Eva NIEMINSKI

Utah Department of Environmental Quality
Division of Drinking Water

GIARDIA AND CRYPTOSPORIDIUM IN US DRINKING WATER: OCCURRENCE, TREATMENT, AND RECENT REGULATIONS

GIARDIA I CRYPTOSPORIDIUM W WODZIE PITNEJ W USA: WYSTEPOWANIE, USUWANIE I NAJNOWSZE UREGULOWANIA PRAWNE

Usuwanie mikroorganizmow takich jak Giardia i Cryptosporidium z wody pitnej nadal pozostaje ciezkim zadaniem dla stacji uzdatniania wody. Obydwa te pierwotniaki wystepuja w wiekszosci wod powierzchniowych, sa trudne do usuniecia ze wzgledu na ich mikroskopijny rozmiar, i ponadto, Cryptosporidium jest odporne na chlorowanie. Dodatkowa trudnoscia jest brak dokladnych, szybkich, i niedrogich metod analitycznych, ktore pozwalalyby na ocenienie liczebnosci tych organizmow w wodzie, ich zywotnosci i zdolnosci do spowodowania infekcji w przewodzie pokarmowym czlowieka.
Przedstawiony tu artykol jest zsumowaniem biezacych informacji o wystepowaniu Giardia i Cryptosporidium w wodach Ameryki Polnocnej, efektywnosci usuwania tych organizmow w procesie uzdatniania wody pitnej i jej dyzynfekcji, oraz metod analitycznych, uzywanych do wykrywania tych organizmow w wodzie. Przedstawiony jest tez w skrocie opis obecnych przepisow, ktore w Stanach Zjednoczonych zostaly ustalone na przeciagu ostatnich lat w celu eliminowania tych organizmow z wody pitnej i poprawiania ochrony zdrowia ludzi.

1. Close encounters with Giardia and Cryptosporidium

1.1. Giardia and Cryptosporidium occurrence in water

Giardia and Cryptosporidium are the most common protozoa of concern in drinking water industry, as they are ubiquitous in surface water supplies. Most typically, Giardia is present in flowing streams and in lakes affected by contamination from wildlife (at typical concentration in the US of 8 to 22/100L), while Cryptosporidium is found in waters contaminated with cattle waste (average concentration 58 to 109/L) [1], [2], [3].

The species that affect human's health are *Giardia lamblia*'s oval cysts (7-14 μm) *(*and *Cryptosporidium parvum*'s spherical oocysts (4-6 μm), causing gastrointestinal diseases in humans, known as giardiasis and cryptosporidiosis, respectively.

Giardia was first described in 1681 by van Leeuwenhoek, while Cryptosporidium was isolated by Tyzzer from mouse in 1907 and only conclusively recognized as agents of human waterborne disease in 1987 by Rose and by Hayes et al. Among these two pathogens, Cryptosporidium presents much more challenge to drinking water professionals, as it is smaller and thus more difficult to remove, and is more resistant to disinfection (withstand chlorination & various other chemical disinfectants). More importantly, while giardiasis is relatively easily cured with flagel, no effective medication has been confirmed for human cryptosporidiosis.

Human cryptosporidiosis is triggered by ingestion and/or inhalation of oocysts-contaminated material. Most common symptoms are profuse and watery diarrhea, abdominal cramping, nausea, vomiting, and fever. The AIDS epidemic presented cryptosporidiosis as a disease of new medical importance. While the infection has duration of 2 to 12 days in most well-nourished, immunocompetent individuals and is usually self-limiting, the individuals with immune deficiencies are at risk due to absence of effective immunostimulatory or chemotherapeutic agents. Infections in the gastrointestinal tract may be spreading to other organs, which may lead to cholecystitis, hepatitis, pancreatitis and respiratory problems and has been recognized as a contributing factor in the deaths of AIDS patients.

Waterborne transmission of Cryptosporidium has received particular attention as large communities of susceptible hosts can be infected (i.e. Milwaukee in 1993: 403,000 individuals affected as a result of treatment deficiencies). Several other waterborne outbreaks were reported in the US: Braun Station, TX in 1984 from sewage in well (2,006 affected); Carrolton, GA in 1987 resulting from improper treatment (13,000 affected); Jackson County, OR in 1992 from source water contamination (15,000 affected).

1.2. Analytical Methods

While there are several analytical methods available for detection of Giardia and Cryptosporidium in water, all of them still lack adequate precision, accuracy, and sensitivity [4]. Research is continuing on improvements of the existing methods and on development of new, genetic-based methods. In the US, the EPA Method 1622/1623 is the approved method for detection and analysis of these protozoa in water [5]. There are three steps in the analysis of water samples for the presence and quantification of *Giardia* cysts and/or *Cryptosporidium* oocysts:

- Sample collection – filtration of 100 L through a membrane capsule filter,
- Concentration and separation of target organisms from other debris in the sample through centrifugation and flotation,
- Assay of the target organisms – identification with immunoassay, confirmation with dyes, and enumeration through microscopy.

These approved and widely used EPA methods do not allow for determination of cyst and oocysts infectivity and lack confirmation of viability, and therefore, can't be applied to evaluation of health risk exposure to Giardia and Cryptosporidium in water. Current research on improvements in detection methods include PCR- or other molecular-based assays for faster identification and confirmation, molecular fingerprinting for source tracking, and cell culture to determine infectivity.

2. Treatment and disinfection

2.1. Evaluation of treatment effectiveness

Conventional treatment can be effective in removal of Giardia and Cryptosporidium if it consistently removes turbidity and particles [6]. Cryptosporidium oocysts, smaller in size, are removed at lower degree than Giardia cysts. Properly operated conventional treatment plants remove at least 2-log of Cryptosporidium and 2.5-log of Giardia. Additional removal may be achieved if the filter effluent turbidity is maintained at 0.1 NTU [6].

Chlorine and chlorine-based disinfectants, effective in inactivation of Giardia cysts, are ineffective in Cryptosporidium oocyst inactivation at the commonly practiced chlorine dosages and contact times. Stronger disinfectants, such as ozone or chlorine dioxide are required to effectively inactivate Cryptosporidium. UV light has proven to be to be highly effective in Cryptosporidium inactivation through damaging the replicating DNA by dimerization of thymine nucleotides. A typical UV reactor, providing a dose of 40 mJ/cm^2 should receive 3-log Cryptosporidium and 3-log Giardia inactivation credit, pending validation of its performance.

2.2. Search for a surrogate

Until more accurate, faster, and less expensive methods become available to monitor Giardia and Cryptosporidium in water, surrogate measures are being used in monitoring and optimizing plant performance for the removal of these pathogens. Currently, the most frequently used parameters are turbidity, particle count, somatic and male-specific coliphage, heterotrophic plate count, coliform bacteria, and aerobic spore-forming bacteria [7]. A search for a better surrogate is still continuing, focusing on identification of surrogates that can represent occurrence of pathogens as well as the removal of pathogens through treatment. An ideal surrogate measure, representing occurrence and removal effectiveness of Giardia and Cryptosporidium should fulfill several requirements: be ubiquitously present in natural waters, be non-pathogenic, should not grow or replicate in treatment plant basins, should be removed at similar rates as the target pathogens, and should be analyzed quickly, easily, and inexpensively.

3. Regulations

3.1. Safe Drinking Water Act

Federal and state regulations are used to establish requirements intended to protect the drinking water quality. The federal Safe Drinking Water Act (SDWA) of 1974 is the vehicle used nationally to address drinking water quality issues. After passage of the SDWA, the federal government became involved in developing national drinking water regulations pursuant to the new law and in conducting research to support these regulations. States implement the federal mandates but also utilize their own statutory and regulatory requirements to protect drinking water quality. For example, the states play a significant role in oversight functions ranging from licensing of water treatment plant operators to the approval of new sources of supply and the approval of new treatment facility design. Local agencies such as health departments, environmental health programs, and building departments implement codes and ordinances.

The SDWA, enacted in 1974 and amended in 1986, 1988, and 1996, provides the statutory bases by which public water systems are regulated [8]. Pursuant to the SDWA, the U.S. Environmental Protection Agency (EPA) is mandated to establish regulations for drinking water in the form of Maximum Contaminant Levels (MCL) and treatment techniques. The SDWA also provides EPA with the authority to delegate the implementation of the SDWA requirements to the states through the process of primacy. Forty-nine of the 50 states have accepted primacy, with Wyoming being the exception.

