

CARBONACEOUS DISINFECTION BY-PRODUCTS IN LOW SUVA WATERS: OCCURRENCE, FORMATION POTENTIAL, AND HEALTH RISK ASSESSMENT

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Abstract. This study aims (1) to determine the regulated carbonaceous disinfection by-products formation potentials under five disinfection scenarios for extremely low specific ultraviolet absorbance water sources, (2) to monitor the spatial and temporal variations of carbonaceous disinfection by-products in two full-scale drinking water distribution system for one-year, and (3) to evaluate carcinogenic and non-carcinogenic health risks of carbonaceous disinfection by-products through multi-pathways. Formation potentials of trihalomethanes and haloacetic acids were in the order of chlorination > ozonation/chlorination > chloramination > ozonation/chloramination > ozonation. Trihalomethanes were the most prevalent disinfection by-products followed by haloacetic acids. Chloroform was the dominant species of trihalomethanes, whereas trichloroacetic acid and dichloroacetic acid were the predominant species of haloacetic acids. No clear seasonality changes in carbonaceous disinfection by-products level were observed in water source with lower dissolved organic carbon values, and higher carbonaceous disinfection by-products values were observed in summer for water sources with higher dissolved organic carbon values. Also, there were no clear correlations between carbonaceous disinfection by-products formations and tested surrogate water quality parameters. Although the non-cancer risk of carbonaceous disinfection by-products was below permissible recommended levels, the average lifetime carcinogenic risk levels for trihalomethanes and haloacetic acids were 6.9E-05 and 5.8E-05, respectively, which were above the negligible risk level.

Keywords: *chlorination, haloacetic acids, multi-pathways exposure, occurrence, SUVA, total lifetime cancer risk, trihalomethanes*

Abbreviations: ANT: Antalya; APR: April; AT: Average Time; AUG: August; BAA: Bromoacetic Acid; BDCM: Bromodichloromethane; BW: Body Weight; C-DBPs: Carbonaceous Disinfection By-Products; C_{air}: THM Concentrations in The Air; CDI: Chronic Daily Intake; CF: Chloroform; Cl: Chlorine; CR: The Cancer Risk; CRT: The Total Cancer Risk; C_w: Concentrations of C-DBPs in Water; DBAA: Dibromoacetic Acid; DBCAA: Dibromochloroacetic Acid; DBCM: Dibromochloromethane; DBP: Disinfection By-Product; DCAA: Dichloroacetic Acid; DEC: December; DOC: Dissolved Organic Carbon; DPD: N, N-Diethyl-P-Phenylenediamine; DS: Distribution System; DUVA: Differential UV Absorbance; ED: Exposure Duration; EF: Exposure Frequency; ET: Exposure Time; FEB: February; FP: Formation Potential; GC/ECD: Gas Chromatography-Electron Capture Detector; HAA: Haloacetic Acid; HI: The Hazard Index; IR: Inhalation Rate; ISP: Isparta; JAN: January; JUL: July; JUN: June; KUM: Kumluca; MAR: March; MCL: Maximum Contaminant Level; MRL: Minimum Reporting Limit; MtBE: Methyl Tert-Butyl Ether; NOM: Natural Organic Matter; NOV: November; OCT: October; PC: Permeability Constant in Water; r: Correlation Coefficient; RfD: Reference Dose; SA: Skin Area; SEP: September; SF: Slope Factors; SUVA: Specific Ultraviolet Absorbance; TBAA: Tribromoacetic Acid; TBM: Tribromomethane; TCAA: Trichloroacetic Acid; TCM: Trichloromethane; The USA: The United States of America; THM: Trihalomethane; TSI: Turkish Statistical Institute; USEPA: United States Environmental Protection Agency; UV: Ultraviolet; UV₂₅₄: 254 nm Ultraviolet

Introduction

The most used method for disinfection is chlorination for water supplies to ensure microbial quality of drinking water, and it has been playing an essential role in preventing waterborne microbial diseases (String et al., 2020). Complex reactions between disinfectants with precursors can unintentionally form carbonaceous disinfection by-products (C-DBPs) which are classified as possible carcinogens to humans (Mashau et al., 2018; Ates et al., 2020). People may be exposed to C-DBPs by multi-pathways such as ingestion, dermal absorption, inhalation. Several studies have found links between C-DBPs exposure and cancer risk of brain, bladder, colon, and rectum (Du et al., 2021). Studies focused on the health risks of C-DBPs through multi-pathways exposure in different countries showed that the cumulative cancer risk was relatively higher than the negligible risk level ($1.0E-06$) (Wang et al., 2007; Siddique et al., 2015; Zhang et al., 2018). Also, C-DBPs were also shown to induce reproductive and neurotoxicological adverse effects as a result of C-DBPs (Du et al., 2021).

Trihalomethanes (THMs) were the first C-DBPs class to be detected in chlorinated drinking water in 1974 (Rook, 1974). C-DBPs have been intensively studied, mainly for the conditions affecting their formation, precursors, toxicity, and their adverse health impacts in waters with high specific ultraviolet absorbance (SUVA) value (Tak and Vellanki, 2018; Ates et al., 2020). More than 800 species of disinfection by-products (DBPs) are reported in disinfected water (Ding and Chu, 2017; Sui et al., 2022). THMs and haloacetic acids (HAAs) make up 25% of the total halogenated DBPs are the predominant classes formed after chlorination (Krasner et al., 2016a; Hao et al., 2017). Four THMs have been regulated in most of the countries around the world. Additionally, five HAAs, chlorite, and bromate are also regulated in The United States of America (The USA) (Krasner et al., 2016a). According to the DBPs Stage 2 Rule, maximum contaminant level (MCL) for total THMs at $80 \mu\text{g/L}$ at each point of the distribution system (DS) by United States Environmental Protection Agency (USEPA). Also, MCL is set $60 \mu\text{g/L}$ for total HAAs at each sampling point in the DS (USEPA, 2006).

Chlorine is the most widely used chemical disinfectant worldwide. However, alternative disinfectants or disinfection scenarios are used to seek for control and reduction of the formation of C-DBPs, especially the regulated C-DBPs. Alternative disinfectants may reduce the formation of C-DBPs, but they may lead the formation of different classes of DBPs with higher toxicity. The type and amount of disinfectant used in the drinking water treatment are some of the significant parameters that affect the DBPs formation (Ebsa and Dibaba, 2022). However, various factors and conditions influence the formation and speciation of DBPs in very complex ways. The species and concentration of DBPs depend on the type of water source (Rodriguez et al., 2003), contact time and DS length (Tian et al., 2017), temperature (Uyak et al., 2014), and other physicochemical properties of water (Bond et al., 2015). The formation potentials (FPs) tests are important to determine indirectly the amount of DBPs precursors. The majority of DBPs studies investigated formation potentials of waters that have higher SUVA values ($>2-3 \text{ mg/L}$) (Tak and Vellanki, 2018). Also, FPs studies based on real waters have generally been limited to chlorination and only for THMs formation. Also, there is a limited study about the FPs tests in low SUVA waters under different disinfection scenarios to examine the presence of C-DBPs precursors in water. Therefore, there is a need to determine the formation and occurrence of DBPs in low SUVA waters. Most of the water supplies in Turkey had low SUVA values. Ates et al.

