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DETERMINATION AND EVALUATION OF SEASONAL CHANGES OF DBPs AFTER CHLORINATION IN NETWORKS USING UNDERGROUND WATER. MUŞ, TURKEY CASE

This study aimed to determine the seasonal change of the concentrations of trihalomethanes (THMs) and one of the newly emerging byproducts haloacetonitriles (HANs), the most abundant group of some disinfection by-products (DBPs) forming as a result of chlorination of drinking water supplied from 2 different reservoirs to the city centre of Muş for disinfection purposes and called chlorinated organic halogens. The quantitative determination of these compounds, some of which may have carcinogenic properties, and the evaluation of their possible effects on public health constitute the importance of the study. The results show that although there is not sufficient chlorination in both water networks and total organic carbon (TOC) values are low in underground water, the total THMs sometimes exceed the 100 μg/dm^3 value applied in Turkey and pose a risk. It was observed that the total HAN values remain below the 2 μg/dm^3 concentration in both networks.

1. INTRODUCTION

Water obtained from resources is subjected to various treatment processes to prevent the possible effects of polluting parameters in water resources on public health and to meet water quality criteria. Through these processes, suspended and colloidal substances in water are removed and, in the following, the water is made microbiologically safe by disinfection [1, 2]. Chlorine is the most widely used for drinking water disinfection because it leaves a residue, is cheap, and is easy to implement [3]. In the 1970s, studies on chlorine chemistry revealed that chlorine does not only react with targeted microorganisms in water but also with natural (NOM) or synthetic organic matter in

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water and forms compounds called disinfection by-products (DBPs), some of which were found to have carcinogenic effects. Among these, THMs, haloacetic acids (HAAs), and HANs are the most abundant by-products [1–4].

Many studies showed that the presence of THMs in drinking water poses a risk to human health due to its carcinogenic effect. However, the amount of nitrogenous DBPs started to increase in recent years as a result of the use of alternative disinfectants, such as chloramine, to reduce the formation of DBPs, such as THMs and HAAs, which are included in the regulations. Nitrogenous DBP types such as HANs and halonitromethanes (HNMs) are becoming a significant threat to public health due to their higher toxicological effects than THMs and HAAs [1–5].

Due to these features, while limit values of 80 μg/dm^3 in USEPA, and 100 μg/dm^3 in the European Union and Turkey are applied for THMs, there is no limit value for HANs yet [1]. However, worldwide research on the subject continues. There are various studies in the literature on the formation of DBPs and the investigation of the precursor compounds involved in the formation of DBPs.

Şahinkaya et al. [6] investigated THM formation potential (THMFP) in 29 lakes from which drinking water is supplied in Turkey. Chloroform was found to be the most important type of THM and made up 86% of THMFP. In their study on the same water resources, Ateş et al. [7] reported that as a result of chlorination, HAA concentrations were 18–149 μg/dm^3, THM 21–189 μg/dm^3 and absorbable organic halogens (AOXs) varied in the range of 378–859 μg/dm^3. With the treatment of water before chlorination, the potential for DBP formation decreased by 50% compared to raw water, but this situation did not affect the type distribution of THM. In general, DBP formation was the lowest in the dry summer period when the amount of precipitation was low. This shows that the precursor compounds in the formation of DBP were soil-derived organics that penetrate the water through precipitation and their amounts varied depending on the season.

Toröz and Uyak [8] stated that the THM concentration in the network fed by the Istanbul Büyükçekmece Drinking Water Treatment Plant increased depending on the distance. With the increase in temperature in summer, THM values, up to 1.2–1.8 times the limit value, were obtained at the endpoint of the network at 24 °C. Uyak [9] sampled tap water from 15 points in Istanbul to evaluate the carcinogenic effect of THM. The most dominant type of THM was chloroform, cancer cases were high in regions with high THM concentration, and therefore the higher the THM concentration, the higher the risk. Baytak et al. [10] conducted THM and HAN measurements for 1 year in two different resources from which the city of İzmir, Turkey, drinking water need is met. 42% of the THM values obtained exceed the limit value of Turkey and 61% exceed the limit value of the US EPA. While the highest THM and HAN concentrations are seen in spring, the values are the lowest in summer.

