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ORIGINAL PAPER

Seasonal and spatial variation in total trihalomethane formation potential in groundwater in Tulkarm and Hebron, Palestine

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Abstract

Water disinfection using processes such as chlorination is required to kill bacteria and harmful biological components. During chlorination, organic components in water react with chlorine, forming harmful disinfection by-products such as trihalomethanes (THMs). These compounds are very harmful to humans, animals, and plants. Thus, the concentration of these substances in groundwater as well as the seasonal variation in this concentration are of immense interest to scientists. A headspace method was used to analyze trihalomethanes (THMs) using an Agilent 6890N GC/MS. Five-milliliter water samples were employed in this analysis. Separation was performed on a J&W-VRX column. A selected ion monitoring (SIM) mode that complied with US EPA method no. 501 was developed for the detection of four THM species. Quantification and method validation were performed using external standard calibration. The total trihalomethane formation potentials (TTHMFPs) in four groundwater wells in the summer and the winter were found to be below the maximum limits specified by environmental agencies. Seasonal variations were more pronounced for the formation of chloroform (CF), which was the dominant THM species formed. The fraction of the TTHMFP that was due to CF increased in the winter in groundwater samples from the Anabta (2), Anabta (3), and Al Rehya wells, whereas the fraction of the TTHMFP that was due to CF was almost the same in summer (43.2%) and in winter (40.3%) in the groundwater samples from the Al Fawar well. These findings are important for the appropriate regulation of THM levels and for achieving a better understanding of environmental public health and epidemiological issues concerning disinfection by-products in Palestine.

Keywords Seasonal · Spatial · Groundwater wells · Trihalomethanes (THMs) · Formation potential (FP)

Introduction

The chlorination of drinking water to prevent waterborne diseases produces disinfection by-products that can cause negative health effects in humans (Baytak et al. 2008; Calderon 2000). Organic precursors and bromide in water react with chlorine, producing many types of halogenated organic compounds that are considered disinfection by-products. These by-products are mainly trihalomethanes (THMs), including chloroform (CF), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform (TBM) (Richardson 2011; Richardson et al. 2007). Several factors, including the physical and chemical properties of the groundwater (i.e., water pH and temperature, type and amount of organic matter present, bromide concentration, disinfectant dose and type, and contact time), affect the formation of disinfection by-products (Liang and Singer 2003). The amount and type of natural organic matter (NOM) and the bromide concentration are the parameters that most

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strongly influence the formation and speciation of disinfection by-products (Liang and Singer 2003; Kanan and Karanfil 2011). The levels and properties of natural organic matter (NOM) vary seasonally and spatially in groundwater in accordance with fluctuations in recharge rates and amounts (Liang and Singer 2003).

Groundwater is the only source of drinking water in the West Bank in Palestine. Drinking water of variable quality is received by consumers after chlorination throughout the year. Some studies on the seasonal variation in the formation of THMs due to the chlorination of surface water show that THM levels are higher in the summer than in the winter due to the increased organic matter in surface water sources during the summer (Williams et al. 1998; Rodriguez and Sérodes 2001; Rodriguez et al. 2004). Ates et al. (2007) have reported increased formation during the winter. There are, however, no general trends in the seasonal and spatial variations in THM formation potential, implying that the type, origin, and amount of the NOM in the groundwater affect the reactivity of the NOM and the formation of THMs (Matilainen et al. 2011; Qurie et al. 2018).

In Palestine, there are significant differences in weather and rainfall patterns between the north and south. These variations are likely to affect THM formation and speciation. It is important to understand temporal and spatial differences in THM formation as they could have significant implications for both regulatory and epidemiological issues. This study investigated the seasonal (temporal) and spatial variations in the total trihalomethane formation potential (TTHMFP) in drinking water samples collected from four groundwater sources in the north (Tulkarm) and the south (Hebron) of the West Bank in Palestine (Fig. 1).