(2007) performed a comprehensive THMs and HAAs formation study in Turkey at 29 different water sources using chlorine as a disinfectant. Kitis et al. (2010) found that the water sources in the Antalya region were characterized by low organic content, low SUVA, and low bromide (Br^-) concentrations. The main purpose of the study is (i) to determine the FPs of THMs and HAAs using different disinfection scenarios in water sources, specifically, with low SUVA values; and (ii) to monitor THMs and HAAs in two different full-scale DSs (Isparta and Kumluca DSs) (iii) to estimate the lifetime cancer and non-cancer risk of C-DBPs through multiple pathways such as ingestion, dermal absorption, and inhalation. The results will contribute to improve the knowledge regarding FPs of THMs and HAAs about under different disinfection scenarios to determine indirectly the amount of DBPs precursors in low SUVA waters. To decrease C-DBPs in the coming years, the use of alternative disinfectants will be inevitable in the legislation that they will become even stricter in the future. This study is the first study for comparison of different disinfection scenarios for C-DBPs formation in low SUVA waters with tracking spatio-temporal occurrence and assessment of cancer/non-cancer risk of THMs and HAAs through ingestion, dermal absorption, and inhalation routes in Turkey.

Methods

Water sources and sampling strategy

The selected water sources and DSs in the south of Turkey are used in this study. The first water source is Egirdir Lake in Isparta city located 915 meters above sea level, which is a drinking water source that supplies approximately 265,000 people. The second water source is the Karaagac water source, located 900 meters above sea level which is a drinking water source for approximately 50,000 people, on the west side of Antalya city. In addition to the FPs tests, C-DBPs were monitored in two DSs: Isparta DS and Kumluca DS that is supplied from Egirdir Lake and Karaagac Water Source, respectively. Water samples were collected monthly from two full-scale water DSs between October 2017 and November 2018. To have representative samples from the DSs, different 5 points along the DSs were selected from the closest to the disinfection unit to the farthest. Distribution points for Isparta and Kumluca DSs were numbered from 1 to 5 (one is the closest point, 5 is the farthest point). The distance between the disinfection unit of the Isparta water treatment plant and the furthest point of the water distribution system is approximately 25 kilometers, and the drinking water distribution system of Kumluca is approximately 10 kilometers. In both water DSs, chlorine is used as a disinfectant (Ozgur, 2019). Water samples were quenched using 1:1 sodium sulphite (Na_2SO_3 (Sigma Aldrich)) to end the disinfectant activity. All samples were transferred to the lab and analyzed as soon as possible (no later than 2 days). Analytic methods of selected water quality parameters are shown in *Table 1*. The SUVA is calculated by dividing the ultraviolet (UV) absorbance of the sample (in cm^{-1}) by the dissolved organic carbon (DOC) of the sample (in mg/L) and then multiplying by 100 cm^3/M . THMs and HAAs analyses were carried out in three repetitions for twelve months at ten points in two separate water distribution networks. Moreover, C-DBPs formation potential tests in both water sources were performed in triplicate over twelve months. Statistical analysis of the water quality data was performed based on t-statistics and 95% confidence intervals were calculated from parallel tests and triplicate measurements.

Table 1. Water quality parameters and methods

Parameter	Measurement methods	Instruments	Minimum detection limit
pH	SM 4500 H +	Multi 340i, WTW, Weilheim-Germany	
Temperature	SM 2550		
Free chlorine	Colorimeter/DPD	Pocket Colorimeter™ II, HACH, Colorado, USA	0.1 mg/L
Dissolved organic carbon (DOC)	SM* 5310B	TOC-L Series, Shimadzu, Kyoto, Japan	0.1 mg/L
UV absorbance	SM 5910	BioSpec 1601 UV-Vis Spectrophotometer, Shimadzu, Kyoto, Japan	± 0.005 cm ⁻¹
Br	USEPA Method 300	The Dionex ICS-3000 Ion Chromatography, California, USA	0.01 mg/L
SUVA	Calculation		

Formation potential tests and analysis of disinfection by products

FPs tests were conducted under five different disinfection scenarios, (1) chlorination, (2) chloramination, (3) ozonation, (4) ozonation/chlorination, and (5) ozonation/chloramination. All FPs tests were conducted in triplicates using 130 mL headspace free amber glass bottles. Chlorine was prepared from a stock sodium hypochlorite solution (10-15%) (Merck). The chloramine stock solution was prepared by mixing very slowly (drop by drop) 500 mg/L chlorine solution to a 500 mg/L ammonium sulphate solution at a pH 9 to a mass ratio of 3.5:1 chlorine/ammonium sulfate (Cl₂/N). Free chlorine and chloramine were determined using N, N-Diethyl-P-Phenylenediamine (DPD) ferrous titrimetric method (APHA, 1995). The chlorine and chloramine dose in the FPs test was determined using *Equations 1* and *2* respectively. Ozone was produced with Degremont Technologies (North America, The USA), Ozonia LAB2B model ozone generator (producing up to 10 g/h using oxygen), and ozone gas was applied 1:1 (Ozone/DOC) ratio according to DOC concentrations. All FP tests were carried out at room temperature in a dark and cool environment for 72 h as previously performed by Krasner (2009). After 72 h, the oxidant concentration in the samples was quenched with sodium sulphite (Cl₂:Na₂SO₃ 1:1). Ozonation + chlorination and ozonation and chloramination scenarios were performed by applying chlorine or chloramine on ozonated water samples. In these processes, the Ozone/DOC ratio was used as 1:1. Ozone concentration in water was measured using AccuVac® Ampules (HACH). Dilutions were made according to DOC concentration (Krasner, 2009).

$$Cl_2(mg/L) = 3 * DOC + 8 * NH_3^- - N * NO_2^- - N + 10 \quad (\text{Eq.1})$$

$$NH_2Cl(mg/L) = 3 * DOC + 5 * NO_2^- - N \quad (\text{Eq.2})$$

THMs analysis was performed by USEPA Method 551.1 with inconsequential modifications (USEPA, 1995). A total of six calibration standards (1, 5, 10, 25, 50, and 75 µg/L) were prepared. The minimum reporting limit for THMs measurements was 0.5 µg/L. HAA was analyzed by liquid/liquid extraction using methyl tert-butyl ether (MtBE), followed by derivatization with acidic methanol, and analyzed by gas chromatography-electron capture detector (GC/ECD) (Agilent 6890) according to the USEPA method 552.2 (USEPA, 1995). Standard solutions at concentrations ranging from 0.1 to 2000 µg/L were prepared for the HAAs calibration curve. The minimum

reporting limit (MRL) for HAAs species measurements was 1.0 µg/L. To eliminate the effects of extraction efficiency, water samples were extracted according to the same protocol as the calibration standards. Agilent 6890 gas chromatograph with an electron capture detector was used for both THMs and HAAs measurements.

