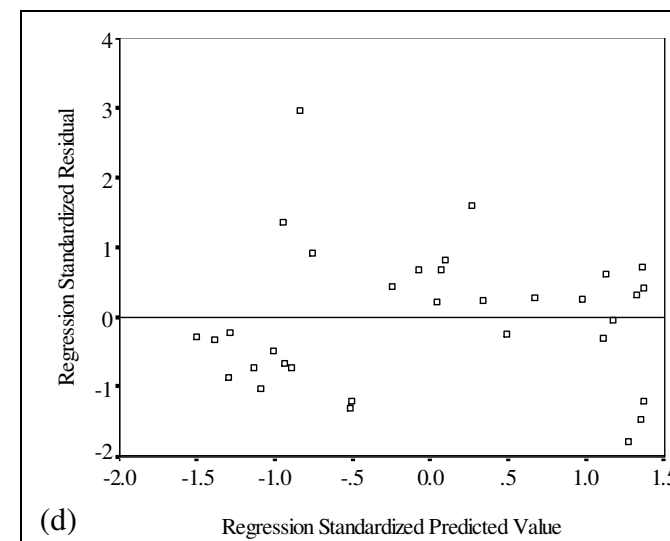
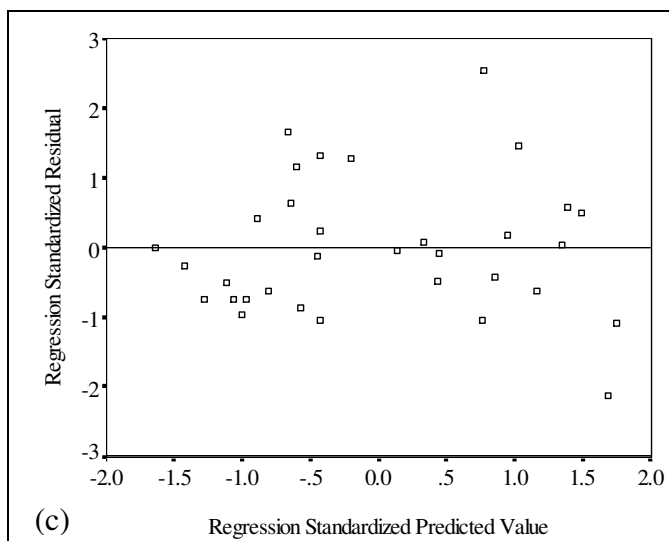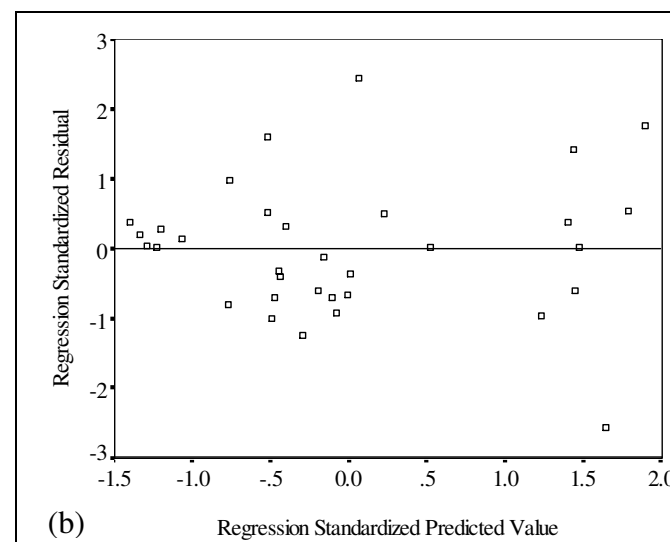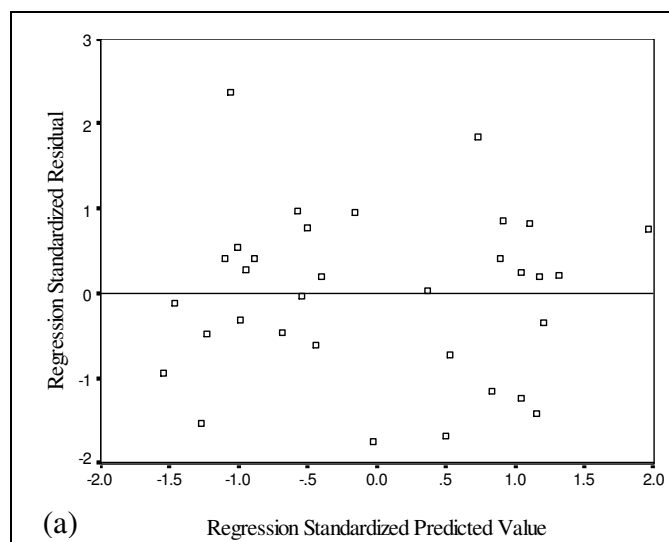Figure 4.16. Normal probability plots for selected models