In the study conducted by Avşar et al. [1] in Istanbul Büyükçekmece and Ömerli surface water resources, it was determined that the hydrophobic part of the NOM was

the most active in the formation of THMs, and the transphilic part was the most active in the formation of HAN. Guilherme and Rodriguez [5] measured THMs and HAAs in small water distribution systems of 2 existing cities in Canada. The mean concentration of THMs was 75 μg/dm^3, and the mean concentration of HANs was 2.5 μg/dm^3. The level decreased in autumn and winter and reached the highest level in summer. Shanks et al. [11] observed that in the drinking water network, the concentrations of trichloroacetonitrile (TCAN) and dichloroacetonitrile (DCAN) which are HAN types increased in summer months, and the concentration of HAN increased as the residence time of water in a network prolonged.

Serrano et al. [12] investigated the effect of the processes in various units of the drinking water treatment plant on the formation and removal of different DBPs. It was determined that aldehydes were completely removed and 15–50% of HAAs were removed by sand filtration, but THMs, HNMs (halonitromethanes) and HANs increased by around 70%. In the Yuqiao reservoir located in Tianjin, China, it was seen that raw water quality had an important role in the formation of DBP, and the formation of THMs, HAAs and HANs decreased by using chloramine instead of chlorine [13].

Guo et al. [14] examined various factors affecting the formation of THMs, HANs and HNMs in water subjected to UV-chlorination and chloramination following filtration in a drinking water treatment plant. Generally, more THMs formed in the UV-chlorination process, while more HANs and HNMs formed in the UV-chloramination. Hsu et al. [15] measured the concentrations of THMs in raw water and chlorinated water taken from three drinking water treatment plants in Taiwan. They calculated THMs-reasoned lifetime cancer risk and determined that chloroform was the most important type of THM and constituted the most important part of the lifetime cancer risk (87.5–92.5%). In the area where 3 facilities provide water, the calculated lifetime cancer risk in tap water for 4 THM types was greater than 10^{-6}. The total THMs calculated for tap water in Southern Taiwan are less than the risk level of 1.94×10^{-4}. This level is higher than the EPA acceptable risk (10^{-6}).

Hong et al. [3] detected water quality deterioration and associated high THM formation in the Dongjiang River, which is the most important drinking water source in Hong Kong. The control of THM formation primarily depended on the reaction time and the bromide concentration in the water. The study by Siddique et al. [16] examined the lifetime cancer risk in humans exposed to THMs present in drinking water via multiple exposure routes in an urban industrial area located in Karachi, Pakistan. The lifetime cancer risk for ingestion and skin exposure was at the low-risk level ($\geq1.0\times10^{-6}$; $\leq5.1\times10^{-5}$) according to the USEPA, while exposure by inhalation was in the acceptable high-risk ($\geq5.0\times10^{-6}$; $\leq1.0\times10^{-4}$) category. However, in some urban industrial areas, the calculated risk of respiratory tract cancer for chloroform was found to be at an unacceptable risk ($\geq1.0\times10^{-4}$) level.

Amjad et al. [17] carried out THMs-reasoned cancer risk assessment in urban drinking water sources in Rawalpindi and Islamabad, Pakistan. THMs were monitored at a total of 20 points in two cities, and it was observed that the concentration range changed between

21 and 373 μg/dm^3; the average concentrations were 142 and 260 μg/dm^3 levels, respectively. Chloroform was the most important THM component (>85%). The lifetime cancer risk was found as 0.74×10^{-4} and 1.24×10^{-4} for Rawalpindi and Islamabad, respectively. Ingestion is the most important route of exposure, followed by respiratory and dermal routes, respectively. In a study conducted in Spain between 2008 and 2013, Ribera et al. [18] observed that exposure to THM through drinking water increased the risk of bladder cancer, and chloroform might be associated with breast cancer.

Krasner et al. [19] investigated newly emerging carbonaceous and nitrogenous DBPs in the effluent of 14 drinking water treatment plants. They found that the precursor compounds and/or disinfection processes involved in the formation of these compounds were different from THMs. The amounts of 2-halogenated HAN types were similar in the chlorination and chloramination processes, and varied as 0.9–12 (median 3.4) and 0.7–7.5 (median 3.2) μg/dm^3, respectively. There was a significant correlation between 2-halogenated HANs formed as a result of chlorination and DOM and UV ($R^2 = 0.76$, $R^2 = 0.73$, respectively), but no significant correlation ($R^2 = 0.24$) could be detected with dissolved organic nitrogen (DON). In a 3-year study conducted in Korea by Shin et al. [20], it was determined that THMs constituted 60% of all DBPs measured in drinking water, HAAs constituted 20%, HANs 12%, halo ketones (HKs) 5%, chloropicrin (KP) 3%. Chloroform was the most important THM component and constituted 77% of THM. Chen et al. [21] stated that DBPs were formed less in chloramination and the toxicity was less than in chlorination, but ozonation increased the formation of brominated DBP types, thus causing an increase in toxicity. Daniel et al. [22] stated that drinking water pollutants such as chlorinated and brominated HANs were formed as a result of chlorination and that these chemicals had carcinogenic activity potential and showed genotoxic properties that might mean a human health hazard.