The SDWA applies to public water systems, which can be publicly or privately owned. Public water systems are defined as providing drinking water to at least 25 people or 15 service connections for at least 60 days per year. Currently, 51 organic chemicals, 16 inorganic chemicals, seven disinfectants and disinfectant byproducts, four radionuclides, and coliform bacteria are monitored for compliance with the SDWA, including such things as arsenic, fluoride, and volatile synthetic organic compounds [9].

The 1996 amendments to the SDWA mandated that EPA conduct research to strengthen the scientific foundation for standards that limit public exposure to drinking water contaminants. Specific requirements were given for research on waterborne pathogens such as Cryptosporidium and Norwalk virus, disinfection by-products, arsenic, and other harmful substances in drinking water.

3.2. Surface Water Treatment Rule

In 1989, the EPA published the final Surface Water Treatment Rule (SWTR) in response to Congress' mandate to require systems that draw their water from surface water sources (rivers, lakes, and reservoirs) and groundwater under the influence of surface water to filter, where appropriate, and to disinfect their water before distribution [8]. The SWTR seeks to reduce the occurrence of unsafe levels of disease causing microbes, including viruses, *Legionella* bacteria, and the protozoan *Giardia lamblia*.

The SWTR requires water systems that filter to meet specific turbidity limits and achieve reductions in *Giardia lamblia* cysts (99.9 % or 3 log) and viruses (99.99 % or 4 log). Water systems are also required to maintain a detectable residual disinfectant concentration in the distribution system measured as total chlorine, combined chlorine, or chlorine dioxide [9]. Surface Water Treatment Rule specified the MCL for turbidity in combined filter effluent at 0.5 NTU and requires 3 log removal of Giardia. The rule provides 2.5 log credit for conventional treatment and 2 log credit for direct filtration. Disinfection with chlorine, ozone, or chlorine dioxide is required for all surface waters to further reduce Giardia and Cryptosporidium in drinking water.

3.3. Interim Enhanced Surface Water Treatment Rule

The Interim Enhanced SWTR (IESWTR), promulgated in December of 1999 and implemented in January 2002, is the first regulation to specifically address chlorine resistant pathogens such as Cryptosporidium [9]. The IESWTR applied to public water systems serving greater than 10,000 people that were subject to the original SWTR. The IESWTR establishes a requirement for the reduction of Cryptosporidium and a more stringent turbidity requirement for filtered water supplies. The IESWTR also requires certain water systems to evaluate their disinfection practices to ensure that there will be no significant reduction in microbial protection as the result of modifying disinfection practices to reduce formation of disinfection by-products.

In addition to the requirements of the Surface Water Treatment Rule, this rule establishes a Maximum Contaminant Level Goal (MCLG) of zero for Cryptosporidium, and set a 2-log Cryptosporidium removal requirement for systems that filter. It also lowered the combined filter effluent turbidity standard to less than or equal to 0.3 NTU in 95 percent of all measurements. At no time can any one turbidity measurement exceed 1.0 NTU. Water systems that meet the turbidity standard are assumed to provide at least 2-log Cryptosporidium removal through filtration. This rule also establishes criteria for systems that must establish a disinfection profile by collecting additional data related to the disinfection process and DBP formation. The rule provides specific guidance for individual filter turbidity monitoring, disinfection profiling and benchmarking, requirements for covers on new finished water reservoirs, and sanitary surveys conducted by states for all surface water systems regardless of size.

The IESWTR, which tightened turbidity performance criteria and required individual filter monitoring, was designed to optimize treatment reliability and to enhance physical removal efficiencies to minimize the Cryptosporidium levels in finished water. In addition, the rule included disinfection benchmark provisions to assure continued levels of microbial protection while facilities take the necessary steps to comply with new DBP standards.

3.4. Long Term 1 Enhanced Surface Water Treatment Rule

In 2002 EPA promulgated the Long Term 1 Enhanced Surface Water Treatment Rule (LT1ESWTR) [9]. The LT1ESWTR applies to public water systems that use surface

water or groundwater under the direct influence of surface water and serve fewer than 10,000 persons. The purposes of the LT1ESWTR were to improve control of microbial pathogens, specifically Cryptosporidium, in drinking water and to address risk trade-offs with disinfection byproducts. The rule required systems to meet strengthened filtration requirements as well as to calculate levels of microbial inactivation to ensure that microbial protection is not jeopardized if systems make changes to reduce formation of disinfection by-products. The only difference between this rule and the IESWTR is the size of the affected community.

3.5. Long Term 2 Enhanced Surface Water Treatment Rule

In 2003, EPA proposed the Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) [10]. The LT2ESWTR applied to public water systems that use surface water or groundwater under the direct influence of surface water. The purpose of this rule is to reduce disease incidence associated with Cryptosporidium and other pathogenic microorganisms in drinking water. The LT2ESWTR supplements existing regulations by targeting additional Cryptosporidium treatment requirements to higher risk systems.

The LT2ESWTR also contains provisions to mitigate risks from uncovered finished water storage facilities. Water systems with uncovered finished water storage reservoirs are required to cover the reservoir and treat the reservoir discharge to the distribution system to achieve a 4-log virus inactivation or implement a risk mitigation plan, which must address control of physical access, preventing surface water run-off and the introduction of animal and bird waste, and continuous water quality assessment [10].

Finally, to ensure that systems maintain microbial protection as they take steps to reduce the formation of disinfection by-products (DBPs), the LT2ESWTR requires water systems that proposed to modify their disinfection process to reduce DBPs to assess the existing levels of disinfection that the system provides. Systems are required to establish a benchmark, which is the system's lowest monthly average microbial inactivation. If the benchmark is more than the required inactivation of 3-log removal for Giardia and 4-log removal for viruses, the system may consider decreasing the amount of disinfectant added, contact time, or altering other disinfection practices to lower DBP levels [10].

A summary of US regulations concerning Giardia and Cryptosporidium in drinking water is presented in Table 1. The additional treatment requirements for Cryptosporidium inactivation are presented in Table 2. They are based, in part, on the assumption that conventional treatment plants in compliance with the IESWTR achieve an average of 3-log removal of Cryptosporidium. Therefore, the total Cryptosporidium removal requirements for the action bins with 1-log, 2-log and 2.5-log additional treatment correspond to total Cryptosporidium removals of 4-log, 5-log and 5.5-log, respectively. EPA has created a "microbial toolbox" of treatment options to assign log removal credit to different treatment techniques utilities can use to meet the Cryptosporidium removals required by the assigned bin number. These incremental credits, given for addition of specific treatment practices, are presented in Table 3.

The action bins are assigned based on the estimate of the water source vulnerability to the presence of Cryptosporidium. According to the requirements of the Long-Term 2 Enhanced Surface Water Treatment Rule, EPA required large systems to monitor monthly for Cryptosporidium in 2006-2008 and small systems to monitor for *E. coli* for two years starting in October 2008. As stated in the M/DBP2 Agreement in Principle, EPA "will work with stakeholders to evaluate alternative indicators and systems characterization scenarios for predicting Cryptosporidium occurrence in small systems" [10]. Another round of source water monitoring for Cryptosporidium is scheduled for 2011-2013.

