ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

A COMPARATIVE EXAMINATION OF TRIHALOMETHANE AND N-NITROSODIMETHYLAMINE FORMATION

M.Sc. THESIS

Nur Hanife ORAK

Department of Environmental Engineering

Environmental Science and Engineering Program

JANUARY 2012

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

A COMPARATIVE EXAMINATION OF TRIHALOMETHANE AND N-NITROSODIMETHYLAMINE FORMATION

M.Sc. THESIS

Nur Hanife ORAK

501091774

Department of Environmental Engineering

Environmental Science and Engineering Program

Thesis Advisor: Assoc. Prof. Elif PEHLİVANOĞLU-MANTAŞ

JANUARY 2012

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

TRİHALOMETAN VE N-NİTROSODİMETİLAMİN OLUŞUMUNUN KARŞILAŞTIRMALI OLARAK İNCELENMESİ

YÜKSEK LİSANS TEZİ
Nur Hanife ORAK

501091774

Çevre Mühendisliği

Çevre Bilimleri ve Mühendisliği Programı

Tez Danışmanı: Doç. Dr. Elif PEHLİVANOĞLU-MANTAŞ

OCAK 2012

Nur Hanife ORAK, a **M.Sc.** student of ITU **Graduate School of Science Engineering and Technology** student ID 501091774, successfully defended the **thesis/dissertation** entitled "**A COMPARATIVE EXAMINATION OF TRIHALOMETHANE AND N-NITROSODIMETHYLAMINE FORMATION**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor: **Assoc. Prof. Elif PEHLİVANOĞLU-MANTAŞ**

İstanbul Technical University

Jury Members: **Prof. Dr. İsmail TORÖZ**

İstanbul Technical University

Prof. Dr. Miray BEKBÖLET

Boğaziçi University

Date of Submission: 19 December 2011

Date of Defense: 24 January 2012

To my patient family,

FOREWORD

I would like to express my deep appreciation and thanks to my advisor Assoc. Prof. Elif PEHLİVANOĞLU MANTAŞ for sharing her valuable knowledge and time during my work.

I would like to thank to Assist. Prof. Esra ATEŞ GENCELİ, Assoc. Prof. Melike GÜREL, Res. Assist. Egemen AYDIN, Res. Assist. Emel TOPUZ and Res. Assist. Esra ERDİM for their experimental and emotional support.

I would like to send the most sincere thanks to my mother Vasfiye ORAK and my father Abdulhadi ORAK who have supported me all the time in line with my aims.

I hope I could provide a little contribution to the science world with this work.

This work is supported by The Scientific and Technological Research Council of Turkey, Project No : 108Y311.

December 2011 Nur Hanife ORAK

Environmental Engineer

TABLE OF CONTENTS

Page

ABBREVIATIONS

ÇOK **:** Çözünmüş Organik Karbon
NOM **:** Natural Organic Matter
TOC **:** Total Organic Carbon
DBP **:** Disinfection by-products
DOC **:** Dissolved Organic Carbon
TTHM **:** Total Trihalomethanes
THM **:** Trihalomethane
THMFP **:** Trihalomethane Formation Potential
TKN **:** Total Kjeldahl Nitrogen
HAAs **:** Haloacetic Acids
NDMA **:** N-Nitrosodimethylamine
NDMAFP **:** N-Nitrosodimethylamine Formation Potential
SUVA **:** Specific Ultraviolet Absorbance
WQP **:** Water quality parameters

LIST OF TABLES

Page

LIST OF FIGURES

A COMPARATIVE EXAMINATION OF TRIHALOMETHANE AND N-NITROSODIMETHYLAMINE FORMATION

SUMMARY

Disinfection process which is used for inactivation of disease-causing microorganisms in drinking water leads to formation of various disinfection by-products (DBP) depending on the disinfectant used and the type of precursors present in the water. However, the relation between the DBP precursors and DBPs is not very clear. In this context, this thesis is constructed to examine the presence of precursors of two different disinfection by-products, N-Nitrosodimethylamine (NDMA) and Trihalomethanes (THMs) in a drinking water watershed and the comparative formation of NDMA and THM in a drinking water treatment plant upon disinfection. Moreover, the formation of these DBPs was compared in lab-scale tests using different types of disinfection methods (e.g., chlorination, chloramination and stepwise chloramination).

Büyükçekmece Lake Basin is in the south of the Trakya peninsula and near the Sea of Marmara. The basin covers Silivri, Büyükçekmece and Çatalca settlements which are suspected to contribute to the amount of disinfection by-products formed in Büyükçekmece Drinking Water Treatment Plant. Samples were taken both from Büyükçekmece Lake and its tributaries as well as the drinking water treatment plant. In addition to the measurement of THM, NDMA and their precursors, several water quality parameters are measured to examine the probable relationship between DBPs and water quality parameters. Lab-scale experiments are conducted with lake water obtained from Büyükçekmece Lake as well as lake water spiked with two NDMA precursors (i.e., dimethylamine and ranitidine). The tests are conducted to investigate the effect of disinfection methods, amount of disinfectant and the presence of different types of DBP precursors on DBP formation.

The presence of high DBP precursors in some of the tributaries in the watershed suggests that there are anthropogenic sources of DBP precursors in addition to natural sources. These sources could either be untreated domestic or industrial wastewater discharges or the presence of agricultural runoff leading to diffuse pollution. Although some tributaries seem to be severely polluted, the concentrations of both DBP precursors are low enough in the lake so that the concentrations of DBP at the end of the WTP which uses chlorination are not significant. Nevertheless, the presence of DBP precursors at low concentrations might lead to the formation of NDMA during chloramination which was tested with the lab-scale tests.

During lab-scale tests, NDMA does not form in short contact time (2 hours) in lake water. Especially during chlorination and stepwise chloramination NDMA

concentrations obtained are low even at high concentration of 10 mg/L. THM formation is observed in both chlorination and stepwise chloramination trial, but its concentration is below the maximum allowable limit. The experiments with ranitidine suggest that the presence of NDMA precursors might have a significant effect on NDMA formation even at very low concentrations, especially in the distribution system if chloramination is used. Moreover, depending on the structure of the NDMA precursor, high THM concentrations may also form during chlorination.

Chloramination is currently not used in Turkey, but this study will be useful for its possible future application in drinking water treatment plants. Although THM concentrations are below the current standards, chloramination may be an alternative if their MAC is decreased further. The only foreseeable problem is the presence of NDMA precursors which are hard to detect due to their low concentrations. However, when best management practices and a better watershed protection plan is applied to remove the possible anthropogenic sources of NDMA precursors, the NDMA that will form during chloramination of naturally occurring organic matter will not be high enough to affect public health.

.

TRİHALOMETAN VE N-NİTROSODİMETİLAMİN OLUŞUMUNUN KARŞILAŞTIRMALI OLARAK İNCELENMESİ

ÖZET

İçme sularındaki hastalık yapıcı mikroorganizmaların etkisiz hale getirilmesi için kullanılan dezenfeksiyon işlemi, kullanılan dezenfektana ve suda bulunan öncü maddelerin cinsine bağlı olarak farklı dezenfeksiyon yan ürünlerinin (DYÜ) oluşmasına yol açabilir. Ancak, DYÜ öncü maddeleri ile DYÜ arasındaki ilişki tam olarak ortaya konulmuş değildir. Bu bağlamda, bu tez iki farklı DYÜ olan N-nitrosodimetilamin (NDMA) ve Trihalometanlar (THM)'ın öncü maddelerinin bir içme suyu havzasında varlığının ve bu iki DYÜ'nün bir içme suyu arıtma tesisinde karşılaştırmalı olarak oluşmasının incelenmesi amacıyla gerçekleştirilmiştir. Ayrıca, bu DYÜ'lerin oluşumu farklı dezenfeksiyon yöntemleri (klorlama, kloraminleme, kademeli kloraminleme) kullanılarak laboratuvar ölçekli testlerde karşılaştırılmıştır.

THM'lar kanserojen olduğu bilinen ve hakkında çok araştırma yapılmış olan klorlama sonucu oluşan en önemli DYÜ'dür. Klorlamaya alternatif bir metot olarak dezenfeksiyon için ozonlama yapılması sonucunda bromat oluşurken, kloraminle dezenfeksiyon yapılması durumunda da NDMA oluşmaktadır. Ülkemizde şu anda kloraminleme kullanılmasa da THM konsanstrasyonu ile ilgili getirilmiş olan sınırlamalar farklı dezenfektan arayışlarına yol açabilecektir. Nitrosaminler içinde en zararlı olanlarından olan N-Nitrosodimetilamin çevrede en çok rastlanılan nitrosamin türüdür. NDMA US EPA tarafından 'kanserojen olması muhtemel' olarak sınıflandırılmış olmasına rağmen NDMA'nın çok yakın bir zamana kadar DYÜ olarak bilinmemesi çoğu ülkede NDMA için içme suyu standardının daha mevcut olmamasına yol açmıştır. NDMA'nın DYÜ olarak tanımlanması yeni olmasına rağmen (Mitch ve Sedlak, 2002a, Mitch ve diğ., 2003a), NDMA'nın peynir, soya yağı, et ürünleri ve konserve meyvalar gibi gıda maddelerinde ve bira gibi içeceklerde de bulunduğu bilinmektedir (Mitch ve diğ., 2003a). Ayrıca NDMA sıvı roket yakıtı olan 1,1-dimethylhydrazine (UDMH) üretiminde ve bazı endüstriyel proseslerde antioxidan, yumuşatıcı ya da plastikleştirici olarak da kullanılmaktadır. NDMA ayrıca bu maddeyi içeren bromacil, benazolin, 2,4-D, dicamba, MCPA, ve mecoprop gibi pestisitlerin kullanılması sonucunda çevreye yayılabilmektedir (WHO, 2002). Endüstriyel atıksuların içme sularına karışması sonucunda da NDMA oluşabilir.

Nitrosaminlerin çoğu kanserojen, mutajen ve teratojen etki gösterir (Loeppky, 1994). NDMA ile ilgili yeni ortaya çıkan verilerden ve halk sağlığı ile ilgili endişelerden dolayı ABD'de Kaliforniya Eyaleti'nde aksiyon/önlem seviyesi olarak 10 ppt konulmuştur (CDPH, 2006; CDPH, 2008). NDMA ile ilgili yürürlükte olan standartların olduğu diğer bir ülke de Kanada olup 1992'de

maksimum izin verilebilir konsantrasyon olarak 9 ng/L belirlenmiştir (OME, 2003). Ayrıca, Arizona'da Arizona Department of Environmental Quality (AzDEQ) NDMA'yı deşarj izinleri için izlenen parametreler listesine almıştır. Kronik olarak solunum ve sindirim yoluyla maruz kalma durumunda NDMA'nın karaciğer ve böbrek tümörlerini arttırdığı tespit edilmiş ve NDMA ile ilgili hayvanlar üzerinde yürütülen çalışmalarda NDMA'nın kanserojen olduğu ortaya konulmuştur (USEPA Technology Transfer Network, 2003). İnsan sağlığı üzerindeki etkileri ile ilgili yeterli veri bulunmamakla birlikte USEPA Integrated Risk Information Services 1/1000000 kanser riski yaratacak NDMA konsantrasyonunu 0,7 ng/L (USEPA, 2008) olarak; The Office of Environmental Health Hazard Assessment (OEHHA) ise 0.002 ppb (2 ng/L) (OEHHA, 2006) olarak belirlemiştir. Bu da NDMA'nın eskiden kanserojen olduğu düşünülen kloroform gibi diğer DYÜ'den farklı olarak içme sularında bulunduğu konsantrasyonda tehlike yaratacağını ortaya koymaktadır (USEPA, 2008, Charrois ve diğ., 2007). Çeşitli epidemiyolojik çalışmalar sonunda içme suyunda bulunan DYÜ'lere maruz kalma sonucunda mesane kanserine yakalanma (Villanueva ve diğ., 2004) ya da üreme yolları ile ilgili hastalıkların (Nieuwenhuijsen ve diğ., 2000) riskinin arttığı ortaya konmuştur. NDMA'nın etki mekanizmasının araştırıldığı çalışmalarda da insanlarda ve kemirgenlerde NDMA'nın etki bölgesinin mesane olduğu belirlenmiştir (IARC, 1978; Shank ve Magee, 1981).

Çeşitli kaynaklardan suya karışabilecek NDMA'in yanısıra, sularda ve atıksularda hem THM hem de NDMA'in öncü maddesi olarak davranacak çeşitli maddeler bulunabilir. Bunlar doğal olarak su ortamlarında bulunan organik maddeler olabileceği gibi insan kaynaklı organik kirleticiler de suyun klorlanması ya da kloraminlenmesi durumunda THM ve NDMA oluşumuna katkıda bulunabilir.

Büyükçekmece Gölü Havzası Trakya Yarımadası'nın güneyinde ve Marmara Denizi'nin yanında bulunmaktadır. Havza, Silivri, Büyükçekmece ve Çatalca yerleşim alanlarını da içermekte olup, bu yerleşimlerden Büyükçekmece İçme Suyu Arıtma Tesisi'nde oluşan DYÜ'lerine katkıda bulunan öncü maddelerin geldiği düşünülmektedir. Numuneler hem Büyükçekmece Gölü ve ona dökülen derelerden hem de içme suyu arıtma tesisinden alınmıştır. THM, NDMA ve bu DYÜ'lerin öncü maddelerinin ölçümlerinin yanı sıra birçok su kalite parametresi de ölçülerek DYÜ'leri ile ilişkisi incelenmiştir. Laboratuvar ölçekli testler Büyükçekmece Gölü'nden alınan su numuneleri ve iki NDMA öncü maddesinin (dimetilamin ve ranitidin) enjekte edildiği göl numuneleri ile gerçekleştirilmiştir. Testler, dezenfeksiyon metotları, dezenfektan konsantrasyonları ve farklı DYÜ öncü maddelerinin DYÜ'lerinin oluşmasına etkisini incelemek üzere gerçekleştirilmiştir.

Bu çalışmada havzadaki bazı derelerde yüksek konsantrasyonda DYÜ öncü maddelerinin varlığının tespiti doğal kaynaklara antrapojenik kaynaklı DYÜ öncü maddelerin karıştığını göstermektedir. Bu kaynaklar arıtılmamış evsel veya endüstriyel atıksu deşarjları olabileceği gibi yayılı kirliliğe neden olan tarımsal yüzeysel akış da olabilir. Bazı derelerin ciddi olarak kirlenmesine karşın her iki DYÜ öncü maddeleri de gölde yeterli derecede düşük konsantrasyondadır, bu nedenle DYÜ'lerinin klorlama yapan su arıtma tesisi çıkışındaki konsantrasyonu önemli miktarda değildir. Yine de, laboratuvar ölçekli çalışmalarda incelendiği gibi, düşük konsantrasyonlarda dahi olsa DYÜ öncü maddelerinin varlığı kloraminleme yapılması durumunda NDMA oluşumuna neden olabilir.

Laboratuvar ölçekli testlerde göl suyunda kısa temas süresinde (2 saat) NDMA oluşumu gözlenmemiştir. Özellikle klorlama ve kademeli kloraminlemede NDMA konsantrasyonu, yüksek (10 mg/L) dezenfektan konsantrasyonunda bile düşük ölçülmüştür. THM oluşumu klorlama ve kademeli kloraminleme denemelerinde gözlenmiş olmakla birlikte, konsantrasyonu azami izin verilebilir konsantrasyon değerinin altında kalmıştır. Ranitidin ile yürütülen deneyler özellikle dağıtım sisteminde kloraminleme kullanılıyorsa, çok düşük konsantrasyonlarda bile NDMA öncü maddelerinin varlığının NDMA oluşumuna önemli ölçüde katkıda bulunabileceğini göstermiştir. Ayrıca NDMA öncü maddesinin yapısına bağlı olarak klorlama sırasında yüksek konsantrasyonda THM oluşumu da gözlenmektedir. Çalışmanın önemli sonuçlarından bir tanesi TOK ve DYÜ'leri (THM ve NDMA) arasındaki ilişkinin incelenmesidir.

Gölün ÇOK değeri 6 mg/L'dir. Göl suyuna ilave edilen NDMA öncü maddelerinin ÇOK eşdeğerleri ise sırasıyla DMA ve ranitidin için 0.52 mg/L ve 1.7 E-4 mg/L'dir. Bu ÇOK değerleri de toplamın % 8.7 ve % 0.003'üne denk gelmektedir. Ancak DMA ve ranitidin'in THM oluşumuna katkısı sırasıyla % 11.5 ve % 23'tür. Bu sonuç DMA'nın dönüşüm oranının THM için DOM'e benzediğini ama ranitidin'in dönüşüm oranının çok yüksek olduğunu göstermektedir. Literatürde THM ve ranitidin, DMA arasında bir dönüşüm oranı bulunmamakla birlikte, çalışma sonucunda elde ettiğimiz dönüşüm oranları DMA için 147 mol THM/mol DMA iken ranitidin için 11765 mol THM/mol ranitidin'dir. İlk defa bu çalışmada ranitidin'in sadece NMDA öncü maddesi değil aynı zamanda THM öncü maddesi olduğu elde edilmiştir. Literatürde belirtilen NDMA dönüşüm oranları; DMA için % 0.76 iken ranitidin için % 62'dir. Bu değerlere karşılık olarak çalışma sonucunda elde edilen dönüşüm oranlar DMA için % 14 iken, ranitidin için % 57'dir.

Kloraminleme şu an Türkiye'de kullanılmamakla birlikte, ileride içme suyu arıtma tesislerinde kloraminleme uygulanmasının irdelenmesi açısından bu çalışma önem taşımaktadır. THM konsantrasyonları her ne kadar mevcut standartların altında kalıyorsa da azami izin verilebilir konsantrasyonun düşürülmesi durumunda kloraminleme alternatif bir metot olabilir. Bununla ilgili karşılaşılması muhtemel tek problem düşük konsantrasyonda bulunan NDMA öncü maddelerinin varlığıdır. Ancak, en iyi yönetim uygulamaları ve daha iyi bir havza koruma planı uygulanması durumunda olası antropojenik NDMA öncü maddesi kaynaklarının giderilmesi mümkün olup, doğal organik maddelerin kloraminlenmesi sonucunda oluşan NDMA konsantrasyonunun da halk sağlığını etkileyecek düzeylerde olmayacağı tahmin edilmektedir.

1. INTRODUCTION

1.1 Aim and Scope

Trihalomethanes (THMs) and N-Nitrosodimethlyamine (NDMA) are examples of disinfection by-products that form mainly during the chlorination and chloramination processes, respectively. THM are known carcinogens and the maximum allowable concentration in drinking water is 150 µg/L (TS 266, 2005). However, the maximum allowable amount will be 100 µg/L after December 2012. This decrease in concentration will require extra efforts to control the THM concentrations in three possible ways: decreasing the DBP concentration after chlorination, decreasing the DBP precursor concentration before chlorination or using a different disinfection method such as chloramination. Among these methods chloramination needs to be evaluated further since chloramination will decrease THM concentrations but may lead to NDMA formation in drinking water treatment plants. The aim of this thesis, therefore, is the comparative evaluation of THM and NDMA formation.

In this context, this thesis is constructed to examine the presence of precursors of two different disinfection by-products, Nitrosodimethylamine (NDMA) and Trihalomethanes (THMs) in a drinking water watershed and their comparative formation in a drinking water treatment plant upon disinfection. Moreover, the formation of these DBPs have been compared in lab-scale tests using different types of disinfection methods, namely, chlorination, chloramination, and stepwise chloramination both in the presence and absence of various types of DBP precursors.

Büyükçekmece Watershed is selected as the project area because although it is one of the main drinking water sources for Istanbul, it covers Silivri, Büyükçekmece and Çatalca districts where the settlements and industries may contribute to the disinfection by product precursors. In addition, agriculture is one of the land use practices in the watershed and the diffuse pollution may contribute to the DBP precursors in the watershed as well.

Samples are taken from Büyükçekmece Lake, its tributaries and the Büyükçekmece Drinking Water Treatment Plant. In addition to the measurement of THM, NDMA and their precursors for the occurrence study in the watershed and throughout the treatment plant, several water quality parameters are measured to examine the probable relationship between DBPs and water quality parameters.

For the lab-scale tests, lake water and lake water spiked with DBP precursors are used. The tests are conducted to investigate the effect of disinfection methods, amount of disinfectant and the presence of DBP precursors on the formation of NDMA and THM simultaneously.

1.2 Significance of the Work

Drinking water disinfection is a vital process for public health. Before widespread disinfection of drinking water in the world, water-borne diseases such as cholera and typhoid were serious problems. After disinfectants are started to be used in the early 1900s, number of deaths from water-borne pathogens decreased significantly in developed nations. However, with the use of disinfection chemicals, new problems such as disinfection by-products have emerged and some of these DBPs such as THMs are regulated in drinking water standards.

Since one of the possible methods to decrease the concentration of THM is to switch from chlorination to chloramination for disinfection, it is really important to evaluate the formation of NDMA during this process. With this study, one of the first studies for comparative formation of THM and NDMA in a drinking water treatment plant is conducted. The change of THM, NDMA and their precursors within the treatment plant also lays the ground for further studies to remove these DBPs in the WTP.

Since the sources of THM and NDMA precursors are Büyükçekmece Lake and its tributaries, the occurrence data which is the final part of an ongoing study conducted at ITU, provide information on the seasonal effects on DBP precursors. Moreover, the monitoring of DBP precursors in the watershed will point to the contamination hotspots, which then could be removed/treated to decrease the concentration of DBP precursors coming to the drinking water treatment plant.

Since the formation pathways are different for THMs and NDMA, the use of chlorination, chloramination or stepwise chloramination will lead to high concentrations of either THMS or NDMA. The results of lab-scale tests are conducted to shed light on the occurrence data in the WTP and also to provide information for the drinking water utilities which may want to change their disinfection practice. The results can be used as an indicator for the selection of the appropriate disinfection method and the disinfectant concentration in the treatment plant to minimize DBP formation.

2. DISINFECTION, DBP AND DBP PRECURSORS

2.1 Importance of Disinfection and Description Methods

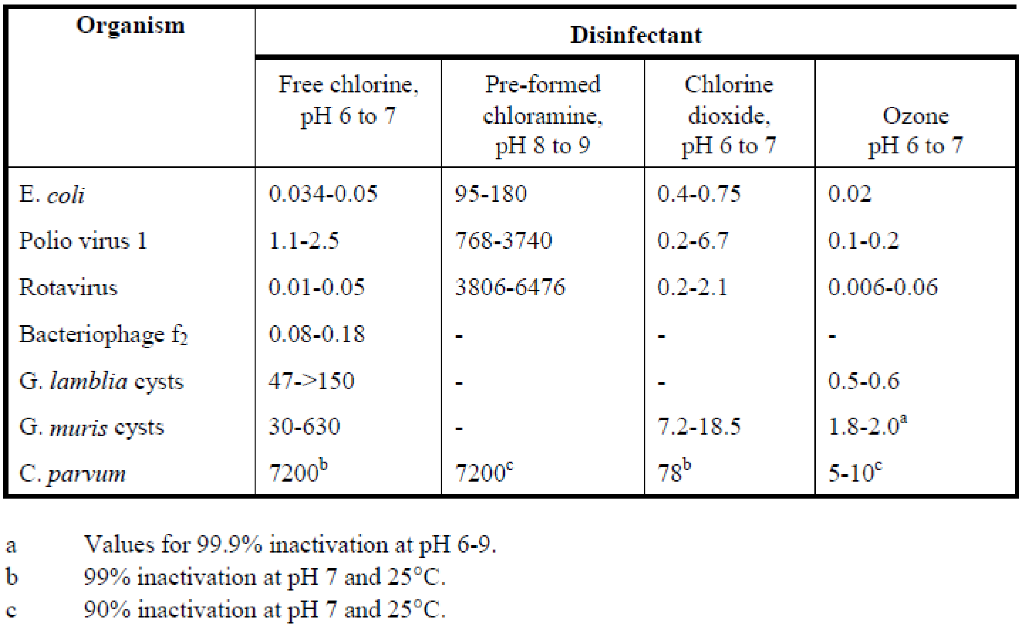
Disinfection is an essential process in drinking water treatment plants to inactivate pathogens. There are many disinfectants which are preferred in different countries such as chlorine, chlorine dioxide, ozone and chloramine. Chlorination for disinfection is firstly used in 1902 in Middlekerke (Belgium) and ozone is used in Nice (France) in 1906 (MWH, 2005).

During disinfection process disinfectants generally react with natural organic matter which is already in water and cause disinfection by- products (DBPs). Moreover, the intentional or unintentional presence of wastewater-derived organic matter may add to the formation of DBPs. There are many types of disinfection by-products due to the use of different disinfectants and the presence of different types of organic matter. More than 600 disinfection by-products have been reported in the literature for the major disinfectants (Krasner et al., 2006).

There are various disinfection methods but to decide on the most appropriate method for disinfection a number of issues should be considered. The disinfectant should be able to destroy all types of pathogen, it should not cause the water to become toxic or unpalatable, it should be safe and easy to handle and it should provide residual protection against recontamination and it should be economic.

Efficiency of disinfectants is related to their C.t values. C is the concentration of disinfectant in mg/L and t is the contact time in minutes to inactivate a specific percentage of microorganisms. Summary of C.t values for inactivation of several types of pathogens are provided in Table 2.1.

Table 2.1 : Summary of C.t values (mg/L.min) for 99% inactivation (Clark et al, 1994)



Organism	**Disinfectant**			
	Free chlorine, pH 6 to 7	Pre-formed chloramine, pH 8 to 9	Chlorine dioxide, pH 6 to 7	Ozone pH 6 to 7
E. *coli*	0.034-0.05	95-180	0.4-0.75	0.02
Polio virus 1	1.1-2.5	768-3740	0.2-6.7	0.1-0.2
Rotavirus	0.01-0.05	3806-6476	0.2-2.1	0.006-0.06
Bacteriophage f_2	0.08-0.18	-	-	-
G. *lamblia* cysts	47->150	-	-	0.5-0.6
G. *muris* cysts	30-630	-	7.2-18.5	1.8-2.0[a]
C. *parvum*	7200[b]	7200[c]	78[b]	5-10[c]

[a] Values for 99.9% inactivation at pH 6-9.
[b] 99% inactivation at pH 7 and 25°C.
[c] 90% inactivation at pH 7 and 25°C.

Efficiency of pathogen inactivation is an important but not the only issue to decide the most appropriate disinfectant. Disinfectants features should be analyzed more detailed.

Chlorination has been the most common method used all over the world. Chlorine is very effective for removing almost all microbial pathogens and can be used as both a primary and secondary disinfectant. Moreover, it is very cheap to provide. Historical developments of chlorine usage in the world are given in Table 2.2. Chlorination can be applied by different disinfectants such as chlorine (gas), sodium hypochlorite solution, and solid calcium hypochlorite. When chlorine added to water the following reaction 2.1 occurs:

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \qquad \textbf{(2.1)}$$

As a result of chlorination, several disinfection by-products are formed which include trihalomethanes (THM), halogenated acetic acids, halogenated acetonitriles, chloral hydrate and chlorinated phenols (WHO, 2004).