In this study, seasonal and distance-related changes of THMs and HANs, forming after chlorination, were determined in the samples taken from two different reservoirs providing drinking water to Muş city center and the distribution network of these reservoirs, and their possible effects on public health were evaluated. Studies in the literature mostly examine the formation of DBP in surface waters while data on places where drinking water is obtained from underground water, such as Muş, are quite limited.

2. MATERIALS AND METHOD

Sampling points. Seasonal changes of trihalomethanes (THMs) and haloacetonitriles (HANs) as disinfection by-products (DBPs) formed as a result of chlorination in 2 reservoirs and the connected network that supplies water to Muş City Center and their changes depending on the distance in the network were determined. Within the scope of the study, the sampling analysis study was carried out in the summer (20.07.2017), autumn (26.10.2017), winter (08.01.2018) and spring (07.03.2018) seasons. Two different networks distribute water in the city. A significant part of the water supplied to

Muş city center is supplied from the main pumping center and there are 17 boreholes for this purpose. The water obtained from the wells is pumped into the main tank, where it is chlorinated with liquid chlorine and then supplied to the network. Apart from the main pumping center, there is also a mountain spring. The water coming from this source is pumped into the Murat Paşa water tank and from there, it feeds the city center after being chlorinated [23]. A peristaltic pump mechanism is used for chlorination, and Muş municipality does not carry out any measurement/analysis/monitoring studies regarding chlorination and DBP formation in the reservoir and network.

In the reservoir and distribution networks specified in the study, THMs and HANs as DBPs forming after chlorination were monitored. Also, water quality at the raw water sources was monitored. The sampling points in both distribution networks are given in Table 1, in the order from the source to the last point.

Table 1

Location of sampling points

Main reservoir and its network			
No.	Sampling point	Sample type	Coordinates
1	main reservoir	raw water	38.727294; 41.580537
2	main reservoir exit	chlorinated tap water	38.727801; 41.580370
9	Muş city center reservoir inside No. 3		38.736459; 41.496992
7	city center restaurant		38.740921; 41.496384
4	city center Atatürk children's park		38.745588; 41.499400
10	city center bus station garden		38.747446; 41.507699
3	mains endpoint		38.760184; 41.512072
Murat Paşa reservoir and its network			
5	Murat Paşa reservoir exit	raw water	38.731482; 41.482136
6	city center castle park	chlorinated tap water	38.730002; 41.485636
8	city center reservoir front No. 3		38.736480; 41.497141

Parameters and methods of analyses. Within the scope of the study, the water quality parameters of the raw water supplied to both networks were monitored seasonally. In this context, pH, conductivity, oxidation-reduction potential (ORP), temperature, free chlorine, total chlorine, alkalinity, nitrate, bromide, turbidity, UV_{254} absorbance, total organic carbon (TOC) and total nitrogen (TN) were measured. The measurement method and the devices used were described elsewhere [24].

DBPs measured within the scope of the study were THMs and HANs. Four THM compounds were chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform. Four HAN compounds were trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromodichloroastonitrile (BCAN), dibromoacetonitrile (DBAN). All of the compounds were determined according to the EPA 551.1 method developed by the Environmental Protection Agency (USEPA). This method is based on the conversion of THM and HAN types in water from the water phase to the solvent

phase with the help of methyl tertbutylether (MTBE) and concentration and purification in this phase. Components concentrated in the solvent phase were analyzed by a gas chromatograph equipped with a micro electron capture detector (GC-μECD) [1, 24].

Risk assessment. Minimum, maximum and average concentrations were calculated from the data obtained in both networks and it was evaluated whether this situation poses a lifetime risk in people exposed to these concentrations. For this purpose, the risk was calculated for 4 THM types using methods available in the literature [25]. Risk assessment is a method used to reveal the effects of DBPs on public health. A similar evaluation was used by Gan et al. [26] in calculating the risk of THMs and HAAs in pool water on swimmers. Risk assessment of HANs could not be performed within the scope of this study, due to the low concentrations of HAN and the lack of necessary constants for HANs in the referenced methodology.