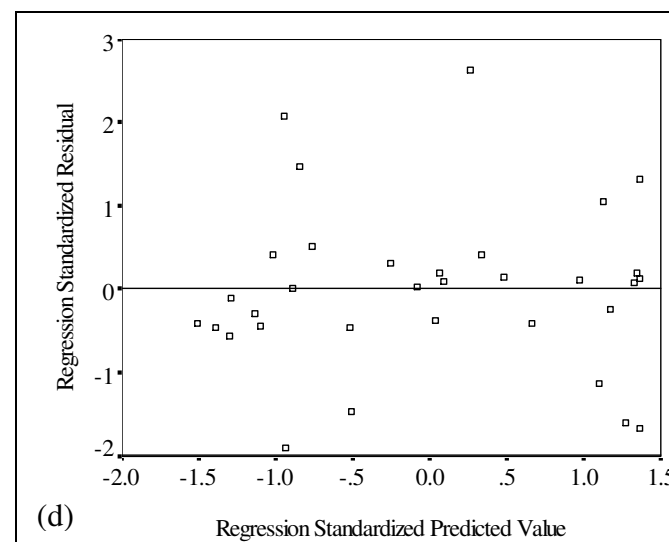Figure 4.17. Residuals vs predicted values of (a) CF, (b) THAN, (c) BDCM, (d) n(Br)HAN
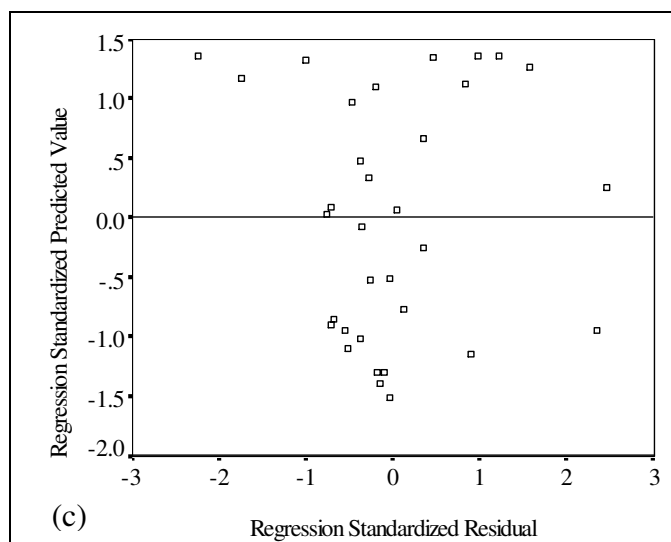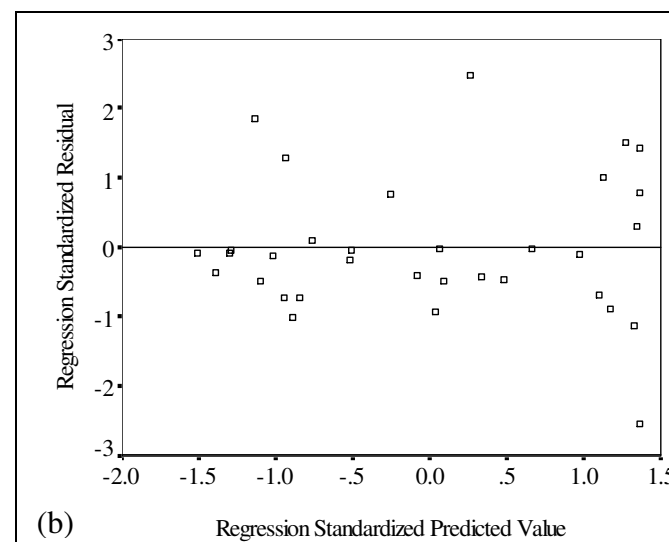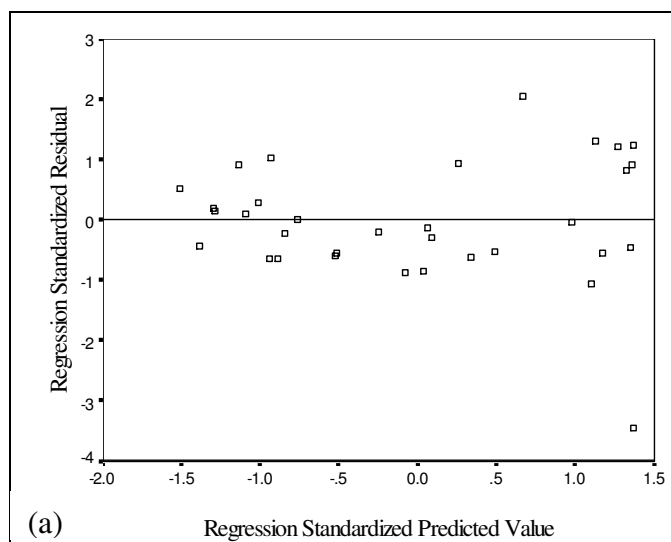
Figure 4.18. Residuals vs predicted values of (a) BF, (b) TotBr-THM, (c)TotBr-HAN, (d) n(Br)THM