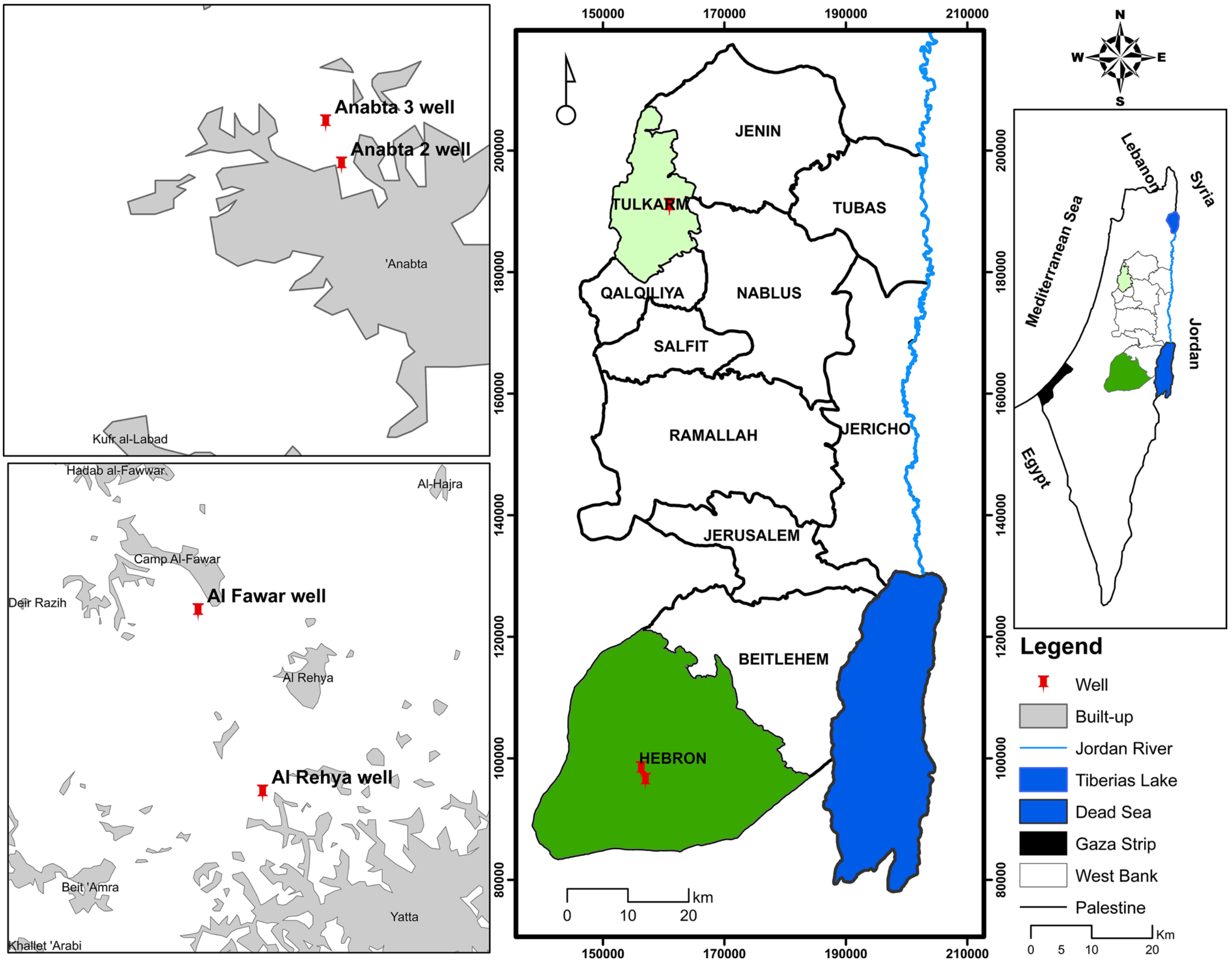

Fig. 1 The study area (Tulkarm and Hebron, West Bank, Palestine), showing the locations of the groundwater wells from which samples were obtained for this study

Materials and methods

Sampling

Groundwater samples for TTHMFP analysis were collected from two districts in the north and the south of the West Bank in Palestine (Fig. 1). They were collected from two wells (Anabta 2 and Anabta 3) in Tulkarm and two wells (Al Fawar and Al Rehya) in Hebron. Tulkarm is located in the northwestern part of the West Bank, very close to the coastal plain, 15 km east of the Mediterranean Sea. The climate in Tulkarm is subtropical, and winter is the rainy season. The average temperature during the winter ranges from 8 to 16 °C, whereas it ranges from 17 to 30 °C during the summer (ARIJ 1996). The Tulkarm area lies on the western slopes of the West Bank, with plains to the west and mountainous terrain to the east. Hebron is in the southern part of the West Bank. It is an arid to semi-arid area, with the aridity increasing towards the desert in the south. The monthly average temperature in Hebron is 7 °C in the winter and 21 °C in the summer. The minimum temperature is about – 3 °C in January and the maximum is about 40 °C in August. Most of the rain falls during the period from December through February, although there may be rain during other periods of the winter season (ARIJ 1995, 1996).