3. RESULTS

3.1. EXPERIMENT RESULTS

Results of seasonal raw water quality analysis of the networks (the minimum, maximum, average and standard deviation) and comparison with limit values (Turkish Standards, TS 266) are given in Table 2. The values in the table are calculated by considering a total of 4 samples taken once per season for each raw water source.

Table 2

Raw water quality results of 2 reservoirs and comparison with Turkish limit values

Parameter	Main reservoir				Murat Paşa reservoir				TS266 limits
	Min	Max	Av.	Std. dev	Min	Max	Av.	Std. dev	
pH	6.98	7.87	7.55	0.34	6.82	7.54	7.32	0.30	6.5–9.5
Conductivity, μS/cm	285	473	371	76	323	455	387	58	2500
ORP, mV	174.2	415.0	256.7	93.2	141.2	249.0	193.6	38.6	–
Temperature, °C	8.5	15.8	12.0	2.6	36	21.1	11.5	6.3	–
Free chlorine, mg/dm^3	0	0			0	0			–
Total chlorine, mg/dm^3	0	0			0	0			–
Alkalinity, mg $CaCO_3$/dm^3	116	154	140	16	154	230	186	28	–
Nitrate, mg/dm^3	2.0	4.8	3.6	1.1	1.1	3.4	2.1	0.9	50
Bromide, mg/dm^3	<0.1	0.44	0.32	0.12	0.12	0.44	0.28	0.14	–
Turbidity, NTU	0.10	0.65	0.27	0.22	0.09	4.19	1.20	1.73	1
UV_{254} absorbance, 1/cm	0.002	0.014	0.006	0.005	0	0.005	0.00	0.00	–
TOC, mg/dm^3	<0.05	0.3553	0.1787	0.1766	<0.05	0.3052	0.2070	0.0982	–
TN, mg/dm^3	1.9166	2.4552	2.2773	0.2152	0.6358	1.0441	0.8729	0.1523	–

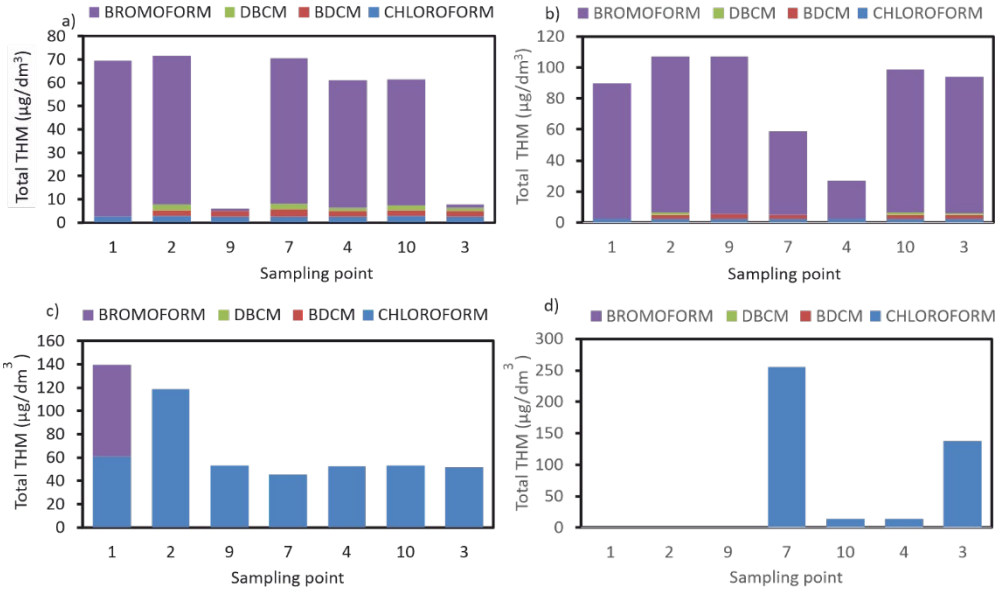

Fig. 1. THM types in the Muş main reservoir and distribution network in a) summer (20.07.2017), b) autumn (26.10.2017), winter (08.01.2018), and spring (07.03.2018) periods