Table 2.2 : Historical developments of chlorine usage in the world (Oğur et al., 2004)

Year	Development
1870s-1880s	It was scientifically proven that microorganisms can cause diseases
1896	Chlorine was first used in the U.S.A. (Louisville state)
1897	Chlorine was used in United Kingdom for drinking water disinfection
1905	Drinking waters were chlorinated regularly in United Kingdom
1908	Drinking waters were chlorinated regularly in the U.S.A, Chicago and Jersey
1909	Liquid chlorine was produced commercially
1912	Liquid chlorine was used for the first time to Niagara Fall water
1915	USA had released he first drinking water bacterial standard
1917	Chloramine compounds were introduced for the first time in the USA and Canada
1918	Chlorine was used over 1000 cities in the U.S.A
1920s	Liquid chlorine was chosen for disinfection of water instead of other forms of chlorine
1925	Bacterial drinking water standards were settled and began to be applied in the United States legally
1932	First time in our country chlorination was started with calcium chloride in Istanbul Terkos drinking water treatment plant
1936	Drinking water of Ankara Çubuk dam was chlorinated with chlorine gas regularly
1940s	Chlorination process was widespread throughout Turkey
1960s	Chlorine disinfection of water had become widespread throughout the world
1970	Chlorine dioxide became more popular for drinking water treatment than other chlorinated compounds
1974	As result of chlorination disinfection by-products were recognized

Chloramination is not as widely used as chlorination but it is an effective method for most of the pathogens. Chloramine is a weak disinfectant and monochloramine is about 2000 and 100.000 times less effective than free chlorine for the inactivation of E. coli and rotaviruses, respectively (WHO, 2004). However, chloramines cause less disinfection by-products compared to chlorination and its weak disinfectant properties make chloramine a more suitable secondary disinfectant, especially when recontamination is suspected during water distribution. Chloramine is generated onsite with the addition of ammonia after chlorination of water and the formation reaction rate is very fast.

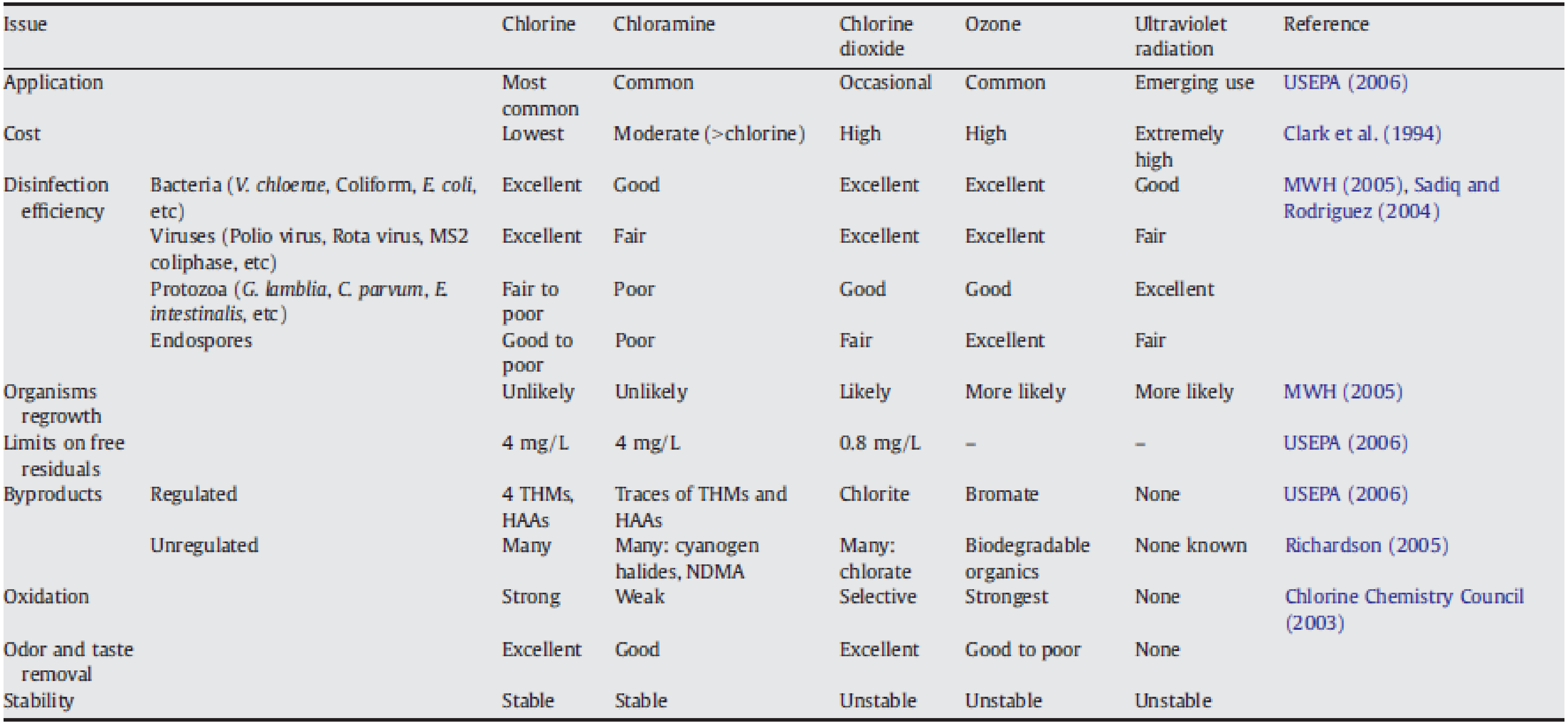
Chlorine dioxide (ClO_2) is a strong disinfectant and generally produces less halogenated disinfection by-products than chlorine (Richardson, 1998). Chlorine dioxide has to be produced onsite. For drinking water applications sodium chlorite ($NaClO_2$) used as premise raw material to produce chlorine dioxide. It is widely produced in the USA and in addition to being a good disinfectant it is used for paper and textile industries for its oxidative effects. The most important physical feature is its high solubility in water; it is soluble in water 10 times more than chlorine (above 11 ^{0}C) and is also highly volatile. It is more expensive than chlorine and hard to produce.

Ozone is an allotrope of oxygen having 3 atoms in each molecule and it is a powerful oxidizing and disinfecting agent. It is formed by passing dry air through a system of high voltage electrodes. This method requires shorter contact time and smaller concentrations than chlorine to achieve effective disinfection and hence ozone is widely used as a primary disinfectant in some parts of the world. Ozone gas must be generated onsite due to its instability. One of the problems with ozone as the primary disinfectant is the need to use a different secondary disinfectant such as chlorine, because ozone does not maintain an adequate residual in water distribution system. Also, the formation of DBPs such as bromate are a concern in ozonation process (von Gunten et al., 2003) and it is believed that ozonation may form more DBPs such as NDMA than currently known (Schmidt and Brauch, 2008).

For disinfection using Ultraviolet Light (UV); a special lamp is used to create the radiation. When UV radiation penetrates the cell wall of an organism, the cell’s genetic material is disrupted. Therefore, UV radiation effectively destroys bacteria and viruses. As with ozone, a secondary disinfectant must be used to prevent regrowth of microorganisms. UV radiation is unsuitable for water with high levels of suspended solids, turbidity, color, or soluble organic matter. These materials can react with or absorb the UV radiation, reducing the disinfection performance.

Comparison of all disinfectants based on their specifications is provided in Table 2.3.

Table 2.3 : Basic comparison of disinfectants (Chowdhurny, 2009)



Issue		Chlorine	Chloramine	Chlorine dioxide	Ozone	Ultraviolet radiation	Reference
Application		Most common	Common	Occasional	Common	Emerging use	USEPA (2006)
Cost		Lowest	Moderate (>chlorine)	High	High	Extremely high	Clark et al. (1994)
Disinfection efficiency	Bacteria (*V. chloerae*, Coliform, *E. coli*, etc)	Excellent	Good	Excellent	Excellent	Good	MWH (2005), Sadiq and Rodriguez (2004)
	Viruses (Polio virus, Rota virus, MS2 coliphase, etc)	Excellent	Fair	Excellent	Excellent	Fair	
	Protozoa (*G. lamblia*, *C. parvum*, *E. intestinalis*, etc)	Fair to poor	Poor	Good	Good	Excellent	
	Endospores	Good to poor	Poor	Fair	Excellent	Fair	
Organisms regrowth		Unlikely	Unlikely	Likely	More likely	More likely	MWH (2005)
Limits on free residuals		4 mg/L	4 mg/L	0.8 mg/L	–	–	USEPA (2006)
Byproducts	Regulated	4 THMs, HAAs	Traces of THMs and HAAs	Chlorite	Bromate	None	USEPA (2006)
	Unregulated	Many	Many: cyanogen halides, NDMA	Many: chlorate	Biodegradable organics	None known	Richardson (2005)
Oxidation		Strong	Weak	Selective	Strongest	None	Chlorine Chemistry Council (2003)
Odor and taste removal		Excellent	Good	Excellent	Good to poor	None	
Stability		Stable	Stable	Unstable	Unstable	Unstable	

2.2 General Information on and Formation Mechanism of Important DBPs

Disinfection by-products are first recognized in 1974, and since then various toxicological studies have been conducted to establish their effect, especially carcinogenicity on animals. Moreover several investigations have been carried out to establish a relationship between occurrence of cancer and chlorinated drinking water. Based on epidemiological studies and research on animals; U.S. Environmental Protection Agency (EPA), limited the presence of DBPs in drinking water with "Stage 1 Disinfectants/Disinfection Byproducts Rule" in 1998. This rule requires water systems to use treatment methods to reduce the formation of disinfection by-products and sets the following standards:

Total trihalomethanes (TTHM) measured as the sum concentration of chloroform, bromoform, bromodichloromethane, and dibromochloromethane) at 80 parts per billion (ppb), haloacetic acids (HAA5) (measured as the sum concentration of monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid) at 60 ppb, bromate at 10 ppb, and chlorite at 1.0 parts per million (ppm) (EPA,1998).

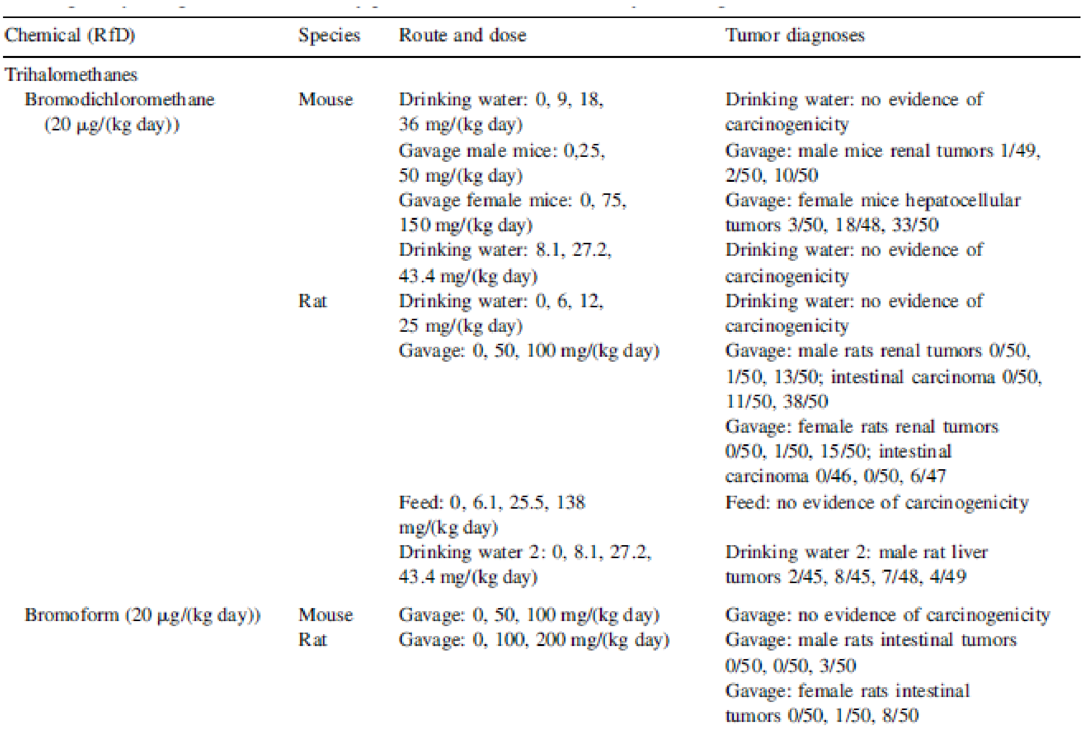
After 30 years, various epidemiological studies have done about DBPs, and their mutagenic and genotoxic properties are investigated. All four of the regulated THMs are carcinogenic in rodents (Richardson et al., 2007). Carcinogenicity of disinfection by-products is shown in Table 2.4.

After having many strong results about the effects of DBPs, many regulations include limitations for DBPs. DBPs for which standards have been established in drinking water are trihalomethanes, haloacetic acids, bromated and chlorite. There are several guidelines and standards developed by different countries for DBPs in drinking water. In 1996 World Health Organization (WHO) published guideline values for Trihalomethanes in drinking water. USEPA has standards for THM and HAA in 2003. Latest version is Stage 2 Rule. The current standards in the world are given in Table 2.5.

Chlorination causes high level of THMs, so that chloramines are used by many treatment plants in USA instead of chlorine. However, as a result of this treatment NDMAs may occur in water as an important DBP (Mitch et al., 2003). The California Department of Health Services established an action level for NDMA of

0.002 µg/L in 1998. California Department of Public Health calculated 10^{-6} cancer risk levels for 3 ng/L NDMA in drinking water (CDPH, 2008). Only two countries have a place in their regulations for NDMA, USA (only California) has 10 ng/L and has 9 ng/L maximum allowable concentration (MAC) limitations (Schafer et al., 2010). WHO has established a guideline value of 100 ng/L for NDMA in drinking water according to a lifetime carcinogenicity risk of 10^{-5} and 60 kg average weight for an adult consuming 2 L of water per day (Canada Guideline, 2011).

Table 2.4 : Carcionogenity of disinfection by-products in rodents based on 2-year dosing studies (Richardson et al., 2007)

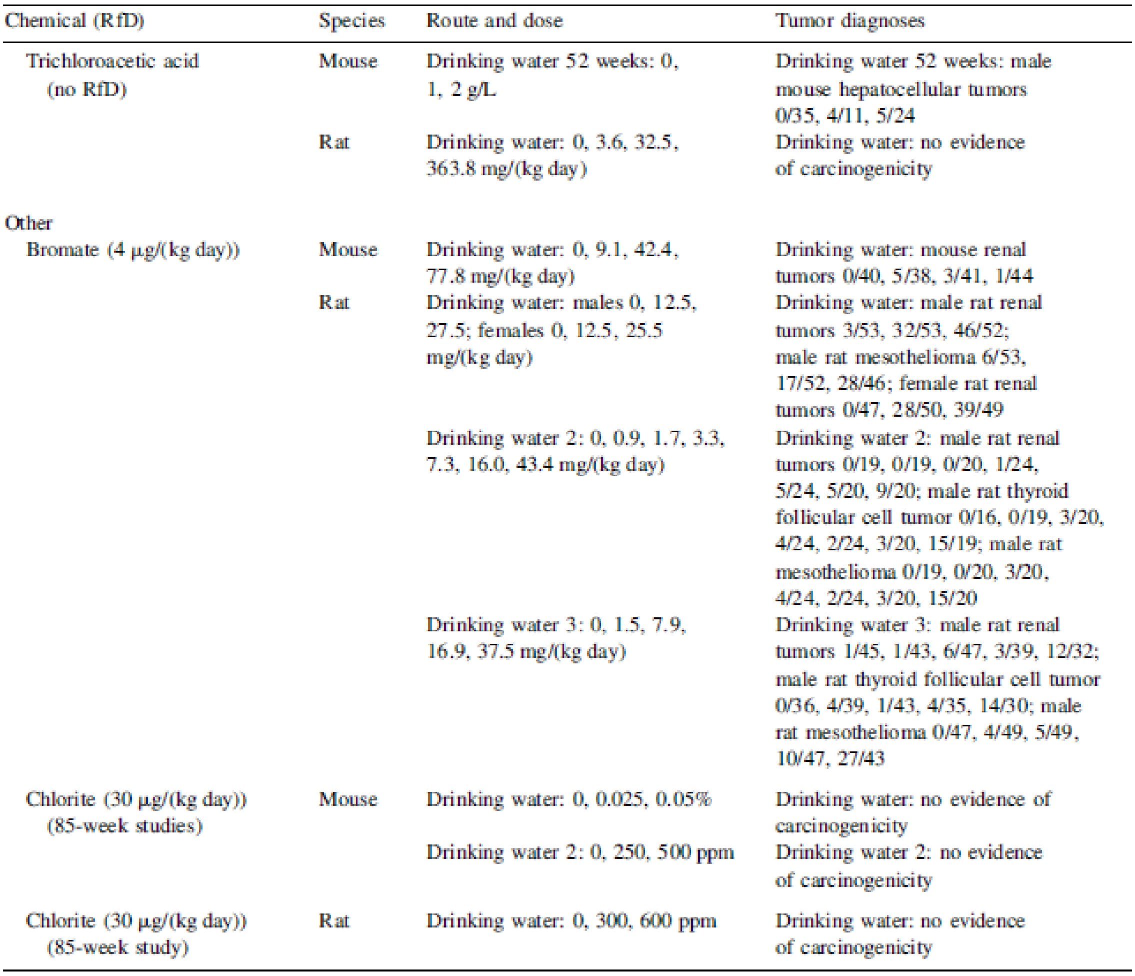


Chemical (RfD)	Species	Route and dose	Tumor diagnoses
Trihalomethanes			
Bromodichloromethane (20 µg/(kg day))	Mouse	Drinking water: 0, 9, 18, 36 mg/(kg day)	Drinking water: no evidence of carcinogenicity
		Gavage male mice: 0,25, 50 mg/(kg day)	Gavage: male mice renal tumors 1/49, 2/50, 10/50
		Gavage female mice: 0, 75, 150 mg/(kg day)	Gavage: female mice hepatocellular tumors 3/50, 18/48, 33/50
		Drinking water: 8.1, 27.2, 43.4 mg/(kg day)	Drinking water: no evidence of carcinogenicity
	Rat	Drinking water: 0, 6, 12, 25 mg/(kg day)	Drinking water: no evidence of carcinogenicity
		Gavage: 0, 50, 100 mg/(kg day)	Gavage: male rats renal tumors 0/50, 1/50, 13/50; intestinal carcinoma 0/50, 11/50, 38/50 Gavage: female rats renal tumors 0/50, 1/50, 15/50; intestinal carcinoma 0/46, 0/50, 6/47
		Feed: 0, 6.1, 25.5, 138 mg/(kg day)	Feed: no evidence of carcinogenicity
		Drinking water 2: 0, 8.1, 27.2, 43.4 mg/(kg day)	Drinking water 2: male rat liver tumors 2/45, 8/45, 7/48, 4/49
Bromoform (20 µg/(kg day))	Mouse	Gavage: 0, 50, 100 mg/(kg day)	Gavage: no evidence of carcinogenicity
	Rat	Gavage: 0, 100, 200 mg/(kg day)	Gavage: male rats intestinal tumors 0/50, 0/50, 3/50 Gavage: female rats intestinal tumors 0/50, 1/50, 8/50

Table 2.4 - (continued)

Chemical (RfD)	Species	Route and dose	Tumor diagnoses
Chlorodibromomethane (20 µg/(kg day))	Mouse	Gavage: 0, 50, 100 mg/(kg day)	Gavage: male mice hepatocellular tumors 23/50, 27/50 Gavage: female mice hepatocellular tumors 6/50, 10/49, 19/50
	Rat	Gavage: 0, 40, 80 mg/(kg day)	Gavage: no evidence of carcinogenicity
Chloroform (10 µg/(kg day))	Mouse	Gavage: males 0, 138, 277 mg/(kg day); females 0, 238, 477 mg/(kg day)	Gavage: male mice hepatocellular tumors 3/50, 18/50, 49/50 Gavage: female mice hepatocellular tumors 0/50, 40/50, 48/50
		Drinking water: 0, 34, 65, 130, 263 mg/(kg day)	Drinking water: no evidence of carcinogenicity
	Rat	Gavage: males 0, 90, 180 mg/(kg day); females 0, 100, 200 mg/(kg day)	Gavage: male rats renal tumors 0/50, 4/50, 12/50
		Drinking water: 0, 19, 38, 81, 160 mg/(kg day)	Drinking water: male rat renal tumors 4/301, 4/313, 4/148, 3/48, 7/50
		Inhalation males (0, 25, 50, 100 ppm, 6 h/day, 5 day/week) combined with drinking water (1000 ppm): total dose was 0, 73, 93, 135, mg/(kg day)	Combined exposure: renal tumors 0/50, 4/50, 4/50, 18/50
Haloacetic acids			
Chloroacetic acid (not listed on IRIS)	Mouse	Gavage: 0, 50, 100 mg/(kg day)	Gavage: no evidence of carcinogenicity
	Rat	Gavage: 0, 15, 30 mg/(kg day)	Gavage: no evidence of carcinogenicity
		Drinking water: 0, 3.5, 26.1, 59.9 mg/(kg day)	Drinking water: no evidence of carcinogenicity
Bromoacetic acid (not listed on IRIS)	Mouse	No data	No data
	Rat	No data	No data
Dibromoacetic acid (not listed on IRIS)	Mouse	Drinking water: 0, 50, 500, 1000 mg/L	Male hepatocellular tumors 28/49, 41/50, 42/50, 47/50; male lung tumors 12/49, 12/50, 22/50, 47/50 Female hepatocellular tumors 22/49, 28/50, 37/50, 37/49
	Rat	Drinking water: 0, 50, 500, 1000 mg/L	Male mesothelioma 3/50, 1/50, 0/50, 10/50; male leukemia 17/50, 31/50, 24/50, 13/50 Female mesothelioma 11/50, 13/50, 16/50, 22/50
Dichloroacetic acid (4 µg/(kg day))	Mouse	Drinking water 52 weeks: 0, 1, 2 g/L	Drinking water 52 weeks: male mouse liver tumors 0/35, 0/11, 7/24
		Drinking water: 0, 8, 84, 168, 315, 429 mg/(kg day)	Drinking water: male mouse hepatocellular tumors 13/50, 11/33, 12/24, 23/32, 13/14, 8/8
	Rat	Drinking water: 0, 3.6, 40.2, 139.1 mg/(kg day)	Drinking water: male rat hepatocellular tumors 1/33, 0/26, 7/29, 8/28

Table 2.4 - (continued)



Chemical (RfD)	Species	Route and dose	Tumor diagnoses
Trichloroacetic acid (no RfD)	Mouse	Drinking water 52 weeks: 0, 1, 2 g/L	Drinking water 52 weeks: male mouse hepatocellular tumors 0/35, 4/11, 5/24
	Rat	Drinking water: 0, 3.6, 32.5, 363.8 mg/(kg day)	Drinking water: no evidence of carcinogenicity
Other			
Bromate (4 µg/(kg day))	Mouse	Drinking water: 0, 9.1, 42.4, 77.8 mg/(kg day)	Drinking water: mouse renal tumors 0/40, 5/38, 3/41, 1/44
	Rat	Drinking water: males 0, 12.5, 27.5; females 0, 12.5, 25.5 mg/(kg day)	Drinking water: male rat renal tumors 3/53, 32/53, 46/52; male rat mesothelioma 6/53, 17/52, 28/46; female rat renal tumors 0/47, 28/50, 39/49
		Drinking water 2: 0, 0.9, 1.7, 3.3, 7.3, 16.0, 43.4 mg/(kg day)	Drinking water 2: male rat renal tumors 0/19, 0/19, 0/20, 1/24, 5/24, 5/20, 9/20; male rat thyroid follicular cell tumor 0/16, 0/19, 3/20, 4/24, 2/24, 3/20, 15/19; male rat mesothelioma 0/19, 0/20, 3/20, 4/24, 2/24, 3/20, 15/20
		Drinking water 3: 0, 1.5, 7.9, 16.9, 37.5 mg/(kg day)	Drinking water 3: male rat renal tumors 1/45, 1/43, 6/47, 3/39, 12/32; male rat thyroid follicular cell tumor 0/36, 4/39, 1/43, 4/35, 14/30; male rat mesothelioma 0/47, 4/49, 5/49, 10/47, 27/43
Chlorite (30 µg/(kg day)) (85-week studies)	Mouse	Drinking water: 0, 0.025, 0.05%	Drinking water: no evidence of carcinogenicity
		Drinking water 2: 0, 250, 500 ppm	Drinking water 2: no evidence of carcinogenicity
Chlorite (30 µg/(kg day)) (85-week study)	Rat	Drinking water: 0, 300, 600 ppm	Drinking water: no evidence of carcinogenicity

Table 2.5 : Guidelines and Standards in the World

DBP	**USEPA Drinking water standards (mg/L)**	**WHO Guidelines for Drinking Water (mg/L)**	**European Union Drinking Water Standards (µg/L)**	**Guidelines for Canadian Drinking Water (µg/L)**	**Turkey Drinking Water Standards (µg/L)**
Total THMs	0.080	1	100	0.10	100 (It is 150 µg/L till 2012)
5 Haloacetic acids	0.060			0.08	
Bromate	0.010	0.010	10	10	
Chlorite	1.0	0.7		1000	
Chloroform		0.3			
Bromodichloromethane		0.06		16	
Dibromochloromethane		0.1			
Broform		0.1			
Bromate	0.01	0.01	10	10	10
Chlorite	1.0	0.7		1000	
Chloralhydrate (trichloroacetaldehyde)					
Dichloroacetonitrile		0.02			
Dibromoacetonitrile		0.07			
Cyanogen chloride (as CN)		0.07			
2,4,6-Trichlorophenol		0.2			
Formaldehyde					
NDMA		0.0001		0.009	

2.2.1 Chlorination disinfection by-products

The most widely studied chlorination by-products are trihalomethanes. THM formation process can be described basically (2.2):

Precursor(s) + $HO_x \rightarrow CHX_3$ **(2.2)**

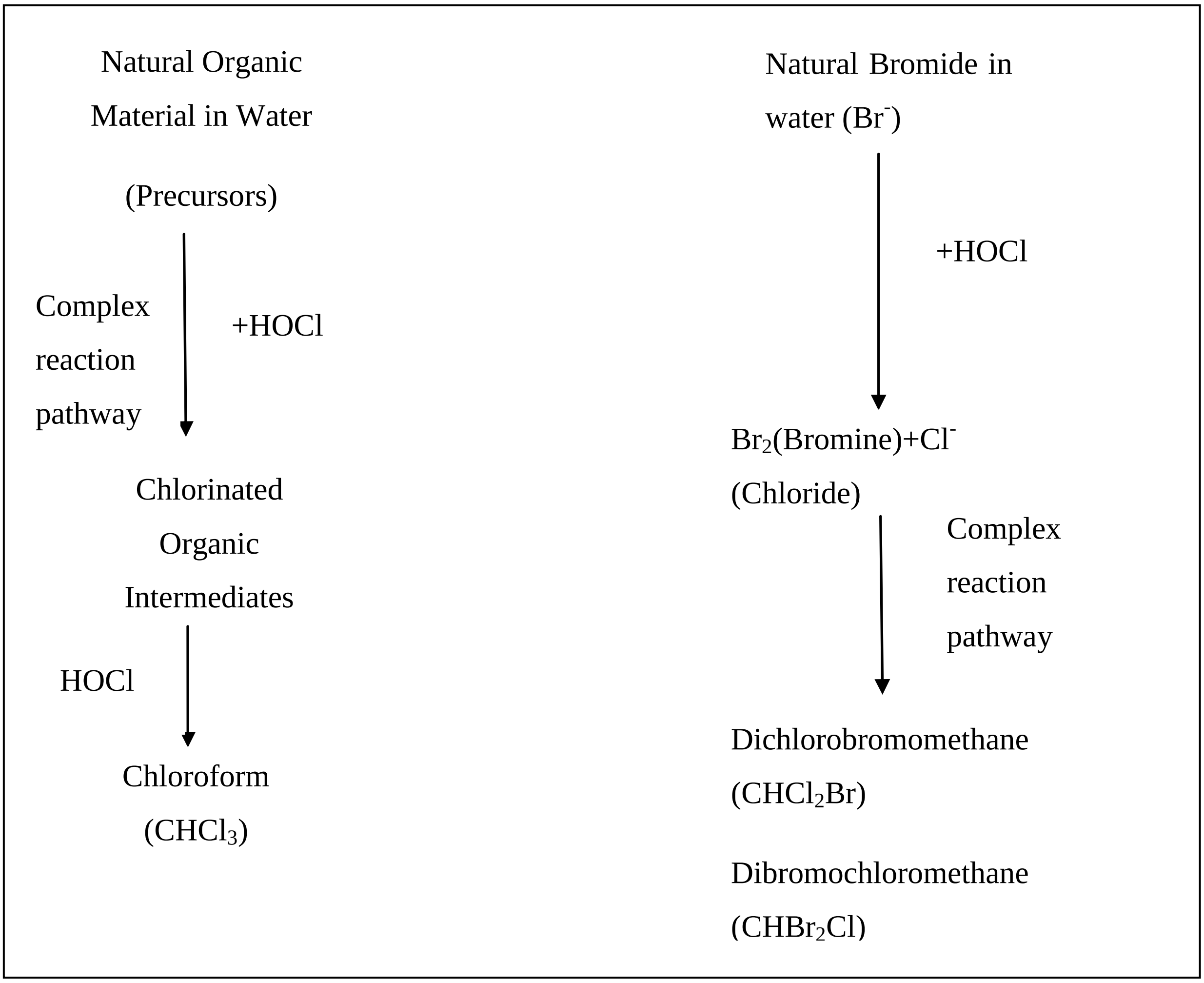
X : Cl, Br

CHX_3 : general formula of Trihalomethanes

(Chawla, 1983)

Actually, this is a complex mechanism and following parameters are important;

- Concentration and type of precursors
- Concentration of chlorine (disinfectant)
- Temperature
- pH

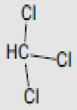
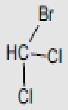
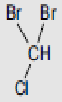
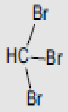


THM formation continues until either chlorine or precursors are exhausted.