4.3.2. Logistic Regression Analysis

Logistic regression analysis was performed to estimate the susceptibility of TDWTP to generating high levels of THMs. This analysis was aimed at estimating the probability to exceed THM thresholds based on water quality and operational parameters. Logistic regression models were developed for THM threshold levels of 80 and 100 µg/L as well as the mid-level of two thresholds (90µg/L). Explanatory variables used for modeling were raw and treated water NPOC levels, pH, temperature, pre-, final and total chlorine doses. In addition, interaction terms were also used as in the case for multivariate regression analysis.

First, logistic regression models were developed for each threshold and by using each explanatory variable. The statistical significance of the variables was assessed by using the χ^2 values, which measure the ability of the model to adapt and adjust to available observations. The models were developed by using the results of univariate regression models for each of the independent variables. Then, regression models were obtained by adding the variable of the univariate model with the second highest χ^2 and so on, to the univariate model with the highest value for χ^2.

Table 4.9 presents the χ^2 and p-values of models based on water quality and operational parameters. The results obtained for 80 µg/L threshold were not satisfactory. The χ^2 values for this threshold were considerably lower than χ^2 of models of other thresholds. All p-values were higher than 0.05 indicating that the models were not statistically significant for 80 µg/L. For 90 µg/L threshold temperature and the cross product term of temp*pH were found to be statistically significant parameters (p<0.05). Therefore, a two variable logistic regression model was developed for this threshold and the p-value of the final model was 0.021.

In the case of for the 100 µg/L threshold, results were quite satisfactory in spite of the fact that threshold is situated at the extreme end of THM distribution. The final model for this threshold included five independent variables and three of them were interaction terms. It is also important to note that each time an explanatory variable is added, model precision also increases. This may be observed in systematic increase of the value of χ^2. Highest χ^2 values were obtained for the models with maximum number of variables.

