

Assessment of Halonitromethanes Formation Potentials Under Different Disinfection Scenarios in Low SUVA Water

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Abstract

The main objective of this project is to investigate the formation of halonitromethanes, an emerging class of disinfection by-products (DBPs) identified in drinking waters in recent years, which are currently unregulated but highly toxic. Halonitromethanes formation potentials tests were investigated under five different disinfection conditions in Eğirdir Lake with low specific ultraviolet absorbance (SUVA) value. The results showed that ozone/chlorine formed the highest halonitromethanes followed by in the order of ozone/chloramine and chlorine only. When chloramine or ozone were used alone, the halonitromethanes concentration was below the minimum detection limits. The highest halonitromethanes was determined 2.5 µg/L for ozone /chlorine scenario and the lowest halonitromethanes concentration was 1.7 µg/L in ozone /chlorine scenario. In the ozone/chlorine scenario, a dramatic decrease for halonitromethane formation was detected from spring to winter. Chloropicrin has been the only measurable halonitromethanes species. In the correlation analysis between halonitromethanes and water quality parameters, the highest correlation was found between halonitromethanes and dissolved organic nitrogen. Besides dissolved organic nitrogen, different organic/inorganic compounds and disinfectants also contribute to the formation of halonitromethanes. These results can be used to control the formation of N-DBPs in the disinfection of low SUVA waters.

Keywords

Formation Potentials, Halonitromethanes, Nitrogenous Disinfection by Products

Düşük SUVA Değerine Sahip Kaynak Sularında Farklı Dezenfeksiyon Senaryolarında Halonitrometan Oluşum Potansiyellerinin Değerlendirilmesi

Özet

Su dağıtım sistemlerinde tespit edilen tüm kanserojen dezenfeksiyon yan ürünleri arasında, halonitrometanlar diğerlerine nazaran en toksik sınıflardan biridir. Bu araştırmanın temel amacı, düşük SUVA'ya sahip içme suyu kaynaklarında halonitrometan oluşumunun sistematiği araştırılmasıdır. Eğirdir Gölü'nde beş farklı dezenfeksiyon senaryolarında halonitrometan oluşum potansiyelleri testleri gerçekleştirilmiştir. Ozon + klor senaryosunun en yüksek halonitrometan oluşumuna sebep olduğu, müteakip ozon + kloramin/klorun oluşturduğu gözlenmiştir. Sadece Kloramin veya ozon senaryolarında, halonitrometan konsantrasyonu genellikle minimum tespit limitlerinin altında kalmıştır. Ozon + klor senaryosunda en yüksek halonitrometan konsantrasyonu 2.5 µg/L olarak belirlenmiştir. Ozon + klor senaryosunda tespit edilen en düşük halonitrometan konsantrasyonu ise 1.7 µg/L'dir. Ozon + klor senaryosunda halonitrometan konsantrasyonlarında ilkbahardan kışa doğru kayda değer bir düşüş tespit edilmiştir. Kloropikrin, ölçülebilir tek halonitrometan türü olmuştur. Halonitrometanlar ile su kalitesi parametreleri arasındaki analizlerde en yüksek korelasyon halonitrometanlar ile çözünmüş organik azot arasında bulunmuştur. Bununla birlikte, farklı doğal organik maddeler: inorganik maddeler veya dezenfektanlar da halonitrometan oluşumuna katkıda bulunmaktadır. Bu sonuçlar, düşük SUVA'ya sahip suların dezenfeksiyonunda azotlu dezenfeksiyon yan ürünlerinin (A-DYÜ) oluşumunu kontrol etmek için kullanılabilir.

Anahtar Kelimeler

Oluşum Potansiyeli, Halonitrometanlar, Azotlu Dezenfeksiyon Yan Ürünleri

1. Introduction

Since trihalomethanes were first discovered in drinking water, disinfection by-products (DBPs) issues have become a major regulatory driving force in the U.S. Over the last 30 years, significant amount of research efforts has been directed toward improving our understanding of DBPs, and to date more than 800 DBPs have been identified in drinking waters. One of the major challenges for drinking water treatment is to control DBPs formation. DBPs are possible human carcinogen and genotoxic and are formed by the reaction of disinfectants with natural organic matter (NOM). Undoubtedly, the disinfection process is an undeniably complementary step for drinking water treatment.