Chlorination by-products are; trihalomethanes (chloroform, bromodichloromethane, dibromochloromethanes, bromoform), haloacetic acids (monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid, bromodichloroacetic acid, dibromochloroacetic acid, monobromoaceticacid, dibromoacetic acid, tribromoacetic acid), haloacetonitriles (trichloroacetonitrile, dichloroacetonitrile, bromochloroacetonitrile, dibromoacetonitrile

, bromoacetonitrile), haloketones (1,1-dichloroacetone, 1,1,1-trichloroacetone), miscellaneous chlorinated organics (chloral hydrate, chloropierin), cyanogen halides (cyanogen chloride, cyanogen bromide), oxyhalides (chlorite, chlorate, bromate), aldeyhydes (formaldehyde, acetaldehyde, giyoxal, methyl giyoxal, isobutyraldehyde, isoavaleraldehyde, 2-methylbuyraldehyde, phenyacetaldehyde), aldoketoacids (pyruvic acid, ketomalonic acid), carboxylic acids (formate, acetate, oxalate), maleic acid, chlorophenols (chlorophenol, dichlorophenols, trichlorophenols), chloroanisoles, haloacids (3,3-dichloropropenoic acid, 3-bromo-3-chloro-4-oxypentanoic acid, 2,3-diboromopropanoic acid,3,3-dibromo-4-oxopentanoic acid, 3,3-dibromopropenoic acid, cis-2,3-dibromopropeoic acid, trans-2,3-dibromobutenedioic acid, tribromopropeoic acid, cis-2-bromo-3-methylbutenedioic acid, 2-bromobutanoic acid, 3-bromo-3iodopropenoic acid, trans-4 bromo-2-butenoic acid, bromoiodoacetic acid, cis-4-bromo-2butenoic acid, 3-bromo-3iodopropenoic acid, trans-2,3-dibromo-2 butenoic acid, 2-iodo-3-methylbutanedioic acid, iodoacetic acid), haloacetates, halo-nitromethanes, iodoacids, iodo-tri halomethanes, halo-acetonitriles, halo-ketones, halo-aldehydes, haloamides, carbonyls, halopyrrole and NDMA. This study focused on trihalomethanes as and NDMA as chlorination by-products of which THMs are listed in Table 2.6. Since NDMA formation during chlorination is believed to be due to the reaction of monochloramine to form an unsymmetrical dimethylhydrazine (UDMH) intermediate (Mitch et al., 2003). NDMA and its formation will be explained in more detail in Section 2.2.2.

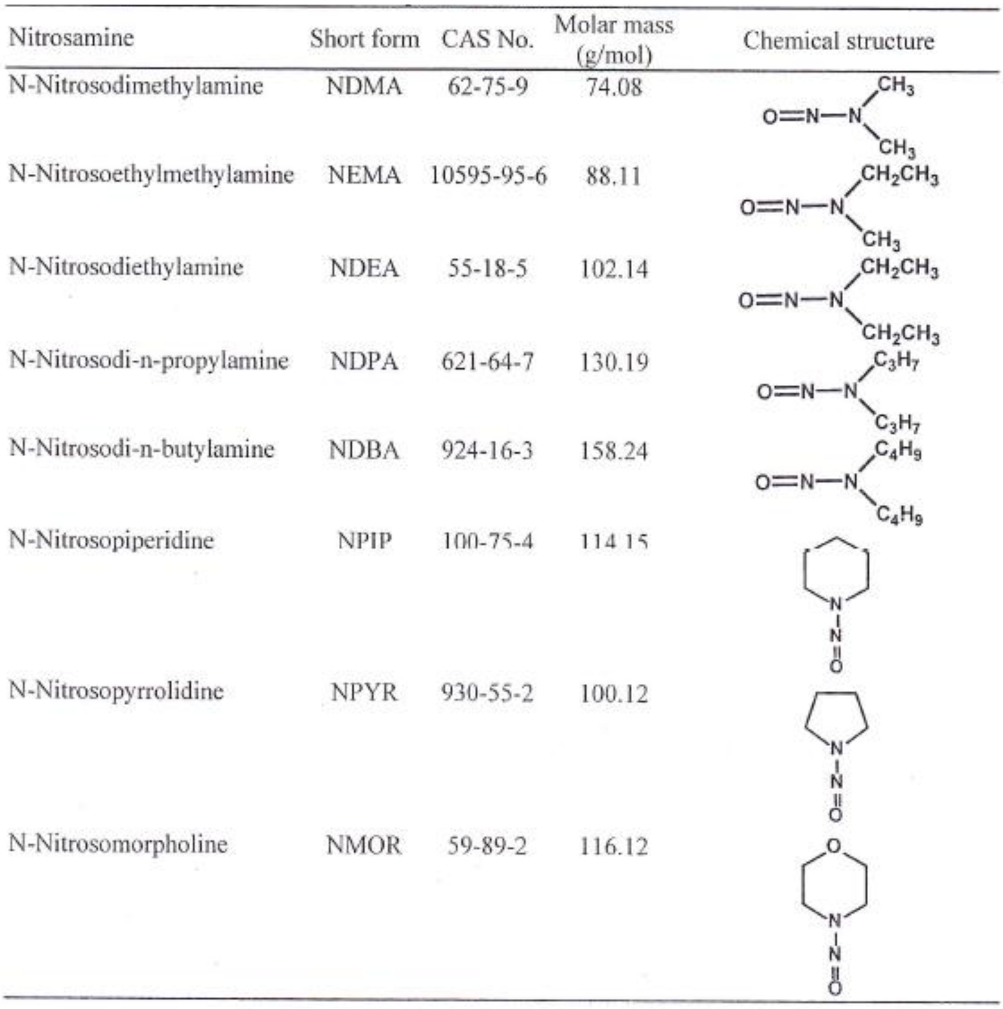
Table 2.6 : Trihalomethanes (THM4) (Hrudey, 2009)

General class	Name	Structure
Trihalomethanes THMs (collectively: THM4)	Chloroform	
	Bromodichloromethane	
	Dibromochloromethane	
	Bromoform	

2.2.2 Chloramination disinfection by-products

Trihalomethanes form either at low concentrations or not at all during chloramination. Nitrosamines are the main disinfection by-products formed during chloramination and their structures and physical and chemical properties are provided in Figure 2.1. and Table 2.7 (Sacher et al., 2008).

Although nitrosamines have carcinogenic, mutagenic and teratogenic effects (Loeppky, 1994), N-Nitrosodimethylamine is considered the most important and highly occurring DBP of chloramination.



Nitrosamine	Short form	CAS No.	Molar mass (g/mol)	Chemical structure
N-Nitrosodimethylamine	NDMA	62-75-9	74.08	
N-Nitrosoethylmethylamine	NEMA	10595-95-6	88.11	
N-Nitrosodiethylamine	NDEA	55-18-5	102.14	
N-Nitrosodi-n-propylamine	NDPA	621-64-7	130.19	
N-Nitrosodi-n-butylamine	NDBA	924-16-3	158.24	
N-Nitrosopiperidine	NPIP	100-75-4	114.15	
N-Nitrosopyrrolidine	NPYR	930-55-2	100.12	
N-Nitrosomorpholine	NMOR	59-89-2	116.12	

Figure 2.1 : Structures of NDMA and other nitrosamine DBPs (Sacher et al., 2008)

Table 2.7 : Physical and chemical properties of important nitrosamines (Sacher et al., 2008)

Nitrosamine	Density (g/mL)	Water solubility (g/100 mL)	Vapor pressure (hPa)*	Boiling point (°C)**
NDMA	1.006 (at 20 °C)	> 10 (at 19 °C)	2.1	151-153
NEMA	0.9448 (at 18 °C)	-	1.1	163
NDEA	0.9431 (at 20 °C)	9.3	0.81	175-177
NDPA	0.9163 (at 20 °C)	0.9894	0.086	206
NDBA	0.8997 (at 20 °C)	slightly soluble	0.03	235
NPIP	1.06 (at 20 °C)	1 – 5 (at 22 °C)	0.092	217-219
NPYR	-	-	0.072	214
NMOR	-	> 10 (at 19 °C)	0.036	224-225

* at 20 °C ** at 760 mmHg

It has been identified that NDMA is carcinogenic for animals. NDMA increased liver and kidney tumors in the case of chronic exposure through the respiratory and digestive systems (USEPA Technology Transfer Network, 2003). Experiments on animals showed that NDMA cause liver hemangiosarcomas, hepatocellular carcinomas, and kidney and lung tumors (WHO, 2007). Tumors due to exposure to NDMA have also been observed in rats, hamsters, rabbits, guinea pigs, ducks and fish (Sacher et al., 2008 and references there in).

U.S. Department of Health and Human Services settled risk levels for each nitrosamine in 2005, NDMA concentration for 10^{-6}cancer risk level is 0.7 ng/L (Sacher et al., 2008 and references there in). NDMA is classified as a ‘probable human carcinogen’ by the International Agency for Research on Cancer (Schafer, 2010), and food, cosmetics and cigarette smoke are among the exposure pathways in addition to drinking water. Several epidemiological studies shows that DBP in drinking water cause high risk for bladder cancer (IARC, 1978; Shank and Magee, 1981; Villanueva et al., 2004) or reproductive tract diseases (Nieuwenhuijsen et al., 2000). Moreover, there are studies relating the presence of NDMA and other DBPs in the drinking water with premature abruption of membranes (Joyce et al., 2008). Although NDMA is classified as 'possibly carcinogenic' by U.S. EPA, since it has not been defined as a DBP until recently, NDMA is not present in the drinking water standards in most countries (2003). Nevertheless, the USEPA Integrated Risk Information Services identified NDMA concentration for 10^{-6} risk of cancer as 0.7 ng/L (USEPA, 2008). Moreover, the Office of Environmental Health Hazard Assessment (OEHHA) identified concentration for 10^{-6} risk of cancer as 3 ng/L (OEHHA, 2006).

Nitrosamine formation chemistry is generally very complex involving several different reactions occurring at the same time. Monochloramine and organic nitrogen compounds (i.e., either dimethylamine or tertiary amines with dimethylamine functional groups) are the two key precursors (Mitch et al, 2003).

There are three formation mechanisms for NDMA. First one is nitrosation of nitrogen containing compounds by nitrosating agents (Mitch et al., 2003); second one is formation by UDMH explained before (Section 2.2.1), third one is reaction of monochloramine with aliphatic amines to chlorinated UDMH and subsequent oxidation to nitrosamines (Sacher et al., 2008).

General formation mechanism of nitrosamines is given in Figure 2.2.

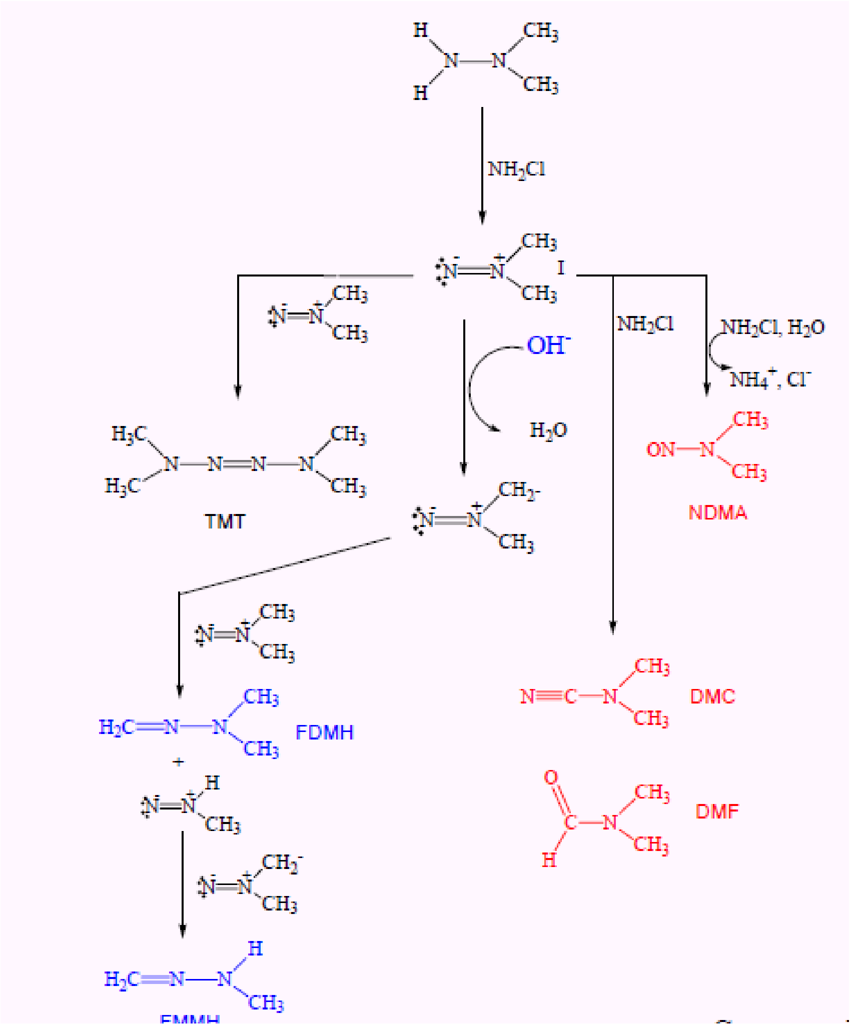


Figure 2.2 : Formation mechanism of nitrosamine (Mitch and Sedlak, 2002)

Moreover, reaction of DMA with ozone may lead to the formation of NDMA (Andrzejewski et al., 2005).

In the light of existing information, NDMA is not included among water quality parameters for drinking water as TOC, alkalinity, but because of the potential impact on public health it should be investigated in near future and it is one of the emerging contaminants which mean probably it will be included in the drinking water quality standards among time.

2.3 Occurrence

2.3.1 THMs

THM concentration is related to water quality parameters. Several investigations are conducted during last decade. Fate of THM is investigated in low TOC surface water in Korea (Kim, 2009) which on 30 conventional surface treatment plant samples in which total organic carbon ranges between 0.74 mg/L and 6.20 mg/L. THMs level is measured 4.5–84 mg/L, TOC range changes seasonally related that THMs concentration changes. Bromide plays a very important role for THM formation, total THMs increases with initial bromide concentration (Sorlini et al., 2005). Organic matter is an important DBP precursor (Sorlini et al., 2005; Chen et al., 2008). Moreover algae are behaving as a THM precursor (Chen et al., 2008). A study showed that the highest THM formation in dam lake water is in Istanbul, that means DOM is not just formed by fulvic and humic acid it also formed by other synthetic organic materials (Ateş et al., 2007a).

Disinfection method is effective on occurrence of THMs. Several long term studies are completed in different countries. Chlorination converts precursors to THMFP more than HAA, also THMFP concentrations are measured higher than THMs (Zhang et al., 2011). Chlorine, chlorine dioxide and ozone disinfectants are compared in oxidation batch tests, and results shows that total THMs increased with chlorine dosage, chlorine dioxide and ozone cause 97% less TTHM formation (Sorlini et al., 2004). Effects of disinfectants (chlorine, chloramine and ozone- total chlorine usage changes between 0.1 mg/L up to 5.75 mg/L) on DBPs formation in treatment plant and distribution system is examined and it is realized that chloroform, dichloroacetic acid and trichloroacetic are the major found DBPs (Williams et al., 1997). During a study where Terkos lake water is focused, enriched coagulation and activated carbon adsorption effects on DBPs formation is examined (Uyak et al., 2007).

THM concentrations in drinking water may change seasonally. In winter, especially in cases where the water's surface is covered with ice THM concentrations are lower; both low water temperature and decreased amount of the DOM takes a role on this situation (Sadiq et al., 2007, and in the references), this relation is available for treatment plants (Williams et al., 1997). Higher THM concentrations found in drinking water distribution networks during high summer temperatures (Health

Canada, 2006). Similarly, the studies conducted on 3 dam lakes and 3 water treatment plant reservoirs, lowest THMFP is determined in winter months and during spring months these values are increased, and finally reached its maximum value in fall semester (Uyak et al., 2008). During winter months in Büyükçekmece water treatment plant network's end point THM concentrations were found 100 mg/L, however during summer months where water temperature is higher than 10 °C THM concentration reaches 120-180 μg / L (Toröz and Uyak, 2006). In another study done in Turkey, on the contrary, the highest concentrations of THMs were found in winter, the lowest THM concentrations were measured in summer (Ateş et al., 2007a). One year long monitoring project showed that the highest THMs and HAAs formation potential (500 μg/L) occurred in autumn, and the lowest (100 μg/L) were in spring (Chen et al., 2008).

Studies on disinfection by-products in Turkey are accelerated since the early 2000s. Developing and accessibility of analytical techniques play a role for this situation, as well as the new limitations on clean drinking water. As a result of a study conducted on 29 dam lake all over Turkey, the THMFP value range is introduced between 21-189 μg/L (Ateş et al., 2007a). Yet another study held on 29 dam lake (161-137 mg / L) similar THM formation potential were obtained (Şahinkaya et al., 2005). Despite measuring 86% of THMs is chloroform, 11% is bromodichloromethane, 2.5% is dibromochloromethane and 0.25% is bromoform averagely, higher brominated compounds concentrations are expected because there is an interference from the sea water to the study place Büyükçekmece Lake. Indeed, due to the high bromide concentrations (274 mg/L) in Büyükçekmece Lake high bromoform concentrations were found (Bekbolet et al., 2005). In this study the specific total THM formation potential is measured on the samples taken from Ömerli and Büyükçekmece Lakes 42.1 and 44.2 μg/L respectively.

2.3.2 NDMA

NDMA was first measured in Canada drinking water in 1989 (OME, 2003). Later, NDMA was measured in the groundwater around rocket engine test areas in California, USA (CDHS, 2002; CDPH, 2008). This facility used unsymmetrical dimethyldrazine (UDMH)-based rocket fuel for engine testing. NDMA concentration is found 400.000 ng/L on site and 20.000 ng/L off site (Mitch et al., 2003).

Again in California Orange Municipality, 0.03 and 0.04 µg/L NDMA concentrations are measured in well waters near a wastewater treatment plant which is used for groundwater recharge, which lead to the closing of wells in 2000 (Hrudey, 2009). In 2000, in Los Angeles NDMA were found between 0.032 and 0.076 µg/L range in well waters, probably due to aircraft fuel plants. Moreover, NDMA is found more than 0.03 µg/L in a drinking water treatment plant which uses resin to remove nitrate in Los Angeles (Luo, 2006).

NDMA has been detected in drinking water treatment plants at low concentrations in the world. The highest reported concentration is 20.9 ng/L (Planas et al., 2008). In Canada where standards for NDMA exist, several studies about NDMA formation in drinking water treatment systems are conducted. NDMA concentrations are mostly below the maximum allowable concentration even at treatment plants which use chloramination for disinfection (Charrois et al., 2007). Nevertheless, NDMA has been detected in a treatment plant which uses only chlorine, in a number of cases up to 10 times of the standard.

Researchers tried to understand the effect of chlorination on drinking water about NDMA formation, so that 16 samples collected from a drinking water treatment plant and one chlorinated sample from a reservoir; NDMA is measured higher than 10 ng/L in reservoir and treated drinking water samples concentrations. Moreover the highest concentrations are measured after chlorination and ozonation process (Planas et al., 2008). Like Canada USA investigated drinking water treatment plants which use monochloramine as disinfectant and NDMA is found higher than 10 ng/L in four of ten drinking water treatment plants. NDMA levels range between 3 ng/L and 48 ng/L (Luo, 2006). After having some information about NDMA occurrence, comparison of disinfection methods and disinfection by-products (NDMA and THMs) become important, so that a comparison of disinfection by-products in chlorinated and chloraminated drinking waters is conducted in Scotland. Seven water treatment works are analyzed which are chosen according to different water sources, different treatment processes and different disinfection practices. Experiments are done through three seasons. Measured DBPs are: trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), trihalonitromethane, iodinated THMs and nitrosamines. There is not any difference of nitrogenous DBPs between chlorination or chloramination using treatment works. Only NDMA is found in one treatment work in one season. It is shown that in chlorinated works THM is increased during the water transfer from distribution system; however there is no difference occurs in chloramines works. Only in one exceptional work NDMA is found (8.6 ng/L) in treatment plant using chloramines for disinfection (Goslan et al., 2009). The effect of natural organic matter on formation of NDMA is not clear, to transcribe this relation a study is conducted in Japan on raw and finished water samples from drinking water treatment plants. The seasonal results shows that in summer raw water samples give maximum 2.6 ng/L NDMA concentrations while finished samples NDMA concentrations are up to 2.2 ng/L. In winter raw water samples give NDMA concentrations up to 4.3 ng/L while finished samples NDMA concentrations are up to 10 ng/L (Asami et al., 2009). Also NDMA and seven other nitrosamines are analyzed in six UK drinking water supply systems and only in one distribution system NDMA is measured more than detection limit (0.9 ng/l) (Templeton et al., 2010).

Furthermore NDMA is formed not only as a result of chlorination/chloramination but also as a result of ozonation of water containing dimethylamine (DMA) (Andrzejewski et al., 2007). Although NDMA formation via ozonation requires long contact time and low ozone / DMA ratio there is a possibility of NDMA formation even at treatment plant using ozonation, but there is not enough research. Also in USA a study conducted in 56 lakes of Missouri show that water with higher fluorescence intensity generally exhibited higher trihalomethanes formation potential. Waters with fluorescence center in the range of excitation 290–310 nm and emission 330–350 nm were related high NDMA and TTHM formation potentials. Fluorescence EEM fingerprints are important to be used as surrogate parameters for monitoring (Hua et al., 2006).

In addition to NOM, anthropogenic organic matter can act as a DBP precursor. For example chloramination of contaminated drinking water can lead to higher NDMA concentrations. Chloramination of drinking water caused 10 ng/L NDMA concentrations, but as a result of waste water chlorination 100 ng/L NDMA was formed. Therefore, in cases where drinking water is contaminated with waste water NDMA concentration in drinking water is expected to increase (Pehlivanoğlu-Mantaş and Sedlak, 2006a). Chlorination of wastewater before irrigation causes formation of NDMA in wastewaters containing ammonia (Pehlivanoğlu-Mantaş et al., 2006b). That situation can create hazard to public health with contamination of drinking water with irrigation water or consuming foods irrigated with recycled water.

Other sources of anthropogenic pollution could be diffuse pollution, especially agricultural runoff. (NDMA) can be formed during chlorination of water containing the herbicide diuron (N′-(3,4-dichlorophenyl)-N,N-dimethylurea) but presence of ammonia (chloramination) results higher NDMA formation. Groundwater can be contaminated by agricultural runoff which may contain diuron and high total nitrogen concentrations (Chen and Young, 2009). Moreover several other pesticides and pharmaceuticals could be DBP precursors (Le Roux et al., 2011). Therefore, it is possible to find other DBP precursors in surface waters due to possible pollution of anthropogenic sources as wastewater discharge and surface agricultural runoff.

3. BÜYÜKÇEKMECE BASIN AND WATER TREATMENT PLANT

3.1 Watershed

Büyükçekmece Basin covers 620 km^2 area of southwest of İstanbul. Büyükçekmece Lake has become a 36 km^2 lake after withdrawal a set around lagoon in 1985 (Baykal et al., 2000; Maktav and Erbek, 2005; Örgün et al., 2003). The lake is fed by seven streams. According to year 2000 data, approximately 2500 people of 76000 people live in absolute protection area, 2500 live in the field of short-distance protection area, 900 live middle distance protection area, rest of them live long-distance protection area (Baykal et al., 2000).

There are 129 industrial facilities in the basin; 16 of them are in the absolute protection area, 23 of them are in the short-distance protection area, 13 of them are in middle distance protection area, rest of them is in the long-distance protection area (Baykal et al., 2000). Although these data are not very recent, since the number of people living in the basin and the number of industrial facilities located in the basin have increased since the cite study; we can assume that the current state of the basin is more polluted than 1994 and 2000. Büyükçekmece Lake water quality parameters are given in Table 3.1.