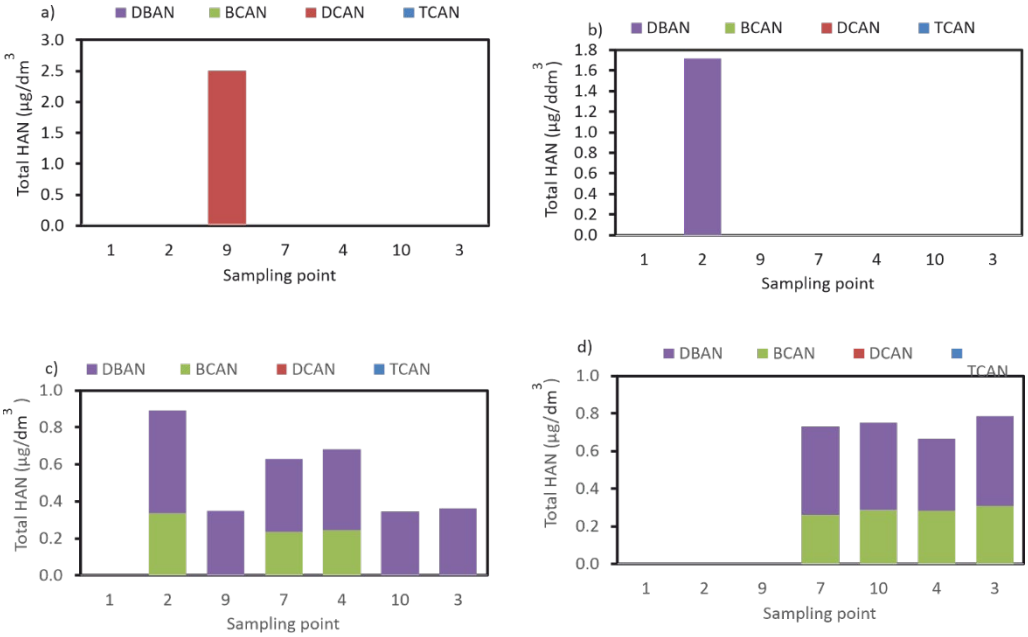

Fig. 2. HAN types in the Muş main reservoir and distribution network in a) summer (20.07.2017), b) autumn (26.10.2017), c) winter (08.01.2018), d) spring (07.03.2018) periods

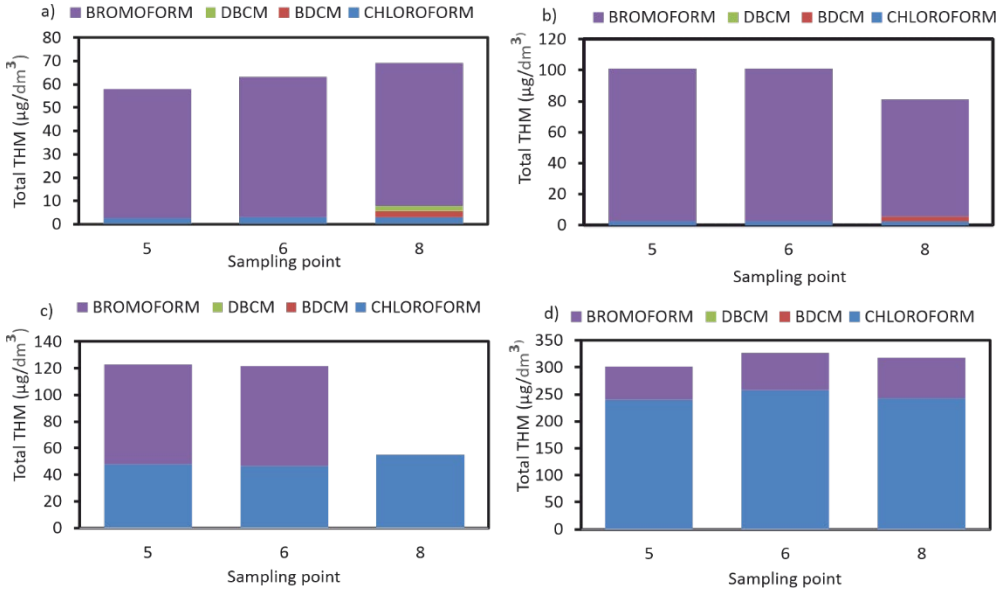

Fig. 3. THM types in the Murat Paşa main reservoir and distribution network in a) summer (20.07.2017), b) autumn (26.10.2017), winter (08.01.2018), and spring (07.03.2018) periods

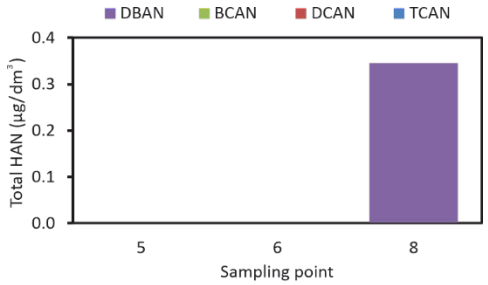

Fig. 4. HAN types in the Murat Paşa main reservoir and distribution network in the winter period (08.01.2018)