Table 4.9. Values of χ^2 for each selected thresholds

Explanatory Variables	Threshold (µg/L)		
	80	90	100
NPOCi	0.057	1.263	0.685
	(0.811)	(0.261)	(0.408)
NPOCo	1.486	2.986	2.309
	(0.223)	(0.084)	(0.129)
pH	0.03	0.011	0.003
	(0.863)	(0.918)	(0.955)
Temp	0.19	4.477	5.964
	(0.662)	(*0.034*)	(0.015)
PreCl$_2$	0.156	1.919	3.566
	(0.683)	(0.166)	(0.059)
FinalCl$_2$	0.128	0.837	1.688
	(0.721)	(0.360)	(0.194)
TotCl2	0.165	1.941	3.63
	(0.684)	(0.164)	(0.057)
pH*preCl$_2$	0.164	2.183	4.051
	(0.685)	(0.139)	(*0.044*)
pH*TotCl$_2$	0.145	0.156	4.265
	(0.465)	(0.678)	(*0.039*)
pH*Temp	0.213	5.119	6.788
	(0.645)	(*0.024*)	(*0.009*)
PreCl$_2$*Temp	0.079	2.396	4.315
	(0.778)	(0.122)	(*0.038*)
TotCl$_2$*Temp	0.097	2.641	4.654
	(0.755)	(0.104)	(*0.031*)
Temp + (pH*Temp.)	-	7.776	10.062
		(*0.021*)	(*0.007*)
Temp + (pH*Temp.) + (TotCl$_2$*Temp.)	-	-	13.362
			(*0.004*)
Temp. + (pH*Temp) + (TotCl$_2$*Temp.) + (pH*TotCl$_2$)	-	-	14.019
			(*0.007*)
Temp. + (pH*Temp.) + (TotCl$_2$*Temp.) + (pH*TotCl$_2$) + TotCl$_2$	-	-	15.537
			(*0.008*)

Note: Numbers in parentheses are p-values. Blanks within the table are result of methodology for model development. Models for each threshold consider different order of variable inclusion according to obtained χ^2 values.

The logistic regression models obtained for 90 and 100 µg/L are presented in Table 4.10. The χ^2 value as well the overall significance of the model was found to be higher for 100 µg/L threshold. However, the percent correct prediction levels of two models were equal. The models may be useful for determining strategies aimed at reducing standard violations in drinking water utilities, and therefore reducing the risk associated with exposure to these chemicals.

Table 4.10. Logistic regression models for selected thresholds

Threshold	Variables	β	χ^2	percent correct prediction
90 µg/L	Const.	4.312	7.776 (0.021)	76
	Temp.	1.444		
	Temp.*pH	-0.222		
100 µg/L	Const.	13.61	15.507 (0.008)	76
	Temp.	16.58		
	temp*pH	-2.089		
	Temp*TotCl$_2$	0.020		
	pH*TotCl$_2$	4.838		
	TotCl$_2$	-42.34		

Numbers in parenthesis are p-values

CHAPTER 5

SUMMARY AND CONCLUSION

The most frequently detected DBPs in İzmir drinking water were CF, DBCM, BF, DCAN, BCAN and DBAN. Among all DBPs, THMs were the most abundant DBP group followed by HANs, CP and HKs. Concentration of THMs ranged between 2.86 and 183 µg/L whereas HANs ranged from 0.25 to 88.40 µg/L. CF was detected at highest concentration among all DBPs with a concentration range of 0.03-98.39 µg/L.

The level of DBP concentrations as well as the species distribution was affected by the type of water source. In tap water samples derived from surface water (Tahtalı and Balçova reservoirs) chlorinated DBPs were the predominant species whereas in tap water samples from ground water (Urla) brominated ones were detected at highest concentrations. In water samples from urban area, CF contributed about 51 % of the THMs, while in drinking water of Urla BF was the 95 % of TTHMs. The speciation of HANs was also similar to THMs. While DCAN was found to be the major HAN compound for Tahtalı and Balçova reservoirs, brominated HANs, DBAN and BCAN, were the most abundant HAN species in Urla.

The highest DBP levels were detected at Hatay sampling point where drinking water is supplied from Tahtalı Reservoir. Although THM levels in all samples complied with the current drinking water regulations of Turkey, 61 % of the samples from Hatay exceeded the maximum contaminant level of USEPA (80 µg/L).

Seasonal evaluation of DBP concentrations suggested that all DBPs were highest in spring and lowest in summer and fall. The variability of all DBPs according to seasons was found to be statistically significant except for DCAN in the distribution system of Balçova Drinking Water Treatment Plant and CF in Urla. For three water sources, intra-seasonal variations were also observed for THM levels possibly due to short-term fluctuations in operational parameters and drinking water quality.

The effect of water temperature on DBP formation was also evaluated. The concentrations of all DBPs except CF were found to be lower at water temperatures below 17 $^{\circ}$C. The decrease in THM levels were also found be statistically significant except for TTHMs and DCAN.

Concentration of DBPs increased in distribution system as the residence time increased. Highest DBP formation was observed in Güzelbahçe district which represented the system extremity. The re-chlorination of drinking water before this sampling location also resulted in further DBP formation.