Table 3.1 : Water quality parameters of Büyükçekmece Lake (Özdemir, Toröz, 2010)

Parameter	Unit	Value
Temperature	^{0}C	17.1
pH	-	8.19
Alkalinity	mgCaCO3/L	114
Turbidity	NTU	3.24
DOC	mg/L	4.71
UV254	cm-1	0.095
SUVA	L/mg.m	2.02
THMFP	µg/L	230

Streams in Basin:

- Akalın
- Ayvalı
- Çekmece
- Damlı
- Delice
- Eskidere
- Gökçeali
- Hadımköy
- Hamzalı
- İnceğiz
- İnter
- İzzettin
- Kadınlar
- Karasu
- Kavuk
- Kayan
- Kesliçiftliği
- Kestanelik
- Kızılcaali
- Köy
- Örcünlü
- Şeytan
- Tahtaköprü
- Tavşan
- Tepecik

Büyükçekmece Basin streams are shown in Figure 3.1. This figure is modified from the figure presented by DSI in1987.

The main rivers that feed Büyükçekmece are Karasu, Sarısu and Çakıl Streams.

Flowrate observation stations are operated only on two of the streams that feed the basin and study on flood flow; these are number 2-24 Tepecik flowrate observation station on Çakıl stream which is run by the General Directorate of State Hydraulic Works (DSİ) and number 211 Çatalca flowrate observation station on Karasu stream run by the General Directorate of Electrical Power Resources Survey Administration (EİE) (Hepdoğan, 1998).

The distribution of flows into Büyükçekmece Lake in different seasons is :

- 32% is between March-May months
- 1.5% is June-August months
- 6.5% is September-November months
- 60% is between December-February months

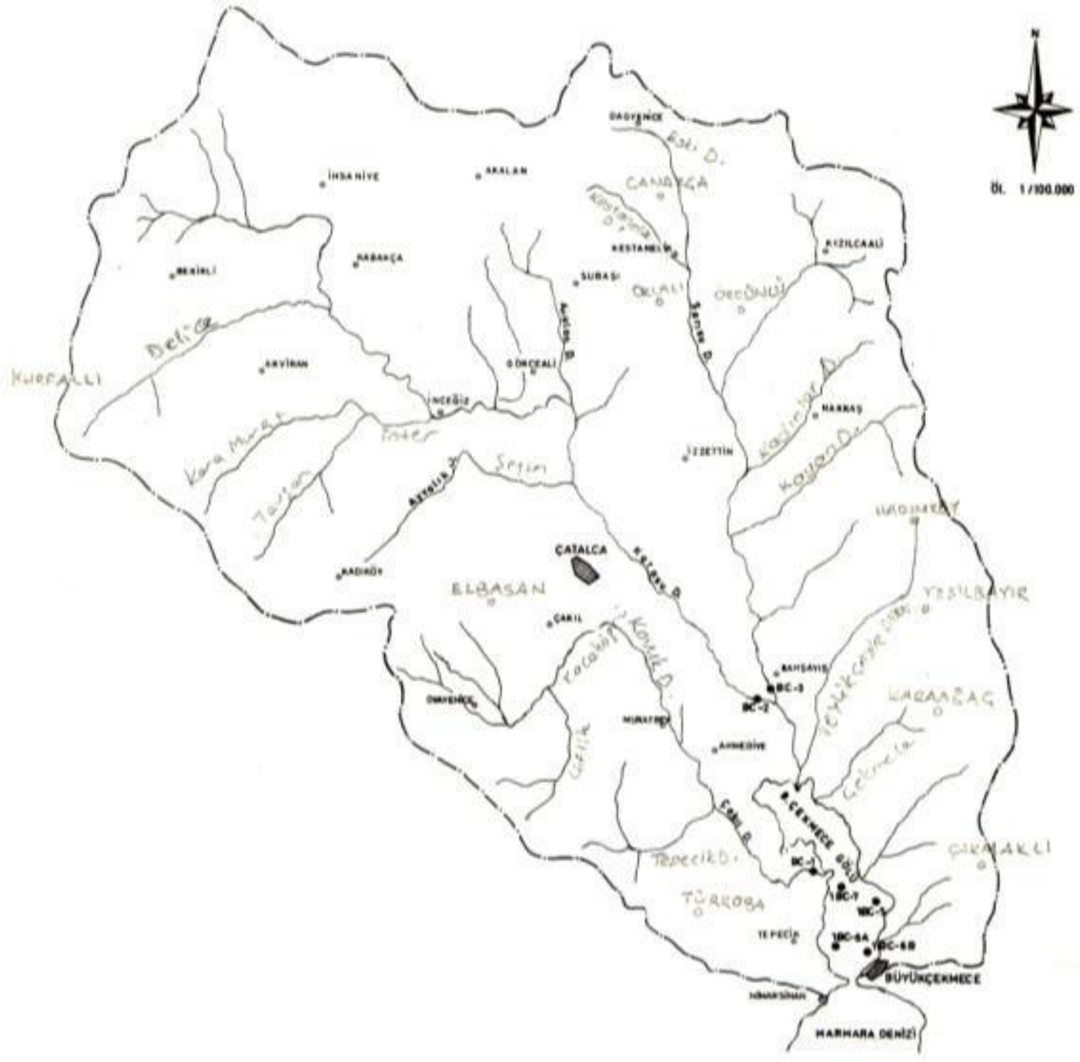


Figure 3.1 : Büyükçekmece Basin Streams

Büyükçekmece Lake

Based on Istanbul provincial environmental status report (İÇDR, 2005) Büyükçekmece Dam Lake is one of the water sources that suffers from pollution Büyükçekmece Dam Lake is contaminated due to domestic and industrial wastewater discharges, natural or human-induced erosion and agricultural activities.

Beler Baykal et al., (2000) classified İstanbul's drinking water supplies (Büyükçemece, Ömerli, Terkos, Darlık, Alibeyköy, Elmalı) according to the Water Pollution Control Regulation (1st class is high quality water). According to this classification, physical and inorganic chemical parameters of Büyükçekmece belong to 3rd class, organic parameters belong to 3rd class, inorganic parameter belongs to 4th class and bacteriological parameters are in the 2nd class.

3.2 Water Treatment Plant

Capacity of the plant is 400.000 m^3 per day, and serving maximum 2.600.000 people in İstanbul. The main residential areas that are fed by the plant are; Büyükçekmece, Beylikdüzü, Kıraç, Gürpınar, Esenyurt, Avcılar, Bahçeşehir, Çatalca, Kavaklı, Mimaroba, Sinanoba, Kumburgaz, Selimpaşa and Tepecik.

Water treatment plant process flow chart is provided in Figure 3.2.

Büyükçekmece drinking water treatment plant is consists of 9 main units;

1. Raw water intake and pump station
2. Aeration basin (tank)
3. Raw water distribution unit
4. Chlorination unit
5. Rapid and slow mixers
6. Sedimentation basin
7. Rapid sand filters
8. Fresh Water Pump Station
9. Energy and power station

3.2.1 Raw water intake and pump station

Raw water entry mouth is a section consists of an intake system with two doors and 5 mm screens; each of entry mouth is suitable for 2 pumps to receive water.

Raw water pump number 3+1
Raw water pump type SEZ.800 (900)-875
Flow rate 162.000 m^3/day
Lifting Height 30 m
Engine power 730 kw

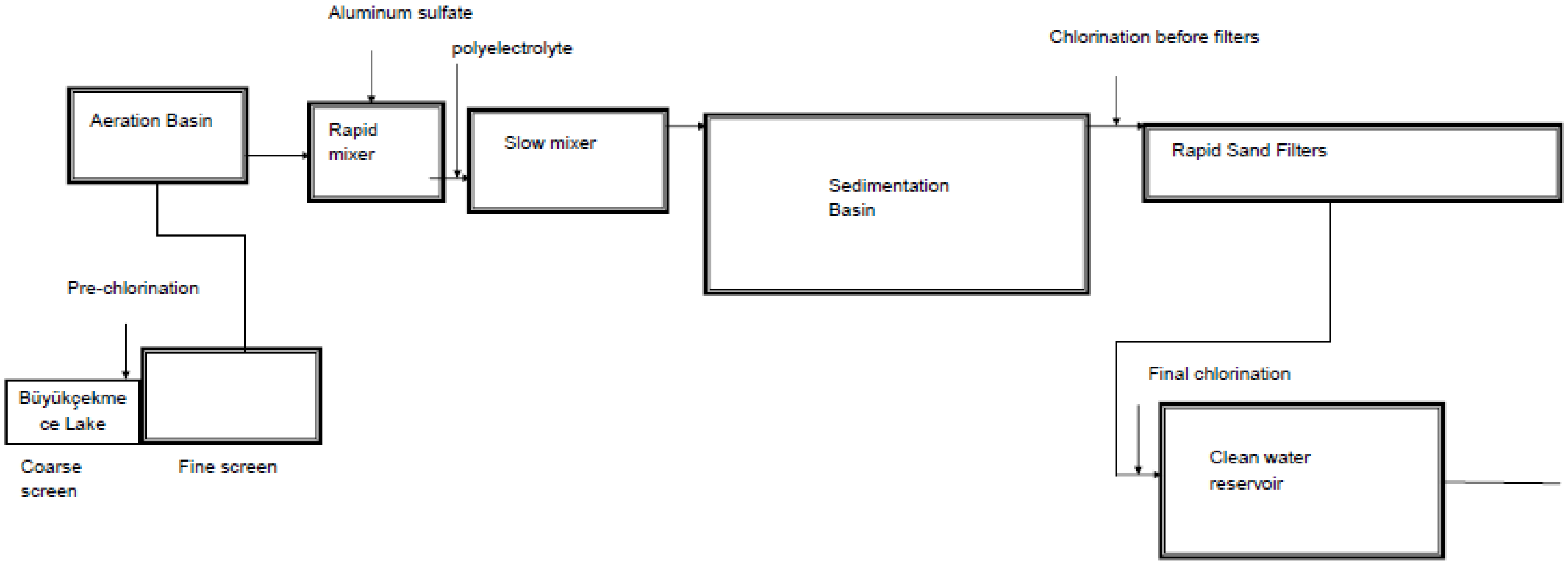


Figure 3.2 : Water Treatment Plant Flow Chart

3.2.2 Aeration basin (tank)

The aeration structure (32 m) was built in order to gain oxygen into water, oxidize iron and mangan. Structure of aeration is equipped with cascades to take 2 m distance during falling from top to the down. Water is pre-chlorinated in the out flow of aeration. Average Raw Water Blur is 5-10 NTU in the Büyükçekmece Liquidation plants; during severe winter conditions and windy weather it can reach more than 300 NTU.

3.2.3 Raw water distribution unit

Water comes from aeration unit is routing to the sedimentation pools in this section; also chemical substances (aluminum sulfate) are injected into the water. It consists of three separate rooms. It is called Mixer 1 (M1) room.

3.2.4 Chlorination unit

The chlorine is stored and prepared for dosing. Chlorine is stored in pressurized tanks as a liquid, but after coming into steam it is mixed with water.

Chlorine concentration (mg/L)	**Minimum**	**Maximum**
Pre-chlorination	1.5	3
Final chlorination	2	3.5

Aim of chlorination:

- Minimize the formation of algae in the raw water entrance (shock chlorination)
- Protect clarifiers against algae (pre-chlorination)
- Protect plant against mussels (shock and pre-chlorination)
- Eliminate or prevent the formation of bacteria that affect human health (pre-chlorination)
- Provide disinfection of the water (final chlorination)

3.2.5 Rapid and slow mixers

Rapid Mixers

After aeration, water goes raw water distribution room with an Ø1870 mm line, and from there it goes rapid mixers. Aluminum Sulfate mixed with water on the weir. Solution is injected into the water with perforated pipes. Mixing is provided with the turbulence of the difference between aeration and this unit level. Approximately water fall over the weir is 300 mm. Rapid mixing time, depending on flow rate, is 1.5-3 minutes.

Slow mixers

This section is the entrance of flat-based clarifying pools, and also polyelectrolyte is injected in this section. Slow mixing time is, depending on flowrate, between12-20 minutes.

3.2.6 Sedimentation basin

There are three sedimentation pools. Each one consists of two sedimentation unit.

As a result of upward flow of water comes from tridents in sedimentation pools sludge blanket is formed. The muddy waters filled into 14 cone-shaped PVC concentrators (hold by steel ropes).

Dimension: 40.5 m x 18 m
Depth: 4.5 m
Total number of tank: 6
Unit area: 729 m^2
Total are: 4.374 m^2
Unit volume: 3280.5 m^3
Total volume: 19.683 m^3

3.2.7 Rapid sand filters

Clean water outflow from sedimentation pools by Ø1400 mm pipes separately, and conjoint with 1600 mm main collector and enter fast sand filters as 2 pipe lines. Suspended particles are kept during passing through the sand filters that make the water clear and clean. In fast sand filters there are 20 cm gravel (5-7 mm) on the nozzles and on that there are 90 cm sand (0.8-1.2 mm).

Number of filter: 28

Filter length: 16 m

Filter width: 4 m (one pool)

Filter area: 64 m^2 (one pool)

Filter unit area : 128 m^2

Total area: 3.584 m^2

The filter backwash water goes to recycling unit from a separate line, and this water recovered by pressing to aeration unit with pumps.

Filtered water goes to maneuvering room and then goes to water tank's separate two units by two-line separately.

3.2.8 Fresh water pumping station

Volume of Büyükçekmece water treatment plant's clean water tank is 28.000 m^3.

There are two groups of pumps in this center. These pumps features are;

	Bahçelievler Pumps	Silivri Pumps
Number of pumps	3+1	2+1
Type of pump	RDL 500 – 790 B	RDL 500 - 790B
Flow rate	3996 m^3/day	3600 m^3/day
Maximum Discharge Height	116 m	128 m
Motor Power	2000 kw	2000 kw

3.2.9 Energy and power station

The plant is fed from double-sided, first feed is from 2.5 km away TEDAŞ Ambarlı-Tepecek power transmission line. Second feed if brought from TEDAŞ Beylikdüzü in 1998. Also a medium voltage substation was built in the middle of the plant.

4. MATERIAL AND METHODS

4.1 Sample Locations

Experiments within the scope of the thesis were conducted in three different phases. The first phase consists of the occurrence of DBP precursors in a watershed. In the second phase, water samples collected from a drinking water treatment plant were analyzed. The third phase consists of lab-scale disinfection studies conducted on real and synthetic samples for comparative analysis of THM and NDMA formation.

4.1.1 Watershed

The samples used in this study are collected from Büyükçekmece Lake and its tributaries Ahlat, Hamza, Beylikçayı, Karasu, and Tahtaköprü streams (Raw water : Water intake structure of drinking water treatment plant) in 10-L teflon-lined polypropylene containers (Nalgene) to prevent any contamination with NDMA precursors and are taken to Istanbul Technical University Environmental Engineering Laboratory on 21.10.2010.

4.1.2 Water Treatment Plant

Six grab samples were taken from Büyükçekmece drinking water treatment plant in 10-L teflon-lined polypropylene containers (Nalgene) to prevent any contamination with NDMA precursors and brought to Istanbul Technical University Environmental Engineering Laboratory on 02.07.2010 and 21.10.2010.

Sample locations are listed below and shown in Figure 4.1.

1- Raw water from the lake just before the water intake structure of the plant
2- Sample is from at the end of aeration unit, before the pre-chlorination
3- Sample is taken from before the fast mixing, after pre-chlorination
4- Sample is taken at the end of clarifier

5- Sample is taken after sand filters, before last chlorination
6- Sample is taken after clean water tank, inside the plant laboratory tap (water comes from the clean water tank)

4.1.3 Lab-scale Comparative Trials

The aim of trials is to compare three different disinfection methods; chlorination, chloramination and stepwise chloramination.

Figure 4.1 : Aluminum foil covered glass tanks

In these different disinfection methods disinfection dosages are determined as 2 mg Cl_2/L, 10 mg Cl_2/L and 100 mg Cl_2/L. 2 mg Cl_2/L and 10 mg Cl_2/L dosages represent real treatment plant chlorination and shock chlorination conditions whereas100 mg/L concentration is selected to be able to observe DBP formation under short contact time and low precursor concentrations.

5 L lake sample is transferred into each water tank. Hypochlorite dose solution with a concentration of 5 mg Cl_2/mL is prepared for chlorination, and then calculated volume of this solution is injected to the chlorination water tank to reach the final target Cl_2 concentration. Ammonium chloride solution is prepared for chloramination and then sodium hypochlorite is added into prepared solution to have a final concentration of 20 mM. This prepared solution is used directly for chloramination.

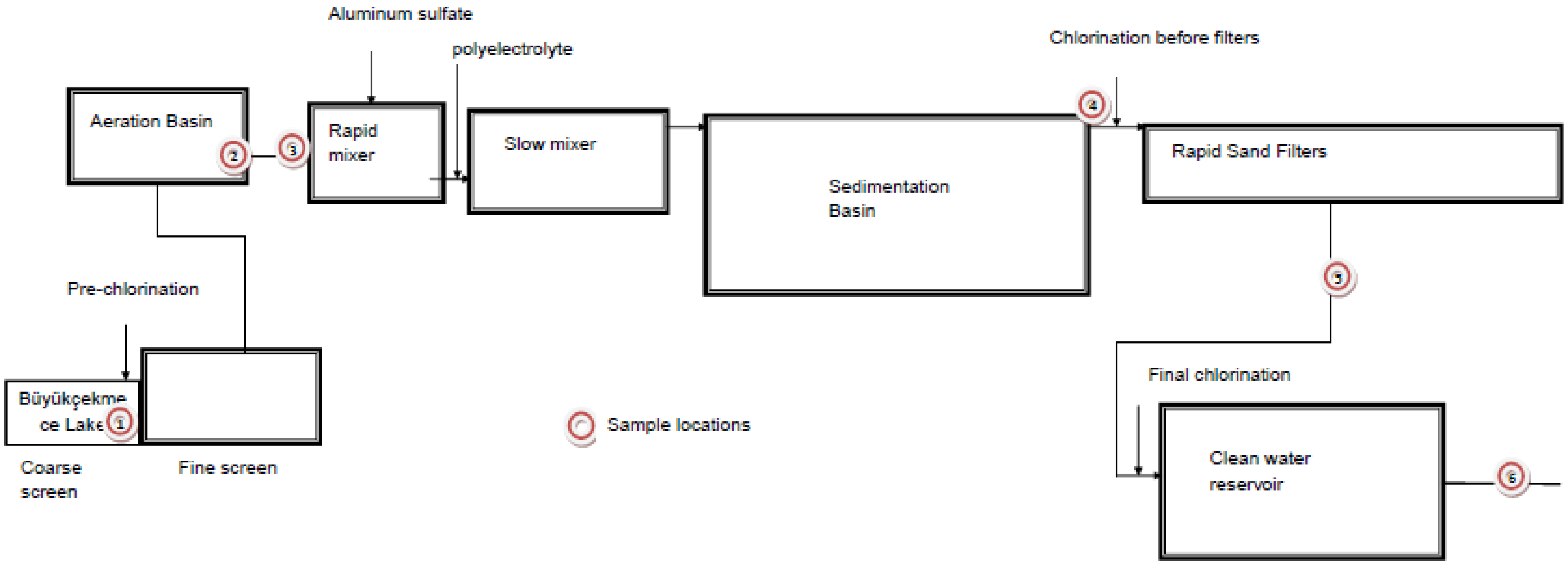


Figure 4.2 : Büyükçekmece Water Treatment sample locations

An appropriate volume of 5 mg Cl_2/mL hypochlorite dose solution is added to the third water tank (5 L) for the stepwise chloramine test. After one hour, the appropriate amount of solid ammonia chloride is added to the tank to reach the final Cl_2 concentration. Disinfection contact time is 2 hours in all trials (Cl_2, chlorination and stepwise chloramination). At the end of contact time, duplicate analysis for NDMA, NDMAFP, THM and THMFP completed.

The second batch of lab-scale trials are conducted with the addition of known NDMA precursors to water samples. Dimethylamine (DMA) and ranitidine are chosen as NDMA precursors (Sacher et al., 2008).

DMA (Figure 4.3) is a common substance in natural rubber stabilization, leather tanning operation, opening petrol wells, solvents, detergent industry and dye industry. It is guessed that 270.000 tones DMA is produced in 2005 (van Gysel and Musin, 2005). Furthermore, DMA is used for rocket fuel production and as a result of that NDMA is firstly measured in polluted underground water (Mitch et al., 2003). Ranitidine (Figure 4.4) is a pharmaceutical used to cure stomach ulcer or to prevent ulcer formation since 1981 (Ellis, West, 1983). Ranitidine becomes the most selling medicine in 1988 in the world. Because of all these reasons there is a possibility to find both two substances in drinking water. The main reasons of choosing these two chemicals are; NDMA can be formed even in low ranitidine concentration in water and DMA is it is the first model compound about NDMA.

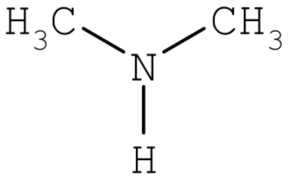


Figure 4.3 : Dymethylamine

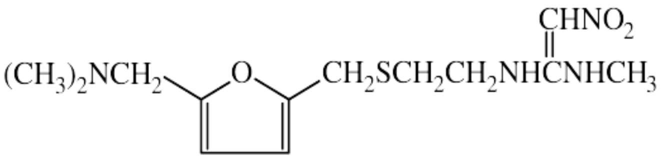


Figure 4.4 : Ranitidine

In lab-scale trials, concentrations of DMA and ranitidine were selected as 1.1 μM and 10 nM, respectively based on their molar conversion rates (0.76% and 62.7%, respectively for DMA to NDMA and ranitidine to NDMA) (Sacher et. al, 2008; Shen and Andrews, 2011). Lab-scale trial summary plan is provided in Table 4.1.

Table 4.1 : Lab-scale trial summary plan

Sample	**Chlorination (mg/L)**	**Chloramination (mg/L)**	**Stepwise Chloramination (Cl_2+NH_3) (mg/L)**
Lake	2	2	2
Lake	10	10	10
Lake	100	100	100
Lake + Ranitidine	10	10	10
Lake +Ranitidine	100	100	100
Lake + Dimethylamine	2	2	2
Lake + Dimethylamine	10	10	10

4.2 Experimental Procedures

Samples are filtered using a Polycap AS-75 brand filter with 0.2 µm pore size in the laboratory and kept at 4 ° C until analyses. Experiments made with dissolved part of samples and also filter-sterilization is provided with the filtration by 0.2 μm filter.

4.2.1 Standard methods

4.2.1.1 pH, temperature and dissolved oxygen measurement

pH, temperature and dissolved oxygen measurements were made in the sampling points with a portable pH meter and the necessary probes (WTW-Oxi330i probe).

4.2.1.2 Dissolved Organic Carbon (DOC) analysis

DOC measurements were done with combustion infrared method as described in Standard Method 3510B by automatic sampling device Shimadzu TOC-5000. Sample is injected a heated reaction room which is filled with platinum oxide catalyst (oxidize organic carbon to CO_2 gasses). Produced inorganic CO_2 is measured with infrared analyzer. General features of TOC device is given in Table 4.2.

Table 4.2 : General features of TOC device

SHIMADZU YOK-5000	
Analyses	TC, TOC,UOK,POK
Method	Combustion infrared gas analysis method
Combustion temperature	680 ^{0}C
Measurement interval	4 ppb - 4000 ppm TOC
Sample injection volume	4-2000 μL

4.2.1.3 UV254 measurement

This parameter provides information about organic substances in water and their aromatic structure. This parameter's measurement was made with Shimadzu 1601 UV-vis Spectrophotometer.

The technique is sending ultraviolet rays between range of 190-1100 nm into the solution and adsorption of ultraviolet rays by substances. Measurements were made at a wavelength of 254 nm at which organic matter has the highest absorbance. Technical features of the device are given in Table 4.3.

4.2.1.4 SUVA parameter

To compare organic substances in different character, UV absorbance of a particular wavelength divides by DOC concentration and this is called specific UV absorbance (SUVA) (L/mg.m). SUVA is semi-quantitative measurement of aromatic structure in the organic carbon content.

4.2.1.5 Anion measurements

Fluoride, chloride, bromide, nitrite, nitrate, phosphate and sulfate anions measurements made with a Dionex ICS-1500 ion chromatograph using EPA 300.0 method. The instrument's technical features are provided in Table 4.4.

4.2.1.6 Measurement of residual chlorine

Free chlorine in the samples was measured at the end of 7-day incubation period using Std. Methods, 4500-Cl G. Technical specifications of spectrophotometer are given in Table 4.5.

Table 4.3 : UV Visible Spectrophotometer Device technical features

UV-1601 VISIBLE SPECTROPHOTOMETER (SHIMADZU)	
Range of wavelength measurement	190-1100 nm
Wavelength indicator	0.1 nm
Sampling interval	1.0 nm 910 nm ≥ λ interval > 500 nm 0.5 nm 500 nm ≥ λ interval > 200 nm 0.2 nm 200 nm ≥ λ interval > 100 nm 0.1 nm 100 nm ≥ λ interval
Photometric system	Dual-light emitting optic
Photometric interval	Absorbance - 0.5-3.999 Abs Transmittance 0-300%
Photometric accuracy	± 0.004 Abs (for 1.0 Abs) ± 0.002 Abs (for 0.5 Abs)
Dimension	550x470x380 (WxDxH)
Weight	18 kg
Power requirement	100, 120, 220, 230, 240 V 50, 160 Hz160 V A

Table 4.4 : Dionex IC-1500 Technical features and working conditions

Dionex IC-1500 Technical features and working conditions	
Mobile phase	8mM Na_2CO_3 +1mM $NaHCO_3$
Stationary phase	AS14 ion chromatograph column
Suppressor	ASRS-4mm
Detector	Conductivity

4.2.1.7 Alkalinity measurements

Alkalinity is an important parameter must be followed during use and soften of process water, chemical treatment of wastewater and industry boiler water. 25 ml sample taken for measurement of alkalinity and titrated with 0.02 N H_2SO_4 until pH 4.5. Alkalinity value is calculated with H_2SO_4 consumption.

4.2.1.8 TKN and NH_3 measurements

Ammonia nitrogen determination method:

Determination method of ammonia nitrogen is selected due to the concentration and presence of substances that can cause interference. Colorimetric methods are applied to be able to measure low ammonia nitrogen concentrations in drinking water, clean surface water, underground water and high quality, nitrified wastewater effluents. Ammonium ions (NH_4^+) are converted to ammonia (NH_3) when pH values are above 7. This transformation is almost complete around pH 9.5. Pre-distillation process is needed in the presence of interference substances and study of a higher sensitivity. Distillation-titration method is especially applied on the samples that concentration of ammonia is higher than 5 mg/L. Distillation process provides separation of ammonia nitrogen from many interference substances. Sample is buffered with borate buffer solution to reduce hydrolysis of organic nitrogen compounds and cyanates at pH 9.5 and then distilled into boric acid solution. During distillation vapor phase is condensed and collected in boric acid solution. And then this solution is titrated by a strong acid to determine ammonia nitrogen.

NH_3-N Phenate method:

Titration method is not available in the case of drinking water samples in which ammonia NH_3- N concentration is very low, for this situation measurements were carried with Standard Methods 4500-NH_3-N Phenate Method. In this method, colored samples were measured on 640 nm with the spectrometer.