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Gönderim Tarihi / Received : 22/01/2022

Kabul Tarihi / Accepted : 21/04/2022

Chlorine is the most used disinfectant, and either alone or in combination with other disinfectants have been adopted (Abusallout 2019; Carter et al. 2019). However, when chlorine is preferred as a disinfectant, carbonaceous disinfection by-products are unintentionally formed in drinking water sources. Alternative disinfectants are getting attention in nowadays instead of chlorine due to the limitation of carbonaceous disinfection by-products (C-DBPs) in regulations/guidelines for DBPs in many countries. However, nitrogenous DBPs (N-DBPs) are formed using alternative disinfectants such as chloramine or ozone. Among the N-DBPs, halonitromethanes (HNMs) are unregulated DBPs with orders of magnitude higher toxicity (i.e., cytotoxicity and genotoxicity) than any of the regulated organic DBPs and one of the most frequently detected HNMs specie is chloropicrin, also known as trichloronitromethane (TCNM) (Hu et al. 2010; Wang et al. 2021).

In the 1970s TCNM had been discovered and has been a source of inspiration for many studies, and research has been carried out on its formation, speciation, and reduction (Shang and Yong-Mei 2010; Chu et al. 2012; Chang et al. 2013; Hermjakob et al. 2013; Zhang et al. 2020). The nine species of HNMs that can be measured in water are trichloronitromethane, bromodichloronitromethane, dibromochloronitromethane, tribromonitromethane, dichloronitromethane, bromochloronitromethane, dibromonitromethane, chloronitromethane, and bromonitromethane (Fang et al. 2013; Dong et al. 2017). HNMs are a type of DBPs that can be found at concentrations of $\mu\text{g/L}$ or lower (Marsa et al. 2017). HNMs are formed by attaching the nitro group to the central carbon atom. The two most important types of HNMs are TCNM and bromonitromethane (BNM). Although TCNM is the dominant specie of HNMs, particular attention should be paid to BNM as brominated HNMs are more reactive than chlorinated nitromethanes (Kim et al. 2015). The main precursors that cause the formation of HNMs are amino groups, nitromethanes, nitro phenols, algae etc. (Zhang et al. 2019). Apart from the nine known HNMs species, different N-DBPs like haloacetonitriles (HANs), haloacetamides (HAcAms) etc. can also be detected in water (Srivastav et al. 2020). The presence of N-DBPs in drinking water can cause serious problems for public health, they must be controlled to reduce health risks (Li et al. 2020). However, due to the low concentration, low molecular weight, and strong hydrophilic properties of N-DBPs, it is very difficult to remove of them with conventional treatment processes (Zhang et al. 2020). The best strategy approaches to N-DBPs control are to remove precursor before it reacts with the disinfect and/or use alternative disinfectants. In some studies, it was determined that the use of ozone before chlorine notably increased the formation of HNM. (Hoigné and Bader 1988; Wang et al. 2021).

The research objectives of the study were (i) to survey the formation potentials of HNMs under different scenarios, (ii) to examine effect of several water quality parameters in estimating the HNMs formation potential (iii) to determine the seasonal variation of HNMs formation potentials, (iv) to examine the correlation between HNMs and water quality parameters. Despite the recent focus on HNMs formation in drinking water, the information about HNMs formation and speciation are limited. Understanding the speciation of these highly toxic DBPs is vital for finding strategies for controlling these compounds. This study provides an important framework for understanding the formation and speciation of HNMs, which is of great significance from a toxicological perspective. To our knowledge this is the first study analyzing the occurrence of seven HNMs for drinking water supply systems in Turkey.

2. Material and Methods

2.1. Sample Collecting and Analysis

In this study, HNM formations and physicochemical properties of water with low SUVA were investigated. Egirdir Lake sample was obtained from the storage tank at drinking water treatment plant in Isparta, Turkey. The samples stored in high density polyethylene (HDPE) bottles with a volume of 5L at $+4^{\circ}\text{C}$ in the dark. HNMs formation potentials were determined under different disinfectant scenarios in the drinking water source, and species and precursors of HNMs were analyzed. pH, UV absorbance, Total Nitrogen (TN), Total Organic Carbon (TOC), nitrate, nitrite, ammonium, bromide, dissolved organic nitrogen (DON), and specific UV absorbance (SUVA) parameters were measured or calculated according to Standard Methods (APHA 2005).