The concentration of natural organic matter (measured as NPOC) for two water sources, Tahtalı and Balçova Water Treatment Plants, were below 5 mg/L, which is typical for unpolluted fresh surface waters. Highest NPOC levels were measured during spring and lowest during winter. Pre- and final chlorine doses for Tahtalı Water Treatment Plant (TDWTP) were about 3-4 times higher than Balçova Water Treatment Plant. Seasonal trend for water temperature and total chlorine dose at TDWTP was nearly identical. Mean concentration of bromide ion in raw water of Tahtalı Water Treatment Plant were 0.26 mg/L whereas it was 1.9 mg/L in tap water of Urla.

Multivariate regression analysis was conducted to develop statistical models for DBPs based on water quality and operational parameters. Correlation of DBPs with temperature and total chlorine dose was relatively high compared to other parameters. The coefficient of determination (R^2) of all models were found to be below 0.5 except for HAN model based on THMs , indicating that all models have poor prediction capacity. Highest R^2 value (0.83) was obtained for the model in which THAN concentrations were predicted by using THM levels. The adequacy of all models was evaluated by residual analysis, and residuals from all models were normally distributed and have nearly constant variance. Logistic regression models correctly exceedance of TTHM thresholds with 76 % efficiency.

REFERENCES

Ates et al. 2006. "Occurrence of disinfection by-products in low DOC surface water in Turkey", *Journal of Hazard. Materials.* doi:10.1016/j.jhazmat.2006.08.076

ATSDR (Agency for Toxic Substances and Disease Registry), 1989. "Toxicological Profile for Bromodichloromethane", U.S. Department of Health and Human Services, Public Health Service, Atlanta, G.A.

ATSDR,1997. "Toxicological Profile for Chloroform", U.S. Department of Health and Human Services, Public Health Service, Atlanta, G.A.

ATSDR, 2005. "Toxicological Profile for Bromoform and Dibromochloromethane", U.S. Department of Health and Human Services, Public Health Service, Atlanta, G.A.

Bellar, T.A., Lichtenberg. J.J., Kroner. R.C. 1974. "The Occurrence of Crganohalides in Chlorinated Crinking Water", *Journal of American Water Works Association* Vol.66. p. 703-706

Butterworth, B.E., 2005. "Science based risk assessments for drinking water disinfection by-products", *Environmental Research*, Vol. 98, p. 276-78

Calderon, R. L.2000. "The Epidemiology of Chemical Contaminants of Drinking Water" *Food and Chemical Toxicology.* Vol 38, p. S13-S20.

Chang, E. E., Lin Y. P., Chiang P. C. 2001. "Effects of bromide on the formation of THMs and HAAs", Chemosphere. Vol. 43, p.1029-1034.

Connell, G.F. 1996. "The chlorination/ chloramination handbook" Denver: *American Water Works Association.*

Çapar G. and Yetiş Ü. 2002, "Removal of THM precursors by GAC: Ankara Case Study", *Water Research*. Vol. 32, p. 1379-1384.

Duong, H. A., Berg, M., Hoang, M. H., Pham, H. V., Gallard, H., Giger, W. and Gunten, U. 2003. "Trihalomethane formation by chlorination of ammonium- and bromide-containing groundwater in water supplies of Hanoi, Vietnam", Water Research. Vol. 37, pp. 3242 –3252.

EC 1998. Council Directive 98/83/EC of the quality of water intended for human consumption, *Official Journal of the European Communities* L 330/32.

Gallard, H. and von Gunten, U., 2002. "Chlorination of Natural Organic Matter: Kinetics of chlorination and of THM Formation", *Water Research*. Vol. 36, p. 65-74.

Glezer V., Harris B., Tal N., Iosefzon B. and Lev O.,1998. "Hydrolysis of Haloacetonitriles: Linear Free Energy Relationship, Kinetics and Products", *Water Research*, Vol. 33, No. 8, p.1938-1948.

Golfinopoulos, S. K., Xilourgidis, K., Kostopoulou, N, Lekkas T. D.,1998. "Use of multiple regression model for prediction trihalomethane formation" *Water Research* Vol. 32, No. 9, p. 2821-2829.