Total Kjeldahl Nitrogen method (TKN):

In the presence of H_2SO_4, potassium sulfate (K_2SO_4) and cupric sulfate ($CuSO_4$) catalyst amino nitrogen of many organic materials is converted to ammonium. Free ammonia also is converted to ammonium. After addition of base, the ammonia is distilled from an alkaline medium and absorbed in boric or sulfuric acid. The ammonia may be determined calorimetrically, by titration with a standard mineral acid (standard methods 4500 B).

4.2.2 THM, THMOP, NDMA, NDMOP methods

4.2.2.1 Measurement of trihalomethane

THMs analysis in drinking water was conducted using Standard Methods 5710 B method. Volatile chlorinated organic in water phase can be extracted easily using pentane solvent. 35 ml water sample contains THM is emptied to 40 ml special vial. 1 ml Na_2SO_3 and 3 ml pentane is added on it. Then, the lid of the vial is closed and the vial is shaken rapidly for one minute. After that, vial waits 3 minutes for phase separation. Pentane phase at the top side is transferred into a 2 ml volume of vial by using a pastor pipette. Then, 2 ml extract is analyzed by Agilent 6890 model gas chromatograph device (Figure 4.5) which has capillary column with electron capture detector. Technical specifications of the device are given in Table 4.6. Detection limit of the device is 0.1 μg/L.

Table 4.5: Scinco SV-1141 vis-Spectrophotometer technical features

Scinco SV-1141 model vis-UV spectrophotometer	
Spectral band width	< 4nm
Wavelength range	340-1100 nm
Sensitivity	< 1 nm
Repeatability	< 0.5 nm
Monochromator	Czerny-Turner tip
Scattered light	<0.1% T at 340 nm
Photometric range	< 0.1-3.0 A,%0-125
Sensitivity	±0.003 A,0-2 A ±%1(read value), 0.3-2 A ±%2(read value), 2-3 A
Balance	± 0.002 A/h
Light source	Tungsten Halogen Lamp
Image mode	LCD
Sample carrier	Standard rectangular cell carrier
Interface ports	RS-232 C
Standard capacity	Absorbance /%conductivity/concentration
Power requirement	AC 100-230 V, 50/60 Hz,1A
Dimension (mm)	300x250x125 (WxDxH)

Figure 4.5 : 6890N GC μECD Device

Table 4.6 : Conditions of Agilent 6890N GC μECD Device

Analytic Column	
Model	DB 1
Producer	J & W Scientific Folsom CA
Product type	Fused silica capillary
Length	30 m
Inner diameter	0.32 mm
Film thickness	1 μm
Injection	
Injection volume	2 μL
Temperature	200 ^{0}C
Detector	
Type	μECD
Temperature	300 ^{0}C
Oven temperature program	It stays 9 min in 35 ^{0}C, then stays 5 min till 40 ^{0}C with 1^{0}C/min increase. Temperature increases to 120 ^{0}C in 13 min with 6 ^{0}C / min. Stays 2 min in 120 ^{0}C. Finally the temperature increases till 150 ^{0}C in 0.5 min with 60 ^{0}C / min and stays for 5 min.
Carrier Gas	
Type	Helium
Carrier stream	13 mL / min
Collector Gas	
Type	Nitrogen
Collector stream	58.7 mL/ min

4.2.2.2 Chlorination of samples and THM formation potential

5ml chlorine dosing solution is completed with double distilled water to 250 ml. Then 100 ml of prepared solution is taken and titrated with 0.02 N Na_2SO_4. Initial chlorine concentration (C_1) is calculated by using of Na_2SO_4 consumption. This value is expected to be around 100 mg/L. Then 5 ml chlorine dosing solution and 5 ml phosphate buffer solution is transferred in to another volumetric flask and completed to 250 ml and mixed. This prepared solution store at 25 ° C for 4 hours and then chlorine is determined. 100 ml is taken from prepared chlorine determination solution and titrated with 0.02 N Na_2SO_4. The amount of residual chlorine (C_R) is determined by using Na_2SO_4 consumption at the end of 4 hours. Chlorine demand (D_{Cl}) is calculated with the difference of these two values.

$$DCl = C1 - CR \tag{4.1}$$

Then, the required dosing solution volume (VD) is calculated.

$$V_D = \frac{D_{Cl} + 3}{5} \times \frac{V_S}{1000} \tag{4.2}$$

After all these processes phosphate buffer solution is added according to the sample bottle volume (1 ml tampon / 50 ml sample), mouth of the bottles are closed with lids, and left in incubator (25 ±2 °C) for 7 day incubation period.

4.2.2.3 Measurement of NDMA

NDMA measurements are conducted with both solid phase extraction (SPE) pre-operations and LC-MS/MS settings (Topuz et al., in review).As a result of these studies appropriate SPE conditions are determined as follows:

SPE Method: Before the start of solid phase extraction d6-NDMA injection is done into the samples according to the last concentration is 100 ng/L. Before sample filtration activated carbon cartridges are conditioned. Bakerbond (Activated spherical carbon SPE column) brand cartridges conditioning procedure is respectively, 2 x 5mL acetonitrile and 2 x 5 ml double distilled water filtration. Then the samples are filtered from carbon cartridge 5 ml / min filtration rate with the help of vacuum pump. During filtering cartridge is completely dried. NDMA in solid phase is collected from cartridge into the liquid phase by using 2 x 5 mL acetonitrile and 2 x 5 mL acetone. Liquid phase which is around 20 ml becomes less than 1 mL by TurboVAP-II instrument (Figure 4.6) under 25 ° C and 2 bar nitrogen gas conditions, after that HPLC-grade is completed to 1 mL with water. The sample is filtered from 0.22 µm injection an then taken to 3 ml vial.

LC-M/MS method: UPLC (Ultra-Performance Liquid Chromatography) (Figure 4.7) was used for the measurement of NDMA and d6-NDMA, and as eluent water with 0.1% formic acid (A) and acetonitrile (B) were used. 400 µL/min flow velocity gradient has been used as eluent flow with UPLC; gradient program is given in Table 4.7. For conversion of NDMA and d6-NDMA respectively, 75.4→ 43.7 and 81.4 →46.7 conversions are used. Mass spectroscopy measurement conditions are given in Table 4.8.

Figure 4.6 : TurboVAP-II instrument

Table 4.7 : Gradient program for UPLC

Time (min)	**%B**
0	5
2	5
4	95
4,1	5
8,35	5

Table 4.8 : MS/MS measurement conditions for NDMA and d6-NDMA

Parameter	Optimum value
Sprey Voltage (V)	5000
Sheath Gas Pressure (arb.)	10
Ion Sweep Gas Pressure (arb.)	0
Auxillary Gas Pressure (arb)	5
Capillary Temperature (°C)	350
Tube Lens Offset (arb.)	37
Skimmer Offset	0
Collision Pressure (mTorr)	1.5
Collision Energy (Volt)	17
Scan Width (m/z)	0.2
Scan Time (s)	0.1

Figure 4.7 : LC-MS/MS instrument

4.2.2.4 Measurement of NDMAFP

A formation potential test based on extreme chloramination is used for the measurement of substances that act as NDMA precursors (Mitch et al., 2003). Chloramine is added into the sample to have a final chlorine concentration of 2 mM with 5 per thousand phosphate buffer solution. At the end of 10 days 10 mL ascorbic acid solution (200 mM) is added into 1000 mL sample to remove residual chlorine. It is shown that added ascorbic acid did not disrupt NDMA (Mitch et al., 2003). The amount of NDMA formed in the sample is determined by the NDMA measurement procedure.

4.2.3 Chloramination methods

4.2.3.1 Preparation of chlorine dosing solution

The necessary amount of stock hypochlorite solution is taken to prepare 5 mg Cl_2/ml chlorine solution and completed to 250 ml with double distilled water into a volumetric flask, and then bottle is wrapped with aluminum foil to protected by sunlight exposure.

4.2.3.2 Preparation of phosphate buffer solution

68.1 grams of potassium dihydrogen phosphate (KH_2PO_4) and 11.7 g of sodium hydroxide (NaOH) are dissolved in double-distilled water and the solution is completed to 1 liter into volumetric flask with double distilled water. Then this solution is stored in the refrigerator.

5. RESULTS AND DISCUSSIONS

Results of experiments conducted in samples collected from the watershed and the water treatment plant as well as results of lab-scale tests are provided in detail in Sections 5.1, 5.2 and 5.3 respectively.

5.1 Büyükçekmece Watershed

The concentration of several water quality parameters as well as the concentrations of DBPs and their precursors (THM, THMFP and NDMAFP) are provided in Table 5.1, Table 5.2, Table 5.3 and Table 5.4. The pH values changes between 7.34 and 8.46; whereas alkalinity range is between 100 mg $CaCO_3$/L and 406 mg $CaCO_3$/L. Chloride concentration is between 39.7 mg/L and 155.4 mg/L. The highest Nitrate-N concentration is 3.66 mg/L. Sulfate concentration range is between 51.5 mg/L and 510.8 mg/L. Bromide and Phosphate-P concentrations are not detected (detection limits are 0.4 mg/L and 0.26 mg/L respectively). The maximum THM concentration is 5.94 μg/L; the biggest part of THM is bromodichloromethane and dibromochloromethane. Bromoform is not detected (detection limit is 0.06 μg/L) where chloroform concentration is maximum 1 μg/L. NDMA concentrations are below the detection limit which might either be because of the lack of NDMA containing discharge to the watershed or the photo degradation of NDMA in the surface water. The highest NDMAFP is measured in Beylikçayı which also has the highest NH_3-N concentration (1.27 mg/L) and TKN concentration (1.27 mg/L). Moreover chloride concentration is likely higher (87.7 mg/L) than other streams except Ahlat. The reason of that situation could be wastewater discharge to the Beylikçayı stream. The highest THMFP is measured in Lake. Further comments are provided in detail in Section 5.1.1.

Table 5.1 : Water quality parameters results in samples collected on 21.10.2010 from several points in the watershed

Sample Point	Sampling Time	pH	T (°C)	Alkalinity mg $CaCO_3$/L	TKN mg/L	NH_3-N mg/L	DON mg/L	DOC mg/L	SUVA L/mg.m	Fluoride mg/L	Chloride mg/L	Nitrite-N mg/L	Bromide mg/L	Nitrate-N mg/L	Phosphate-P mg/L	Sulfate mg/L
Beylikçayı	08 :03	8.1	19	406	1.27	1.27	0	9.64	1.36	0.46	87.7	0.69	<0.4	1.34	<0.26	126.3
Hamza	08 :28	7.9	20	392	0,37	0.02	0.348	10.09	1.49	<0.08	52.2	0.38	<0.4	2.16	<0.26	62.3
Karasu	09 :02	7.2	21	100	1.20	1.20	0	8.73	1.28	0.34	55.7	<0.12	<0.4	1.55	<0.26	90.4
Tahtaköprü	09 :39	8.3	21	374	0.05	0.04	0.012	7.89	1.31	0.35	67.0	<0.12	<0.4	3.53	<0.26	104.8
Ahlat	10 :10	7.7	23	322	0.55	0.31	0.24	7.22	1.28	0.61	155.4	0.51	<0.4	3.66	<0.26	510.8
Lake	10 :30	8.5	23	160	0.08	0.01	0.066	6.87	0.82	<0.08	39.7	<0.12	<0.4	<0.45	<0.26	51.5

Table 5.2 : THM concentrations in samples collected on 21.10.2010 from several points in the watershed (the corresponding WQP's are provided in Table 5.1)

Sample point	Chloroform (µg/L)	BDCM* (µg/L)	DBMCM* (µg/L)	Bromoform (µg/L)	Total THM (µg/L)
Beylikçayı	1	2.62	2.29	<0.06	5.94
Hamza	n.d	n.d.	n.d.	<0.06	n.d.
Karasu	1	1.31	1.14	<0.06	2.97
Tahtaköprü	1	1.31	2.28	<0.06	4.43
Ahlat	n.d	2.59	2.28	<0.06	4.86
Lake	0.44	2.60	2.28	<0.06	5.33

*BDCM : Bromodichloromethane, *DBMCM : Dibromochloromethane, nd. : non-detected

Table 5.3 : THMFP and NDMAFP results in samples collected on 21.10.2010 from several points in the watershed (the corresponding WQP's are provided in Table 5.1)

Sample point	ChloroformFP (µg/L)	BDCMFP* (µg/L)	DBMCMFP* (µg/L)	BromoformFP (µg/L)	Total THMFP (µg/L)	NDMAFP (ng/L)
Beylikçayı	397	209	36	3	644	21.3
Hamza	803	148	16	2	968	19.5
Karasu	678	213	24	2	917	15.2
Tahtaköprü	773	216	26	2	1016	12.1
Ahlat	166	180	36	3	385	106.5
Lake	933	237	29	2	1201	12.3

*BDCMFP : BromodichloromethaneFP, *DBMCMFP : DibromochloromethaneFP

5.1.1 Parameter Relations

Although the importance of THM, THMFP, NDMA and NDMAFP is clear, it is not possible to include these parameters in a standard monitoring program due to time and expertise need to conduct the experiment and the requirement of expensive analytical instruments. Therefore, establishing a relationship between the DBPs and water quality parameters might be useful to obtain a surrogate parameter for the precursors of THM and NDMA. Based on literature research, DOC, DON and SUVA are examined as surrogate parameters of NDMAFP and THMFP (Figure 5.1, Figure 5.2, Figure 5.3, Figure 5.4, Figure 5.5 and Figure 5.6).

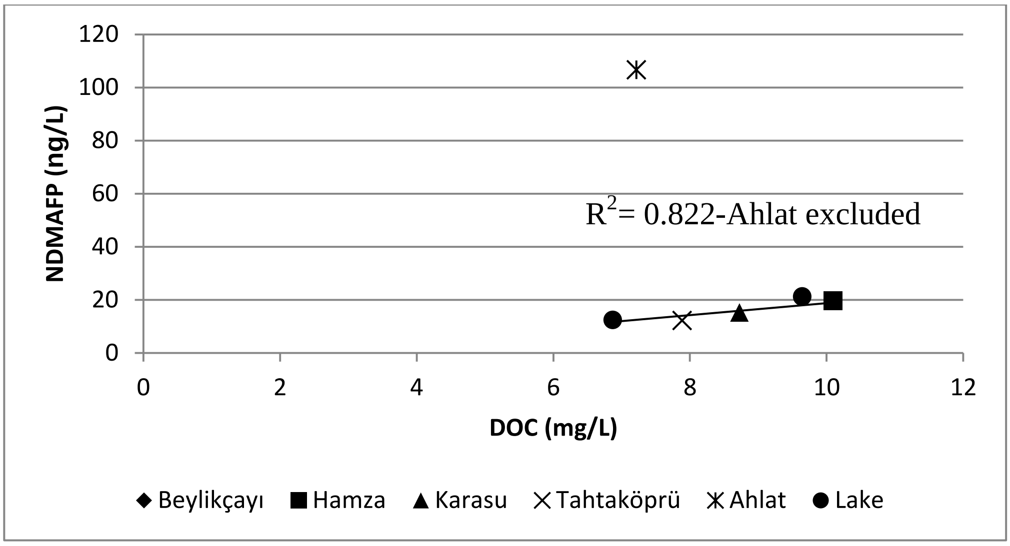


Figure 5.1 : NDMAFP and DOC relation for the watershed samples

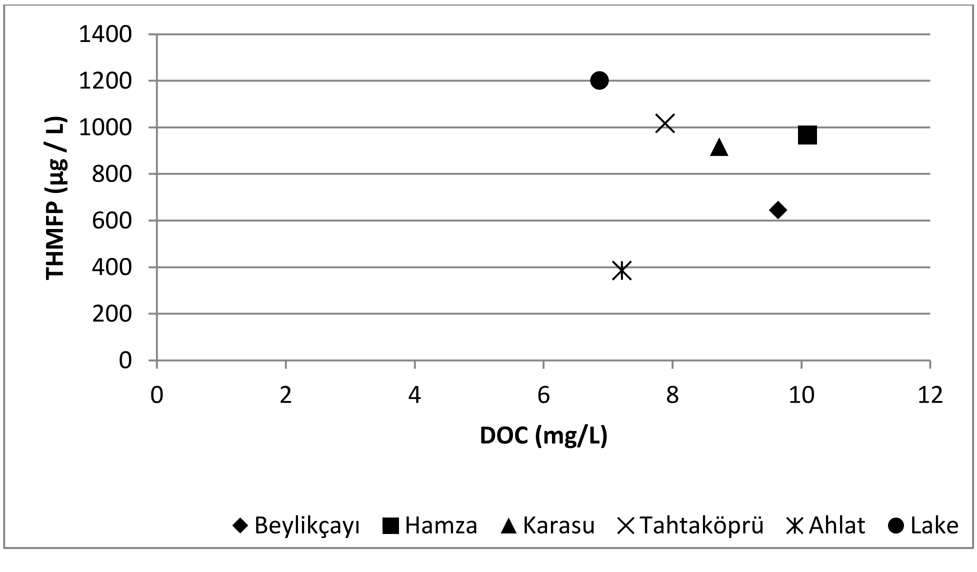


Figure 5.2 : THMFP and DOC relation for the watershed samples

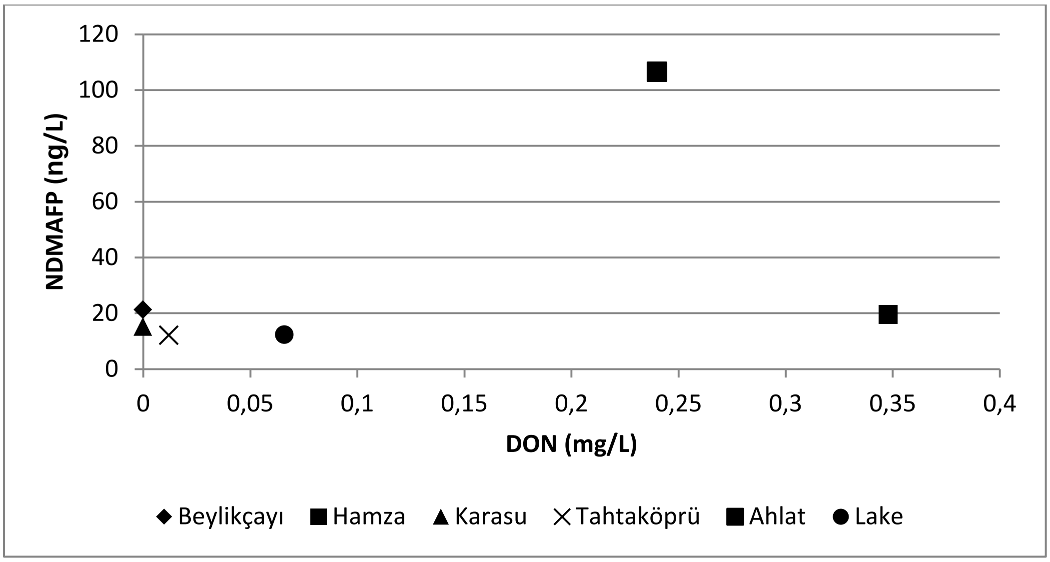


Figure 5.3 : NDMAFP and DON relation for the watershed samples

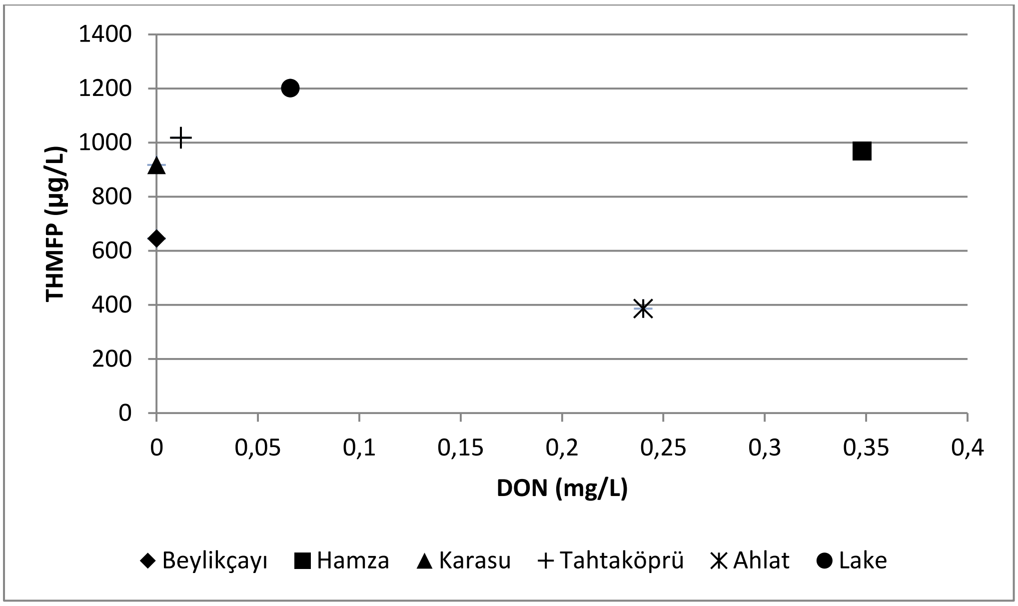


Figure 5.4 : THMFP and DON relation for the watershed samples

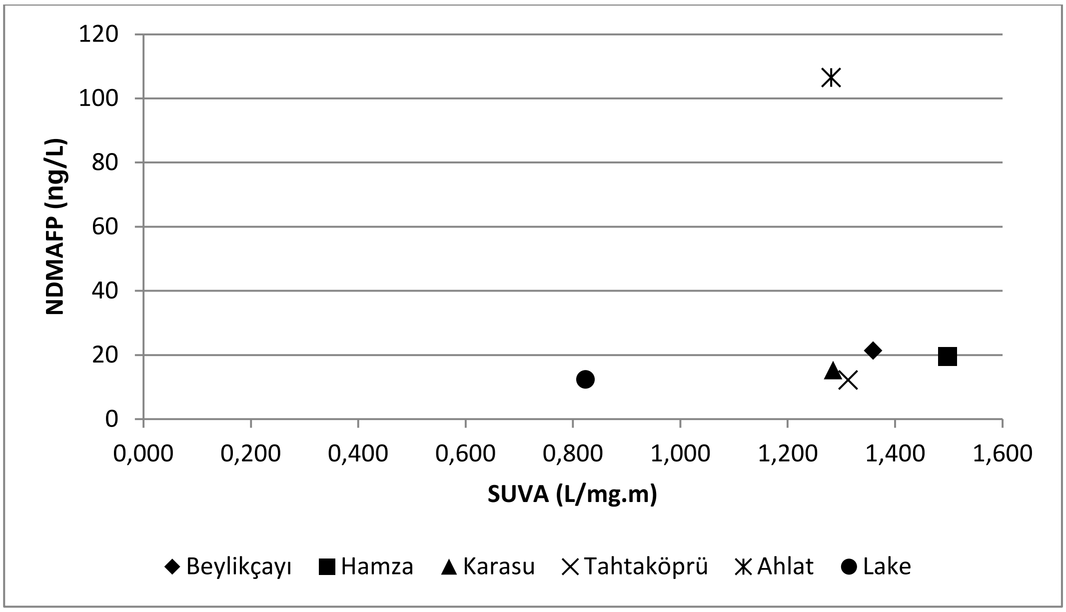


Figure 5.5 : NDMAFP and SUVA relation for the watershed samples

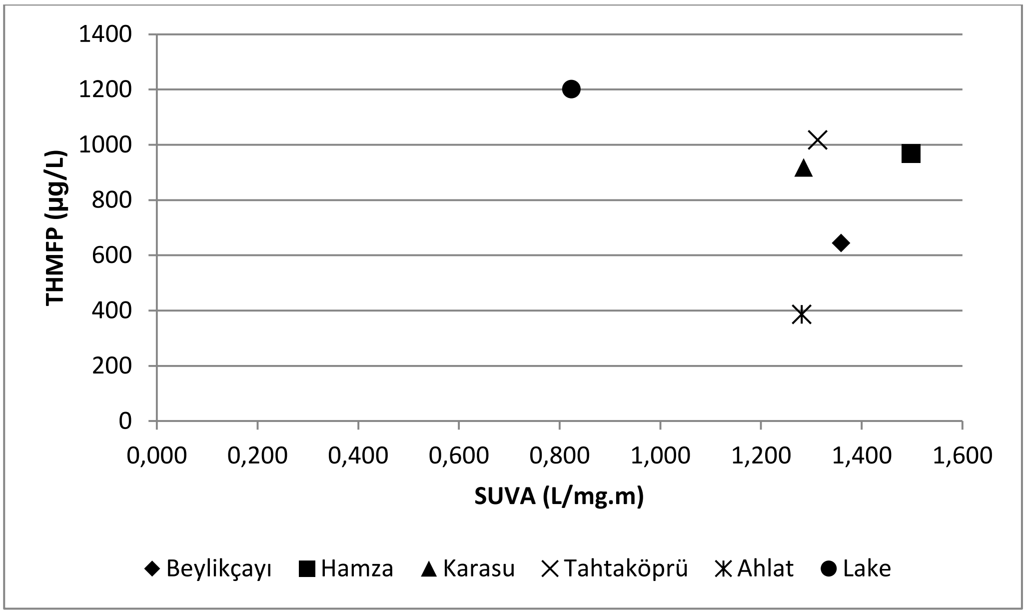


Figure 5.6 : THMFP and SUVA relation for the watershed samples

In stream samples, DOC was between 7 mg/L – 10 mg/L and NDMAFP was around 20 ng/L except in Ahlat stream. A domestic or industrial wastewater contamination is suspected for Ahlat stream, because NDMAFP was very high compared to other streams; therefore Ahlat measurements will be excluded from comments on the relation between DBP precursors and water quality parameters. Figure 5.1 shows that there is a small NDMAFP increase with DOC increase. NDMAFP-DOC relation is not unexpected since organic NDMA precursors will be included in the DOC pool. Also there are studies which reported a relationship between DOC and NDMA

(Sacher et al., 2008 and references there in). However, since DOC pool contains more species than just organic nitrogenous matter, the relationship between DOC and NDMAFP is not very strong. Based on literature data, a relation between NDMA and DON is expected (Westerhoff and Mash, 2002; Xu et al., 2011) but no such relationship was determined (Figure 5.3). The reason for the lack of such a relationship could be the problems associated with DON measurement in the presence of high inorganic nitrogen concentration (Vandenbruwane et al., 2007). Similarly, no relation was determined in our study between THMFP and DON concentrations (Figure 5.4). The NDMAFP and THMFP variations with SUVA values are illustrated in Figure 5.5 and Figure 5.6, and an increase in NDMAFP is observed with increasing values of SUVA. However, no relation could be established between SUVA and THMFP, although SUVA is an indicator for the aromatic organic matter in water which are among THM precursors.

5.2 Büyükçekmece Water Treatment Plant

Samples are taken from six sampling points in the plant (Figure 4.1); Lake water as raw water, pre-chlorination inlet, pre-chlorination outflow, decantation outflow, filter outflow and plant outflow. Since the locations of chlorination were different in July 2010 and October 2010, sampling points were also different. The concentrations of water quality parameters and concentrations of DBPs in two sampling trips are provided in Table 5.4-Table 5.6 and Table 5.7-Table 5.9 in July 2010 and October 2010 respectively.