Results of analyses THM and HAN of the samples are given in Figs. 1–4. The sample points were ordered from the source to the endpoint in both networks. Following the regulation on water intended for human consumption, which is valid in Turkey and based on TS 266, the free chlorine level at the endpoint of the water distribution networks is required to be 0.2–0.5 mg/dm^3. Although free and total chlorine was detected above the 0.5 mg/dm^3 (max free and total chlorine is determined as 1.3 and 1.5 mg/dm^3, respectively) limit value at the outlet of the main reservoir during the entire sampling period, except for January 2018 sampling period, chlorine was not detected at almost any point in the network except July. Probably the most important reasons for this situation are that the network is old, that it causes continuous malfunctions, and that the chlorine dosing system is disabled due to water cuts and power cuts. Furthermore, there

is no control for monitoring the amount of chlorine in the reservoirs and connected networks. All these factors are regarded as the reasons for the failure to provide adequate and proper chlorine concentration in the network.

Residual chlorine was detected in only one of the 12 measurements conducted in the Murat Paşa reservoir (max free and total chlorine were determined as 0.6 and 0.8 mg/dm^3, respectively) and the drinking water network it feeds. This indicates that this tank was not efficiently chlorinated during the monitoring period. In this case, both water networks are open to pollution, and in such a case, it is possible for those living in the city center to be harmed. In addition, the depletion of chlorine in the water is an indicator of the DBP formation potential, and with the increase in the amount of chlorine in the water, the DBP formation in the water may increase further.

According to Table 2, nitrate values in both water reservoirs are below the Turkish Standard TS 266 and 50 mg/dm^3 limit specified by WHO. Total nitrogen (TN) values are also below 8 mg/dm^3 (main reservoir max TN 2.4552 mg/dm^3, Murat Paşa reservoir max TN 0.8729 mg/dm^3) indicating that there was no significant pollution in the water during the monitoring period. This shows that dissolved organic nitrogen compounds that are active in the formation of HAN are not present in significant quantities in the water. This situation is also seen in the HAN measurement results, and the HAN concentrations detected in Muş main reservoir and the connected network, except for July, remained below 2 µg/dm^3. DBAN and BCAN are the most important components (Fig. 2). In the Murat Paşa Network, HANs could not be detected except for January 18 (Fig. 4). As seen in Fig. 4, the only HAN type detected in the Murat Paşa network was DBAN (0.34 µg/dm^3).

Specific ultraviolet absorbance (SUVA) is an indicator of DBP formation potential in the water. To reduce DBP formation, it is desirable to reduce the SUVA value in the water below 2 dm^3/(mg·m) [1, 23–25]. When the calculation was made on the maximum TOC and UV values of 2 reservoirs, it was determined that the SUVA value in the main reservoir increased to 3.9 and in the Murat Paşa reservoir, it was up to 1.6 dm^3/(mg·m). Although the SUVA value in Murat Paşa raw water was below 2 dm^3/ dm^3/(mg·m), it can be seen from the following figures that the THM concentrations in the water can exceed the limit value of 100 µg/dm^3 (Figs. 3c, 3d). It has been determined that THM values in the Murat Paşa network can sometimes increase up to 2.5 times the limit value (255.7 µg/dm^3 for point 7 in March 2018) except in the summer season (Figs. 1b–1d).

According to Table 2, the pH values in both networks are within the limits (6.5–8.5) specified in TS266. Moreover, UV_{254} (<0.02 1/cm), TOC (<1 mg/dm^3) and TN (<8 mg/dm^3) parameters, which characterize the amount of precursor compound in DBP formation, are low in both water reservoirs. The low concentration of TOC in water is another factor in HAN formation being generally below 2 µg/dm^3 (Fig. 2) for the main network and Fig. 4 for the Murat Paşa network). However, although the amount of precursor compound is low, it is seen that THMs can exceed the limit values in both water networks (Fig. 1 for the main network and Fig. 3 for the Murat Paşa network). It is

understood that the amount of brominated THMs in water increases especially with the increase in the amount of bromide in the water (max Br^- 0.44 mg/dm^3 for both reservoirs), and the limit of 100 μg/dm^3 in Turkey is occasionally exceeded in the networks. In the Murat Paşa Network, the values measured in all the remaining samples, except for the summer and autumn samples, are above 100 μg/dm^3 (Fig. 3). This situation shows that although TOC and UV values are low (Table 2) in both water networks, there is a potential for THM formation depending on the high amount of bromide and that the concentration in the water may exceed the limit values from time to time and a significant amount of THM may form. Bromoform and chloroform are the most important THM components in water networks. As stated in the literature, brominated DBPs are more carcinogenic than chlorinated ones. To fully understand the potential of by-product formation in both water networks, it is necessary to determine the DBPFP by taking raw water samples on a seasonal basis. Only through this test, the real by-product formation potential of water can be revealed.