Golfinopoulos, S. K, Arhonditsis, G.B., 2002. "Multiple regression models: a methodology for evaluating trihalomethane concentrations in drinking water from raw water characteristics", *Chemosphere*. Vol 47, pp.107-1018.

Golfinopoulos S. K. and Nikolaou A. D., 2005. "Survey of disinfection by-products in drinking water in Athens, Greece", *Desalination*. Vol. 176, pp.13-24.

Gould, J.P.,Fitchorn, L.E. Urheim, E., 1983. "Formation of brominated trihalomethane: extent and kinetics", Water Chlorination: Environmental Impact and Health Effects, Vol. 4. Ann Arbor Science, Ann Arbor, MI.

Guay C., Rodriguez M., Serodes, J., 2005."Using ozonation and chloramination to reduce the formation of trihalomethanes and haloacetic acids in drinking water", *Desalination.* Vol. 176, pp. 229-240.

Heller L. and Grossman L.,1999. "Formation of Cynogen Bromide and Other Volatile DBPs in the Disinfection of Bromide Rich Lake Water", *Environmental Science and Technology*. Vol. 33, pp. 932-937.

Hsu, C.H., Jeng, W.L., Chang, R.M., Chien, L.C., Han, B.C., 2001. "Estimation of Potential Lifetime Cancer Risks for Trihalomethanes from Consuming Chlorinated Drinking Water in Taiwan", *Environmental Research,* Section A Vol. 85, pp. 77-82.

IARC, 1991. Monograms on the Evaluation Of carcinogenic Risk to Human: e Chlorinated Drinking-water; Chlorination By-products; Some Other Halogenated Compounds; Cobalt and Cobalt Compounds, Vol. 52, WHO.

IARC, 1995. Monograms on the Evaluation Of carcinogenic Risk to Humans. Dry Cleaning, Some Chlorinated Solvents and Other Industrial Chemicals, Vol.63, WHO.

Kampioti, A. A., Stephanou, E. G., 2002. "The impact of bromide on the formation of neutral and acidic disinfection by-products in Mediterranean chlorinated drinking water". *Water Research*, Vol. 36, pp. 2596-2606

Kavcar P., Odabaşı, M., Kitiş, M., Inal F., Sofuoğlu, S.C., 2006. "Occurrence, oral exposure and risk assessment of VOCs in drinking water for İzmir" *Water Research,* Vol. 40, pp. 3219-3230.

Kim, J., Chung, Y., Shin Dongchun, S., Kim, M., Lee, Y., Lim, Y., Lee, D., 2002. "Chlorination By-Products in surface water treatment process", *Desalination*, Vol. 151,pp.1-9.

Komulainen H., 2004. "Experimental Cancer Studies of Chlorinated By-Products", *Toxicology*. Vol. 198, pp. 239-248.

Kawamoto, T. and Makihata N., 2004. "Distribution of Bromine/Chlorine-Containing Disinfection By-Products in Tap water from Different Water sources in the Hyogo Prefecture", Journal of Health Science. Vol. 50, No. 3, pp. 235-247.

Kitiş M., Kilduff, J. E., Karanfil, T., 2001."Isolation of Dissolved Organic Matter from Surface Waters using Reverse Osmosis and its impact on the reactivity of DOM to formation and Speciation of Disinfection By-products", *Water Research*. Vol. 35, No. 9, pp. 2225-2234.

Larson, R. A and Weber, E. J., 1994. "Reactions Mechanisms in Environmental Organic Chemistry, Lewis Publishers, Florida.

Lebel, G.L.,. Benoit, F.M, Williams, D.T., 1997. "A one year survey of halogenated disinfection By-products in the distribution System of treatment plants using three different disinfection processes", Chemosphere. Vol. 34, No. 11, pp. 2301- 2308.

Liang, L. and Singer, P. C., 2003. "Factors influencing the Formation and Relative Distribution of Haloacetic Acids and Trihalomethanes in Drinking water", *Environmental Science and Technogy*. Vol. 37, pp. 2920-2928

Matilainen, A., Lindqvist, N., Korhonen, S., and Tuhkanen, T., 2002."Removal of NOM in the Different Stages of the Water Treatment Process",Environment International. Vol. 28, 457– 465.