In July, pH range was between 7.9 and 8.4, alkalinity was between 136 mg$CaCO_3$/L and 188 mg$CaCO_3$/L. NH_3-N (detection limit is 0.1 mg/L), Nitrite-N (detection limit is 0.03 mg/L), bromide (detection limit is 0.1 mg/L) and Phosphate-P (detection limit is 0.065 mg/L) parameters were below detection limits. Average chloride concentration was 50.92 mg/L, where raw water and plant outflow concentrations were almost equal. The highest sulfate concentration was 98.42 mg/L measured in plant outflow.

In October, pH was between 7.3 and 8.1, alkalinity changes between 122 mg$CaCO_3$/L and 152 mg$CaCO_3$/L. Bromide (detection limit is 0.1 mg/L), Nitrite-N (detection limit is 0.03 mg/L) and Phosphate-P (detection limit is 0.065 mg/L) parameters were below detection limits.

Table 5.4 : Water quality parameter results in samples collected in July 2010 from several points in the WTP

Sample point	pH	Alkalinity (mg $CaCO_3$/L)	NH_3-N (mg/L)	DON (mg/L)	SUVA (L/mg.m)	Fluoride (mg/L)	Chloride (mg/L)	Nitrite-N (mg/L)	Bromide (mg/L)	Nitrate-N (mg/L)	Phosphate-P (mg/L)	Sulfate (mg/L)
Raw water	8.4	188	<0.1	5.10	2.803	0.38	52.38	<0.03	<0.1	0.85	<0.065	62.79
Pre-chlorination inlet	8.4	164	<0.1	6.34	1.969	0.45	54.75	<0.03	<0.1	0.89	<0.065	63.31
Pre-chlorination outflow	8.2	172	<0.1	5.37	2.203	0.38	50.87	<0.03	<0.1	0.77	<0.065	64.33
Decantation outflow	8.0	148	<0.1	4.72	1.019	0.28	45.92	<0.03	<0.1	0.73	<0.065	94.84
Filter outflow	7.9	164	<0.1	3.87	0.965	0.34	49.50	<0.03	<0.1	0.75	<0.065	96.32
Plant outflow	8.1	136	<0.1	4.73	0.739	0.29	52.10	<0.03	<0.1	0.77	<0.065	98.42

Table 5.5 : THM and NDMA results in samples collected in July 2010 from several points in the WTP (the corresponding WQP's are provided in Table 5.4)

Sample point	Chloroform (μg/L)	BDCM* (μg/L)	DBCM* (μg/L)	Bromoform (μg/L)	Total THM (μg/L)	NDMA (ng/L)
Raw water	n.d.	3	2	n.d.	5	<2
Pre-chlorination inlet	n.d.	3	2	1	5	2
Pre-chlorination outflow	17	18	19	5	37	2.4
Decantation outflow	9	14	13	4	40	2.2
Filter outflow	28	26	22	5	76	<2
Plant outflow	28	26	22	5	81	2.5

*BDCM : Bromodichloromethane,*DBMCM : Dibromochloromethane

Table 5.6 : THMFP and NDMAFP results in samples collected in July 2010 from several points in the WTP (the corresponding WQP's are provided in Table 5.4)

Sample point	ChloroformFP (μg/L)	BDCMFP* (μg/L)	DBCMFP* (μg/L)	BromoformFP (μg/L)	Total THMFP (μg/L)	NDMAFP (ng/L)
Raw water	103	48	15	2	167	11
Pre-chlorination inlet	94	43	14	2	153	8.5
Pre-chlorination outflow	99	40	22	5	165	10
Decantation outflow	62	29	17	4	112	6.9
Filter outflow	70	35	24	5	133	8.5
Plant outflow	81	35	23	5	143	6.8

*BDCMFP : BromodichloromethaneFP, *DBMCMFP : DibromochloromethaneFP

THM concentration was low in raw water but not undetected as would be expected before chlorination. In July shock chlorination (10 mg/L Cl_2) was applied. THM concentration ranged from 5 μg/L to 81 μg/L with increases to 37 μg/L and 76 μg/L after pre-chlorination and filter unit, respectively, both of which correspond to chlorination steps. The THMFP on the other hand, did not change as much and the THMFP concentration decreased from 167 μg/L in the inflow to 143 μg/L in the outflow of the WTP, corresponding to a decrease of 14%. When the concentrations of different species of THM and THMFP were compared, one can say that although bromoform and DBCM accounts for a small percentage of both THM and THMFP, these species' concentrations are the same as THM and THMFP. This result suggests that the speciation of THMFP is not always indicative of the THM speciation upon chlorination.

Although no NDMA was detected in the inflow of the WTP, the outflow included a small but detectable amount of NDMA (2.5 ng/L). The NDMAFP decreased by approximately 38% in the treatment plant, but there was a slight increase in NDMAFP concentration after each chlorination step. The increase by 18% and 23% in pre-chlorination and filtration, respectively, could be due to the oxidation of organic material to be converted to NDMA precursors.

Table 5.7 : Water quality parameters results in samples collected in October 2010 from several points in the WTP

Sample point	pH	Alkalinity (mg $CaCO_3$/L)	TKN (mg/L)	DON (mg/L)	DOC (mg/L)	SUVA (L/mg.m)	Fluoride (mg/L)	Chloride (mg/L)	Nitrite-N (mg/L)	Bromide (mg/L)	Nitrate-N (mg/L)	Phosphate-P (mg/L)	Sulfate (mg/L)
Raw water	7.3	152	0.52	0.5	8.3	1.1	0.09	42.52	0.42	<0.4	<0.09	<0.26	52.75
Aeration outflow	7.5	122	0.98	0.9	8.2	0.7	0.09	42.91	0.54	<0.4	<0.09	<0.26	52.42
Decantation inlet	7.8	140	0.37	0.3	6.3	0.6	<0.08	41.52	0.43	<0.4	<0.09	<0.26	73.58
Plant outflow	8.1	130	0.96	0.9	5.3	0.7	0.08	44.62	0.58	<0.4	<0.09	<0.26	73.96

Table 5.8 : THM results in samples collected in October 2010 from several points in the WTP (the corresponding WQP's are provided in Table 5.7)

Sample point	Chloroform (µg/L)	BDCM* (µg/L)	DBCM* (µg/L)	Bromoform (µg/L)	Total THM (µg/L)
Raw water	14	21	27	9	71
Aeration outflow	11	16	22	7	56
Decantation inlet	12	21	29	9	71
Plant outflow	21	23	28	7	78

*BDCM : Bromodichloromethane, *DBMCM : Dibromochloromethane

Table 5.9 : THMFP and NDMAFP results in samples collected in October 2010 from several points in the WTP (the corresponding WQP's are provided in Table 5.7)

Sample point	ChloroformFP (µg/L)	BDCMFP* (µg/L)	DBCMFP* (µg/L)	BromoformFP (µg/L)	Total THMFP (µg/L)	NDMAFP (ng/L)
Raw water	1266	183	43	12	1503	8.53
Aeration outflow	1084	164	40	12	1300	4.44
Decantation inlet	749	155	37	10	951	3.96
Plant outflow	460	105	37	9	611	4.53

*BDCMFP : BromodichloromethaneFP, *DBMCMFP : DibromochloromethaneFP

THM was 71 µg/L in raw water due to shock chlorination applied at the inlet of the WTP; this concentration decreases by 21% after aeration unit due to the volatility of THMs. After aeration outflow THM started to increase through the plant and reached 78 µg/L at the plant outflow. THMFP concentration decreased from 1503 µg/L in the inflow to 611 µg/L in the outflow of the WTP; corresponding to a decrease of 60%. Although the concentration of 1503 µg/L is high compared to most of the THMFP values in the literature, there are other studies which have reported THMFP higher than 1000 μg/L (e.g. White et al., 2002). ChloroformFP was the biggest part of TTHMFP through the WTP. The decrease of chloroformFP was 64% between raw water and plant outflow.

The NDMAFP decreased by approximately 47% in the treatment plant, but there was a slight increase in NDMAFP concentration after decantation unit.

Seasonal variations slightly affected DBPs concentrations. The THMFP in the influent samples are almost one order of magnitude different in the two samples collected in July and October with THMFP concentrations of approximately 170 and 1500 μg/L (Figure 5.14). THM concentrations were approximately 80 μg/L for both of the samples at the end of the WTP. THMFP was measured lower in July although NDMAFP was measured higher in July. THMFP was relatively higher in October compared July. The concentration difference between WTP units was clearer in October than July. In the same month THMFP increases in plant outflow because of final chlorination. THMFP removal efficiencies in the WTP were 14% and 60% in July and October.

5.2.1 Parameter Relations

Similar to watershed samples, DOC, DON and SUVA are examined as surrogate parameters of THMFP and NDMAFP in samples obtained throughout the treatment plant in July and October, 2010 (Figure 5.7- Figure 5.12).

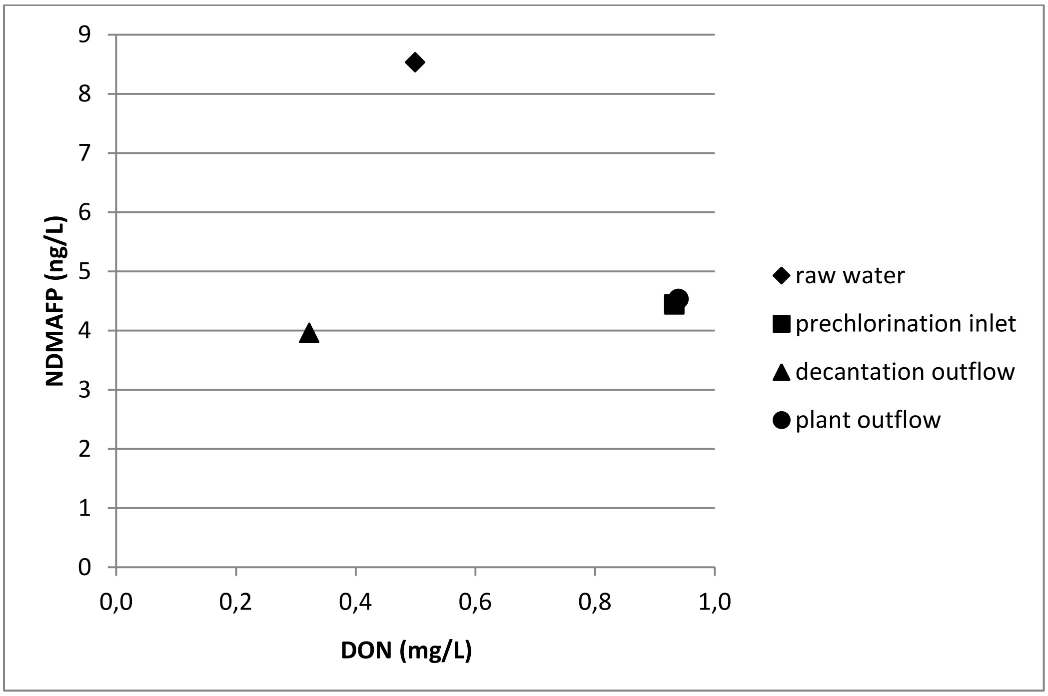


Figure 5.7 : NDMAFP and DON relation for the WTP samples collected in October 2010

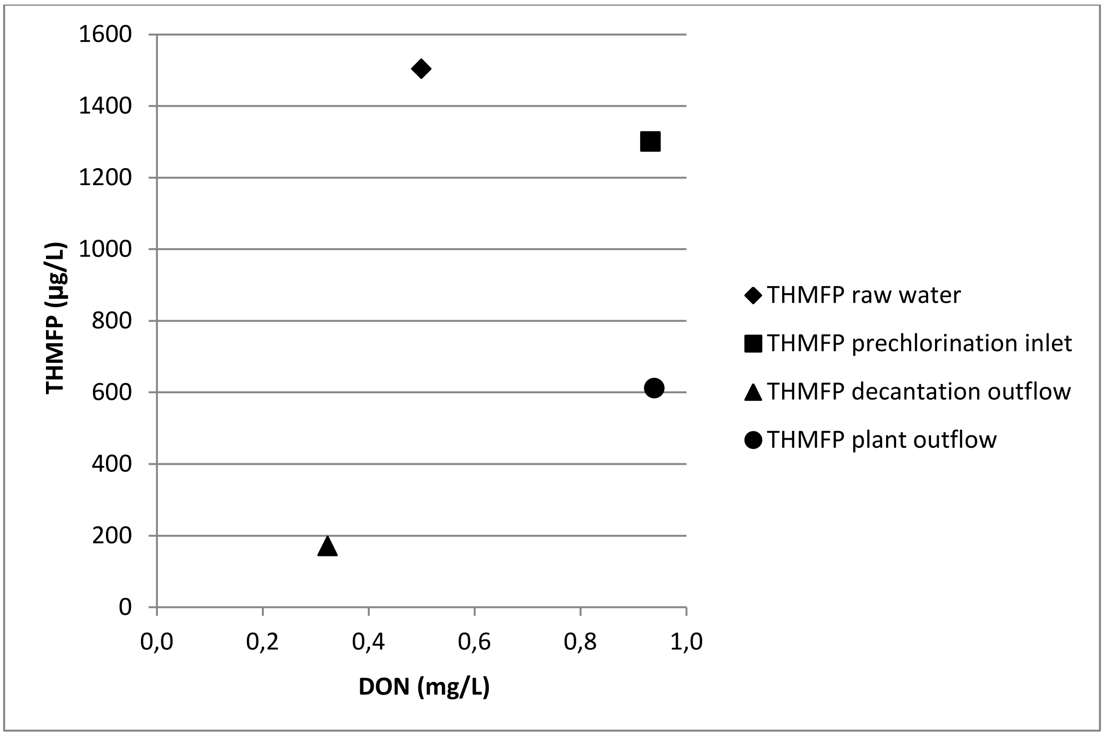


Figure 5.8 : THMFP and DON relation for the WTP samples collected in October 2010

Figure 5.7 and Figure 5.8 shows that there is no direct relation between DON parameter and DBPs formation potential in our data, suggesting that DON is not a good surrogate parameter even for NDMAFP unless the inorganic nitrogen species are removed prior to the measurement of organic nitrogen (Lee and Westerhoff, 2005).

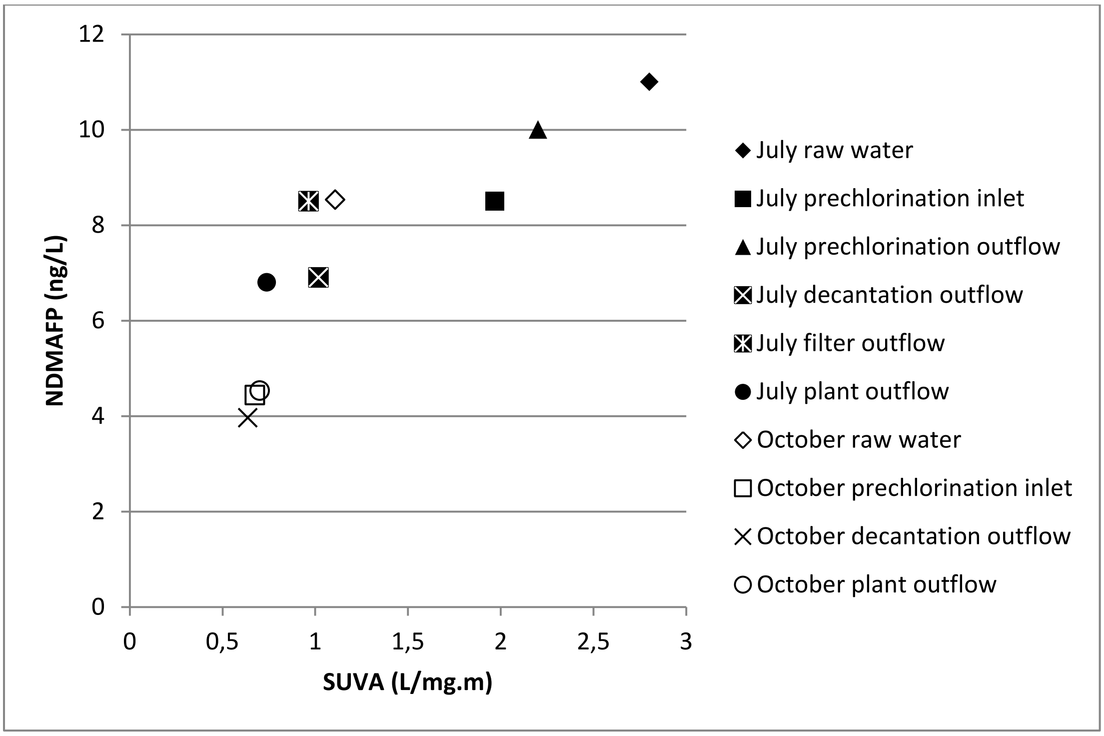


Figure 5.9 : NDMAFP and SUVA relation for the WTP samples

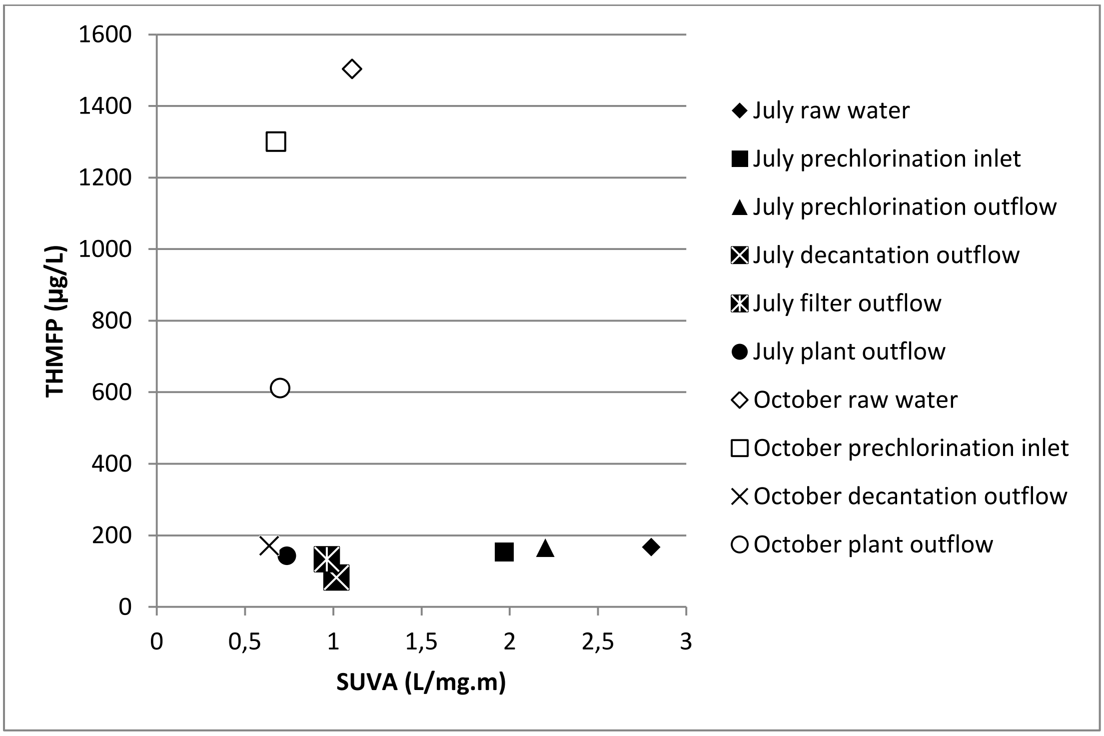


Figure 5.10 : THMFP and SUVA relation for the WTP samples

As seen in the Figure 5.9 the concentration of NDMAFP increases with SUVA increase. However, a relation between THMFP and SUVA is available only for samples collected in July (Figure 5.10).

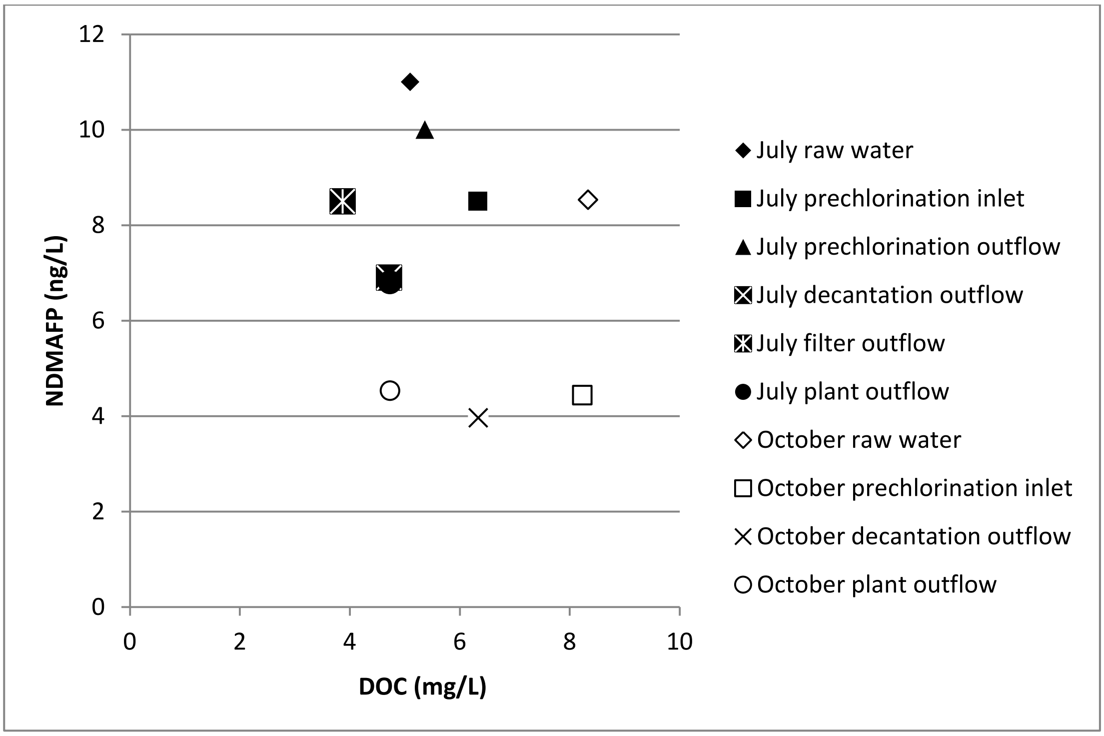


Figure 5.11 : NDMAFP and DOC relation for the WTP samples

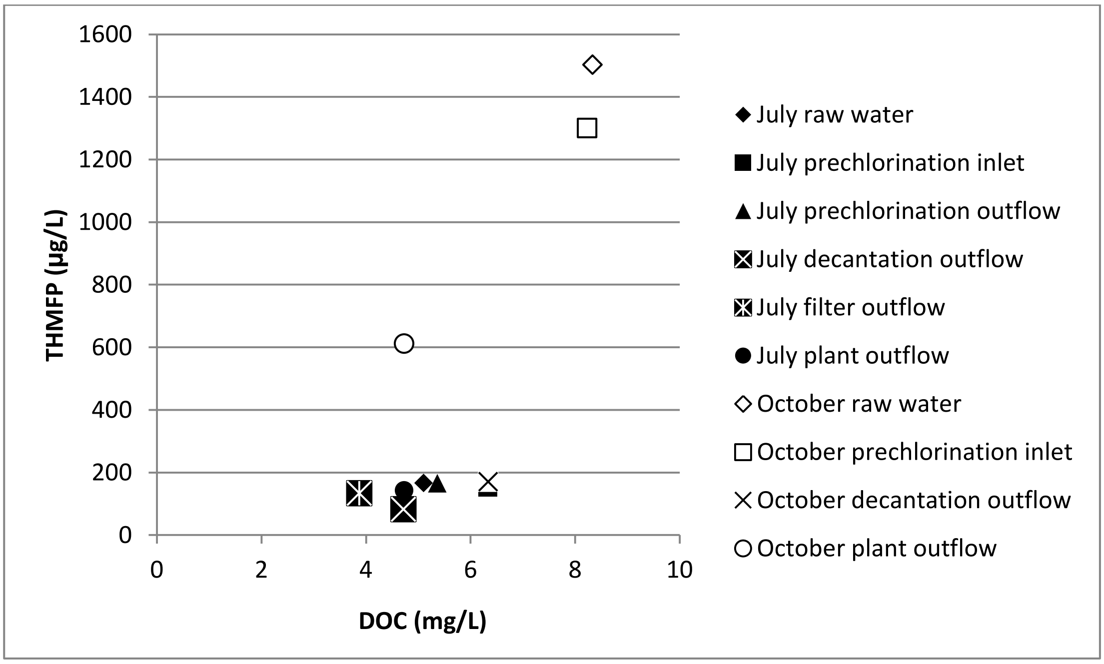


Figure 5.12 : THMFP and DOC relation for the WTP samples

There is no correlation between DOC and NDMAFP (Figure 5.11) although a slight correlation was observed between DOC and NDMAFP in watershed samples. On the other hand, THMFP increases with DOC increase in both July and October even though a good correlation cannot be obtained when data is pooled (Figure 5.12). The lack of relation between DOC, DON and DBPFP suggest that not only the concentration of organic matter (measured as DOC and DON) but its structure affects the formation of DBPs. Therefore, the comparative experiments conducted with different NDMA precursors having different structures will be useful to evaluate the effect of the structure.

5.3 Comparative Trials

Comparative lab-scale trials are conducted in May, July and December 2011. Results of two sets using lake and spiked-lake samples are provided in Tables 5.10-5.11 for three different disinfection techniques. The concentrations of both DBPs and the DBPFPs are measured after two hours of exposure in addition to the raw samples to understand the effect of disinfection both on the formation of DBPs in two hours and on the possible reformation of DBPs.