Cancer risk assessment

The cancer risks (CR) from THMs and HAAs were estimated with calculation using chronic daily intake (CDI) and the corresponding slope factor (SF) (Wang et al., 2019). The total cancer risk (CRT) was the sum of the cancer risks for each species of THMs and HAAs from different exposure pathways. Little's inhalation model was used to the concentrations of THMs in the air in this study (Little, 1992). Parameters used in Little's theory are provided in Ates et al. (2020) study. *Table 2* shows input parameters in cancer/non-cancer risk assessment of THMs and HAAs. The input parameters related on specific to population characteristics were used to represent the accurate assessment using Turkish Statistical Institute (TSI) reports (Ates et al., 2020; TSI, 2022). CR and chronic daily intake (CDI) for each exposure pathway were calculated according to *Equations 3–5*:

$$CR_{ingestion} = CDI_{ingestion} * SF_{ingestion} = \frac{C_w * IR * EF * ED}{(BW * AT)} * SF_{ingestion} \quad (\text{Eq.3})$$

$$CR_{inhalation} = CDI_{inhalation} * SF_{inhalation} = \frac{C_{air} * IR_a * EF * ED * ET}{RW * AT} * SF_{inhalation} \quad (\text{Eq.4})$$

$$CR_{dermal} = CDI_{dermal} * SF_{dermal} = (C_w * SA * PC * EF * ED * ET * CF) / (BW * AT) \quad (\text{Eq.5})$$

Non-cancer risk assessment

The hazard index (HI) was used to estimate the non-carcinogenic risk due to ingestion and dermal and HI of six compounds was calculated by CDI of each compound dividing the reference dose (RfD) according to *Equations 6–7*. Non-cancer risk for inhalation route could not be performed since the RfD values for C-DBPs compounds are not yet evaluated (Kumari and Gupta, 2018). The sum of HI of all each species forms the HI of each pathway. Then the sum of total HI through all the two pathways was the cumulative non-cancer risk of DBPs. Generally, sum of HI < 1 means low non-carcinogenic risk, and sum of HI ≥ 1 means high non-carcinogenic risk.

$$HI_{inaestion} = CDI_{inaestion \text{ for each specie}} / RfD \quad (\text{Eq.6})$$

$$HI_{dermal} = CDI_{dermal \text{ for each specie}} / RfD \quad (\text{Eq.7})$$

Results and discussion

Water characteristics

During the sampling period, samples were collected from Egirdir Lake and Karaagac Water Source and 10 points from Isparta DS and Kumluca DS. The pH values in water sources were in the range of 7.70-8.54. In Isparta DS and Kumluca DS samples, the pH values of all sampling points vary in the range of 7.12-8.62. The results showed that changes on pH values were quite narrow. When the relationship between pH and DBPs

are determined, it is seen that water sources with high pH value cause more DBPs formation (Hung et al., 2017). The average water temperature measured in the Egirdir Lake and Karaagac were 16.4 °C and 14.7 °C, respectively. The maximum water temperature in Isparta DS is 27 °C, the maximum water temperature in Kumluca DS is 28 °C. pH and temperature parameters complied with the water quality standards set by the “Regulation on Waters Intended for Human Consumption” published by the Ministry of Health of Turkey (Ministry of Health Turkey, 2005).

Table 2. Input parameters in assessment of THMs and HAAs

Parameters	Unit	Value/distribution				Data source	
		Male		Female			
Concentrations of C-DBPs in water (C _w)	mg/L					This study	
Ingestion rate (IR _w)	L/d	2				Pan et al., 2014	
Exposure frequency (EF)	d/y	365				Pan et al., 2014	
Exposure duration (ED)	y	75.6		81		TSI, 2022	
Body weight (BW)	kg	77.4		68.4		TSI, 2022	
Average time (AT)	d	75.6×365		81×365		TSI, 2022	
Skin area (SA)	cm ²	18900		17700		TSI, 2022	
Permeability constant in water (PC)	cm/h	0.16 Trichloromethane (TCM)				Zhang et al., 2018	
		0.18 Bromodichloromethane (BDCM)					
		0.20 Dibromochloromethane (DBCM)					
		0.21 Tribromomethane (TBM)					
Exposure time (ET)	h/day	0.12		0.13			
THM concentrations in the air (C _{air})	mg/L	Model calculations				Little, 1992	
Inhalation rate (IR _a)	m ³ /h	0.84		0.66		Pan et al., 2014	
Slope factors (SF)	(mg/kg/day) ⁻¹		TCM	BDCM	DBCM	TBM	Dobaradaran et al., 2020
		Oral ingestion	0.061	0.062	0.084	0.0079	
		Dermal	0.0305	0.0633	0.14	0.0132	
		Inhalation	0.0805	0.13	0.084	0.00385	
		Oral ingestion	DCAA		TCAA		
		0.05		0.07			
Reference dose (RfD)	mg/kg.d	TCM	1.0×10 ⁻²				
		BDCM	2.0×10 ⁻²				
		DBCM	2.0×10 ⁻²				
		TBM	2.0×10 ⁻²				
		DCAA	4.0×10 ⁻³				
		TCAA	2.0×10 ⁻²				

Among water quality parameters monitored, DOC, SUVA and free chlorine were particularly the most important ones that affect the formation of C-DBPs. The water characterization results showed that natural waters used in the FPs tests covered a wide range of average DOC (0.58 mg/L (Karaagac Water Source) and 3.52 mg/L (Egirdir Lake). However, average DOC numbers were quite different, average values of SUVA₂₅₄ of Egirdir Lake and Karaagac Natural Water are approximately 1.0 L/mg-m (between 0.66-1.73 L/mg-L values). For DS samples, average SUVA values were calculated as 1.21 mg/L (Isparta DS) and 0.79 mg/L (Kumluca DS), respectively. The SUVA is a parameter that can be calculated according to the ratio between UV₂₅₄ and DOC. In the studies conducted, it was stated that the waters with a value of < 1.5-2.0 L/mg-m of SUVA generally contain hydrophilic, non-humic and small molecular

weight NOM fragments (Lee and Park, 2022). The UV absorbance measured at a wavelength of 254 nm generally indicates DOM structures containing aromatic DOM fragments and/or unsaturated carbon-carbon bonds in water (Faixo et al., 2021). Bromide values were below measurable levels in all water sources and DSs (Data not shown). Similar results in terms of bromide levels have been found at surface waters in Turkey (Baytak et al., 2008). Another important parameter measured in DS samples is the residual free chlorine concentration. The lowest and highest residual free chlorine concentrations measured in Isparta DS range between 0.10-1.24 mg/L. The highest free chlorine concentration was measured at Isp 1, the closest sampling point to the disinfection unit, and the 0.10 mg/L free chlorine concentration was measured at Isp 4. As it moves away from the disinfection unit, the residual free chlorine concentration decreases because of reactions with organic matter content and decreases depending on the length of the distribution system. However, this free chlorine level did not change in Kumluca DS. This is because of the low organic matter content of Kumluca DS. Average DOC of Kumluca DS is 0.3 mg/L. Since DOC and SUVA values were low, chlorine demand was low in Kumluca DS. The selected characteristics of water samples are summarized in *Table 3*.