Tab. 1. Summary of US regulations concerning Giardia and Cryptosporidium in water

Regulation	Key Requirements
SDWA	• Established national primary and secondary drinking water regulations (MCLs and MCLGs)
SWTR	• Requires removal and disinfection, resulting in a 3 log reduction of *Giardia lamblia* and a 4 log reduction in enteric viruses. Also, requires that a detectable disinfectant residual be maintained at representative locations in the distribution system
IESWTR	• Enhances protection from pathogens, including Cryptosporidium, and tries to prevent increases in microbial risk for large systems while they comply with the Stage 1 D/DBP Rule
LT1ESWTR	• Enhances protection from pathogens, including Cryptosporidium, and tries to prevent increases in microbial risk for systems serving less than 10,000 people while they comply with the Stage 1 D/DBP Rule
LT2ESWTR	• Requires additional Cryptosporidium treatment for high risk systems and maintenance of microbial protection while reducing the formation of DBPs

Tab. 2. Cryptosporidium inactivation requirements per LT2ESWTR

Bin No.	Average *Cryptosporidium* Concentration	Additional Treatment Requirements for Systems with Conventional Treatment
1	Cryptosporidium < 0.075/L	No action
2	0.075/L < Cryptosporidium < 1.0/L	1-log treatment (systems may use any technology or combination of technologies from toolbox as long as total credit is at least 1-log)
3	1.0/L < Cryptosporidium < 3.0/L	2-log treatment (systems must achieve at least 1-log of the required 2-log treatment using ozone, chlorine dioxide, UV, membranes, bag/cartridge filters, or in-bank filtration)
4	Cryptosporidium ≥ 3.0/L	2.5-log treatment (system must achieve >1-log of the required 2.5-log treatment using ozone, chlorine dioxide, UV light, membranes, bag/cartridge filters, or in-bank filtration)

Tab. 3. Credit for additional treatment of Cryptosporidium in water

Approach	0.5 log increase	1.0 log increase	2.0 log increase	2.5 log increase
Pre-treatment				
In-Bank Filtration				X
Pre-settling Basin				
No coagulant addition	X			
Coagulant addition		X		
Off-stream raw water storage				
> 30 days	X			
> 60 days		X		
Improved Treatment				
Lower Finished Water Turbidity to 50% of IESWTR levels (0.15 NTU)		X		
Roughing Filter		X		
Secondary Filters			X	
Membranes (MF, UF, NF, RO)				X
Bag Filters			X	
Improved Disinfection				
Inactivation (disinfection)				
0.5 log inactivation		X		
1.0 log inactivation			X	
> 1.0 log inactivation				X
Peer Review or Other Demonstration / Validation of System Performance				
Demonstration of Performance	X	X	X	X
Peer Review Program (Partnership for Safe Water)		X		

References

[1] AwwaRF (Awwa Research Foundation), 2002. Source Water Assessment: Variability of Pathogen Concentrations. Denver, CO.

[2] AwwaRF (Awwa Research Foundation), 2005. Fate and Transport of Surface Water Pathogens in Watersheds. Denver, CO.

[3] LeChevallier, M.W. et al. 1991. Occurrence of *Giardia* and *Cryptosporidium* spp. in Surface Water Supplies. *Appl. Environ. Microbiol*., 57:9:2610.

[4] Rose, J.B. et al. 1988. Methods for the Recovery of *Giardia* and *Cryptosporidium* From Environmental Waters and Their Occurrence. (P. Wallis and B. Hammond, eds.) Univ. Calgary Press, Calgary.

[5] USEPA, 2005. Method 1623 for Detection of Cryptosporidium in Water. EPA–815–R–05–002, EPA–821–R–01–025, EPA–821–R–99–006, Washington, DC.

[6] Nieminski, E.C., Ongerth, J.E., "Giardia and Cryptosporidium Removal of through Direct Filtration and Conventional Treatment", Jour. AWWA, 87(9):95-106. 1995.

[7] Nieminski, E.C., W.D. Bellamy, "Using Surrogates to Improve Treatment Plant Performance", Jour. AWWA, 92(3):67-78. 2000.

[8] EPA. 1989. National Primary Drinking Water Regulations: Filtration, Disinfection; Turbidity, *Giardia lamblia*, Viruses, Legionella, and Heterotrophic Bacteria; Final Rule (SWTR), 54 Federal Register 27486.

[9] EPA. 2005. FACTOIDS: Drinking Water and Ground Water Statistics for 2004. Washington, DC:EPA

[10] EPA. 2003. National Primary Drinking Water Regulations: Long Term 2 Enhanced Surface Water Treatment Rule, 68 Federal Register 47639.

Anastasia NIKOLAOU[1], Przemyslaw ANDRZEJEWSKI[2]

[1]Faculty of the Environment, Department of Marine Sciences, University of the Aegean, Mytilene, Greece
[2] Faculty of Chemistry, Adam Mickiewicz University, Poznań, Poland

OCCURRENCE PATTERNS OF DIFFERENT CATEGORIES OF DISINFECTION BY-PRODUCTS IN WATER: INFLUENCE OF SOURCE WATER CHARACTERISTICS

WYSTĘPOWANIE PREKURSORÓW RÓŻNYCH GRUP UBOCZNYCH PRODUKTÓW DEZYNFEKCJI W WODZIE: WPŁYW CHARAKTERYSTYKI WODY SUROWEJ

Problem tworzenie się ubocznych produktów dezynfekcji jest przedmiotem zainteresowania od kilku dekad. W prezentowanych badaniach oceniano występowanie prekursorów różnych grup ubocznych produktów dezynfekcji prowadząc eksperymenty z wykorzystaniem wód różnego pochodzenia z Mytilene (Grecja) i odżelazionej wody z Poznania (Polska). Badano tworzenie się różnych grup ubocznych produktów dezynfekcji jak trihalometany, kwasy halogenooctowe, haloacetonitryle, haloketony, wodzian chloralu, chloropikrynę i nitrosodimetyloaminę (NDMA). Zastosowane metody analityczne wykorzystywały techniki chromatografii gazowej z detekcją wychwytu elektronów połączone z ekstrakcją ciecz-ciecz, derywatyzację w analityce kwasów halogenooctowych oraz technikę wykluczania jonowego w systemie wysokosprawnej chromatografii cieczowej z detekcją UV w analityce NDMA.
Eksperymenty obejmowały chlorowanie próbek wody (ozonowanie w przypadku próbek wody w Polsce), w różnych warunkach dla różnych typów wód (chlorowanie) lub różnej charakterystyki wód (ozonowanie). Wyniki badań nad chlorowaniem wód surowych wskazują na znaczne różnice w specjacji jak i poziomie stężeń poszczególnych grup ubocznych produktów dezynfekcji w zależności od charakterystyki źródła wody jak i parametrów procesu (dawka chloru, pH, temperatura i czas reakcji). Charakterystyka źródeł wody, szczególnie zawartość naturalnej materii organicznej i bromków, wysoka w niektórych z badanych wód, wykazała wielki wpływ występowania poszczególnych grup prekursorów na powstające uboczne produkty dezynfekcji, wskazując jednocześnie na konieczność szczegółowego badania źródeł wody w celu optymalizacji procesu dezynfekcji i minimalizacji ryzyka zdrowotnego z nim związanego. Wyniki ozonowania wód podziemnych zawierających dimetyloaminę wskazują, że NDMA powstaję przy specyficznym stosunku molowym ozonu do dimetyloaminy a ilość powstającej NDMA wzrasta wraz ze wzrostem pH.

The formation of disinfection by-products (DBPs) has been an issue of concern during the last decades. Many investigations have revealed the complexity of the subject matter, as their formation can vary according to different factors and water source. In this study, the occurrence patterns of different categories of DBPs are examined, by experimental work regarding surface water of different origins in Mytilene, Greece and deironed ground water in Poznan, Poland. The categories of DBPs investigated included trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), chloral hydrate (CH), chloropicrin (CP) and N-Nitrosodimethylamine (NDMA).The analytical methods used included gas chromatography with electron capture detector (GC-ECD) after liquid-liquid extraction of DBPs, as well as derivatization for HAAs and HPLC-IE-UV for NDMA. Experimental work included chlorination of water samples (ozonation in case of water in Poland) under different conditions for different water sources (chlorination) or different characteristics of water (ozonation). During chlorination of raw water, bromide content was determined by ion chromatograph and natural organic matter (NOM) was measured as UV-272 absorbance. During ozonation of dimethylamine (DMA) containing groundwater, destruction of DMA (NDMA precursor) was determined indirectly by means of measurement of concentration of formic acid, which are formed as the result of oxidation methyl group in DMA molecule. The results of raw water chlorination have shown the differentiation of speciation as well as levels of the DBPs with varying characteristics of the water source as well as other factors (chlorine dose, pH, temperature and reaction time). The characteristics of the water source, especially the NOM content and the bromide content, which in some of the studied waters was particularly high, exhibited a great influence on the occurrence patterns on DBPs stressing out the necessity of detailed investigation of source water characteristics in order to optimize disinfection and minimize health risks associated with it. The results of ozonation of DMA containing ground water have shown that NDMA are formed in specific ozone/DMA ratio (molar ozone/DMA net ratio below 10) and NDMA/DMA conversion rate significantly increase with pH increases.