Table 5.10 : THM results in trials conducted in May

	THM (µg/L)		
	Lake	**Lake+DMA**	**Lake+Ran**
2 mg/L Cl_2	68	60	
10 mg/L Cl_2	120	199	424
100 mg/L Cl_2	1496		3467
2 mg/L chloramine	5	5	
10 mg/L chloramine	5	5	8
100 mg/L chloramine	9		8
2 mg/L Cl_2+NH_3	49	51	
10 mg/L Cl_2+NH_3	66	64	95
100 mg/L Cl_2+NH_3	91		234

Table 5.11: THM results in trials conducted in July

	THM (µg/L)		
	Lake	**Lake+DMA**	**Lake+Ran**
2 mg/L Cl_2	85	71	
10 mg/L Cl_2	117	103	95
100 mg/L Cl_2			177
2 mg/L chloramine	7	6	
10 mg/L chloramine	9	11	5
100 mg/L chloramine	41		16
2 mg/L Cl_2+NH_3	66	62	
10 mg/L Cl_2+NH_3	137	103	80
100 mg/L Cl_2+NH_3	129		132

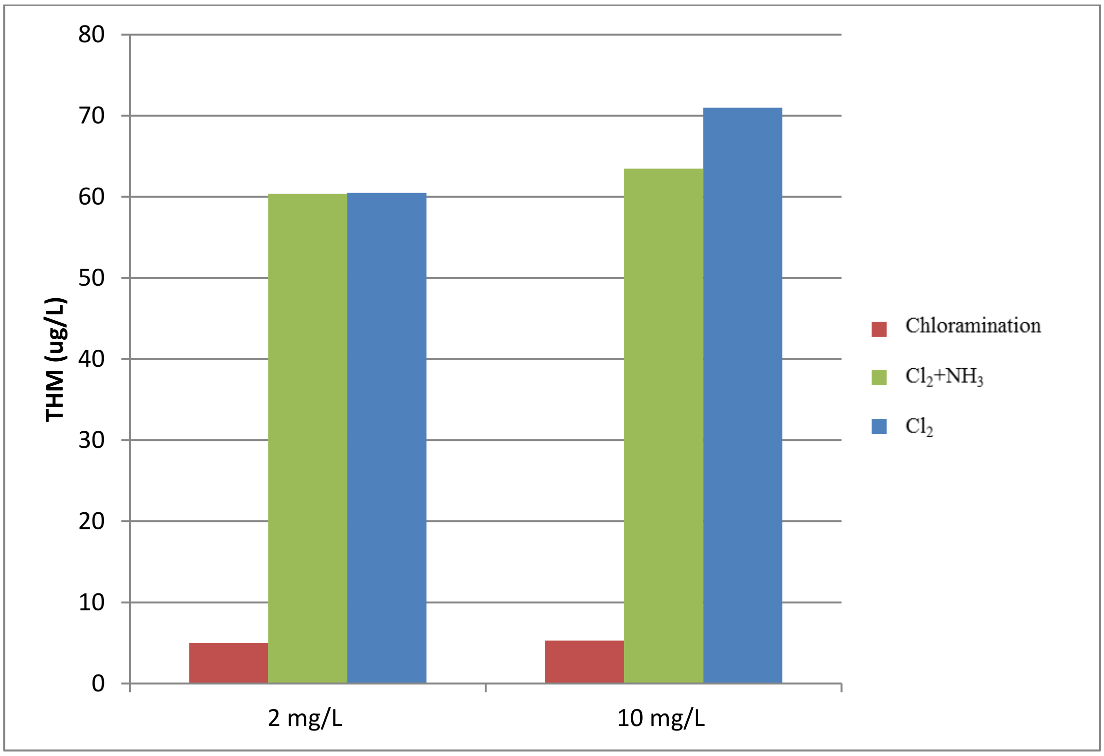


Figure 5.13 : THM concentrations in lake water for different disinfection methods conducted in December

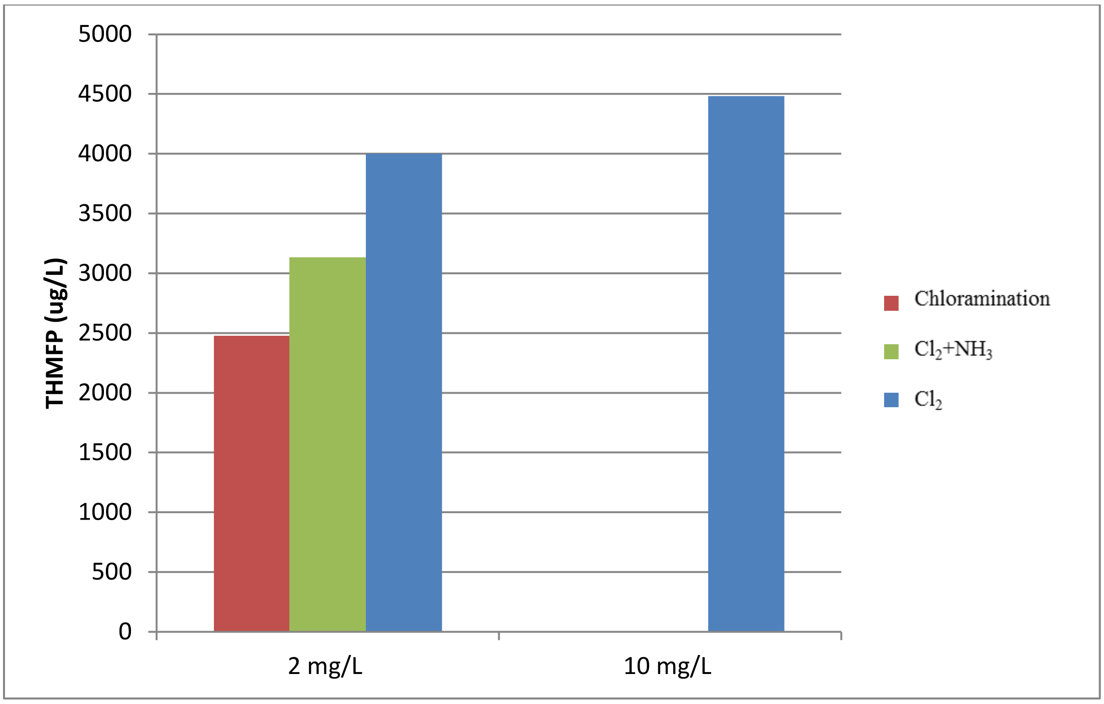


Figure 5.14 : THMFP concentrations in lake water for different disinfection methods conducted in December

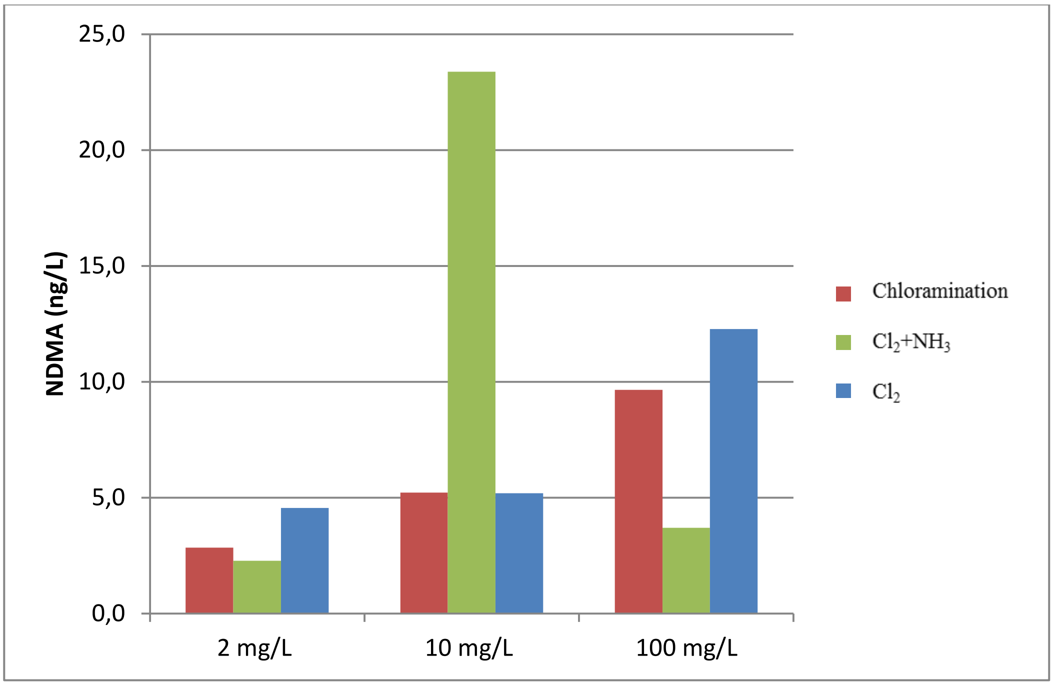


Figure 5.15 : NDMA concentration in lake water for different disinfection methods conducted in December

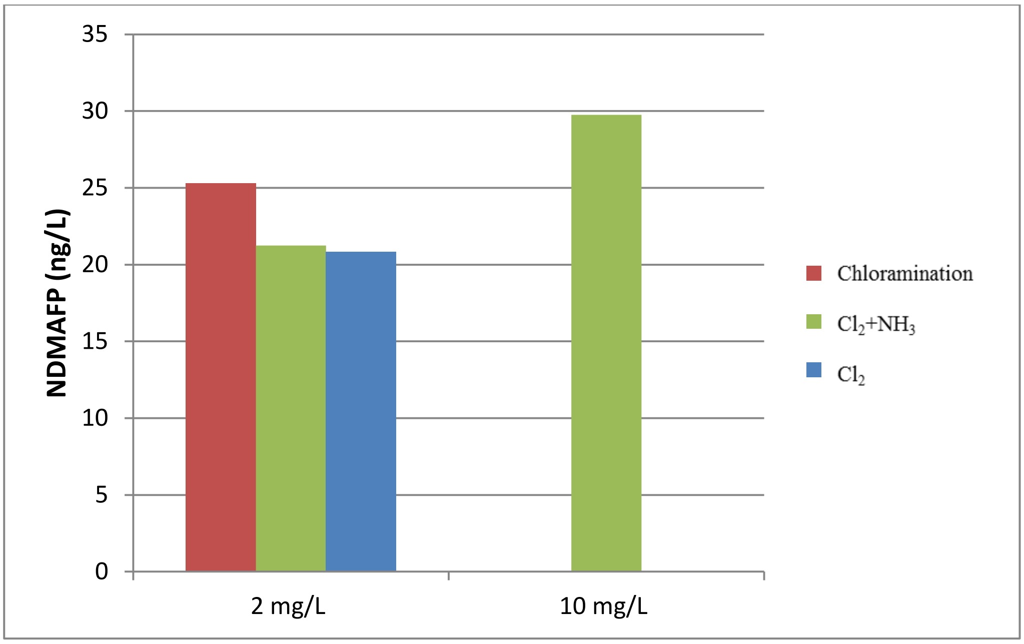


Figure 5.16 : NDMAFP concentration in lake water for different disinfection methods conducted in December

Effect of different disinfection methods using three disinfectant concentrations on THM concentration is provided in Figure 5.13. At the same disinfectant concentration, chloramination causes the lowest THM concentration as expected. THMFP has the highest concentration during chlorination for same disinfectant dosages (Figure 5.14). The expected result for NDMA concentration is $NDMA_{Cl2}<NDMA_{stepwise}<NDMA_{chloramine}$ due to presence of chloramine for the entire duration of the experiment in the chloramination trial. However, NDMA concentrations were different than expectations the reason could be experimental error. When disinfectant concentration increases, higher THM concentration were expected; this result was obtained for all disinfectants except for chloramination where THM concentration stays at same level. The expected result for THM concentration is $THM_{Cl2}>THM_{stepwise}>THM_{chloramine}$; however the results obtained for THM at different disinfectant concentration and disinfection methods did not always follow this prediction. The results obtained for THMFP at different disinfectant concentrations and disinfectant methods were close to expectations. However, the addition of “excess chlorine” probably did not increase the free chlorine concentration significantly, since it was already very high in some cases. THMFP concentration had the highest value during chlorination followed by stepwise chloramination. Chloramination resulted in the lowest THMFP.

When disinfectant concentration was 2 mg/L, the NDMA concentrations were below 5 ng/L for all disinfection types. However, as expected, increasing disinfectant concentrations during chloramination leads to higher NDMA concentrations. Similarly, NDMA concentrations increase with increasing disinfectant concentrations in the other methods as well (Figure 5.15).

When NDMA precursors are added to lake water, they may have two effects. The first one is the direct formation of NDMA during chloramination and the NDMA concentration is expected to increase when disinfectant concentration increases. However, in stepwise chloramination, it is possible to lose some NDMA precursors due to 1 hour-oxidation with chlorine prior to the addition of NH_3. Chlorination is not expected to have much effect on spiked lake water for NDMA formation. However, depending on the precursor structure, it is also possible to form THM during chlorination. For example, the aromatic structure of ranitidine is expected to lead to higher THM concentration than lake water or lake water spiked with DMA. Nevertheless, this effect may also not be observed since the DOC of the added precursors is low (the calculated DOC concentration of added DMA and ranitidine are 1.44 mg/L and 0.17 µg/L, respectively). Ranitidine is expected to form more NDMA than DMA per mole. Added concentration of DMA and ranitidine are 1.1 µM and 10 nM respectively, and in the second trial, DMA concentration was decreased to 0.4 µM and 10 nM. Since both DMA and ranitidine are known NDMA precursors, spiking the lake water with either one is expected to increase the NDMA concentration. However, the addition of these compounds may not affect THM formation the same way. There is no information is available on the formation of THM by these or any other NDMA precursors in the literature and whether the reaction with chlorine will result in THM or not depends on the structure of the compound. Moreover, if the reaction between the compound and chlorine does not result in THM formation, than the addition of an NDMA precursor may actually reduce the THM concentration compared to the unspiked sample. For example, if DMA does not form THM and it reacts faster than the THM precursors within the NOM in lake water with chlorine, then DMA gets oxidized but no THM will form for this amount of chlorine used. If it acts almost the same way as the other THM precursors within the NOM, then a slight increase in the THM concentration in the DMA-spiked water will be obtained.

Effect of different disinfectant methods on DMA-spiked lake water is illustrated in Figure 5.17, Figure 5.18, Figure 5.19 and Figure 5.20. At the same disinfectant concentration, chlorination causes higher THM concentration compared to the other disinfectant methods. THMFP increased significantly under chlorination during 10 mg/L disinfection; while during chloramination the THMFP concentration decreased dramatically with the increase of disinfection concentration. NDMA concentrations were higher at stepwise chloramination for both disinfectant concentrations (i.e., 2 mg/L, 10 mg/L) compared to other disinfectant methods. The reason of this situation could be that chlorination prior to addition of NH_3 may release some NDMA precursors from “pre-precursors” so that when chloramine forms after addition of NH_3, NDMA will form. NDMAFP concentration is almost same for chlorination and chloramination methods for 2 mg/L disinfectant concentration. During high disinfectant concentration, NDMAFP is relatively higher during chloramination.

Effect of different disinfection methods on ranitidine-spiked lake water was illustrated in Figure 5.21, Figure 5.22, Figure 5.23 and Figure 5.24. At the same disinfectant concentration, the lowest THM concentration was occurred during chloramination while the highest concentration was occurred under chlorination. Chlorination formed the highest THMFP concentration for both disinfectant concentrations (i.e., 2 mg/L 10 mg/L) compared to the other disinfection methods. THMFP concentrations were higher after chlorination compared to chloramination, and the highest NDMA concentration occurred at chloramination.

Increasing disinfectant concentration was effective in increasing the THM and THMFP concentrations during all disinfection methods. The increase in disinfectant concentration during chloramination caused higher NDMA concentrations, but it did not have a significant effect on NDMA concentrations for chlorination and stepwise chloramination. The reason of this situation might be the simultaneous formation of THM. During 2 mg/L chlorination trial, most of the precursors were converted to THM (75 mg/L) and during 2 mg/L chloramination trial, most of the precursors were converted to NDMA which lead to low THM concentrations (5 mg/L). The increase of disinfectant concentration during stepwise chloramination had almost no effect on THMFP and NDMA concentrations. One of the problems with stepwise chloramination is the possibility of local reactions forming different types of chloramines (e.g., the formation of dichloramine instead of monochloramine) based on the local NH_3/Cl_2 ratio or the pH. This problem might be overcome with better mixing during the experiments but since this third disinfection type was evaluated as a representation of real life conditions, no additional mixing was provided.

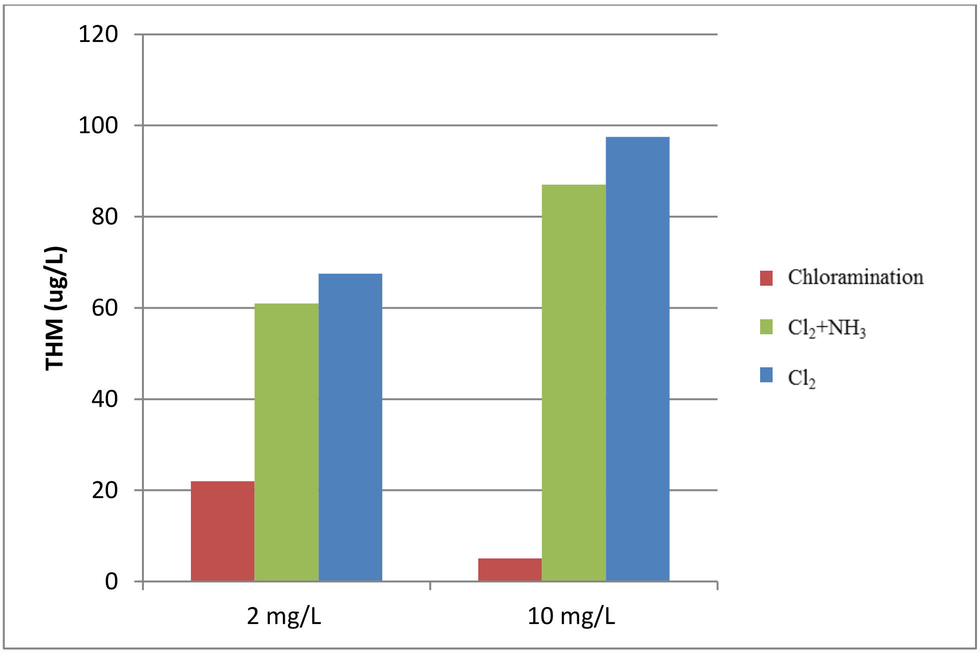


Figure 5.17 : THM concentrations in DMA- spiked lake water for different disinfection methods conducted in December

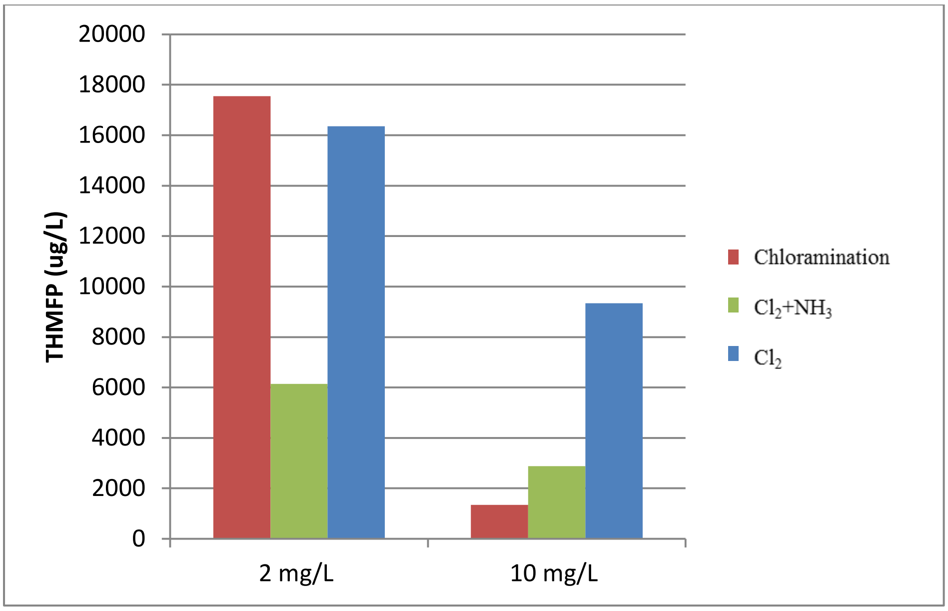


Figure 5.18 : THMFP concentrations in DMA-spiked lake water for different disinfection methods conducted in December

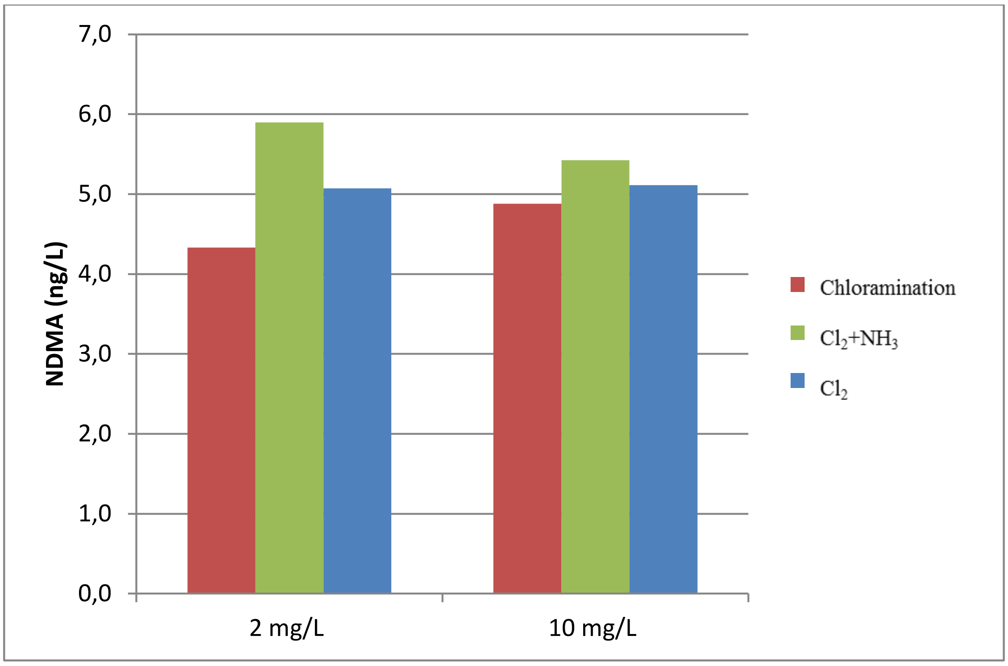


Figure 5.19 : NDMA concentrations in DMA-spiked lake water for different disinfection methods conducted in December

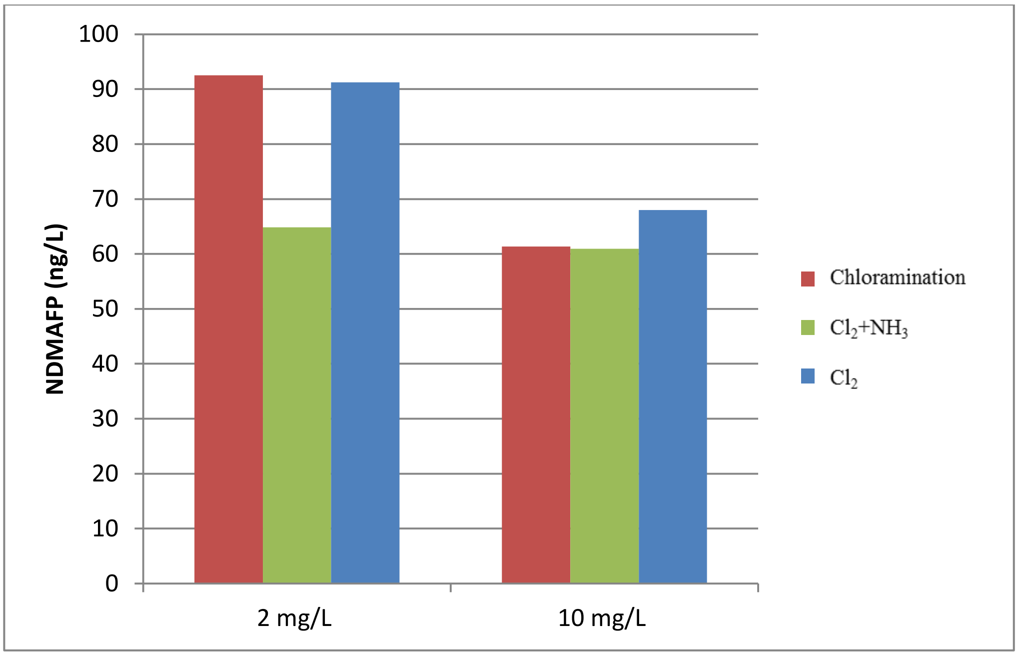


Figure 5.20 : NDMAFP concentrations in DMA-spiked lake water for different disinfection methods conducted in December

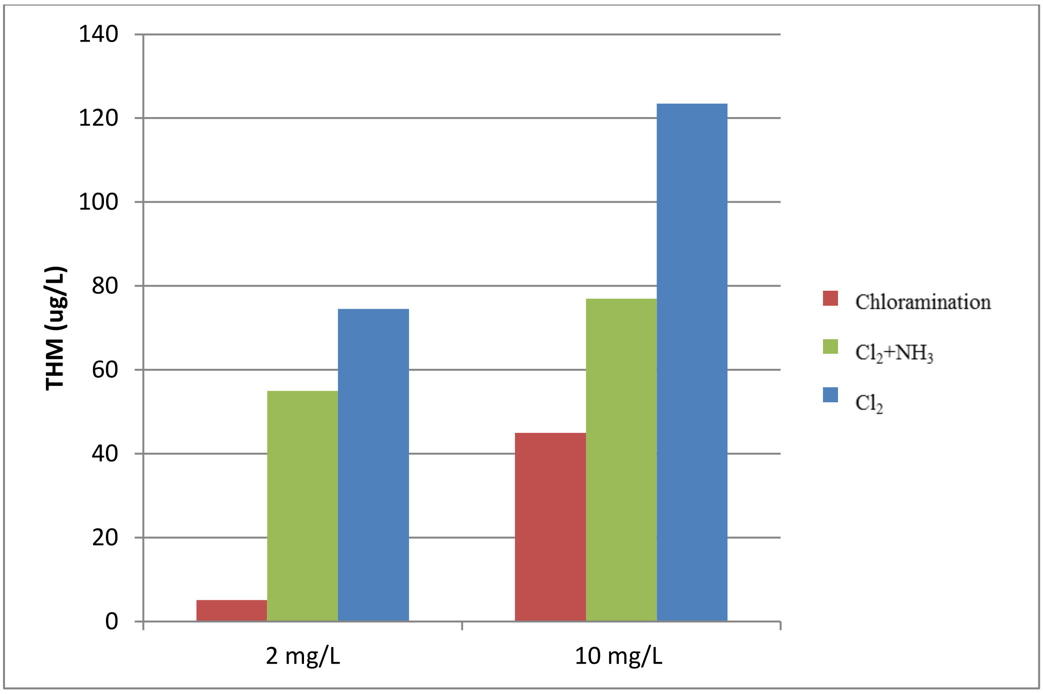


Figure 5.21 : THM concentrations in Ranitidine-spiked lake water for different disinfection methods