Table 3. Water quality data with annual descriptive statistics (average, minimum, maximum) during 12 months of sampling

Sampling point	pH			Temperature (°C)			Residual free chlorine (mg/L)			DOC (mg/L)			UV absorbance (cm ⁻¹)			SUVA (L/mg-m)		
	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.	Min.	Max.	Ave.
Egirdir L.	7.75	8.54	8.32	8.6	25.0	16.3	NA	NA	NA	2.71	4.02	3.52	0.024	0.048	0.034	0.66	1.40	0.98
Karaagac W.S.	7.70	8.42	8.15	11.4	20.5	14.7	NA	NA	NA	0.37	0.98	0.58	0.003	0.023	0.008	0.47	1.73	1.03
Isparta 1	7.52	8.43	8.15	6.8	26.0	14.9	0.48	1.24	0.77	1.07	3.60	2.25	0.016	0.049	0.027	0.83	2.24	1.28
Isparta 2	7.69	8.47	8.21	8.0	26.0	15.9	0.50	0.92	0.68	1.24	3.44	2.25	0.015	0.039	0.026	0.76	2.02	1.21
Isparta 3	7.63	8.62	8.23	8.1	25.0	16.6	0.15	0.49	0.32	1.44	2.88	2.13	0.012	0.033	0.024	0.74	2.08	1.15
Isparta 4	7.81	8.62	8.21	8.6	23.0	16.8	0.10	0.62	0.23	1.46	3.12	2.11	0.006	0.035	0.024	0.41	2.01	1.15
Isparta 5	7.37	8.46	8.19	6.3	27.0	15.7	0.12	0.61	0.35	1.29	2.98	2.18	0.011	0.041	0.026	0.57	2.17	1.25
Kumluca 1	7.12	8.35	8.08	13.6	28.0	19.0	0.10	0.37	0.19	0.17	0.42	0.25	0.001	0.004	0.002	0.56	1.38	0.88
Kumluca 2	7.41	8.38	8.09	11.9	21.0	16.2	0.10	0.30	0.15	0.23	0.51	0.31	0.001	0.005	0.003	0.40	1.61	0.82
Kumluca 3	7.50	8.50	8.13	11.6	16.0	14.1	0.10	0.33	0.22	0.19	0.43	0.32	0.001	0.005	0.003	0.30	1.39	0.78
Kumluca 4	7.55	8.45	8.13	11.9	19.0	15.4	0.10	0.42	0.18	0.20	0.41	0.30	0.001	0.002	0.002	0.24	1.00	0.64
Kumluca 5	7.60	8.35	8.09	4.0	28.0	18.4	0.10	0.41	0.16	0.19	0.38	0.30	0.001	0.004	0.003	0.37	1.58	0.83

*NA: Not available. No chlorine was applied for source water. Min: minimum, Max: maximum, Ave: average

Formation potential of C-DBPs in low SUVA source waters

The FPs of THMs and HAAs of Egirdir Lake and Karaagac water source are shown in *Table 4*. In both tested water sources, the FPs of THMs and HAAs were in the order of chlorination > ozonation/chlorination > chloramination > ozonation/chloramination > ozonation. The maximum FPs of THMs and HAAs concentrations measured in Egirdir Lake were 120 µg/L and 101 µg/L, respectively. The maximum HAAs and THMs FPs concentrations in Karaagac were 44 µg/L and 26 µg/L, respectively. For all disinfection scenarios, C-DBPs concentrations in Karaagac Natural Water were lower than Egirdir Lake. This is expected since DOC values of Karaagac was 0.58 mg/L and DOC values of Egirdir Lake was 3.52 mg/L with similar SUVA values. Precursors reactivity was quantified by specific C-DBPs yields, or µg of C-DBPs formed per mg of DOC to evaluate formation potential of different water sources. Determination of specific C-DBPs yields is important in terms of comparing water sources based on reactivity. The

highest THM formation of 1 mg DOC in Egirdir Lake and Karaagac water is 37 and 119 µg THM/mg for only chlorination, respectively. Similarly, 1 mg of dissolved organic carbon forms 29 µg HAA/mg DOC, while Karaagac water forms 49 µg HAA/mg DOC. This comparison indicates Egirdir Lake had relatively lower precursors reactivity and Karaagac Natural Water has more potential for C-DBPs formation with lower organic matter content than Egirdir Lake. Trichloromethane (TCM) was the dominant species in both water bodies and the speciation in THMs followed the order: TCM > bromodichloromethane (BDCM) > dibromochloromethane (DBCM) > tribromomethane (TBM).

Table 4. THMs and HAAs formation potentials under different disinfection scenarios for 12 months (µg/L)

Scenario	DBPs FP	NOV	DEC	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT
Chlorination	THM ₄ _E	95	87	73	82	84	120	110	88	95	101	91	76
	THM ₄ _K	30	31	37	28	30	36	37	44	34	36	27	35
	HAA ₉ _E	69	58	84	63	65	76	70	101	76	78	89	73
	HAA ₉ _K	16	17	15	12	16	18	20	18	14	19	19	26
Ozonation/chlorination	THM ₄ _E	46	49	41	39	37	50	45	49	47	44	54	45
	THM ₄ _K	22	21	25	25	27	26	25	30	30	32	18	26
	HAA ₉ _E	35	31	42	30	35	39	37	50	36	42	45	39
	HAA ₉ _K	17	18	16	14	17	19	22	19	17	20	21	22
Chloramination	THM ₄ _E	30	35	34	28	27	32	42	41	34	32	35	34
	THM ₄ _K	21	23	19	10	21	25	28	23	12	25	17	19
	HAA ₉ _E	23	27	26	22	23	25	32	31	26	28	37	32
	HAA ₉ _K	11	12	10	5	11	12	14	12	6	13	11	17
Ozonation/chloramination	THM ₄ _E	15	11	16	18	11	18	13	19	22	13	12	11
	THM ₄ _K	13	10	14	17	13	16	12	17	20	16	9	11
	HAA ₉ _E	12	8	12	14	12	13	10	14	17	14	15	12
	HAA ₉ _K	7	5	8	9	7	8	6	10	11	8	9	7
Ozonation	THM ₄ _E	7	9	5	5	9	8	11	6	6	11	14	7
	THM ₄ _K	2	2	1	5	2	2	2	1	6	2	4	3
	HAA ₉ _E	5	7	4	4	5	6	8	5	5	6	9	10
	HAA ₉ _K	1	1	1	3	1	1	1	1	4	1	3	2

E: Egirdir Lake, K: Karaagac Water Source

The dominant HAAs species were trichloroacetic acid (TCAA) in all disinfection scenarios. In similar previous studies, the dominant HAAs species were dichloroacetic acid (DCAA) and TCAA in most of the tested waters in Turkey (Ates et al., 2007). The minimum C-DBPs FP was obtained after ozonation only and the bromide levels were below the detection limit. Similar to our study, it has been reported that the average THMs formation decreased to 10 µg/L after ozonation alone (Vedugo et al., 2020). Pre-ozonation reduces C-DBPs formation and similar results were reported in other studies (Uyak et al., 2014; Meite et al., 2015; Krasner et al., 2016b; Vedugo et al., 2020). The decrease in C-DBPs formation after ozonation/pre-ozonation has been attributed that when pre-ozonation is performed, natural organic materials break down the hydrophobic components into hydrophilic components in high SUVA waters (Vedugo et al., 2020). The results showed that THMs and HAAs formation in chloramination was about 3 times lower than chlorination. Chloramination resulted in lower formation C-DBPs, attributing that the oxidation potential of chloramine is lower than chlorine