1. Introduction

Water chlorination is the most frequent used method of disinfection. Chlorine reacts with naturally occurring matter in water and, as a result, disinfection by-products (DBPs) are generated [1-13]. Among DBPs, trihalomethanes (THMs) have been the focus of particular attention because they are considered potentially carcinogenic [12-15]. Many DBPs have been regulated by the European Union (EU), the WHO and the USEPA. The EU drinking water quality standard for THMs is 100 μg/l [16]. Haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs) and nitrosamines (particularly NDMA) are other categories of DBPs that have been detected in drinking waters during the last years and are subject of current analytical research worldwide [13, 17-18].

Nitrosamines and particularly NDMA, have been known as compounds for more than 100 years. Secondary nitrosamines, mainly the ones of short chain, like N-nitrosodimethylamine (NDMA), N-nitrosomethylethylamine (NMEA) and N-nitrosodiethylamine (NDEA) are highly mutagenic compounds that are suspected of carcinogenic activity to the human body. However, the presence of NDMA in drinking waters was reported in the 1980's and 1990's [19], recently, Choi and Valentine [20] and Mitch and Sedlak [21] in 2002 reported that N-nitrosodimethylamine is formed during the disinfection of water and sewage with chloramine, and they pointed to dimethylamine as the main NDMA precursor. They also proposed mechanism of NDMA formation in this reaction. This mechanism is based on chloramination leading to the formation of 1,1-dimethylhydrazine, known as unsymmetrical dimethylhydrazine (UDMH). Fur-

thermore, 1,1-dimethylhydrazine undergoes oxidation to yield many different by-products, including NDMA. In 2003 Gerecke and Sedlak. reported the formation of N-nitrosodimethylamine as a result of the reaction of NOM with chlorine [22].

Andrzejewski et al. proved the possibility of NDMA formation in water containing dimethylamine (DMA) disinfected with chlorine dioxide [23], ozone [24], hydrogen peroxide [25] and permanganate [26]. Provided that the reactions with chlorine dioxide, ozone, hydrogen peroxide and permanganate take place in the absence of ammonium ions, the mechanism of NDMA formation must be different from the one proposed by Choi and Valentine [21] and Mitch and Sedlak [22]

American Environmental Protection Agency (US EPA) classified NDMA, NMEA and NDEA into group B2 – i.e. compounds which are probably carcinogenic to humans. US-EPA also determined concentrations of these compounds in potable water (oral exposure) at the levels of 7 ng L^{-1} (NDMA), 20 ng L^{-1} (NMEA) and 2 ng L^{-1} (NDEA), associated with the risk of 10^{-5} [27].

Tab. 1. DBPs of different categories in drinking water and their abbreviations

DBP	Category	Abbreviation
Chloroform	THMs	CM
Dichlorobromomethane	THMs	DCBM
Dibromochloromethane	THMs	DBCM
Bromoform	THMs	BM
Monochloroacetonitrile	HANs	MCAN
Trichloroacetonitrile	HANs	TCAN
Dichloroacetonitrile	HANs	DCAN
Monobromoacetonitrile	HANs	MBAN
Dibromoacetonitrile	HANs	DBAN
Bromochloroacetonitrile	HANs	BCAN
Chloral hydrate	-	CH
Chloropicrin	-	CH
1,1,1-Trichloropropanone	HKs	1,1,1-TCP
1,1-Dichloropropanone	HKs	1,1-DCP
1,3-Dichloropropanone	HKs	1,3-DCP
Monochloroacetic acid	HAAs	MCA
Monobromoacetic acid	HAAs	MBA
Dichloroacetic acid	HAAs	DCA
Bromochloroacetic acid	HAAs	BCA
Trichloroacetic acid	HAAs	TCA
Dibromoacetic acid	HAAs	DBA
Bromodichloroacetic acid	HAAs	BDCA
Dibromochloroacetic acid	HAAs	DBCA
Tribromoacetic acid	HAAs	TBA
N-nitrosodimethylamine	N-Nitrosamines	NDMA

The identified DBPs belong to different chemical categories (Table 1) and require different sample preparation and analysis techniques. DBPs are determined mainly by gas chromatographic (GC) methods. THMs and other volatile DBPs (HANs, HKs, CH) are extracted from the aquatic matrix by Purge-and-Trap (PAT) or Liquid-Liquid Extraction (LLE) and then directly detected by GC-ECD. HAAs are targeted through derivatization techniques using diazomethane or acidic methanol. Extraction of the polar dissociated haloacetates from water is traditionally performed after acidification by LLE using organic solvents [9-10].

Determination of N-nitrosamines, particularly NDMA, in water is very difficult because they are present in water at concentrations of a few ng L^{-1} and due to the low maximum admissible concentration in water, which was established for these compounds. Additionally NDMA is characterized by an unfavorably low water/octanol partition coefficient. Almost all the analytical methods developed for NDMA determination are based on application of SPE as preconcentration technique and majority of them employs mass detector as detection system [28].

The formation of DBPs is a function of disinfection processes and chemicals, water source, pH, temperature, chlorine residual, residence time, reaction time, total organic carbon (TOC) or natural organic material (NOM) and bromide content. Results from studies using different water properties, chlorination conditions and studying different compounds often indicate controversial observations, because the chlorination reactions and products are complicated and not fully documented.

Greater chlorine dose and natural organic matter concentration enhance the formation of DBPs. The presence of bromide ion shifts the speciation of DBPs to brominated compounds which is of particular concern, because of the higher toxicity of brominated compounds compared to their chlorinated counterparts [12,17].

Contact time can have positive effect on THMs and some HAAs concentrations and negative effect on the concentrations of HANs, HKs, and some other species of HAAs, possibly due to hydrolysis, reactions with residual chlorine or bacterial decomposition [11-12].

Increased pH values can have positive effect on THMs formation and negative effect on the formation of some other volatile by-products such as HKs, which decrease due to hydrolysis. HAAs have been reported to increase at low pH [4]. According to another study, for dichloroacetic acid not significant changes were observed with pH change, while for trichloroacetic acid a concentration increase was observed during pH increase from 2 to 5, maximum concentration at pH 5 and decrease afterwards [5].

Elevated temperature can have positive effect on DBPs formation, due to faster formation reactions. However, temperature increase also accelerates the decomposition kinetics for some DBPs, such as HANs and HKs [8,11].

This work presents experimental results and observations during bench-scale both chlorination of river water rich in NOM and ozonation of ground water rich in DMA in order to investigate the influence of different factors on the formation of DBPs. The factors studied were ***contact time, pH, temperature, chlorine dose and bromide concentration*** (in the case of NOM chlorination) and ***pH and ozone/DMA molar ratio*** (in the case of DMA ozonation). The investigation of the influence of these factors on the formation of different DBPs categories and species is a fundamental step towards the objective of minimization of their concentrations in water.

2. Materials and Methods

2.1. Sampling

2.1.1. THMs, HAAs and volatile DBPs

Water samples were collected in March 2000 from Tsiknias and Mylopotamos rivers in Mytilene island, Greece. These rivers are the largest on the island, however flow is not constant throughout the year, and does not exist during summer, leading to increased organic matter content and therefore enhanced potential for the formation of DBPs during chlorination. Samples were stored in 1-l amber glass bottles and, kept at 4 oC, they were transported to the Water and Air Quality Laboratory of the University of Aegean, where pH measurements and sample filtration were performed.

2.1.2. NDMA

Groundwater samples were collected from well situated on the University site. Prior to ozonation ground water was deironed by means of aeration/sand filtration and enriched with DMA. On the other hand an influence of pH on NDMA formation was investigated with using model water (buffered high purity water enriched with DMA).

2.2. Analysis of raw water samples

2.2.1. Ions and NOM

Samples were analyzed for chloride, bromide and nitrate ions by a modification of EPA Method 300.0, using a Dionex 2000i ion chromatograph with a Dionex HPIC–AG4A column and a suppressed conductivity detector. UV absorbance measurements were performed at 272 nm by use of a Cary 1E UV-visible spectrophotometer.

2.2.2. DBPs

For the determination of THMs, HANs, HKs, CH and CP, a modification of EPA Method 551.1, which includes liquid - liquid extraction (LLE) with methyl tert butyl ether (MTBE), was performed. For HAAs, acidic methanol esterification was used. These methods have been described in detail in previously published papers [9-10]. A typical chromatogram of a standard solution of HAAs is presented in Fig. 1. For the analysis of nitrosamines, modified ion exclusion chromatography with UV-Vis detection was applied. This technique enabled also the analysis of other byproducts, such as formic acid. The presence of formic acid (the byproduct of DMA oxidation) in the reaction mixture was determined by means of the ion exclusion chromatography with UV-Vis (210 nm) detection. This method i.e. HPLC-IE-UV have been described in our previous papers [23-26].