Ministry of Health, 2005. İnsani Tüketim Amaçlı Sular Hakkında Yönetmelik (Regulation Concerning Water Intended for Human Consumption), Resmi Gazete: 25730, Ankara.

Montgomery D.C., Runger G.C., 2007. Applied Statistics and Probability for Engineer, (John Wiley and Sons Inc).

Muellner, M. G., Wagner, E. D., Mccalla, K., Richardson, S., Woo, Y., Plewa, M. J., 2007. "Haloacetonitriles vs. Regulated Haloacetic Acids: Are Nitrogen Containing DBPs More Toxic?", *Environmental Science and Technology*. Vol. 41. pp. 645-651.

Nikolaou, A.D., Kostopoulou, M.N., Lekkas T.D.,1999."Organic By-Products of Drinking Water Chlorination", GlobalNest: The Int. J. Vol 1, No: 3, pp 143- 146, 1999.

Nikolaou A.D., Lekkas T.D., Golfinopulos S.K and Kostopoulou, M. N., 2004. "DBP levels in chlorinated drinking water: Effect of Humic Substances", *Environmental Monitoring and Assessment*. Vol. 93, pp. 301-319.

Nikolaou A.D., Lekkas T.D., Golfinopulos S.K, 2004a. "Kinetics of formation and decomposition of the chlorination by-products in surface waters", *Chemical Egineering Journal*. Vol.100, pp. 139-148.

Panyapinyapol B., Mathaba T. F., Kanokkantapong V., Pasavant P., 2005. "Characterization pf precursors to Trihalomethane formation in Bangkok Source water", *Journal of Hazardous Materials*. Vol. B120, 229-236.

Peters, R.J. B., De leer, W. B., De Galan, L., 1999. "Chlorination of Cyanoethanoic Acid in Aqueous Medium" *Journal of Environmental Science and Technology*. Vol. 24, pp. 81-86

Pourmoghaddas and Stevens, 1995."Relationship between trihalomethanes and haloacetic acids with total organic halogen during chlorination, *Water Research*, Vol. 29, No. 9, pp. 2059-2062.

Rodriguez, M.J. and Serodes, J.B., 2001."Spatial and temporal evolution of THMs in three water distribution systems", *Water Research*. Vol. 35, No. 6, pp. 1572-1586.

Rodriguez, M.J, Serodes J. B., Levallois, P, 2004. "Behavior of trihalomethanes and haloacetic acids in a drinking water distribution system",*Water Research* Vol. 38, pp. 4367-4382.

Rodriguez, M.J., Vinnete, Y., Serodes, J.B., Bouchard, C., 2003. "Trihalomethanes in drinking water of Greater Quebec Region (Canada): Occurrence, variations and Modeling", *Environmental Monitoring and Assessment*. Vol. 89, pp. 69-93.

Rook J.J., 1974. "Formation of Haloforms During Chlorination of natural waters", *Journal of the society for Water treatment Examination*.Vol. 23, pp. 234–243.

Sadiq, R. and Rodriguez, M. J. 2004. "Disinfection By-Products in drinking water and predictive models for their occurrence: a review, Science of Total Environment". Vol.321. pp.21-46

Simpson, K. L and Hayes, P. H, 1998. "Drinking Water disinfection By-Products: An Australian Perspective", *Water Research*. Vol. 32, No. 5, pp. 1522-1528.

Singer, P.C., Reckhow, D.A., 1999. Chemical oxidation, chapter 12, Water quality and treatment: a handbook of community water 5th ed., American Water Works Association, McGraw-Hill, New York

Sorlini, S. and Collivignarelli, C., 2005. "Trihalomethane formation during chemical oxidation, chlorine dioxide and ozone of ten Italian natural waters, *Desalination.* Vol. 176, pp. 103-111

Standard Methods for the examination of water and wastewater (1995), Eaton A.D., Clesceri L. S., Greenberg A. E., American Public Health Association, Washington DC

Switzer J. A., Rajasekharan, V. V., Boonsale, S., Kulp, E. A. Bohannan, E. W., evidence that monochloramine disinfectant could lead to elevated Pb levels in drinking water, *Environmental Science and Technology.* Vol. 40, pp. 3384-87

Tokmak, B., Çapar G., Dilek F. B., Yetiş U., 2004. Trihalomethanes and associated potential cancer risks in the water supply in Ankara, Turkey, *Environmental Research.* Vol. 96, pp. 345-352.