2.2. Halonitromethanes (HNMs) Formation Potentials Tests

Formation potentials (FP) analyzes were carried out to determine HNMs concentrations in low SUVA water and samples taken from storage tank of Isparta Drinking Water Treatment Plant before chlorine addition to represent Egirdir Lake. In this context, three different disinfectants applied in drinking water treatment plants and their combinations were used. The method developed by Krasner et al. (2009) is used for formation potential tests. Each FP experiments was carried out in amber bottles with a volume of 100 ml. HNMs measurements were analyzed by applying chlorination, chloramine, ozone, ozone/chlorine, and ozone/chloramine scenarios to water source in monthly. NaOCl solution containing 10-15% active chlorine was used as free chlorine main stock. In the analyzes, it was determined that the main stock had 12% active chlorine content and stock concentration was prepared according to the DPD ferrous titrimetric method. In DPD ferrous titrimetric method, 20 ml sample was made up to 100 ml with ultrapure water due to dilution of iron ammonium sulfate.

20 ml/100 ml of the iron ammonium sulfate solution was taken in a separate flask. Phosphate buffer solution (5 ml) and DPD indicator solution (5 ml) were added to a titration beaker. Free chlorine solution (50 ml) was added to the buffer solutions.

The red color of the solution in the titration flask indicates that there is free chlorine residue in the solution. Titration was continued with ammonium sulfate solution until the red color became colorless. The chlorinated samples were kept in a dark and cool environment for 72 hours. In the formation potential test, the chlorine dose is the sum of the required chlorine demands for total organic carbon, ammonia nitrogen, and nitrite nitrogen. The following Equation 1 was used for dosage of chlorine:

$$\text{Cl}_2(\text{mg/L}) = 3 * \text{TOC} + 8 * \text{NH}_3 - \text{N} + 5 * \text{NO}_2^- - \text{N} + 10 \quad (1)$$

The intermediate stock solution used to prepare free chlorine in monochloramine solution was used. Except for the free chlorine solution, 67.3 mg (NH₄)₂SO₄ was added to some ultrapure water in a flask, and the flask was completed with 100 ml of ultrapure water. The pH values of free chlorine solution and ammonium sulfate stock solutions were brought to the range of 9-9.1 using HCl and NaOH. 50 ml of ammonium sulfate solution, whose pH was adjusted, was taken into a flask and 50 ml of free chlorine solution was taken into a burette. The titration was carried out very slowly. A sample of 20 ml was taken from the solution mixture obtained and made up to 100 ml with ultrapure water. 20 ml/100 ml of iron ammonium sulfate solution was taken. Phosphate buffer solution (5 ml) and DPD buffer solution (5 ml) were taken into another beaker and 100 ml of the prepared monochloramine solution was added to it. Color transformation should not be observed after full mixing is achieved. An indication that all free chlorine is bound to ammonia is the absence of color. Then KI salt (0.5 g) was added to the solution. Titration is continued until color conversion occurs. The water samples, which was monochlorinated, were kept in a dark and cool environment for 72 hours. In the formation potential test, the monochloramine dose is the sum of the required chlorine demands for total organic carbon and nitrite nitrogen. The following Equation 2 was used for chloramine:

$$\text{NH}_2\text{Cl} (\text{mg/L}) = 3 * \text{TOC} + 5 * \text{NO}_2^- - \text{N} \quad (2)$$

In ozone experiments, the ozone concentration was chosen in a 1:1 ratio according to the TOC concentration. Degremont Technologies brand, Ozonia LAB2B model ozone generator was used in ozone experiments. With the device using high purity oxygen, maximum 10 mg/L ozone production can be achieved. To obtain maximum efficiency from ozone production, maximum impermeability is provided around the device and around the reactor. The water samples taken from the ozonized samples were kept in a dark and cool environment for 72 hours. Followed by chlorine/chloramine, ozone-enriched ultrapure water injected to Egirdir Lake samples. The water samples which were chlorinated with ozone + chlorine and ozone, were stored in a dark and cool environment for 72 hours.