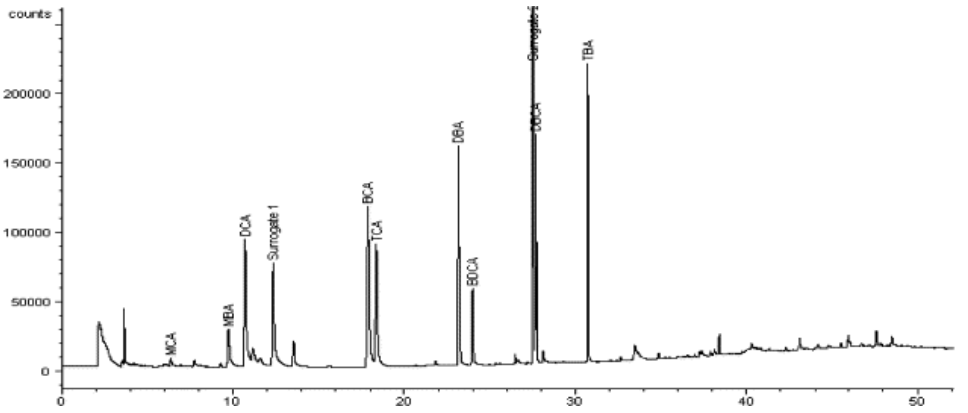


Fig.1. Typical chromatogram of a standard solution of haloacetic acids

2.3. Experimental setup

Chlorination of the samples was performed according to the procedure described in Standard Methods for the Examination of Water and Wastewater (Iodometric Method I 4500B). The chlorine dosages applied ranged from 2 to 30 mg/l, and the pH values tested ranged from 4 to 11. For the investigation of bromide effect concentration, samples were spiked with bromide ion (KBr) at concentration levels ranging from 1 to 30 mg/l before chlorination.

The chlorinated samples were divided into 40-ml amber glass bottles (Pierce 13075). The vials were carefully filled so that trapping of air bubbles inside was prevented. Depending on the experiment, they were incubated at 21 ^{o}C, 35 ^{o}C or 3 ^{o}C for the desired contact times, which ranged from 0 to 120 h. Then, residual chlorine was measured according to the DPD colorimetric method and the quenching agent for depletion of residual chlorine was added. Sodium sulfite was used for the samples analyzed for THMs and other volatile DBPs and ammonium chloride for the samples analyzed for HAAs.

Preliminary experiments on the NDMA formation during DMA ozonation were initially carried out with model deionized water spiked with DMA and subsequently with groundwater (after iron removal) spiked with DMA. Model water was prepared by addition of 7 mM of buffer solution (Na_2HPO_4, >99.5%, Fluka) and DMA solution (40%, Fluka) into high quality pure water (Millipore). The pH of the solution was adjusted with H_3PO_4 (>85%, Fluka) or NaOH (>98%, Fluka) in a range of 6 to 11.

Iron was removed from groundwater by aeration and filtration through an active sand filter, so that the average concentration of Fe in water did not exceed 0.05 mg l^{-1}. The other parameters of groundwater were as follows: pH=7.4, TOC=2.67 mg l^{-1}, ammonia concentration of 0.2 mg l^{-1}, nitrate concentrations of 0.6 mg l^{-1} and nitrite concentrations of 0.06 mg l^{-1}. Water was subsequently spiked with DMA solution (DMA, 40%) and pH was adjusted with either H_3PO_4 or NaOH. The experiments were carried out at different DMA concentrations, varying from 35 to 700 mg l^{-1} (from 0.78 to 15.5 mM).

The ozonation experiments were carried out at room temperature (20 ^{o}C) in a semi-continuous mode. A 400 ml of model solution was transferred to the contact column (capacity, 500 ml), recirculated and continuously treated with ozone (gaseous ozone dosage delivered to the reactor, 0.4 mg l^{-1} min^{-1}) for 1 h. Ozone was generated from pure oxygen and introduced to the reactor through a ceramic sparger at a flow rate of 19.5 ml min^{-1}. Total doses of ozone ranged from 30 to 200 mg O_3/l, while the O_3/DMA ratio ranged from 0.01 do 4.3 (M/M). 2 ml samples of the reaction solution were collected every 15 minutes and quenched with 0.025 M Na_2SO_3 (>98%, Fluka) in order to remove any residual ozone.

3. Results and Discussion

The NOM content measured as UV-272 absorbance was significantly higher for Mylopotamos river (0.139 cm-1) than for Tsiknias river (0.069 cm-1). Moreover, significant concentrations of chloride and bromide ions (10 and 2.4 mg/l respectively) were detected in Mylopotamos river. It must be noted that the sampling point at Mylopotamos river is located near a saltwork. On the contrary, bromide ion concentration in Tsiknias river was not detectable.

The residual chlorine concentrations during the experiments ranged from 0.1 mg/l (Cl dose 2 mg/l) to 12.5 mg/l (Cl dose 30 mg/l) for samples from Tsiknias river and from not detectable (Cl dose 2 mg/l) to 4 mg/l (Cl dose 30 mg/l) for Mylopotamos river.

No DBPs were detected in the raw water samples, while in the chlorinated samples, a large number of DBPs were formed, including CM, DCBM, DBCM, BM, MCA, DCA, BCA, TCA, MBA, DBA. CH, 1,1-DCP, 1,1,1-TCP, BCAN, DBAN, BDCA, DBCA and TBA also occurred at lower concentrations. Brominated species predominated in the chlorinated water with high bromide ion concentration.

Effect of contact time

CM, MCA, DCA and TCA have shown the highest increasing trends over time. Decreasing trends were observed after a particular time interval for some volatile DBPs, especially for 1,1,1-TCP. This compound has been reported to decompose to chloroform, and has been found to decompose over time even in ultrapure water solutions, in the absence of residual chlorine. Increase in total THMs and HAAs concentrations was observed during the first hours of reaction. For reaction times longer than 72 h for THMs and 24 h for HAAs, no significant concentration changes were observed, due to consumption of residual chlorine and completion of their formation reactions (Figure 2).