(Sfynia et al., 2020). Goslan et al. (2009) found that THMs formation with chlorine is 2 times higher than with chloramine. Also, earlier studies reported HAAs after chlorination were 3 times higher than after chloramination (Goslan et al., 2009; Behbahami et al., 2018; Bougeard et al., 2020). Brominated THMs concentrations were considerably lower than chlorinated ones since the bromide concentration was less than 10 µg/L for both water sources. However, the highest brominated THMs concentrations were detected only after ozonation. One-year-long monitoring was performed to evaluate seasonal changes of C-DBPs formation potential the presence of typical drinking water disinfectants. The C-DBPs formation potential for Egirdir Lake varied with changes in seasons. The highest C-DBPs formation potential concentration was determined for both THMs and HAAs in spring and summer months, which could be attributed to the higher concentrations of dissolved organic matter and temperature at that time. No clear seasonality in C-DBPs formation potential for Karaagac Natural Water was observed.

Occurrence of C-DBPs in distribution systems

The seasonal variations of THMs in Isparta DS sampling points are presented in *Figure 1*. The highest THMs average was 41 µg/L in summer and the lowest THMs was 31 µg/L in winter in Isparta DS. A similar temporal trend has been reported in several previous studies (Rodriguez et al., 2003; Scheili et al., 2015). As expected, the total concentrations of THMs in the DSs were lower than those produced in the FPs tests which are attributed to the high disinfectant dose and the long contact time in the FPs tests. Increased THMs concentrations in summer are explained with higher water temperature and higher DOC concentration. In addition, since the sustainability of microbial water quality is more difficult in hot seasons than in cold seasons, higher chlorine doses are used in DSs and a significant increase in free chlorine demand and higher THMs concentrations especially in summer and autumn seasons observed (Rodriguez et al., 2011; Sfynia et al., 2022). Rodriguez et al. (2003) found a good correlation between residual chlorine, temperature and THMs formation in summers. The seasonal variation of THMs in Kumluca distribution points are presented in *Figure 2*. The highest THMs concentrations detected in Kumluca DS was 11 µg/L and the lowest THMs concentration was 3 µg/L. The average THMs concentrations calculated at Kumluca DS sampling points are 7 µg/L. As expected in the Kumluca DS, less THMs formation was observed than Isparta DS. This is explained with the lower UV absorbance and DOC values of Kumluca DS compared to Isparta DS. TCM accounted for average 73% of the THMs in all samples, implying that TCM was dominant species of THMs in both DSs, which is consistent with other similar studies (Summerhayes et al., 2011; Duan et al., 2020). A meaningful seasonal variation could not find in Kumluca DS. The slightly higher THM formation was observed in winter for Kumluca DS. In the Kumluca DS. The seasonal variation of HAAs in Isparta distribution points are presented in *Figure 3*. In Isparta DS, the highest HAAs concentration was 29 µg/L in summer and the lowest HAAs concentration was 18 µg/L in winter. The mean HAA₉ concentrations obtained in the spring and summer seasons were 23 and 22 µg/L, respectively. Rodriguez et al. (2004) found that HAAs concentration was 4 times higher in summer than in winter. The main mechanism responsible for the reduction of HAAs concentration throughout the distribution system is thought to be the biodegradation mechanism produced by the biofilm layer resulting from reduced chlorine concentration (Uyak et al., 2014; Behbahami et al., 2018). The

most dominant HAAs species in the Isparta DS were TCAA and DCAA. Similarly, it was reported that the dominant HAAs species are TCAA or DCAA when surface waters were used as water sources and chlorine was disinfectant (Rodriguez et al., 2004; Muellner et al., 2007; Bougeard et al., 2020). In present study, other HAA species were low due to the very low bromine level (below detection levels). In most studies, while CAA can be measured in many surface waters sources, bromoacetic acid (BAA), dibromoacetic acid (DBAA), dibromochloroacetic acid (DBCAA), tribromoacetic acid (TBAA) could not be measured in chlorine use either in surface water sources or groundwater sources in low bromide levels (Alomirah et al., 2020). The seasonal variation of HAAs in Kumluca distribution points are presented in *Figure 4*. The highest HAAs value measured in Kumluca DS was 8 µg/L at KUM 1 and the lowest HAA value was 2 µg/L at KUM 2. Low HAA concentrations were expected due to low DOC concentrations and low initial chlorine dose.

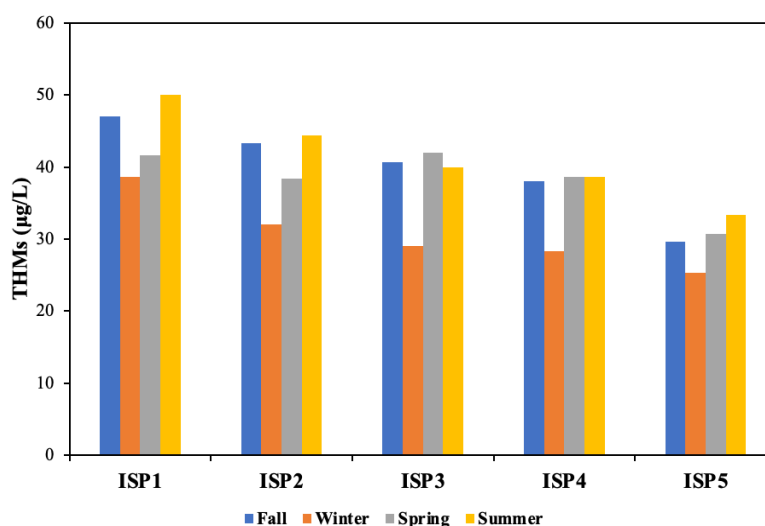


Figure 1. Seasonal average concentrations of THMs in Isparta distribution system sampling points. (Sampling point 1 is the closest while 5 is the farthest sampling point)

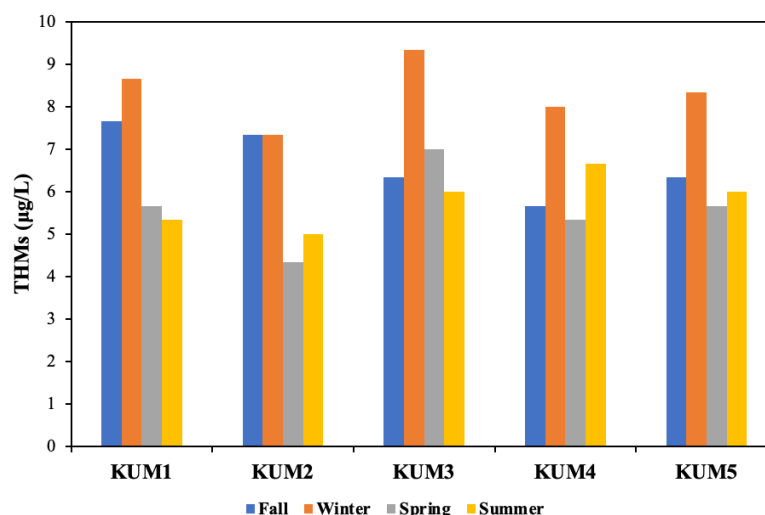


Figure 2. Seasonal average concentrations of THMs in Kumluca distribution system sampling points. (Sampling point 1 is the closest while 5 is the farthest sampling point)