2.3. Analytical Methods

USEPA 551.1 (USEPA 1995) method was used with some modifications for liquid-liquid extraction in HNMs analysis. After adding methyl tertiary butyl ether (MTBE) (10 ml) as organic solvent phase for 10 ml sample, sodium sulfate (Na₂SO₄) (3 g) was added to the sample to increase the ionic strength and copper sulphate (CuSO₄) (1 g) was added to facilitate phase separation. After 30 minutes of mixing, the samples were left for 15 minutes to separate the phases, and then 2 ml of the MTBE phase was transferred to sample bottles using glass pipettes. Prepared samples were analyzed using Gas Chromatography (GC) with electron capture detector (ECD) (Agilent 6890N). The details of the method used in GC are as followed. Column specifications: Inner Diameter: 0.25 mm, film thickness: 0.25 μm, length: 30 m, DB-5 (J&W Scientific). Temperature program: initial oven temperature: 20 minutes at 35 °C, 140 °C in 10 °C min⁻¹ increments, 300 °C in 30 °C min⁻¹ increments. The injector temperature is 117 °C and the detector temperature is 297 °C. Injection volume: 2 μL. Gases: ultra-high purity helium is used as carrier gas and high purity nitrogen gas is used for make-up gas. Flow rate of gases; carrier gas + make-up gas: 62.3 mlmin⁻¹, carrier gas: 1.6 mlmin⁻¹. During the study period, many water quality analyzes were carried out in the water source. The details of analytical methods for water quality parameters are presented in Table 1.

Table 1: Methods and equipment's of water quality parameters

Parameter	Unit	Methods	Equipment	Minimum Detection Limits
pH	---	SM 4500 H+	WTW Multi 340i Set	
TOC	mg/L	SM* 5310B	TOC-L CPH&NHM-1 Shimadzu	0.1
Total Nitrogen	mg/L	High temperature burning	TOC-L CPH&NHM-1 Shimadzu	0.1
254 nm UV absorbance	cm ⁻¹	SM 5910	Shimadzu	±0.005
NO ₃ -N, NO ₂ -N, Br ⁻	mg/L	USEPA Method 300	Dionex ICS-3000	25
NH ₃ -N	mg/L	SM 4500-NH ₃	HACH Test Kit	0.02
SUVA	L/mg TOC.m	Calculation	---	
DON	mg/L	Calculation	---	

3. Findings and Discussions

3.1. Egirdir Lake Water Quality Results

The water samples of Egirdir Lake were taken from storage tank of Isparta Drinking Water Treatment Plant. While determining the physico-chemical water quality of Egirdir Lake, pH, SUVA, TOC, TN, TOC/TN, nitrate, DON, and UV absorbance were measured. The general physico-chemical water quality parameters of raw water samples are shown in Table 2.

Table 2: Physico-chemical water quality parameters of Egirdir Lake

Egirdir Lake	pH	SUVA (L/mg TOC.m)	TOC (mg/L)	DON (mg/L)	TOC/DON (mg/mg)	Nitrate (mg/L)	UV (cm ⁻¹)
November	8.30	0.99	3.43	0.37	9.27	0.28	0.034
December	8.38	1.00	3.81	0.34	11.21	0.32	0.038
January	8.22	1.40	3.43	0.28	12.25	0.80	0.048
February	8.41	1.08	3.62	0.36	10.06	0.65	0.039
March	8.37	0.85	3.89	0.41	9.49	0.61	0.033
April	8.25	0.66	3.62	0.2	18.10	1.28	0.024
May	8.39	0.91	3.53	0.24	14.71	0.50	0.032
June	8.25	0.94	3.52	0.21	16.76	1.08	0.033
July	7.75	0.87	3.55	0.34	10.44	0.31	0.031
August	8.50	1.25	2.71	0.31	8.74	0.31	0.034
September	8.54	1.03	3.12	0.25	12.48	0.20	0.032
October	8.53	0.81	4.02	0.74	5.43	0.22	0.033