Summer and the winter samples were taken during August 2015 and January 2016, respectively, from the four groundwater wells. The samples were collected before the chlorination points of each groundwater well in 3 L amber glass bottles and were transported to the Chemical and Biological Analytical Center at Al-Quds University in an ice box at 4 °C. Formation potential tests and other analyses were conducted within 24 h of sampling. Relevant details of the wells sampled to determine the TTHMFP are summarized in Table 1.

Reagents and glassware

All glassware were scrupulously cleaned with tap water and a detergent. They were then rinsed three times with distilled water and with dilute (1% solution) hydrochloric acid (ACS reagent, cat. no. NC-5844) three times, before finally being rinsed with deionized distilled water. The glassware were dried at 80 °C in an oven to avoid any contamination and dust before use. Amber glass reagent bottles (135 mL) with screw caps were used for the chlorine demand test. Amber glass reagent bottles (135 mL) with screw caps were employed to chlorinate samples. Glass vials (10 mL) with Teflon-lined septa caps were used to determine the trihalomethanes (THMs) in the water samples. The reagent water used in the experiments was deionized and distilled water produced with a Millipore water purification system. 1 N sodium hydroxide was prepared by dissolving 4 g of analytical grade sodium hydroxide (ACS) (Sigma, cat. no. 30620) in 100 mL of deionized distilled water. *N*,*N*-diethyl-*p*-phenylenediamine (cat. no. 21055-69) free chlorine powder pillow kits for 10 mL samples were used. Sodium hydroxide and phosphate buffer solutions (0.2 M NaH_2PO_4 and 0.2 M NaOH) were used to maintain the pH during the THM formation test. Ascorbic acid (L(+)-ascorbic acid, ACS reagent, cat. no. 401471000; 10 mg for a 10 mL sample) was used as a quenching agent to stop the chlorine reaction before measuring the THMs. A HACH model NI-8 ammonia nitrogen test kit (224100) was used for quantitative ammonia analysis.

Table 1 Depths and locations of the groundwater wells in Tulkarm and Hebron that were sampled in this work (PWA 2012)

District	Well	Coordinates		Depth (M)
		X	*Y*	
Tulkarm	Anabta (2)	190,650	160,970	200
	Anabta (3)	190,400	161,100	150
Hebron	Al Fawar	98,110	156,320	150
	Al Rehya	96,200	157,000	495

Total trihalomethane formation potential (TTHMFP) experiments and THM analysis

The groundwater samples were transferred to 135 mL amber glass bottles, chlorinated to maintain excess residual chlorine, incubated at 25 °C, and kept in the dark for 1, 2, 4, 8, 24, 48, 72, 96, and 120 h. At the end of each incubation period, the samples were quenched using ascorbic acid to prevent further formation of THMs. The pH was adjusted to 8 ± 0.3 using NaOH and HCl. Each 5 mL aliquot of treated groundwater was transferred into a 10 mL headspace vial, which was immediately sealed with a stainless steel screw cap with a PTFE-lined septum. The vials were statically incubated at 95 °C for 10 min in a COMPIPAL autosampler (CTC Analytics AG, Switzerland). A 1 mL aliquot of the headspace gas was subsequently withdrawn and injected into an Agilent 6890N GC combined with an Agilent 5973 MS instrument. Separation was performed on a Varian Factor Four capillary column (VF-5 ms, 30 m, 0.25 mm, 0.25 µm).

The column oven temperature was held at 35 °C for 5 min and then ramped to 60 °C at 10 °C/min, before it was finally ramped to 200 °C at 25 °C/min. Injections were made in the pulsed split mode (split ratio 10 after 0.05 min of injection) with the injector temperature at 220 °C. The transfer line and ion source temperatures were maintained at 280 and 230 °C, respectively. A selected ion monitoring (SIM) mode was developed for four compounds (CF, BDCM, CDBM, and BF) according to US EPA method 501. Quantification of the compounds and method validation were performed with calibration using external standards. Calibration curves in the concentration range from 2 to 100 mg/L were prepared using standard solutions (Restek, catalog # 30211).