3.2. RISK ASSESSMENT FOR THMs

The cancer risk of THMs can be calculated in three ways, ingestion and dermal absorption and respiratory tract exposure. However, respiratory tract exposure was not taken into account in the calculation as it is not a suitable exposure route for those who consume mains water [23, 25, 26].

- THM risk of ingestion (THMRI) was calculated with the help of the equation

$$\text{THMRI} = PDS_o \times PF_o \tag{1}$$

where PDS_o is the amount of THM types taken orally per day, mg/(kg·day), PF_o is a potential factor or slope factor

$$PDS_o = \frac{PW \times EF \times ED}{BW \times AT} \tag{2}$$

where PW expresses the concentrations, mg/dm^3, of THM types in the water, In this context, minimum, maximum and average concentrations were determined for four THM types measured in both networks and the risk was calculated for these values. The minimum, maximum and average concentrations used for risk calculation are given in Table 3. WS is the amount of water ingested daily, dm^3/day, taken as 2, EF is the exposure frequency, day/year, taken as 365, ED is the exposure duration. According to TUIK (Turkish Statistical Institute) statistics for the period of 2014–2016, the average human life span in Turkey is 75.3 years for men and 80.7 years for women [27]. BW is the body weight. The average weight for men in Turkey is 75.8; for women, it is 66.9 kg. The average height is 172.6 cm for men and 161.4 cm for women [28]. AT is the expression of the average life in days. Considering the above ED values, it was calculated as 27 484.5 days for men and 29 455.5 days for women.

Table 3

Minimum, maximum and average concentrations of THM types and oral potential factors for both networks

Location	Concentration	THM type			
		Chloroform	BDCM	DBCM	Bromoform
Mains	minimum	0.00240205	0	0	0
	maximum	0.25570	0.00292	0.00267	0.10171
	average	0.03567	0.00130	0.00082	0.03720
Murat Paşa network	minimum	0.002401	0	0	0
	maximum	0.25794	0.00287	0.00207	0.09874
	average	0.07535	0.00070	0.00069	0.06725
PF_o, mg/(kg·day)		0.0061	0.062	0.084	0.0079

The risk was calculated with the above values; the risks of ingestion obtained for women and men are given in Tables 4 and 5.

Table 4

Risk of ingestion in women

Main network					
Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	4.4×10^{-7}	0	0	0	4.4×10^{-7}
Maximum	4.7×10^{-5}	5.3×10^{-7}	$4.9\text{x }10^{-7}$	2.4×10^{-5}	7.2×10^{-5}
Average	6.5×10^{-6}	2.4×10^{-7}	1.5×10^{-7}	8.8×10^{-6}	1.6×10^{-5}
Murat Paşa network					
Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	4.4×10^{-7}	0	0	0	4.4×10^{-7}
Maximum	4.7×10^{-5}	5.2×10^{-7}	3.8×10^{-7}	2.3×10^{-5}	7.1×10^{-5}
Average	1.4×10^{-5}	1.3×10^{-7}	1.3×10^{-7}	1.6×10^{-5}	3.0×10^{-5}

Table 5

Risk of ingestion in men

Main network					
Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	3.9×10^{-7}	0	0	0	3.9×10^{-7}
Maximum	4.1×10^{-5}	4.8×10^{-6}	5.9×10^{-6}	2.1×10^{-5}	$7.3\text{ x}10^{-5}$
Average	5.7×10^{-6}	2.1×10^{-6}	1.8×10^{-6}	7.8×10^{-6}	1.7×10^{-5}
Murat Paşa network					
Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	3.9×10^{-7}	0	0	0	3.9×10^{-7}
Maximum	4.2×10^{-5}	4.7×10^{-6}	4.6×10^{-6}	2.1×10^{-5}	7.1×10^{-5}
Average	$1.2\text{ x}10^{-5}$	1.1×10^{-6}	1.5×10^{-6}	1.4×10^{-5}	2.9×10^{-5}

According to the US EPA, if the probability of an event exceeds one in a million, the acceptable risk level is exceeded in terms of the situation handled [23, 25, 26]. When the values obtained in this context are examined, it is seen that there is a risk for both women and men in terms of maximum and average concentrations.