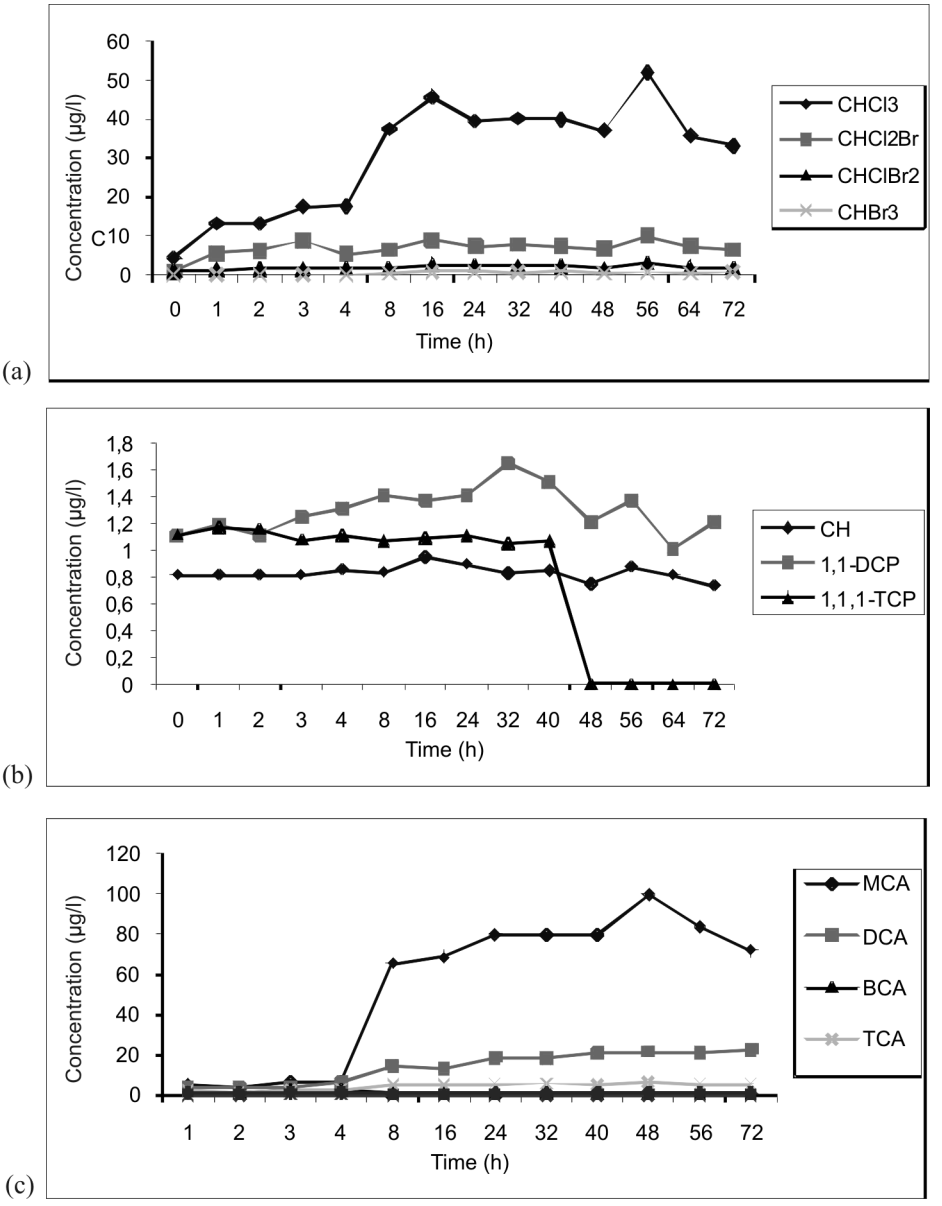
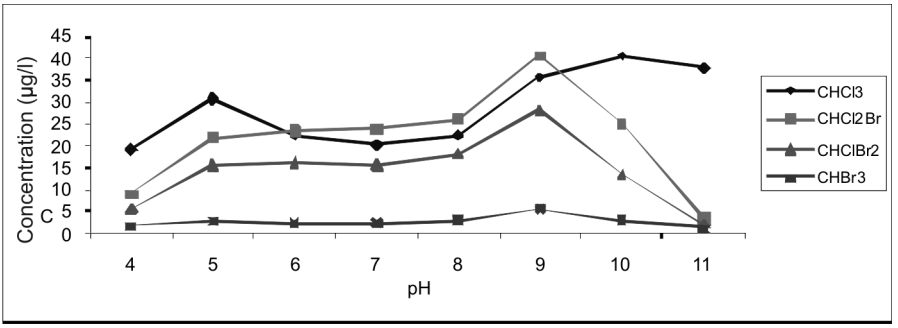


Fig. 2. Influence of contact time on the formation of (a) THMs , (b) volatile DBPs and (c) HAAs in chlorinated water from Tsiknias river (chlorine dose 2 mg/l)

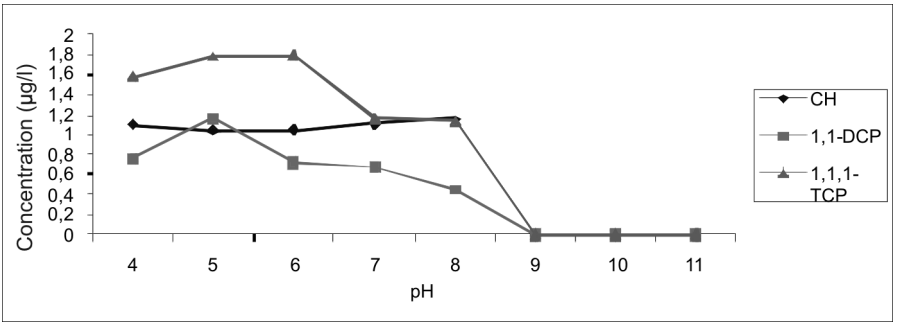
Effect of pH

THMs concentrations increase with increasing pH, in agreement with previous research findings. In contrast, the volatile DBPs CH, 1,1-DCP, 1,1,1-TCP were only formed at pH values lower than 8 and their formation was particularly favored at low pH.

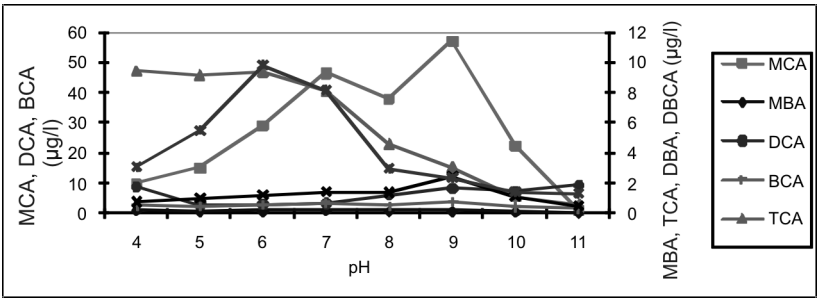
For HAAs, the influence of pH was different for the individual species; MCA and DCA formation is enhanced from high pH, but TCA formation is favored at pH values lower than 7. For BDCA, the optimum pH values are 6 and 7 (Figure 3).



(a)



(b)



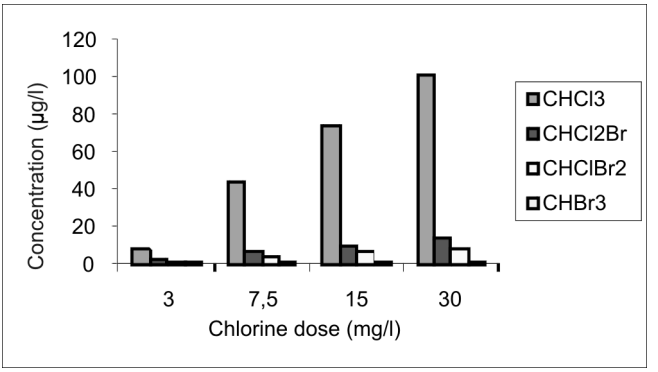
(c)

Fig. 3. DBPs concentrations detected in chlorinated water from Tsiknias river for different pH values (Chlorine dose 4 mg/l, reaction time 4 h): (a) THMs, (b) CH, HKs, (c) HAAs

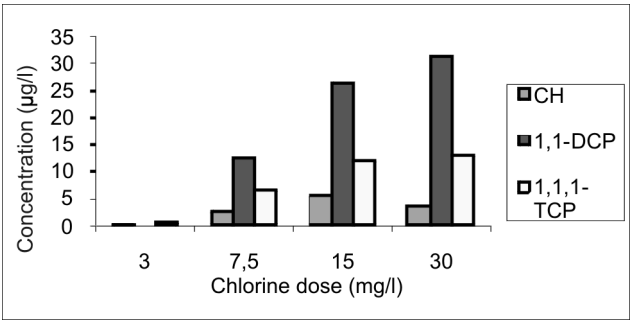
For the total THMs concentrations, increase was observed with increasing pH in both river samples, while the change of total HAAs concentrations showed fluctuations, due to the different effect of pH on the concentrations of individual HAA species. During pH increase from 4 to 11, for chlorine dose 2 mg/l and reaction time 24 h, the average percent increase of the concentrations of total THMs and total HAAs was 145% and 42% respectively.

Effect of chlorine dose

The formation of all DBPs increased with increasing chlorine dose. For chlorine dose 30 mg/l, CM concentration became 10-fold higher, 1,1-DCP concentration 30-fold higher, and TCA concentration 5-fold higher than the corresponding concentrations formed for Cl dose 3 mg/l (Figure 4). In the case of Mylopotamos river, the concentrations of THMs and HAAs formed were significantly higher and the distribution of the different species entirely different, due to the presence of bromide ion, which resulted in elevated concentrations of brominated species, mainly BM. BM concentration after application of Cl dose 30 mg/l was 10-fold higher than after application of Cl dose 3 mg/l.



(a)



(b)

Fig. 4. Influence of chlorine dose on the formation of (a) THMs, (b) volatile DBPs in chlorinated water from Tsiknias river (pH 4, contact time 24 h)

Effect of temperature

In chlorinated water from Tsiknias river, the increase of temperature resulted in increase of concentrations of all DBPs formed, with the highest concentrations occurring at 35 ^{o}C. However, in chlorinated water from Mylopotamos river, decrease of the concentration of MBAN was observed with increasing temperature, while the formation of THMs and HAAs was mostly favored at 21 ^{o}C and not at 35 ^{o}C. This observation could be attributed to different properties of NOM in the two rivers (Figure 5).