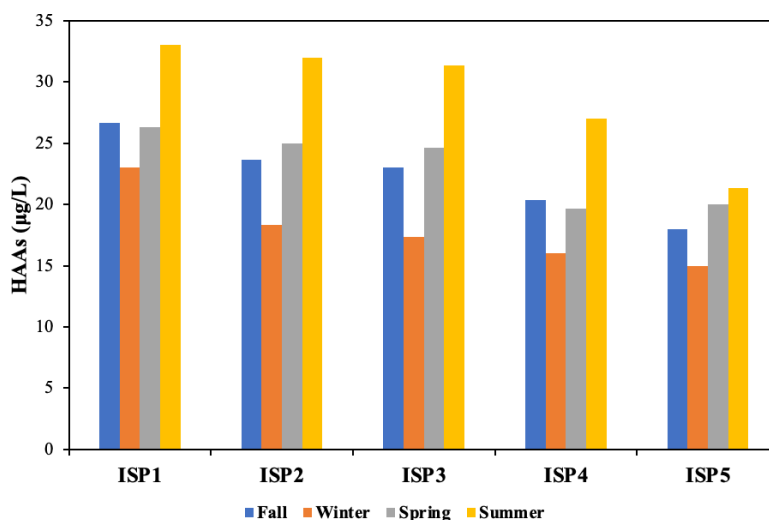


Figure 3. Seasonal average concentrations of HAAs in Isparta distribution points. (Sampling point 1 is the closest while 5 is the farthest sampling point)

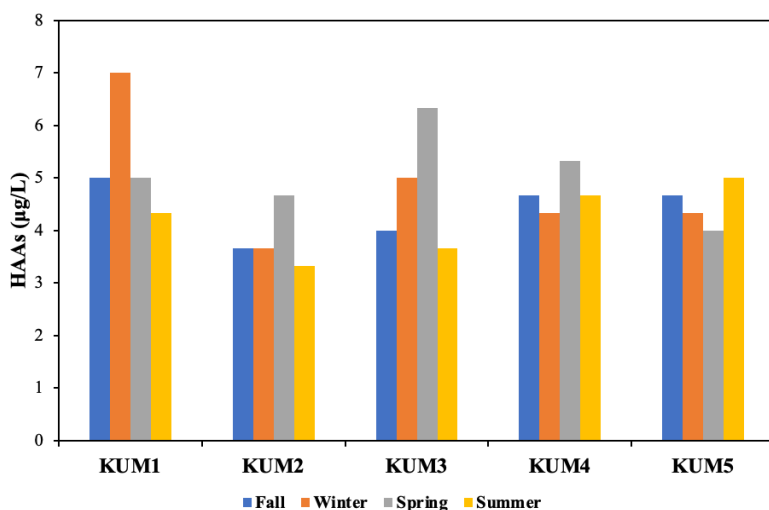


Figure 4. Seasonal average concentrations of HAAs in Kumluca distribution points (Sampling point 1 is the closest while 5 is the farthest sampling point)

Correlations between surrogate parameters and DBPs

Analyses of C-DBPs in water treatment plants and DSs are expensive, complicated and time-consuming, and require specialized laboratories and know-how. A key aim of many studies has been to find a surrogate readily measurable water quality parameters to predict C-DBP formation. Among the water quality parameters, DOC, UV₂₅₄, SUVA, and differential ultraviolet absorbance (DUVA) are the most associated surrogate parameters (Li et al., 2017). At this stage of the study, data analysis was performed with surrogate of the water quality parameters (such as pH, temperature, free chlorine, DOC, UV₂₅₄, SUVA) with THMs and HAAs in DSs. Pearson's correlation matrix was used to perform data analysis. *Table 5* present the correlation coefficients among total THMs and its species with surrogate parameters. Although strong correlations were reported between THMs formation with DOC, SUVA, UV₂₅₄,

and differential UV absorbance in the DBPs literature, THMs and its species did not correlate well with almost all parameters. THMs were low correlations with DOC and free chlorine with 0.26 and 0.35 correlations coefficients, respectively. Especially SUVA and UV did not correlate well with the formation and speciation of THMs and HAAs. The results may explain that low- or non-UV-absorbing NOM moieties play important roles in the formation of C-DBPs in waters with low SUVA waters. Fu et al. (2017) found low correlations ($r < 0.25$) between DBPs types and water quality parameters. *Table 6* present the correlation coefficients among total HAAs and its species with surrogate parameters. Like THMs results, low correlations ($r < 0.3$) were found between HAAs types and water quality parameters. Studies in the literature reported that Pearson correlation (P) values for the DOC and the chlorine dosages are 0.786 and 0.865 for HAAFPs, respectively for high SUVA waters (Alver and Kılıc, 2018). Ates et al. (2007) reported that no strong correlations between SUVA and HAAs formations were found in low SUVA waters. These different trends showed that the effectiveness of surrogate parameters in correlating with C-DBPs formation is water specific. Kumluca water distribution systems, Pearson Correlation Matrix between THMs and parameters did not yield significant results (Data not shown). For the Kumluca water distribution system, this situation can be explained by the very low total organic concentration in groundwater (Kitis et al., 2010). According to the Pearson correlation matrix in the Kumluca water DS, the lower correlation between THMs and free chlorine can be explained by the fact that the DS length is quite short, and the chlorine demand of the water is very low. The reason of poor correlation between chlorine and THMs formation is because of relatively little organic matter in the sample.

Table 5. The Pearson's correlations matrices of surrogate parameters and THMs in Isparta DS

	THM	TCM	BDCM	DBCM	TBM	pH	Temp.	Free Cl.	DOC	UV	SUVA
THM	1										
TCM	0.68	1									
BDCM	0.30	-0.34	1								
DBCM	0.47	0.54	-0.27	1							
TBM	-0.14	-0.59	0.03	-0.13	1						
pH	-0.02	-0.33	0.50	-0.17	0.06	1					
Free Cl.	0.35	0.17	0.17	0.05	0.02	-0.03	-0.15	1			
DOC	0.26	-0.20	0.58	0.07	0.14	0.39	0.42	-0.01	1		
UV	-0.15	-0.31	-0.02	-0.05	0.42	0.03	-0.10	0.15	0.18	1	
SUVA	-0.33	-0.13	-0.37	-0.12	0.19	-0.15	-0.37	0.13	-0.47	0.73	1

The relationship between THM and HAA concentrations detected in the Isparta DS and the measured water quality parameters was evaluated with the Pearson correlation matrix is statistically significant ($\alpha < 0.05$). While a positive correlation was found between DOC - free chlorine and THM formation, a negative correlation was found between SUVA - UV and THM formation. Regression analysis was not statistically significant ($\alpha > 0.05$) for THM and HAA in the Kumluca distribution system.