Results and discussion

Chemical and physical characteristics of the groundwater samples

Chemical and physical parameters of all the groundwater samples were determined and are shown in Table 2. The temperature ranged from 15 to 21 °C in the summer and from 14.5 to 16.5 °C in the winter. These groundwater temperatures in the summer and the winter are within maximum allowable temperatures according to Palestinian standards (25 °C) and the relevant WHO standard (PWA 2012; WHO 2011). The pH of the groundwater samples varied from 7.1 to 7.7 in both the summer and the winter. These pH values are typical for the area, and are influenced by the carbonate rocks—limestone ($CaCO_3$) and dolomite ($MgCO_3$)—present in the Tulkarm and Hebron governorates (Scarpa et al. 1998). Ammonia was the most reduced inorganic form of nitrogen present in the water samples. It occurred as dissolved ammonia (NH_3) and ammonium (NH_4^+). An ammonia nitrogen test kit was used to analyze the level of ammonia in the groundwater samples. Natural water typically has an ammonia concentration of less than 0.2 mg/L according to the WHO (2011). The ammonia concentrations in the Anabta (2) and Anabta (3) samples were 0.43 mg/L and 0.45 mg/L, respectively, which are lower than the maximum allowable concentration (0.5 mg/L) according to the relevant Palestinian standard (PWA 2012). However, the ammonia concentrations in the Al Fawar and Al Rehya samples were 0.51 mg/L and 1.12 mg/L, respectively; both of these values exceed the maximum allowable concentration of ammonia according to the Palestinian standard (PWA 2012), which may indicate the presence of fresh sewage pollution or animal waste contamination.

Seasonal variation in trihalomethane formation potential

The TTHMFPs in the four groundwater samples were below the maximum levels proposed by WHO (100 µg/L) and USEPA (80 µg/L) in both the summer and the winter (Hoen et al. 2004). However, the concentrations of both bromodichloromethane and bromoform in the four groundwater samples exceeded the USEPA MCLs for these THMs (zero) (Kavlock et al. 1996). In this study, significant seasonal variation in the TTHMFP was observed. TTHM formed at a low rate during the first two days of incubation of the four summer water samples. However, TTHM (mainly CF) formed at a higher rate during the first 8 h of incubation of the samples collected in the winter from Anabta (2), Anabta (3), and Al Fawar. That said, the TTHMFP was low during the first two days in the sample collected from Al Rehya.

Such seasonal variations in the formation and occurrence of THMs have been reported previously, and occur because the characteristics and composition of organic precursors in the summer differ from those of the precursors during the winter (Brown et al. 2011). The TTHMFP in the winter samples was higher than that in the summer samples collected from three groundwater wells (Anabta (2), Al Fawar, and Al Rehya). The seasonal variation was even more obvious for the formation of CF. In the summer samples, CF formation corresponded to 29.2%, 41%, and 54.6% of the TTHMFP after five days in chlorinated groundwater water samples from Anabta (2), Anabta (3), and Al Rehya, respectively. The fraction of the TTHMFP that was due to CF was even higher in the winter samples: 48.3%, 54.8%, and 62.3% in samples from the Anabta (2), Anabta (3), and Al Rehya wells, respectively. However, the fraction of the TTHMFP that was due to CF in the Al Fawar well samples showed little seasonal variation (CF was 43.2% and 40.3% of the TTHMFP in the summer and the winter, respectively), although the formation rate during the first 8 h in the winter samples was higher than that in the summer samples from the Al Fawar well.