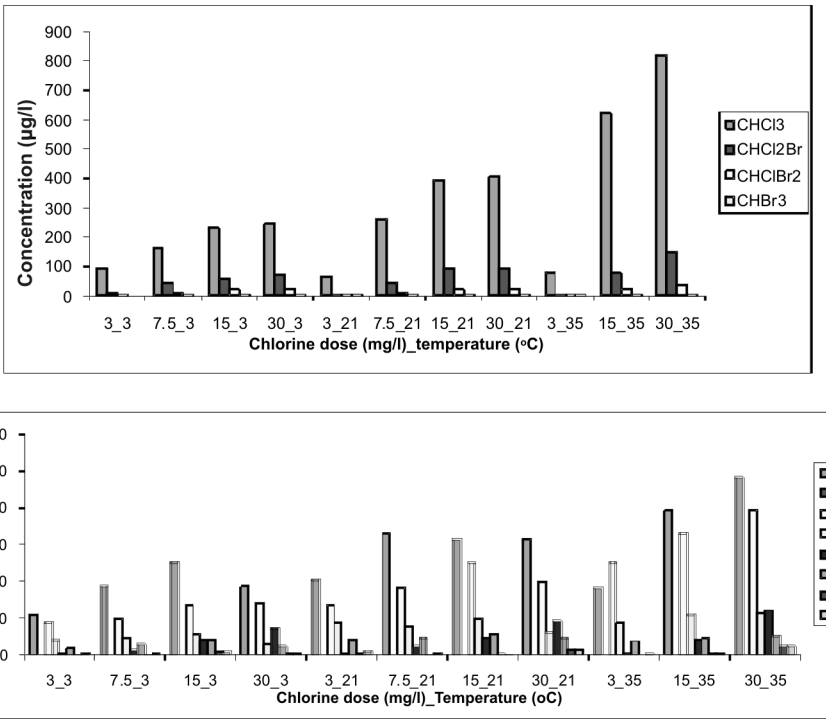


Fig. 5. DBPs concentrations detected in chlorinated water from Tsiknias river as function of temperature and chlorine dose (a) THMs (b) HAAs

Increased concentrations were observed with increasing chlorine dose and temperature. From the THMs, CM was the DBP mostly favored from temperature and chlorine dose increase. When chlorine dose increased from 3 mg/l to 30 mg/l, CM concentration became 6-fold higher at 3 ^{o}C, 10-fold higher at 21 ^{o}C and 20-fold higher at 35 ^{o}C. 1,1-DCP was the compound showing the greatest increase among the rest volatile DBPs. When chlorine dose increased from 3 mg/l to 30 mg/l, 1,1-DCP concentration became 16-fold higher at 3 ^{o}C, 30-fold higher at 21 ^{o}C and 120-fold higher at 35 ^{o}C. The HAA compound mostly favored from temperature and chlorine dose increase was TCA. When chlorine dose increased from 3 mg/l to 30 mg/l, TCA concentration became 11-fold higher at 3 ^{o}C, 22-fold higher at 21 ^{o}C and 18-fold higher at 35 ^{o}C.

Effect of bromide concentration

The speciation of DBPs formed in chlorinated waters containing Br- concentrations 1 and 15 mg/l (Cl dose 30 mg/l, reaction time 24 h) is presented in Figure 6. The presence of Br- results in significant changes in the distribution of DBPs species. The concentrations of chlorinated species (CM, DCBM, DBCM, CH, 1,1,1-TCP, MCAN, MCA, DCA, BCA, BDCA, DBCA) decreased and the concentrations of brominated species (BM, MBA, DBA, TBA) increased.

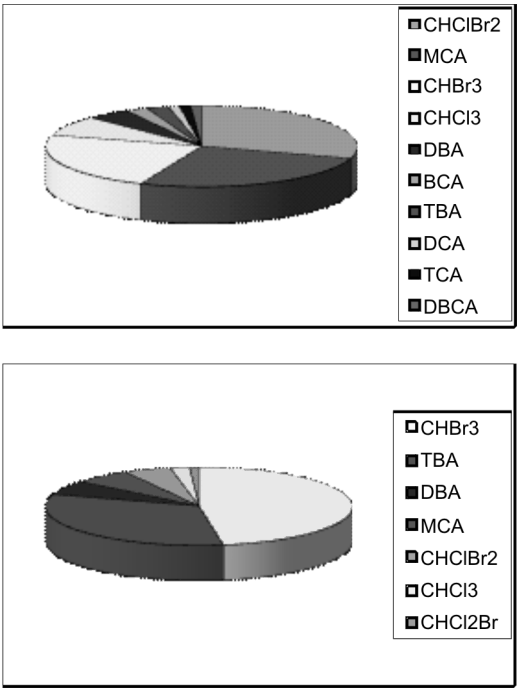


Fig. 6. Speciation of DBPs for bromide ion concentrations (a) 1 and (b) 15 mg/l (Cl dose 30 mg/l, reaction time 24 h)

The percent distribution of the DBPs concentrations detected in chlorinated water from Tsiknias river without and with bromide ion spiking is shown in Table 6.

Tab. 6. Percent distribution of the DBPs concentrations in chlorinated water from Tsiknias river before and after spiking with Br- (chlorine dose 3 to 30 mg/l, Br- concentration 1 to 30 mg/l, reaction times 2 to 48 h)

Distribution of DBPs before spiking with Br^-	***Distribution of DBPs after spiking with Br^-***
$CHCl_3$ (47%)	$CHBr_3$ (28%)
DCA (12%)	TBA (18%)
TCA (11%)	$CHCl_3$ (15%)
1,1-DCP (9%)	$CHClBr_2$ (10%)
$CHCl_2Br$ (8%)	$CHCl_2Br$ (8%)
MCA (4%)	MCA (6%)
1,1,1-TCP (2%)	BCA (4%)
$CHClBr_2$ (2%)	DBA (4%)
BCA (2%)	DBCA (2%)
BDCA (1%)	1,1-DCP (2%)
CH (1%)	CP (1%)
DBA (1%)	DCA (1%)
	BDCA (1%)

NDMA

PH influence on yield of NDMA formation.

The pH clearly influences the formation of NDMA. An increase of NDMA formation with increased pH and contact time is shown in Figure 7. Increased NDMA formation with increased pH may indicate the following phenomena:

- According to Muñoz and von Sonntag, only free amine reacts with ozone, thus the initial destruction of DMA (which supplies a nitrogen atom for the nitroso group) is faster at a higher pH (Muñoz and von Sonntag 2000) [29], due to a decreased share of protonated DMA at increasing pH in the total amine amount,
- Radical reactions are important in the destruction of DMA and/or formation of NDMA,
- Both effects combined.

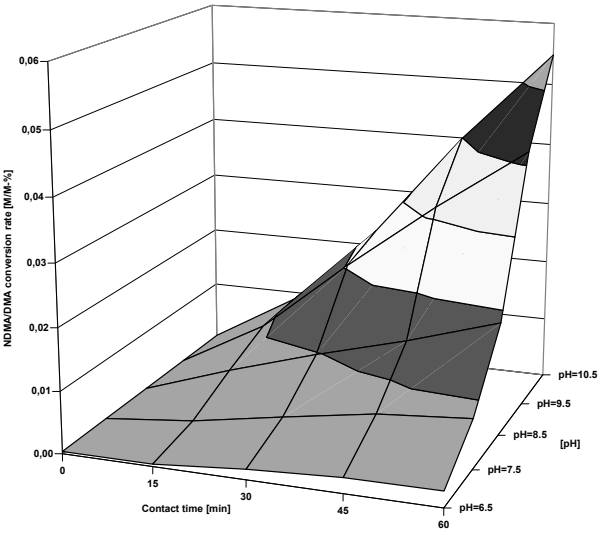


Fig. 7. NDMA/DMA conversion rate vs. pH

NDMA formation in deironed groundwater containing DMA

The experiments were carried out with groundwater spiked with DMA. The influence of contact time and the molar ratio of ozone/DMA on the formation of NDMA were examined The results presented in Figure 8 show the following trends:

- Longer contact time leads to higher NDMA yield but only for ozone/DMA ratio below 4,2. Further contact time increase (i.e. also ozone dose) leads to decreasing of NDMA yield as the result of excessive DMA destruction or product (NDMA) destruction.
- Higher ozone/DMA ratio (higher then 2,6) leads to lower NDMA formation

Since this set of experiments was carried out at pH 7.67, a generally lower yield of NDMA formation is observed over higher pHs (see Figure 8).