Table 6. The Pearson's correlations matrices of surrogate parameters and HAAs in Isparta DS

	HAA	CAA	BAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA	pH	Temp.	Free Cl.	DOC	UV	SUVA
HAA	1															
CAA	-0.25	1														
TCAA	0.53	0.08	1													
DCAA	0.45	-0.23	-0.27	1												
BCAA	0.13	-0.27	-0.37	0.04	1											
BAA	-0.02	-0.19	-0.42	-0.12	0.88	1										
DBAA	-0.40	0.01	-0.21	-0.20	-0.15	-0.14	1									
BDCAA	-0.01	-0.23	-0.18	0.06	0.10	0.16	0.08	1								
DBCAA	-0.10	0.06	-0.23	0.19	-0.05	-0.12	0.10	-0.06	1							
TBAA	0.19	-0.29	-0.38	0.41	-0.11	-0.20	0.10	0.02	0.18	1						
pH	-0.23	0.16	-0.29	0.00	0.26	0.25	-0.05	0.03	0.03	-0.14	1					
Free Cl.	0.30	-0.07	0.10	0.00	0.32	0.13	0.12	-0.02	-0.02	0.12	-0.03	-0.15	1			
DOC	0.12	-0.02	0.02	0.05	0.32	0.27	-0.39	-0.11	0.12	-0.22	0.39	0.42	-0.01	1		
UV	-0.19	0.25	0.09	-0.14	-0.10	-0.12	0.21	-0.11	0.07	-0.28	0.03	-0.10	0.15	0.18	1	
SUVA	-0.31	0.17	-0.02	-0.15	-0.23	-0.23	0.52	0.01	0.00	-0.12	-0.15	-0.37	0.13	-0.47	0.73	1

Cancer risk and non-cancer risk assessment

Figure 5 shows the lifetime cancer risk of THMs for males and females through different exposure pathways in Isparta DS. The highest values of the total cumulative cancer risk posed by exposure to THMs for males and females in Isparta DS were 8.3E-05 and 8.1E-05, respectively. The average values of total lifetime cancer risks for males were 1.77% higher than those for females. The average lifetime total cancer risk was 60–70 times higher than negligible cancer risk (1.0E-06). The lifetime cancer risk for total THMs through each pathway in both males and females exceeds 1.0E-06, the negligible cancer risk level recommended by USEPA. Inhalation exposure made the most contribution (average 59%) to the total lifetime risk, followed by ingestion (average 29%), whereas dermal absorption showed the least contribution (average 12%) for both males and females. Similarly, the inhalation route was the most prominent exposure pathway to lifetime cancer risk in the studies of multi-pathway risk assessment for THMs (Siddique et al., 2015; Kujlu et al., 2020). However, other studies found that ingestion was the main contributor pathway (Uyak, 2006; Kumari et al., 2015; Mishaqa et al., 2022). The average total cancer risk for HAAs for males and females was calculated as 3.3E-05 and 4.4E-05 respectively (Data not shown). TCAA was the compound contributing the most (80%) to the total CDI of HAAs, followed by DCAA (20%) though ingestion. The average values of the total lifetime cancer risk posed by exposure to THMs for males and females in Kumluca DS were 1.4E-05 and 1.2E-05, respectively. The average values of the total lifetime cancer risk posed by exposure to HAAs for males and females in Kumluca DS were 7.6E-06 and 7.6E-06, respectively (data not shown).

Table 7 shows the average specific cancer risks for each THM species through different pathways for Isparta DS. While BDCM made the highest percentage contribution of the total risk through ingestion, TCM is the main contribution to the total risk through both inhalation and dermal adsorption. These results are explained by the product of the concentration of individual THMs and its SF of exposure pathways (Kumari et al., 2015; Mishaqa et al., 2022). The total cancer risk through ingestion for THMs followed the order: BDCM (61%) > TCM (23%) > DBCM (14%) > TBM (2%). A similar trend of higher BDCM percent contribution through ingestion has been

observed in previous studies (Lee et al., 2004; Uyak et al., 2006). TCM made the highest percentage contribution (52%) to average lifetime cancer risk through dermal exposure, followed by BDCM (23%), DBCM (14%), and TBM (2%). The percentage contribution of each THMs to the cancer risk though inhalation followed the pattern: TCM (70%) > BDCM (26%) > DBCM (3%) > TBM (1%). In several studies, it is shown that TCM was the major contributor for inhalation route since TCM has a lower boiling point than other THMs (Uyak et al., 2006; Wang et al., 2019).

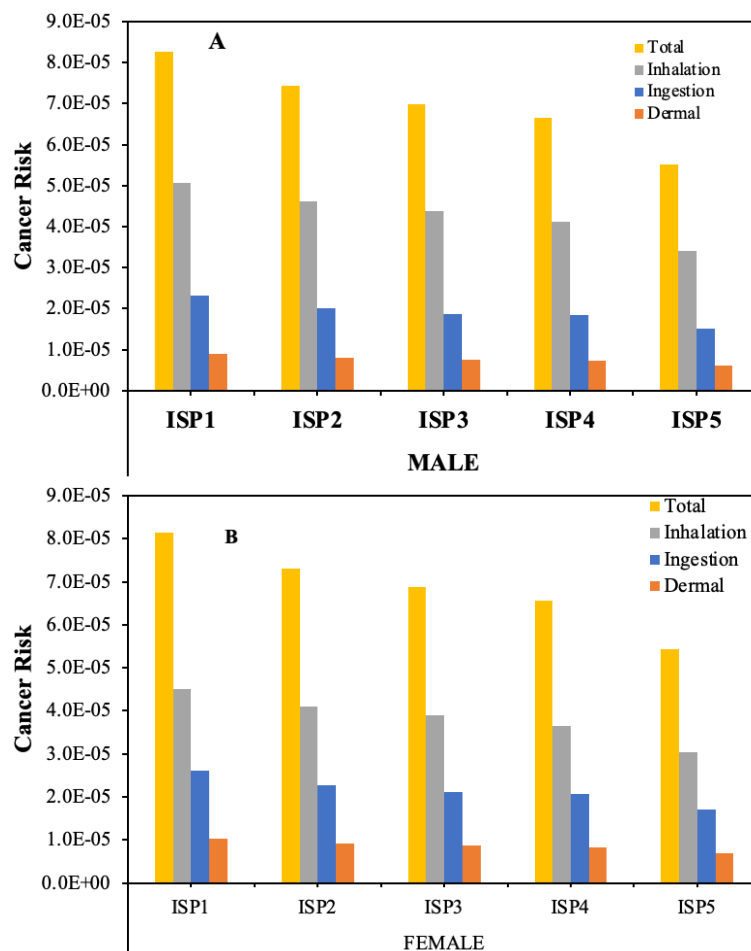


Figure 5. Lifetime cancer risk of THMs through all exposure routes in males (A) and females (B) for Isparta DS

For the non-carcinogenic risk, the total HI of C-DBPs through ingestion (A) and dermal (B) for Isparta DS are provided in Figure 6. The total HI of C-DBPs from all exposure routes was ranged from 0.18 to 0.25. Dermal exposure resulted in slightly HI than ingestion route. The major HI of THMs and HAAs via dermal exposure was the HI of TCAA. Of the four THMs compounds, TCM had the highest HI value for both dermal and ingestion routes. HI values of THMs species followed an order of TCM > DBCM > TBM > DCBM for both dermal and ingestion routes. For HAA species, TCAA had a higher HI value than DCAA. In conclusion, the non-carcinogenic risk of C-DBPs in the distribution system was less than 1, which was in the allowable range for C-DBPs. Similar results were reported in the studies from Kumari et al.