Table 2 Physical and chemical characteristics of the groundwater samples obtained in this work

Well sampled	Season	Temp (°C)	pH	EC (µs/cm)	TDS (mg/L)	Ammonia (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)
Anabta (2)	Summer	15.5 ± 0.7	7.2 ± 0.0	1040 ± 85	487.5 ± 3	0.43 ± 0.02	0.49 ± 0.02	0.39 ± 0.07
	Winter	14.5 ± 0.7	7.3 ± 0.0	985 ± 7	495 ± 7			
Anabta (3)	Summer	15 ± 0.0	7.1 ± 0.0	835 ± 7	420 ± 14	0.45 ± 0.07	0.32 ± 0.02	0.29 ± 0.01
	Winter	14.5 ± 0.7	7.3 ± 0.1	730 ± 14	345 ± 7			
Al Fawar	Summer	18.5 ± 0.7	7.2 ± 0.2	1115 ± 69	552.5 ± 31	0.51 ± 0.01	0.49 ± 0.01	0.40 ± 0.00
	Winter	15.5 ± 0.7	7.3 ± 0.1	865 ± 7	437.5 ± 10			
Al Rehya	Summer	21 ± 0.0	7.7 ± 0.1	695 ± 7	345 ± 7	1.12 ± 0.02	1.04 ± 0.05	0.89 ± 0.01
	Winter	16.5 ± 0.7	7.6 ± 1.0	555 ± 7	288.5 ± 2			

Taking only the samples from Tulkarm into account, the dominant THM species present after 5 days (120 h) of incubation after chlorination during both the winter and the summer was CF. The fraction of the TTHMFP that was due to CF was 29.2% in the summer samples and 48.3% in the winter samples (Fig. 2a and b). This increase in the formation of CF during the winter may be due to the increased fresh organic matter in groundwater wells during this period, which increases the formation of THMs. The increase in organic matter is most likely due to the higher groundwater recharge rate during the winter.

When we only considered the samples collected from wells in Hebron (Al Fawar and Al Rehya), CF was again found to be the most abundant species formed. More CF was formed in the winter samples than in the summer samples (Fig. 2a and b), and it mainly formed during the initial period of incubation, as more fresh and reactive organic matter were available due to rainfall and groundwater recharge.

Other studies of surface water samples have shown that the TTHMFP is higher in the summer due to the effect of higher temperatures, which enhance the formation of THM (Rodriguez and Sérodes 2001). Experiments conducted on the formation potential of THMs showed that total THM was higher in the winter samples than in the summer samples (Fig. 3a and b), and that THM formation occurred mainly during the first 8 h of incubation (although it increased in Anabta (3) well samples after 48 h of incubation).

THM formation was greater during the winter than during the summer in the samples from wells in Hebron (Al Fawar and Al Rehya), especially during the first few hours of incubation (Fig. 3c and d). The results also indicated that the formation potential of BF was higher during the winter than the summer in both wells in Hebron (Fig. 4c and d).

Spatial variation in total trihalomethane formation potential during the winter and summer

It is clear from our results that the TTHMFP differs between the two districts (north and south), regardless of the season. In the winter, the TTHMFP at the end of incubation was 18.3, 15, 20, and 15.8 µg/L for samples from the Anabta (2), Anabta (3), Al Fawar, and Al Rehya groundwater wells, respectively. In the summer, the corresponding values were 13.9, 18.3, 21, and 12.7 µg/L. These results imply that the precursors of disinfection by-products in the north are different from those in the south, most likely due to differences in