Source water SUVA values was low throughout the year. Waters with low SUVA values lead less formation in terms of disinfection by-product. If the SUVA <2 L mg⁻¹, it can be said that these waters contain hydrophilic natural organic substances with smaller molecular weights. Humic and fulvic acids are found in small amounts in such waters and the organic materials present are not rich in aromatics, which means less disinfection by-product formation (Kaplan-Bekaroglu 2010). Considering that about SUVA values, it can be concluded that the natural organic substances in the samples contain hydrophobic substances are predominantly hydrophilic and humic substances are in small amounts. If the SUVA value of a water source is >3.5-4 L mg⁻¹, these waters are generally defined as waters rich in humic substances, containing larger molecular weights and more hydrophobic natural organic substances. The highest and lowest SUVA values were determined as 1.40 and 0.66 L mg⁻¹, respectively, and the annual average SUVA value was determined as 0.98 L mg⁻¹. Average SUVA values for autumn-winter-spring-summer seasons were 0.94; 1.16; 0.81 and 1.02 L mg⁻¹, respectively. The highest, lowest, and average TOC concentrations of Egirdir Lake were 4.02, 2.71 and 3.52 mg/L, respectively. Average TOC values in autumn-winter-spring-summer seasons are 3.52; 3.62; 3.68 and 3.26 mg/L, respectively. Although there is no standard for the TOC parameter in our country, this parameter is a very important parameter in terms of water quality. In the "Regulation on Water Intended for Human Consumption" published by the Ministry of Health, TOC is included as an indicator parameter.

However, it is recommended to provide TOC levels of <2 mg/L in networks for disinfection by-product control after chlorine and to minimize the risks of taste, odor, color, and microbial regrowth in the network. TOC parameter is now included in the legislation in developed countries (etc. USA) (WHO 2018).

The highest and lowest DON values of Egirdir Lake were 0.74 and 0.20 mg/L, and the annual average DON value is 0.34 mg/L. The DON values determined in autumn-winter-spring-summer seasons were 0.45; 0.33; 0.28; 0.29 mg/L, respectively. DON values ranged between 0.1 to 10 mgN/L and an average concentration of 0.3 mgN/L in surface waters (Westerhoff and Mash 2002; Lee et al. 2007). In another study, the average DON concentration in 28 treatment plants was determined as 0.19 and 0.15 mg/L for raw water and treated water, respectively. Although DON is generally present in very low amounts in natural waters, it reacts with chlorine during the disinfection process and leads to the formation of more toxic N-DBPs. While the TOC/DON ratio in water can be used to roughly estimate the potential for N-DBPs formation, there is a positive correlation between the amino sugar: aromatic ratio and the N-DBPs FP (Lee et al. 2007; Hua et al. 2015). It is important to monitor the seasonal variation of DON, one of the precursors of N-DBPs, to define its relationship with the formation of N-DBPs. The highest and lowest TOC DON⁻¹ values of Egirdir Lake are 18.10, respectively; It is 5.43 mg/L, and the annual average TOC DON⁻¹ value is 11.57 mg/L. The highest and lowest nitrate nitrogen values of Egirdir Lake were 1.28 and 0.20 mg/L. The highest, lowest, and average TN values of Egirdir Lake were 0.78, 0.33 and 0.47 mg/L respectively. The nitrite nitrogen, ammonia nitrogen and bromide ion concentrations measured in Egirdir Lake could not be found at measurable levels during the sampling period.

3.2. HNMs Formation Potentials

In the HNMs calibration, 0, 1, 5, 10, 25, 50, 75 and 100 µg/L calibration intermediate stock solutions were obtained from the main stock solution. Correlation coefficients for each species are shown in Table 3.

Table 3: Correlation coefficients for HNM intermediate species

HNM Intermediate Species	Correlation Coefficient (R ²)
Chloronitromethane (CNM)	0.93
Dichloronitromethane (DCNM)	0.99
Trichloronitromethane (TCNM)	0.93
Bromonitromethane (BNM)	0.99
Bromochloronitromethane (BCNM)	0.99
Tribromonitromethane (TBNM)	0.96
Dibromonitromethane (DBNM)	0.99

HNMF concentrations vary between $<$ MRL and 2.5 µg/L for five different disinfection scenarios. TCNM is the only specie of HNM detected in this study, which is known as chloropicrin. HNMs formation potential results obtained monthly for five different disinfection scenarios in Egirdir Lake water samples are shown in Table 4.