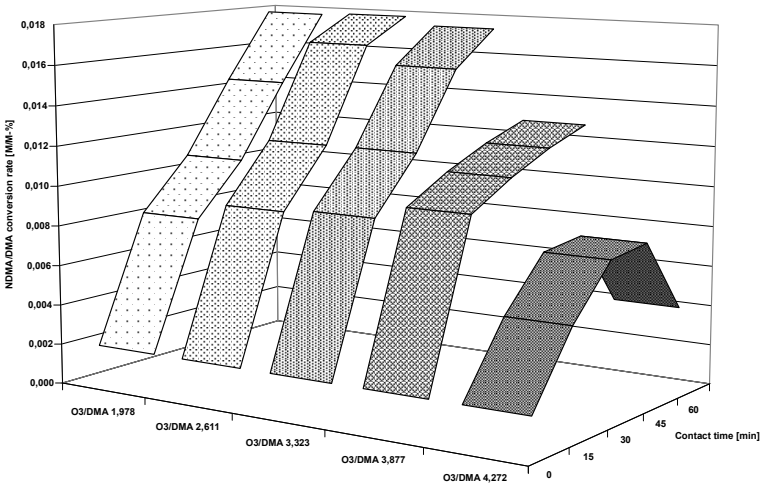


Fig. 8. NDMA/DMA conversion rate vs. contact time and the molar ratio of ozone/DMA

4. Conclusions

The formation and behaviour of disinfection by-products (DBPs) was studied during laboratory disinfection of waters from Greece and Poland. The parameters investigated were time, pH, disinfectant dose, temperature and bromide ion concentration. The DBPs investigated were THMs, HAAs, HANs, HKs, CH, CP and NDMA.

Different behaviour trends were observed for the different categories and species of compounds in regard to the formation parameters as well as in regard to the raw water characteristics. Ozonation of dimethylamine dissolved in deionized and natural waters leads to the formation of N-nitrosodimethylamine. The yield of reaction of NDMA formation during DMA ozonation significantly increases with pH and depends strongly on the ozone/dimethylamine ratio.

The results of this investigation stress the necessity for detailed evaluation of the formation and fate of different DBPs species towards the assessment of the actual health risks associated to their presence in drinking water.

References

[1] Rook, J.J. Formation of haloforms during chlorination of natural waters, Wat. Treat. Exam., 1974, 23, 234-243

[2] Christman, R.F., Norwood, D.L., and Millington, D.S. Identity and yields of major halogenated products of aquatic fulvic acid chlorination, Env. Sci. Technol., 1983, 17, 625-628

[3] Krasner, S.W., McGuire, M.J., Jacangelo, J.G., Patania, N.L., Reagan, K.M., and Aieta, E.M. The occurrence of disinfection by-products in US drinking water, J. AWWA, 1989, 81, 41-53

[4] Nieminski, E.C., Chaudhuri, S., and Lamoreaux, S.-T. The occurrence of DBPs in Utah drinking waters, J. AWWA, 1993, 85, 98-105

[5] Summers, R.S., Hooper, S.M., Shukairy, H.M., Solarik, G., and Owen, D. Assessing DBP yield: uniform formation conditions, J. AWWA, 1996, 88, 80-93

[6] Williams, D.T., Lebel, G.L., and Benoit, F.M. Disinfection by-products in Canadian drinking water, Chemosphere, 1997, 34, 299-316

[7] Golfinopoulos, S.K., Xylourgidis, N.K., Kostopoulou, M.N., and Lekkas, T.D. Use of a multiple regression model for predicting trihalomethane formation, Wat. Res., 1998, 32, 2821-2829

[8] Nikolaou A.D., Golfinopoulos S.K. and Lekkas T.D. Formation of organic by-products during chlorination of natural waters, Journal of Environmental Monitoring, 2002, 4(4), 910-916

[9] Nikolaou A.D., Lekkas T.D., Golfinopoulos S.K., Kostopoulou M.N. Application of different analytical methods for determination of volatile chlorination by-products in drinking water, Talanta, 2002, 56(4), 717-726

[10] Nikolaou, A.D., Golfinopoulos, S.K., Kostopoulou, M.N., Lekkas, T.D. Determination of haloacetic acids in water by acidic methanol esterification-GC-ECD method, Wat. Res., 2002, 36, 1089-1094

[11] Nikolaou, A.D., Kostopoulou, M.N., and Lekkas, T.D. Organic By-products of Drinking Water Chlorination: a Review, Global Nest: The International Journal, 1999, 1, 143-156

[12] Richardson, S.D., Simmons, J.E. and Rice, G. Disinfection byproducts: the next generation, Environ. Sci. Technol., 2002, 36 (9), 198A-205A

[13] Andrzejewski P. and Nawrocki J. Analytics of MX and NDMA, two disinfection byproducts, in water, Global Nest Journal (special issue on DBPs), 2005, 7(1), 27-42

[14] Pereira, M.A., Daniel, F.B., and Lin, E.L.C. Relationship between metabolism of haloacetonitriles and chloroform and their carcinogenic activity, In: Water Chlorination: Chemistry, Environmental Impact and Health Effects, Lewis Publishers, USA, 1986, Vol. 5, pp 229-236

[15] Bull, R.J., and Robinson, M. Carcinogenic activity of haloacetonitrile and haloacetone derivatives in the mouse skin and lung, In: Water chlorination: Chemistry, Environmental Impact and Health Effects, Lewis Publishers, USA, 1986, Vol. 5, pp. 221-227

[16] EEC: 1998, 'Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption', Official Journal of the European Communities, L 330/32, 5.12.98

[17] LeBel, G.L., Benoit, F.M., and Williams, D.T. A one-year survey of halogenated DBPs in the distribution system of treatment plants using three different disinfection processes, Chemosphere, 1997, 34, 2301-2317

[18] Golfinopoulos, S.K., and Nikolaou, A.D. Disinfection by-products and volatile organic compounds in the water supply system of Athens, Greece, Env. Sci. Health, 2001, A36(4), 483-499

[19] Jobb D.B., Hunsinger R.B., Meresz O., Taguchi V.Y. *Proc. Am. Water Works Assoc. Water Qual. Technol. Conf.* Denver, CO, USA, 1995;103

[20] Choi J., Valentine R.L. Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloroamine : a new disinfection by-product. *Water Research*, 2002, 36:817-824

[21] Mitch W.A., Sedlak D.L. Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination. *Environmental Science and Technology*, 2002, 36, 588-595

[22] Gerecke A.C., Sedlak D.L. A; Precursors of *N*-Nitrosodimethylamine in Natural Waters; Environ. Sci. Technol., 37, 1331-1336 (2003).

[23] Andrzejewski P., Kasprzyk-Hordern B., Nawrocki J. The hazard of N-nitrosodimethylamine (NDMA) formation during water disinfection with strong oxidants. *Desalination*, 2005, 176, 37-45

[24] Andrzejewski P., Kasprzyk-Hordern B., Nawrocki J. N-nitrosodimethylamine (NDMA) formation during ozonation of dimethylamine-containing waters. *Water Research*, 2008, 42, 863-870

[25] Andrzejewski P., Nawrocki J. N-nitrosodimethylamine formation during treatment with strong oxidants of dimethylamine containing water. *Water Science and Technology*, 2007, 56, 125–131.

[26] Andrzejewski P., Nawrocki J. N-nitrosodimethylamine (NDMA) as a product of potassium permanganate reaction with aqueous solutions of dimethylamine (DMA). *Water Research*, 2009, 43, 1219-1228.

[27] USEPA (2007). www.epa.gov/iris/subst/index.html

[28] Andrzejewski P, Dabrowska A., Nikolaou A. Analytical techniques for DBP measurements in ADVANCES IN CONTROL OF DISINFECTION BY-PRODUCTS. ISBN 1-60021-322-7, Eds.: A. Nikolaou, Luigi Rizzo and H. Selcuk, © 2007 Nova Science Publishers, Inc. NOVA BOOK:

[29] Muñoz F., von Sonntag C. The reactions of ozone with tertiary amines including the complexing agents nitrilotriacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) in aqueous solution. Journal of The Royal Society of Chemistry, Perkin Trans. 2, 2000, 2029–2033.