(2015) and Wang et al. (2019). For Kumluca HI of C-DBPs through dermal and ingestion exposure were 0.033, meaning they were in the allowable range.

Table 7. Specific cancer risks for each THM species for Isparta DS

		Male				Female			
		TCM	BDCM	DBC	TBM	TCM	BDCM	DBC	TBM
Ingestion	ISP1	5E-06	1E-05	3E-06	4E-07	6E-06	2E-05	4E-06	5E-07
	ISP2	5E-06	1E-05	3E-06	3E-07	5E-06	1E-05	3E-06	3E-07
	ISP3	5E-06	1E-05	3E-06	3E-07	5E-06	1E-05	3E-06	3E-07
	ISP4	4E-06	1E-05	3E-06	3E-07	5E-06	1E-05	3E-06	4E-07
	ISP5	4E-06	9E-06	2E-06	3E-07	4E-06	1E-05	3E-06	3E-07
Dermal	ISP1	5E-06	3E-06	1E-06	2E-07	5E-06	3E-06	1E-06	2E-07
	ISP2	4E-06	3E-06	1E-06	1E-07	5E-06	3E-06	1E-06	1E-07
	ISP3	4E-06	2E-06	1E-06	1E-07	5E-06	3E-06	1E-06	1E-07
	ISP4	4E-06	2E-06	1E-06	1E-07	4E-06	3E-06	1E-06	2E-07
	ISP5	3E-06	2E-06	9E-07	1E-07	4E-06	2E-06	1E-06	1E-07
Inhalation	ISP1	4E-05	1E-05	1E-06	7E-08	3E-05	1E-05	1E-06	6E-08
	ISP2	3E-05	1E-05	1E-06	5E-08	3E-05	1E-05	1E-06	4E-08
	ISP3	3E-05	1E-05	1E-06	4E-08	3E-05	1E-05	1E-06	4E-08
	ISP4	3E-05	1E-05	1E-06	5E-08	3E-05	1E-05	1E-06	5E-08
	ISP5	2E-05	9E-06	1E-06	5E-08	2E-05	8E-06	8E-07	5E-08

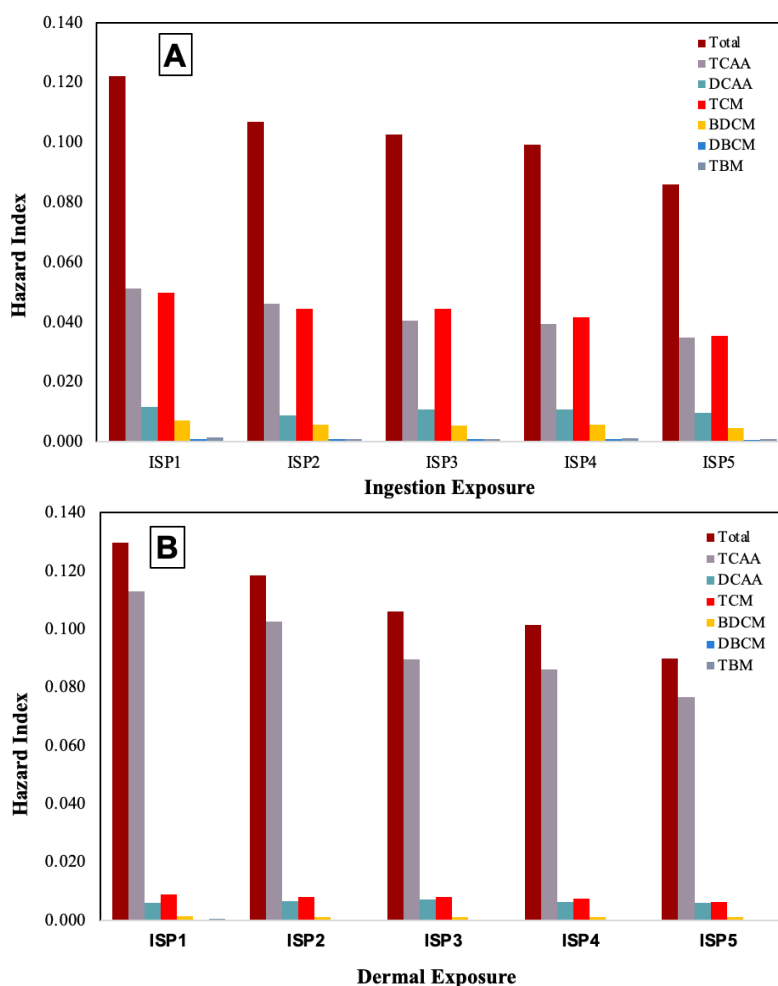


Figure 6. Lifetime hazard index of C-DBPs through ingestion (A) and dermal exposure (B) for Isparta DS

Conclusions

In this study, a systematic investigation was conducted for tracking spatio-temporal occurrence and formation potential of C-DBPs in low SUVA water sources. Also one of objectives of this study was to evaluate the lifetime cancer risk and the hazard index caused by THMs and HAAs. Results of FPs tests showed that chlorination produced the highest THMs and HAAs followed by in the order of ozonation/chlorination, ozonation/chlorination, chloramination, ozonation/chloramination and ozonation. Pre-ozonation may be recommended for the drinking water treatment plants, in consideration of trade-off control of C-DBPs in case of low bromide ion levels. Disinfectants can react not only with NOM and other organic pollutants but also with inorganic compounds form DBPs. Therefore, greater variety of DBPs precursors may form greater quantity and variety of DBPs. Further studies are required to explain and understand better the underlying chemical reaction with precursors and disinfectants in low SUVA waters. A one-year-long monitoring was conducted to evaluate the concentrations of THMs and HAAs in the presence of chlorine for DSs which are low SUVA waters. According to Pearson correlation coefficients, the C-DBPs formation prediction capability of DOC, UV and SUVA were weak in waters with low SUVA waters. Overall, it is apparent that C-DBPs formation in low-SUVA waters may not be estimated by simple surrogate parameters. Although the non-cancer risk of C-DBPs was below permissible recommended levels, the average lifetime carcinogenic risk levels for THMs and HAAs in Isparta DS were $6.9E-05$ and $5.8E-05$, respectively, which is higher than negligible risk level ($1.0E-06$). The results of THMs cancer risk reveal that the ingestion had the highest impact on lifetime cancer risk. Males were found to be at a slightly greater risk of cancer, and the values was found relatively close. The non-carcinogenic hazard index of THMs via dermal was found higher than ingestion. The study would benefit the water management authority and health departments to control the level of C-DBPs. Besides C-DBPs, future studies must focus on improving our understanding of emerging DBPs formation in low SUVA waters (both laboratory-scale and full-scale studies).

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