- Risk of dermal exposure to THMs (THMRDE) is calculated with the help of the equation

$$\text{THMRDE} = PDS_{\text{d}} \times PD_{\text{D}} \tag{3}$$

where PDS_{d} is the amount of pollutant taken daily through the skin, mg/(kg·day), PF_{d} expresses the potential factor or slope; the values used in the calculation are given in Table 6.

$$PDS_{\text{d}} = \frac{PW \times SSA \times SPC \times DE \times EF \times ED}{BW \times AT} \tag{4}$$

where *SSA* is the skin surface area, m^2, taken as 1.76 for men and 1.64 for women, *SPC* is the type-specific skin permeability constant, *DE* is the exposure duration, h/day, calculated by assuming that showering is taken 3 times a week for 15 min a day.

Table 6

Dermal potential factors and type-specific permeability constants of THM types used for calculation

Variable	Chloroform	BDCM	DBCM	Bromoform
PF_{d}, mg/(kg·day)	0.0061	0.062	0.084	0.0079
SPC, m/min	0.000089	0.000058	0.000039	0.000026

The risk values due to dermal exposure calculated for men and women depending on the values taken as a basis are given in Tables 7 and 8.

Table 7

Risk of dermal exposure in women

Main network					
Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	3.4×10^{-12}	0	0	0	3.4×10^{-12}
Maximum	$3.6\ \text{x}10^{-10}$	2.7×10^{-11}	2.3×10^{-11}	5.5×10^{-11}	4.7×10^{-10}
Average	5.1×10^{-11}	1.2×10^{-11}	7.0×10^{-12}	2.0×10^{-11}	9.0×10^{-11}
Murat Paşa network					
Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	3.4×10^{-12}	0	0	0	3.4×10^{-12}
Maximum	$3.7\times^{-10}$	2.7×10^{-11}	1.8×10^{-11}	5.3×10^{-11}	4.6×10^{-10}
Average	1.1×10^{-10}	6.6×10^{-12}	5.9×10^{-12}	3.6×10^{-11}	1.6×10^{-10}

Table 8

Table 8. Risk of dermal exposure in men

Main network					
Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	3.2×10^{-12}	0	0	0	3.2×10^{-12}
Maximum	3.4×10^{-10}	2.6×10^{-11}	2.2×10^{-11}	5.2×10^{-11}	4.4×10^{-10}
Average	4.8×10^{-11}	1.2×10^{-11}	6.6×10^{-12}	1.9×10^{-11}	8.5×10^{-11}
Murat Paşa network					
Risk	Chloroform	BDCM	DBCM	Bromoform	Total
Minimum	3.2×10^{-12}	0	0	0	3.2×10^{-12}
Maximum	3.5×10^{-10}	2.6×10^{-11}	1.7×10^{-11}	5.0×10^{-11}	4.4×10^{-10}
Average	1.0×10^{-10}	$6.2\times^{-12}$	5.6 10^{-12}	3.4×10^{-11}	1.5×10^{-10}

When the obtained values are examined, it is understood that taking a shower 3 days a week and for 15 minutes a day does not pose a risk to women and men. Consequently, the risk of ingestion for men and women for average and maximum values is further increased when dermal exposure is involved.

4. CONCLUSION AND RECOMMENDATIONS

The parameters in terms of water quality may exceed the limit values given in Turkish Standards (TS 266) from time to time in terms of turbidity for Murat Paşa reservoir. It was observed that proper and sufficient chlorination was not carried out in both water networks and chlorine could not be detected in almost the entire measurement period in both networks. To ensure the continuity of the chlorination process, it would be beneficial to carry out weekly controls by the municipality.

Despite the lack of sufficient chlorine in both water networks and low TOC, TN and UV absorbance values, the THM values obtained in both networks may occasionally exceed the limit value of 100 $\mu g/dm^3$. In particular, the values obtained in the Murat Paşa Network exceeded the limit value throughout the monitoring process.

The high amount of bromide in both water networks caused the formation of brominated THM types in the water. For HANs, on the other hand, the concentrations in the mains generally remained below 2 $\mu g/dm^3$, while HANs could not be detected in the Murat Paşa network in general.

In the risk calculation made for THMs, it was observed that there is a risk of ingestion for the average and maximum THM concentrations in both water networks and dermal exposure does not pose a risk alone but increases the overall risk potential.

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