Table 4: HNMs formation potentials in different disinfection scenarios of Egirdir Lake (µg/L)

Disinfection Scenarios	Chlorine	Chloramine	Ozone	Ozone+ Chlorine	Ozone + Chloramine
November	0.7	$<$ MDL	$<$ MDL	2.1	1.1
December	0.6			2.3	1.0
January	0.7			1.9	1.2
February	1.0			1.7	1.3
March	0.6			2.1	0.9
April	0.8			2.3	1.2
May	0.7			2.5	1.1
June	0.8			2.1	1.3
July	1.1			1.9	1.4
August	0.7			2.3	1.0
September	0.6	1.9	0.9		
October	0.7	2.0	0.8		

According to the results of the HNMF tests, the highest HNMF was found in the ozone/chlorine scenario, followed by the ozone/chloramine and chlorine. Concentrations of HNM were below the detection limit with only chloramines and only ozone. Figure 1 shows the relationship between Egirdir Lake HNMF concentrations in the ozone /chlorine scenario, and a slight decrease was detected from spring to winter. HNMs was not formed by using only chloramine and ozone alone.

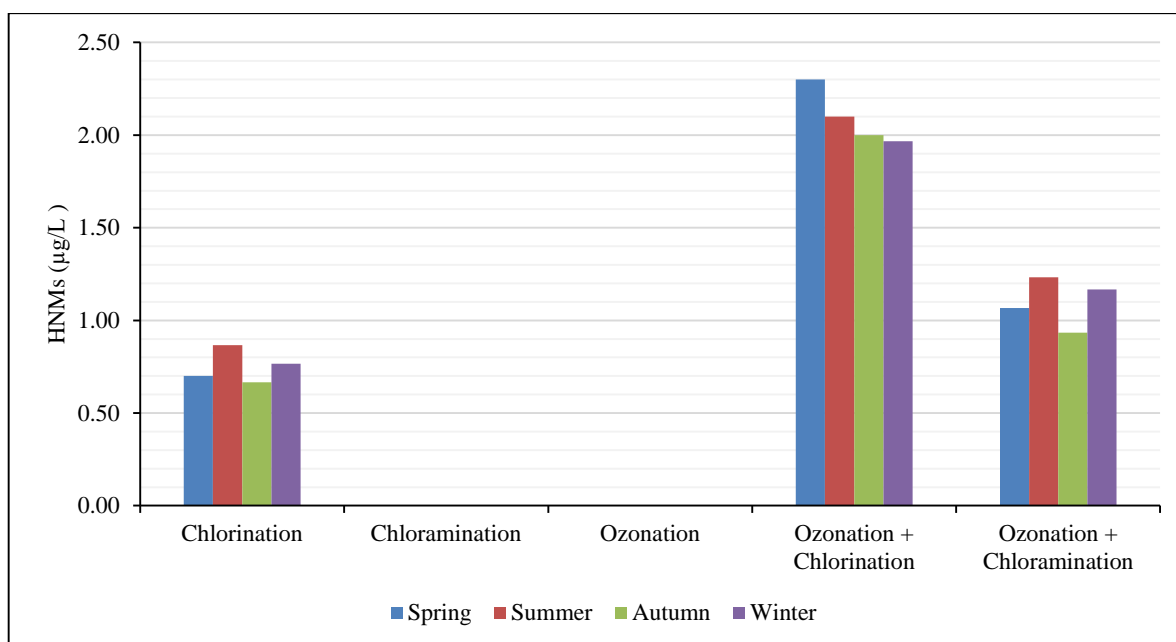


Figure 1: Seasonal effect on HNM formation potentials

Similar to our study, [Montesinos et al. \(2011\)](#) detected only chloropicrin in water samples at a measurable level. [Richardson et al. \(1999\)](#) were able to detect HNMs in the use of ozone/chlorine and ozone/chloramine in their study. It was shown that HNMs formation increased with pre-ozone ([Hong et al. 2015](#)). In our study, the highest HNMs concentration was determined in the ozone/chlorine scenario with similar to previous studies ([Merlet et al. 1985](#); [Hoigné and Bader 1988](#); [Hu et al. 2010](#)). [Hoigné and Bader \(1988\)](#) found that chloropicrin formation enhanced 4-5 times with ozone before chlorine in a lake water. [Hu et al. \(2010\)](#) investigated HNMs formation in different disinfection scenarios of drinking water containing organic substances with different characteristics, and one of the most important findings in the study is that HNMs formation increases significantly in case of ozone/chlorine. [Merlet et al. \(1985\)](#) postulated two mechanisms for chloropicrin formation via ozonation followed by chlorination: 1) oxidation of amine groups in organic molecules to nitro groups by ozone, 2) nitration of organic molecules by nitrogen oxides (N_xO_y) formed during ozonation of air in the ozone generator. [von Gunten \(2003\)](#) reported that intermediates formed because of partial oxidation of organic molecules of ozone and that the intermediates formed are precursors that increase the formation of chloropicrin. For example, phenolic compounds formed because of the reaction of hydroxyl radicals that may occur during ozone with aromatic compounds, and methyl ketones formed because of oxidation of alkenes with ozone are potential HNMs forming precursors ([von Gunten 2003](#)). Following the ozone/chlorine scenario, the second highest HNMs formation was detected in ozone/chloramine scenario. While the lowest HNMs formation was detected in the use of chlorine alone, the HNMs concentration was below than measurable levels in the use of chloramine and ozone. [Hua and Reckhow \(2007\)](#) showed that HNMs formation at very low concentrations using only chloramine in their study. [Goslan et al. \(2009\)](#) found the chloropicrin concentration in all samples below the detection limits. [Hu et al. \(2010\)](#) found chloropicrin and bromodichloronitromethane were dominant species in their study and emphasized that the use of ozone/chlorine increased HNMs levels and lower HNMs were formed in the use of ozone/chloramine. Since the HNMs concentration is detected at very low concentrations, there is not a clear association between seasonal changes.