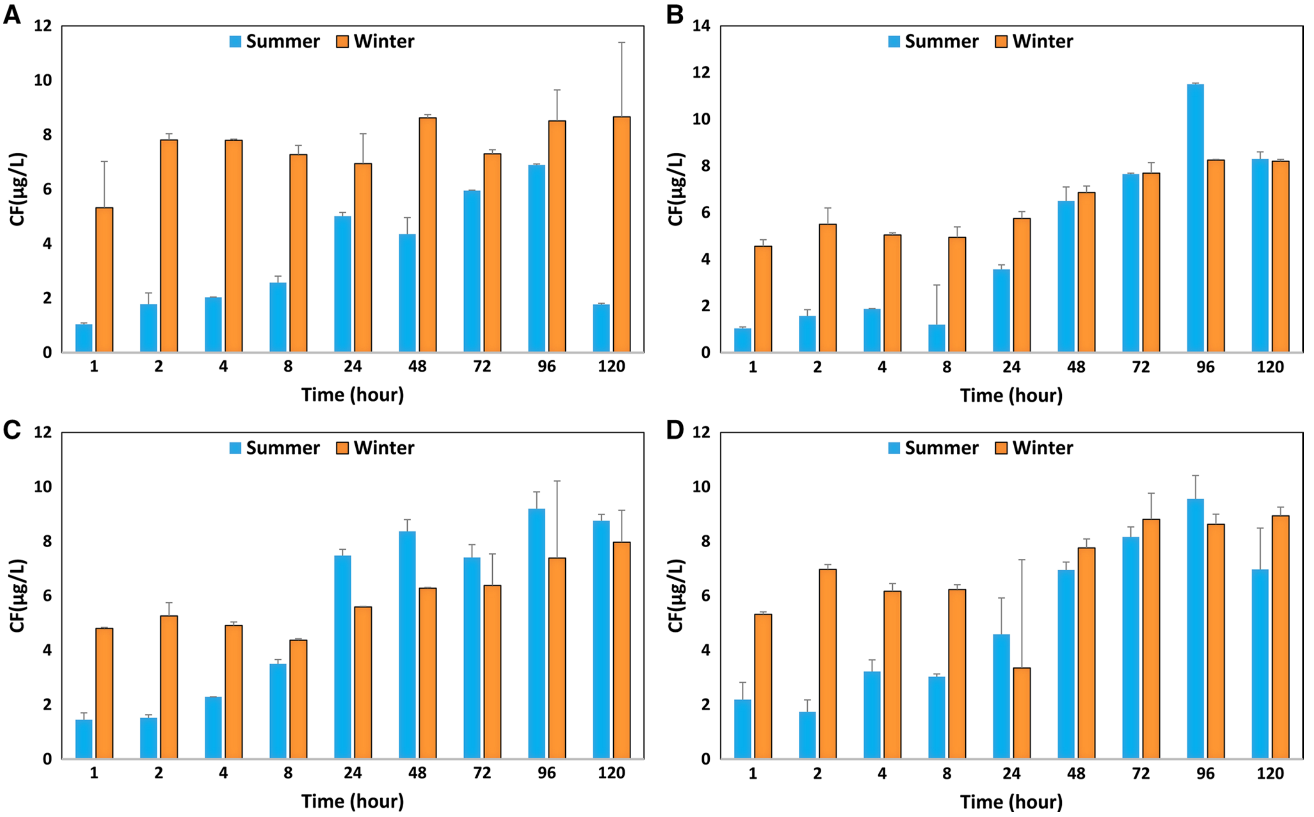

Fig. 2 Chloroform (CF) formation in groundwater from **a** the Anabta (2) well during the winter and the summer, **b** the Anabta (3) well during the winter and the summer, **c** the Al Fawar well during the winter and the summer, and **d** the Al Rehya well during the winter and the summer. Each error bar shows the standard deviation of replicate measurements