Toroz, I. and Uyak, V. 2005."Seasonal variations of trihalomethanes (THMs) in water distribution networks of Istanbul City", *Desalination.* Vol. 176, pp. 127-141.

Ott, R.L. and Longnecker, M., 2001. An Introduction to Statistical Methods and Data Analysis, (Duxbury), p. 625-627, p.758.

USEPA, 1995. Method 551.1, Determination of chlorination Disinfection By-products, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Gas choramotography with Electron Capture Detection, Revision 1. USEPA, Office of Water

USEPA, 1997, Guiding Principles for Monte Carlo Analysis, Risk Assessment Forum U.S., EPA/630/R-97/001, Washington, DC 20460

USEPA, 1998. 40 CFR Parts 9, 141, and 142. National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts Final Rule, Federal Register Part IV, 63: 241, 69389- 69476.

USEPA, 1999. Alternative Disinfectants and Oxidants Guidance Manual, United States Environmental Protection Agency, Office of Water 4607.

USEPA, 1999a. Microbial and Disinfection Byproduct Rules Simultaneous Compliance Guidance Manual, United States Environmental Protection Agency, EPA 815-R-99-015.

USEPA, 2000. Guidance for Data Quality Assessment: Practical Methods for Data Analysis, Office of Environmental Information, Washington, DC, EPA/600/R-96/084

USEPA, 2006. 40 CFR Parts 9, 141, and 142. National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts Final Rule, Federal Register Part II, 71: 387-493.

Uyak V., 2006. "Multi-pathway risk assessment of trihalomethanes exposure in Istanbul drinking water supplies" *Environment International.* Vol. 32, pp. 12 – 21

Villanova R.J.G., Garcia C., Gomez J. A., Garcia M.P. and Ardanuy R., 1997. "Formation, evolution and modeling of trihalomethanes in the drinking water of a town: II. In the distribution system", *Water Research.* Vol. 31, No. 6, pp.1405-1423.

Villanueva C. M., Cantor P. K., Cordier S., Jakkola J. J. K., King W. D., Lynch F. C., Porru S., Kogevinas M., 2004. "Disinfection by-products and bladder cancer", *Epidemiology.* Vol. 5, pp. 357-367.

Von Gunten U., 2003. "Ozonation of drinking water: Part II. Disinfection and by product formation in presence of bromide, iodide or chlorine", *Water Research*, Vol. 37, pp. 1469-1487

Villanueva, C.M., Kogevinas, M., Grimalt, J.O., 2003."Haloacetic acids and trihalomethanes in finished drinking water from heterogeneous sources",*Water Research.* Vo. 37, pp. 953-958.

WEB_1,2006. Health Canada, Guidelines for Canadian Drinking Water Quality. 15/03/07, http://www.healthcanada..gc.ca/waterquality

WEB_2, 2007. Environmental Protection Agency Integrated Risk Information System. 22/02/07, http://www.epa.gov/iris

WEB_3, 2007. NIST/SEMATECH, e-Handbook of Statistical Methods,14/05/07 http:// www.itl.nist.gov/div898/handbook/

Westerhoff P. Chao, P., Mash H., 2004. "Reactivity of Natural Organic Matter with aqueous chlorine and bromine", *Water Research.* Vol. 38, pp. 1502-1513.

WHO (World Health Organization), 2000. Disinfectants and Disinfection By-products: Environmental Health Criteria 216, World Health Organization, Geneva.

WHO, 2004. Guidelines for Drinking-water Quality, Third Edition,Volume 1, Recommendations, World Health Organization, Geneva.

White, G.C.1992, Handbook of chlorination and alternative disinfections, 3rd Ed. New York,Van Nostrand Reinhold Publisher, Inc.

Williams, D.T., Benoit, F.M., Lebel G.L, 1998. "Trend in Levels of Disinfection by-products", *Environmetrics.* Vol. 9, pp. 555-563.

Xu X.,. Mariano T. M., Laskin J. D. and Weisel C. P., 2002. "Percutaneous Absorption of Trihalomethanes, Haloacetic Acids, and Haloketones", *Toxicology and Applied Pharmacology.* Vol. 184, pp. 19-26.