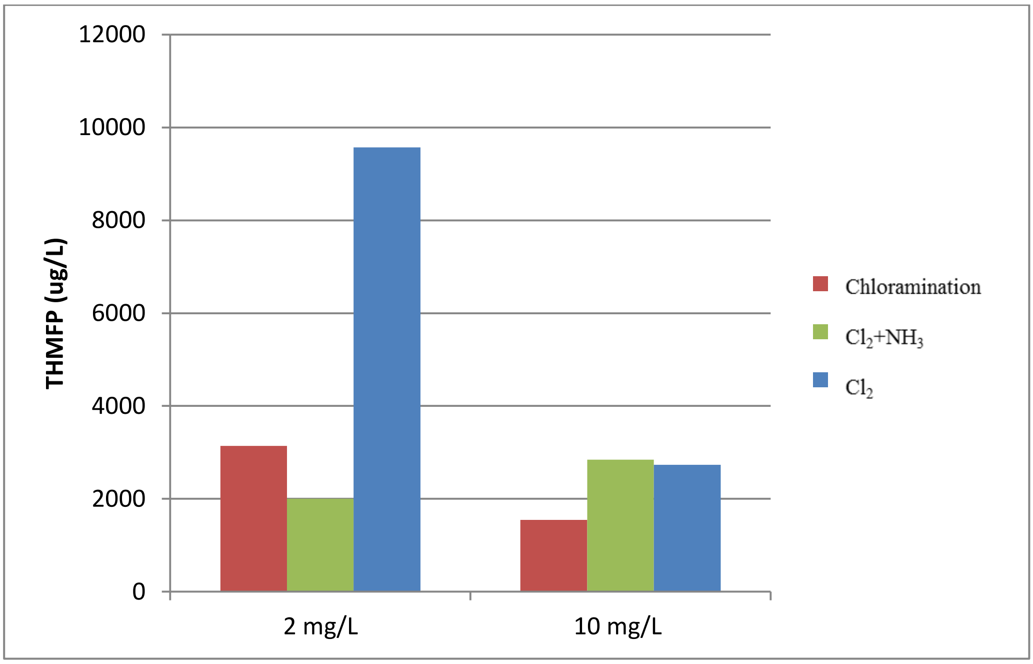


Figure 5.22 : THMFP concentrations in Ranitidine-spiked lake water for different disinfection methods conducted in December

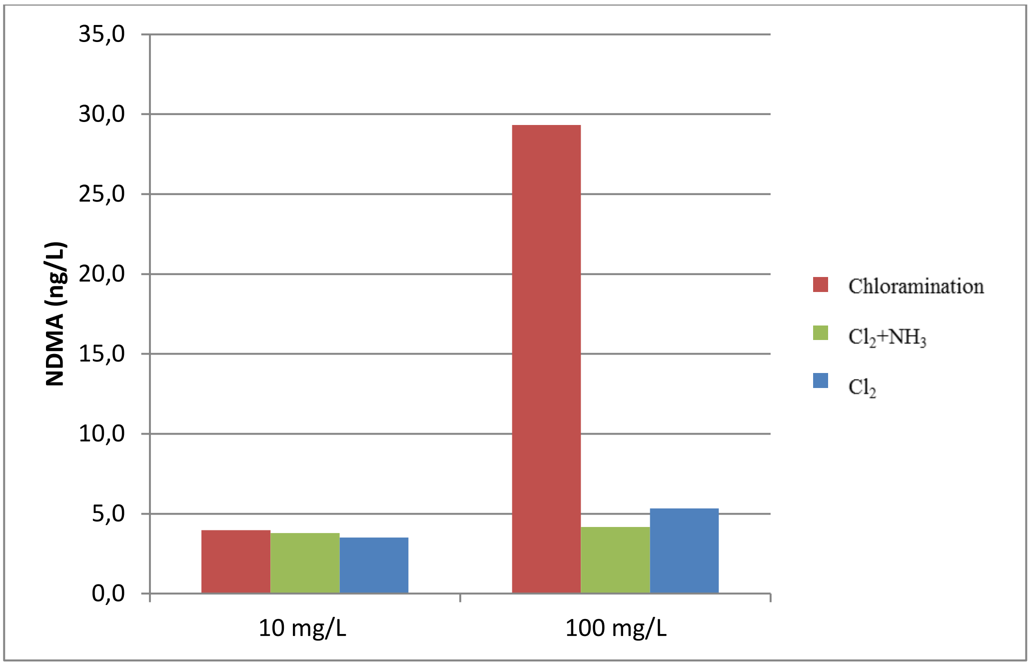


Figure 5.23 : NDMA concentrations in Ranitidine-spiked lake water for different disinfection methods conducted in December

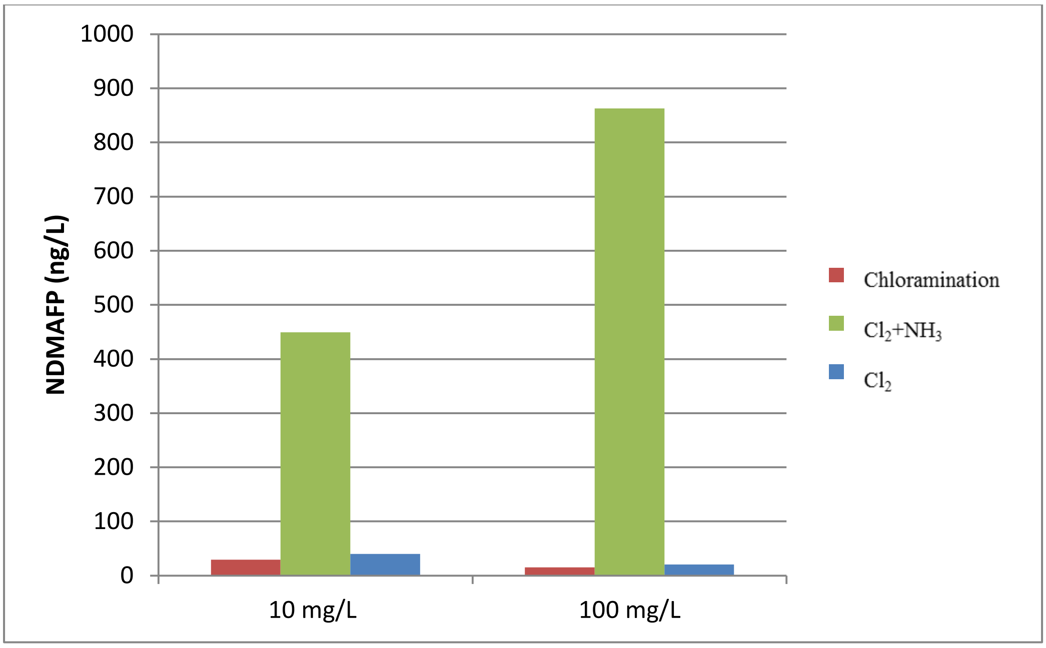


Figure 5.24 : NDMAFP concentrations in Ranitidine-spiked lake water for different disinfection methods conducted in December

One of the most important results of this study is the data obtained on the formation of DBPs from known precursors and the conversion rates based on their DOC values. NDMA conversion rates in the literature are reported as 62% and 0.76% for ranitidine and DMA, respectively (Sacher et al., 2008 and references there in). Our results are 57 % and 14%, for ranitidine and DMA, respectively. The higher conversion rate for DMA can be due to the fact the conditions used for NDMA formation potential test are somewhat different with longer reaction times (10 days vs. 7 days) and higher chloramine concentrations (140 mg/L vs. 30 mg/L) in our study.

Although a few recent studies are present on the conversion of NDMA precursors to NDMA, this is the first study to our knowledge that reports the conversion rates of NDMA precursors to THM.

DOC of lake is 6 mg/L. DOC equivalence of DMA and ranitidine are 0.52 mg/L and 1.7 E-4 mg/L respectively. These DOC values equal to 8.7% and 0.003% of total DOC respectively. However 0.52 mg/L level of DOC (DMA) forms 11.5% of total THM when 1.7 E-4 mg/L TOC forms 23% of total THM. This result shows that ranitidine is not only an NDMA but also a THM precursor and DMA behaves like NOM. Moreover this result might also explain the lack of DOC vs. THMFP and DOC vs. NDMAFP relation. In this study 1 mol DMA formed 147 mol THM and 1 mol ranitidine formed 11765 mol THM.

6. CONCLUSIONS AND RECOMMENDATIONS

Disinfection by-products, including THM and NDMA have adverse effects on human health including carcinogenicity; hence it is important to have a low DBP concentration in the drinking water while maintaining pathogen-free water. Different disinfection methods (i.e., chlorination and chloramination) favoring the formation of one type or another DBP should be evaluated in order to achieve the lowest DBP concentration in drinking water. This study shed light on the formation potential of NDMA and THMs in Büyükçekmece watershed and their formation at the water treatment plant.

Although Büyükçekmece Lake is used as a drinking water source, several point or non-point sources are thought to affect the concentration of DBPFP in the watershed. While the effect of anthropogenic sources is especially important in some tributaries, the volume of the lake enables the concentration of the DBP precursors to be diluted. Moreover, several processes might take place in the lake that affect the fate of DBP precursors and lead to a decrease in their concentrations.

The results obtained in the WTP suggest that at the current situation the formation of neither THM nor NDMA will present a problem for public health since their concentrations are below the maximum allowable concentration and advisable concentration, respectively. However, as it was observed during the sampling in the watershed, there are some important DBP precursor sources at the watershed and their presence may be more pronounced during a drought and adversely affect public health.

The lab-scale studies indicated that although the outcomes of chlorination and chloramination may be foreseen, the stepwise chloramination which is the method that is applied for chloramination at the treatment plants, may result in different concentrations than would be predicted by chlorination and chloramination. The reason of the inconsistency is believed to be the wide range of chloramination reactions which leads to different forms of chloramines with different efficiencies.

The tests with NDMA precursors indicated that the presence of some precursors such as ranitidine even at concentrations when they cannot be detected with DOC or DON, may lead to the formation of NDMA even at short contact times such as 2 hours. Due to the stability of chloramines, the precursors in the water might actually form significant NDMA in the distribution system.

Moreover, the presence of NDMA precursors might also increase the THM concentration depending on their structure. Based on the experimental results of this study, NDMA conversion rates were calculated as 57% and 14%, for ranitidine and DMA, respectively which are similar to the few studies in the literature. Moreover, the results of this study indicated that 1 mol DMA forms 147 mol THM and 1 mol ranitidine forms 11765 mol THM during chlorination. This is the first study to our knowledge, where NDMA precursors are shown to result in significant THM levels even at very low concentrations. The conversion rate of ranitidine, a pharmaceutical, is very high for THM and it is possible that the presence of ranitidine in a surface water used for the abstraction of drinking water, due to anthropogenic pollution, might result in THM concentrations above the MAC upon chlorination in the drinking water. Therefore, it is important not to allow NDMA precursors to reach the lake through better watershed protection plans that can deal with both point and non-point sources of anthropogenic pollution. Another possibility is to remove the precursors during the processes in the water treatment plant. Studying the presence of NDMA precursors in different fractions of water may provide information on how to treat them in the WTP based on their hydrophilicity/hydrophobicity or molecular weight distribution.

REFERENCES

Andrzejewski, P., Nawrocki, J., 2005: N-Nitrosomethylethylamine (NMEA) and N-Nitrosodiethylamine (NDEA), two new potential disinfection byproducts; formation during water disinfection with chlorine

Andrzejewski, P., Kasprzyk-Hordern, B., Nawrocki, J., 2007: N-nitrosodimethylamine (NDMA) formation during ozonation of dimethylamine-containing waters, Water Research., 42(4-5) : 863-870

Asami, M., Oya, M., Kosaka, K., 2009: A nationwide survey of NDMA in raw and drinking water in Japan, The Science of the total environment, 407(11), 3540-5. Elsevier B.V. doi :10.1016/j.scitotenv.2009.02.014

Ates, N., Kaplan, S. S., Sahinkaya, E., Kitis, M., Dilek, F. B., Yetis, U., 2007a: Occurrence of disinfection by-products in low DOC surface waters in Turkey. Journal of hazardous materials, 142(1-2), 526-34. doi :10.1016/j.jhazmat.2006.08.076

Bekbolet, M., Uyguner, C. S., Selcuk, H., Rizzo, L., Nikolaou, A. D., 2005: Application of oxidative removal of NOM to drinking water and formation of disinfection by-products. Methods, 176, 155-166. doi :10.1016/j.desal

Baykal, B.B., Tanik, A., Gonenc, I.E., 2000: Water Quality in Drinking Water Reservoirs of a Megacity, Istanbul, Environmental Management, 26(6) :607-614

Canada federal territorial committee on drinking water, 2010: *N*-Nitrosodimethylamine (NDMA) in Drinking Water

CDHS, California Department of Health Services, 2002: NDMA in California Drinking Water, http ://www.dhs.ca.gov/ps/ddwem/chemicals/NDMA /history.htm, date retrieved : 01.10.2011

CDPH, California Department of Public Health, 2008: NDMA and Other Nitrosamines - Drinking Water Issues, California of Department of Public Health, http ://www.cdph.ca.gov/CERTLIC/DRINKING WATER/Pages/NDMA.aspx (Last Update : July 1, 2008)

Charrois, J.W.A., Boyd, J.M., Froese, K.L., Hrudey, S.E., 2007: Occurrence of N-nitrosamines in Alberta public drinking-water distribution systems, Journal of Environmental Engineering and Science, 6(1): 103-114

Chen, B.Y., Westerhoff, P., 2010: Predicting disinfection by-product formation potential in water Water Res. 44, 3755-3762

Chen, W., Young, T.M., 2008: NDMA formation during chlorination and chloramination of aqueous diuron solutions. Environ. Sci. Technol. 42 (4), 1072e1077

Chowdhury, S., Champagne, P., McLellan, P. J., 2009: Models for predicting disinfection byproduct (DBP) formation in drinking waters: a chronological review. The Science of the total environment, 407(14), 4189-206. Elsevier B.V. doi :10.1016/j.scitotenv.2009.04.006

Clark, R., Rice, E., Pierce, B., Johnson, C., Fox, K., 1994: Effect of aggregation on Vibrio cholerae inactivation. Journal of Environmental Engineering, pp. 875–887

Ellis, G.P., West, G.B., 1983: Progress in Medicinal Chemistry, Volume 20

EPA, United States Environmental Protection Agency, 1998: Stage 1 Disinfectants and Disinfection Byproducts Rule (Stage 1 DBPR) 63 FR 69390, December 16, 1998, Vol. 63, No. 241

Goslan, E. H., Krasner, S. W., Bower, M., Rocks, S. a, Holmes, P., Levy, L. S., Parsons, S. a., 2009 : A comparison of disinfection by-products found in chlorinated and chloraminated drinking waters in Scotland. Water research, 43(18), 4698-706. Elsevier Ltd. doi :10.1016/j.watres.2009.07.029

Health Canada, 2006: Drinking Water Chlorination, http ://www.hc-sc.gc.ca/hl-vs/alt_formats/pacrb-dgapcr/pdf/iyh-vsv/environ/chlor-eng.pdf

Hepdoğan, R., 1998: Büyükçekmece Baraj Gölü Havzası'nın Hidrolojik ve Hidrolik Karakteristikleri, İTÜ Fen Bilimleri Enstitüsü, Yüksek Lisans Tezi, İstanbul

Hua, B., Veum, K., Koirala, A., Jones, J., Clevenger, T., Deng, B., 2006: Fluorescence fingerprints to monitor total trihalomethanes and N-nitrosodimethylamine formation potentials in water. Environmental Chemistry Letters, 5(2), 73-77. doi :10.1007/s10311-006-0085-7

Hrudey, S. E., 2009: Chlorination disinfection by-products, public health risk tradeoffs and me. Water research, 43(8), 2057-92. Elsevier Ltd. doi :10.1016/j.watres.2009.02.011

IARC, International Agency for Research on Cancer, 1978: IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans: Some N-Nitroso Compounds, Vol. 17. IARC, Lyon, France, p. 365

İÇDR, İl Çevre Durum Raporu, İstanbul Valiliği, 2005: İl Çevre ve Orman Müdürlüğü, İstanbul

Joyce, S., Angus, C., 2008: Water disinfection by-products and prelabor rupture of membranes, American Journal of Epidemiology, Volume : 168 Issue : 5 Pages : 514-521 DOI : 10.1093 /aje/kwn188

Kim, J., 2009: Fate of THMs and HAAs in low TOC surface water. Environmental research, 109(2), 158-65. doi :10.1016/j.envres.2008.11.003

Krasner, S. W., Weinberg, H. S., Richardson, S. D., Pastor, S. J., Chinn, R., Sclimenti, M. J., Onstad, G. D., 2006: Occurrence of a New

Generation of Disinfection Byproducts. Environmental Science & Technology, 40(23), 7175-7185. doi :10.1021/es060353j

Kruwai, K., Sacher, F., Werner, A., Müller, J., Knepper, T. P., 2004: Chemical water quality in Thailand and its impacts on the drinking water production in Thailand, Science of the Total Environment

Lee, J.W., Westerhoff, P., 2005: Dissolved organic nitrogen measurement using dialysis pretreatment, Environ. Sci. Technol. 39, 879-884

Le Roux, J., Gallard, H., Croue, J.P., 2011, Chloramination of nitrogenous contaminants (pharmaceuticals and pesticides): NDMA and halogenated DBPs formation, Water Research, 45(10), pg 3164–3174

Loeppky, R.N., 1994: Nitrosamine and N-Nitroso Compound Chemistry and Biochemistry - Advances and Perspectives, Nitrosamines and Related N-Nitroso Compounds, 553 : 1-18.

Luo X., 2006: Formation studies on n-nitrosodimethylamine (ndma) in natural waters, Dissertation, University of Missouri-Columbia

Maktav, D., Erbek, F.S., 2005: Analysis of urban growth using multi-temporal satellite data in Istanbul, Turkey, International Journal of Remote Sensing, 26(4) :797-810.

Mitch, W. A, Sedlak, D. L., 2002: Formation of N -Nitrosodimethylamine (NDMA) from Dimethylamine during Chlorination. Environmental Science & Technology, 36(4), 588-595. doi :10.1021/es010684q

Mitch, W. A, Sharp, J. O., Trussell, R. R., Valentine, R. L., Alvarez-Cohen, L., Sedlak, D. L., 2003: N -Nitrosodimethylamine (NDMA) as a Drinking Water Contaminant : A Review. Environmental Engineering Science, 20(5), 389-404. doi :10.1089/109287503768335896

MWH, 2005: revised by Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., Tchobanoglous, G., Water Treatment Principles and Design, second ed. Wiley, Hoboken, NJ.

Nieuwenhuijsen, M.J., Toledano, M.R., Eaton, N.E., Fawell, J., Elliott, P., 2000: Chlorination disinfection by-products in water and their association with adverse reproductive outcome : a review. Occup. Environ. Med. 57, 73–85.

OEHHA, 2006: Office of Environmental Health Hazard Assessment, California, USA. http ://www.oehha.ca.gov/water/phg/pdf/122206NDMAphg.pdf

Oğur, R., Tekbaş, Ö.F., Hasde, M., 2004: Klorlama rehberi; içme ve kullanma sularının klorlanması, Gülhane Askeri Tıp Akademisi

OME, 2003: Ontario Ministry of Environment, Canada. http ://www.ene.gov.on.ca/envi sion/gp/4449e.pdf

Örgün, Y., 2003 : İstanbul-Çatalca Muratbey Köyü civarında yapılan Madencilik Faaliyetlerinin Büyük Çekmece Göl Havzasında Yeralan Yeraltı Sularına ve Çevreye Olan Etkisi", Türkiye Kuvaterner Çalıştayı IV, İstanbul

Özdemir, K., Toröz, I., 2010 : İçme suyu kaynaklarında klorlama yan ürünlerinin diferansiyel UV spektroskopi yöntemi ile izlenmesi, itü dergisi, 20(2), 59-69

Pehlivanoglu-Mantas, E., Sedlak, D.L., 2006a: Fate of Wastewater-Derived NDMA Precursors in the Aquatic Environment, Water Research, 40(6) : 1287-1293

Pehlivanoglu-Mantas, E., Hawley E., Deeb, R., Sedlak, D.L., 2006b: Formation of Nitrosodimethylamine (NDMA) During Chlorine Disinfection of Wastewater Effluents Prior To Use In Irrigation Systems, Water Research, 40 : 341-347

Planas, C., Palacios, O., Ventura, F., Rivera, J., Caixach, J., 2008: Analysis of nitrosamines in water by automated SPE and isotope dilution GC/HRMS Occurrence in the different steps of a drinking water treatment plant, and in chlorinated samples from a reservoir and a sewage treatment plant effluent. Talanta, 76(4), 906-13. doi :10.1016/j.talanta.2008.04.060

Richardson, S.D., 1998: Drinking water disinfection by-products. In : Meyers, R.A. (Ed.), The Encyclopedia of Environmental Analysis and Remediation, vol. 3. John Wiley & Sons, New York, pp. 1398–1421

Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R., Demarini, D. M., 2007: Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water : a review and roadmap for research. Mutation research, 636(1-3), 178-242. doi :10.1016/j.mrrev.2007.09.001

Sacher, F., Schmidt, C.K., Lee, C. and Gunten, U.V., 2008: Strategies for minimizing nitrosamine formation during disinfection. Awwa Research Foundation, Denver, CO (Report No. 91209)

Sadiq, R., Rodriguez, M.J., Imran, S.A., Najjaran, H., 2007: Communicating human health risks associated with disinfection by-products in drinking water supplies : a fuzzy-based approach, Stochastic Environmental Research and Risk Assessment, 21(4) : 341-353

Schäfer, A. I., Mitch, W., Walewijk, S., Munoz, A., Teuten, E., Reinhard, M., 2010: Drinking water as a source of human exposure to xenobiotics : The case of disinfection by-product N-nitrosodimethylamine (NDMA), Desalination

Sahinkaya, E., Ateş, N., Atlı, E., Tokmak, B., Çapar, G., Sanin, F.D., Celtemen, P., Baltacı, F., Yetiş, Ü., Dilek, F.B., 2005 : İçme suyu amaçlı baraj göllerinde trihalometan oluşum potansiyeli, TMMOB Çevre Mühendisleri Odası 6. Ulusal Çevre Mühendisliği Kongresi, Bildiriler Kitabı, pp. 11-22, İstanbul

Schmidt, C. K., Brauch, H.-J., 2008: N,N -Dimethylsulfamide as Precursor for N - Nitrosodimethylamine (NDMA) Formation upon Ozonation and its Fate During Drinking Water Treatment. Environmental Science & Technology, 42(17), 6340-6346. doi :10.1021/es7030467

Shank, R.C., Magee, P.N., 1981: Toxicity and carcinogenicity of N-nitroso compounds, Mycotoxins and N-Nitroso Compounds : Environmental Risks, vol. 1 CRC Press, Boca Raton, FL (1981), pp. 185–217.

Shen, R., Andrews, S., 2011: Demonstration of 20 pharmaceuticals and personal care products (PPCPs) as nitrosamine precursors during chloramine disinfection. Water Res. 45 (2), 944e952

Sorlini, S., Collivignarelli, C., 2005: Trihalomethane formation during chemical oxidation with chlorine, chlorine dioxide and ozone of ten Italian natural waters. Desalination, 176(1-3), 103-111. doi :10.1016/j.desal.2004.10.022

Templeton, M. R., 2010: Practical Paper NDMA and seven other nitrosamines in selected UK drinking water supply systems. Water, (Cepa 2006), 277-284. doi :10.2166/aqua.2010.077

Toroz, I., Uyak, V., 2005: Seasonal variations of trihalomethanes (THMs) in water distribution networks of Istanbul City. Desalination, 176(1-3), 127-141. doi :10.1016/j.desal.2004.11.008

USEPA Technology Transfer Network, 2003: Air toxic website. N-Nitrosodimethylamine, http ://www.epa.gov/ttn/atw/hlthef/nitrosod.html

USEPA, 2008: Integrated Risk Information System, United States Environmental Protection Agency, http ://www.epa.gov/ncea/iris/subst/0045.htm

Uyak, V., Ozdemir, K., Toroz, I., 2008: Seasonal variations of disinfection by-product precursors profile and their removal through surface water treatment plants. The Science of the total environment, 390(2-3), 417-24. doi :10.1016/j.scitotenv.2007.09.046

Uyak, V., Toroz, I., Meriç, S., 2005: Monitoring and modeling of trihalomethanes (THMs) for a water treatment plant in Istanbul. Desalination, 176(1-3), 91-101. doi :10.1016/j.desal.2004.10.023

Uyak, V., Toroz, I., 2006: Modeling the formation of chlorination by-products during enhanced coagulation. Environmental monitoring and assessment, 121(1-3), 503-17. doi :10.1007/s10661-005-9150-0

Uyak, V., Yavuz, S., Toroz, I., Ozaydin, S., Genceli, E. A., 2007: Disinfection by-products precursors removal by enhanced coagulation and PAC adsorption. Desalination, 216(1-3), 334-344. doi :10.1016/j.desal.2006.11.026

Westerhoff, P., Mash, H., 2002: Dissolved organic nitrogen in drinking water supplies, AQUA, 51, pp. 415–448

White, D.M., Garland, J.S., Narr, J., Woolard, C.R., 2003: Natural organic matter and DBP formation potential in Alaskan water supplies, Water Research, 37(4)

WHO, World Health Organization, 2004 : Guidelines for drinking-water quality, 3rd ed.

Williams, D. T., Lebel, G. L., Benoit, F. M., Centre, E. H., Canada, H., 1997: by-products in Canadian Drinking Water. Water, 34(2)

World Health Organization, International Agency for Research on Cancer, 2007: IARC monographs on the evaluation of carcinogenic risks to humans, volume 89, smokeless tobacco and some tobacco-specific n-nitrosamines

Xu, B., Ye, T., Li, D. P., Hu, C. Y., Lin, Y. L., Xia, S. J., Tian, F. X., Gao, N. Y., 2011: Measurement of dissolved organic nitrogen in a drinking water treatment plant: Size fraction, fate, and relation to water quality parameters, Science of The Total Environment, Volume 409, Issue 6, Pages 1116-1122

Van Gysel, A.B., Musin, W., 2005: Ullmann's Encyclopedia of Industrial Chemistry, 2005 Wiley-VCH Verlag, Weinheim

Vandenbruwane, J., Neve, S. D., Qualls, R. G., Salomez, J., Hofman, G. 2007 : Optimization of dissolved organic nitrogen (DON) measurements in aqueous samples with high inorganic nitrogen concentrations. *The Science of the total environment*, *386*(1-3), 103-13. doi :10.1016/j.scitotenv.2007.06.025

Villanueva, C.M., Cantor, K.P., Cordier, S., Jaakkola, J.J., King, W.D., Lynch, C.F., Porru, S., Kogevinas, M., 2004: Disinfection byproducts and bladder cancer: a pooled analysis, Epidemiology, 15, 357–367

Von Gunten, U., 2003 : Ozonation of drinking water : part I. Oxidation kinetics and product formation. *Water research*, *37*(7), 1443-67. doi :10.1016/S0043-1354(02)00457-8

Zhang, J., Yu, J., An, W., Liu, J., Wang, Y., Chen, Y., Tai, J., 2011: Characterization of disinfection byproduct formation potential in 13 source waters in China. Journal of Environmental Sciences, 23(2), 183-188. The Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences. doi :10.1016/S1001-0742(10)60440-8

CURRICULUM VITAE

Name Surname: Nur Hanife ORAK

Place and Date of Birth: Istanbul, 27.02.1987

Address: İTÜ, İnşaat Fakültesi, Çevre Mühendisliği Bölümü, K 316, Maslak, İstanbul

E-Mail: orakn@itu.edu.tr

B.Sc.: ITU Environmental Engineering

Professional Experience and Rewards: ITU Research Assistant, Istanbul Technical University research groups, The Association for the Art of the Harp

List of Publications and Patents:

T. Ölmez-Hancı, N.H. Orak, A. Tetik, I. Kabdaşlı, T. Ohno, İ. Arslan-Alaton, O. Tünay,2009, Visible Light-Induced Photocatalysis of Formic and Oxalic Acids with S-Doped, Fe-Loaded Titania; Environmental Technology