3.3. Correlation Analysis of HNMs formation with water quality parameters

Correlations between HNMs and various water quality parameters in disinfection conditions (ozone/chloramine) in natural waters were investigated. HNMs concentrations showed a moderate correlation with DON of water sources. HNMs concentrations did not show a clear trend with TOC, SUVA, and other water quality parameters. The results of the water quality analysis show that both the type and concentration of organic precursors are important in the formation of HNMs, since both organic carbon and nitrogen content in natural waters are expected to be important for HNMs formation. The correlation between HNMs and DON was calculated as 0.35. This indicates that there are certain types of natural organic matter components that probably react with nitrogen, especially in the ozone/chlorine scenario, and exhibit high HNMs formation even at very low levels. DON/DOC ratio along with SUVA can be a simple metric for water utilities to determine and assess the presence of HNM precursors in source waters. To date, the type of HNM precursors is not clearly identified in natural waters but formation of emerging NDBPs related to the concentrations and composition of dissolved organic nitrogen (DON) in water ([Krasner et al. 2009](#))

4. Conclusion

HNMs formation potentials in Egridir Lake as low SUVA water were examined under different disinfection conditions. The results showed that HNMs formation potential were the highest for ozone/ chlorine, followed by ozone/chloramine, and chlorine. Pre-ozonation significantly enhanced HNMs formation. The highest HNMs concentration was 2.50 µg/L in the spring season in the ozone/chlorine scenario. A dramatic decrease was detected from spring to winter. In the ozone/chlorine scenario, the lowest HNMs concentration measured in winter is 1.97 µg/L. The lowest measurable HNMs concentration in the study was 0.67 µg/L in the autumn season in the chlorine scenario. A higher correlation was found between DON and HNM formation compared to other water quality parameters. Although HNM formation and distribution were varied systematically in this study, there are still several aspects of HNM formation and distribution that need further investigation: the kinetics of HNM formation and distribution under typical treatment conditions, the effect of temperature on HNM formation, the stability and fate of HNMs in the distribution system containing in the presence of dissolved oxygen and disinfectants, and the fate HNM precursors. Also, waters from other parts of the country and under different influences (e.g., wastewater discharges, algae growth, nonpoint discharges, and storm events) should be beneficial to examine in terms of HNM formation potentials and HNM precursors.

Acknowledgment

This study named “Assessment of Halonitromethanes Formation Potentials Based on Different Disinfection Scenarios in Source Water with Low SUVA Value” was produced from the master's thesis of Sebnem Genisoglu and was financially supported by the University of Suleyman Demirel Scientific Research Projects Coordination Unit with project number 4226-YL1-14.

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