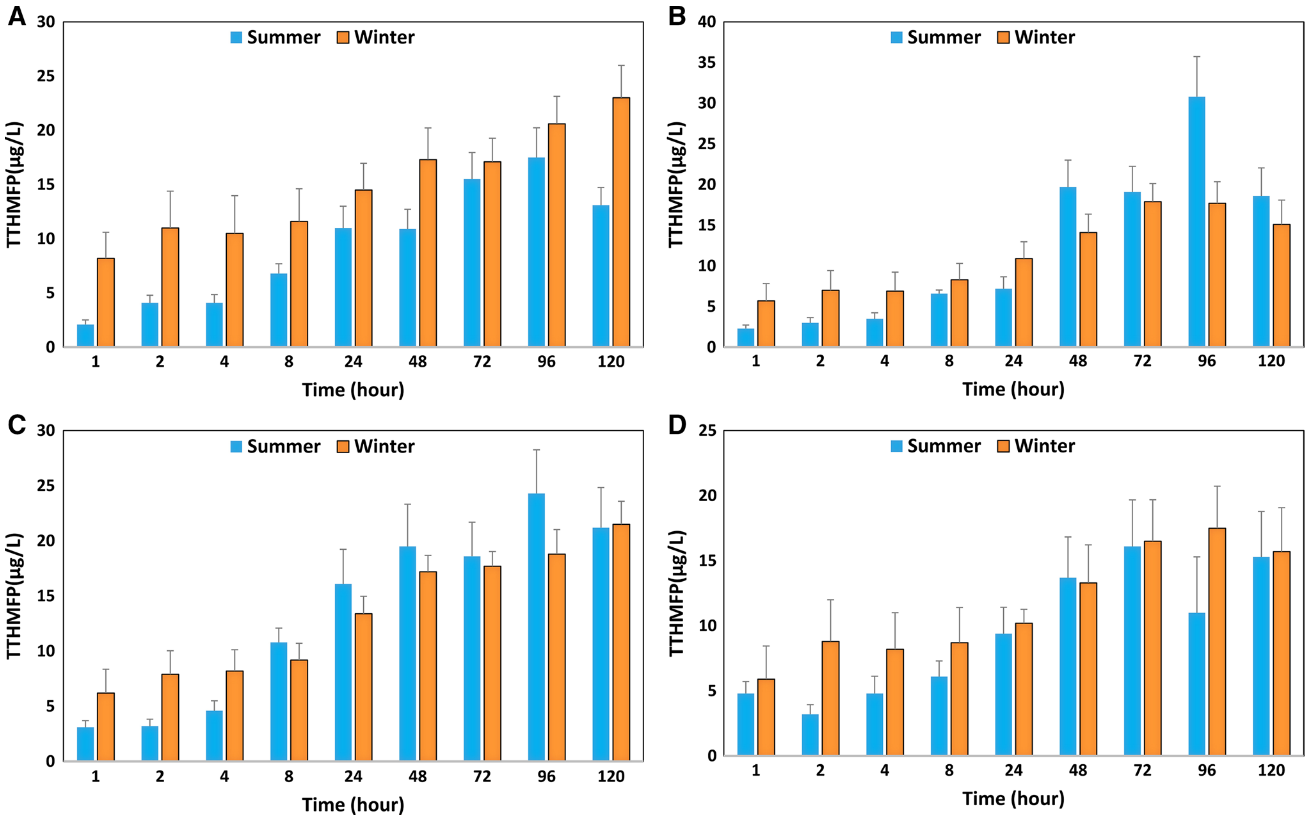

Fig. 3 Total trihalomethane formation (TTHMFP) in groundwater samples from **a** the Anabta (2) well in the winter and the summer, **b** the Anabta (3) well during the winter and the summer, **c** the Al Fawar well during the winter and the summer, and **d** the Rehya well during the winter and the summer. Each error bar shows the standard deviation of replicate measurements

the meteorological and hydrological characteristics of those regions and different well depths. The TTHMPs in the samples from the wells in the north (Anabta (2) and Anabta (3)) and the south (Al Fawar and Al Rehya) during both seasons are shown in Fig. 5.

Conclusion

There is seasonal (summer–winter) variation in the TTHMFP in the groundwater wells of the Hebron and Tulkarm governorates. There is also spatial variation in the TTHMFP in Hebron and Tulkarm, most likely due to differences in the meteorological characteristics and well depths of those regions, in addition to differences in land use. Differences between the two regions in the age of the organic matter in the groundwater as well as in land-use patterns lead to variations in the structure and origin of that organic matter. This, in turn, implies that the behavior of the organic matter in the groundwater will depend on the region considered. Such variations are of great importance when devising regulations for drinking water in Palestine, or when attempting to understand the impact of groundwater consumption throughout the year on the health of the Palestinian population. In addition, climate change may affect rainfall patterns, so groundwater recharge is another factor that should be considered when devising regulations for THMs or when attempting to predicting their behavior in harsher environmental conditions.

The fraction of the TTHMFP accounted for by CF in the groundwater samples from the Anabta (2), Anabta (3), and Al Rehya wells was 29.2%, 41%, and 54.6%, respectively, in the summer. The corresponding values in the winter were higher: 48.34%, 54.77%, and 62.25%. The fraction of the TTHMFP accounted for by CF showed hardly any variation with the season for groundwater samples from the Al Fawar well: it was 43.2% in the summer and 40.3% in the winter. However, there was greater THM formation in the first 8 h during the winter than during the summer. The TTHMFP also showed spatial variation in both the summer and the winter. In the summer, the TTHMFP was 13.9, 18.3, 21, and 12.7 µg/L in groundwater from the Anabta (2), Anabta (3), Al Fawar, and Al Rehya wells, respectively, while the corresponding values in the winter were 18.3, 15, 20, and 15.8 µg/L. These results indicate that the disinfection by-product precursors present in the groundwater differ depending on the region considered. This may

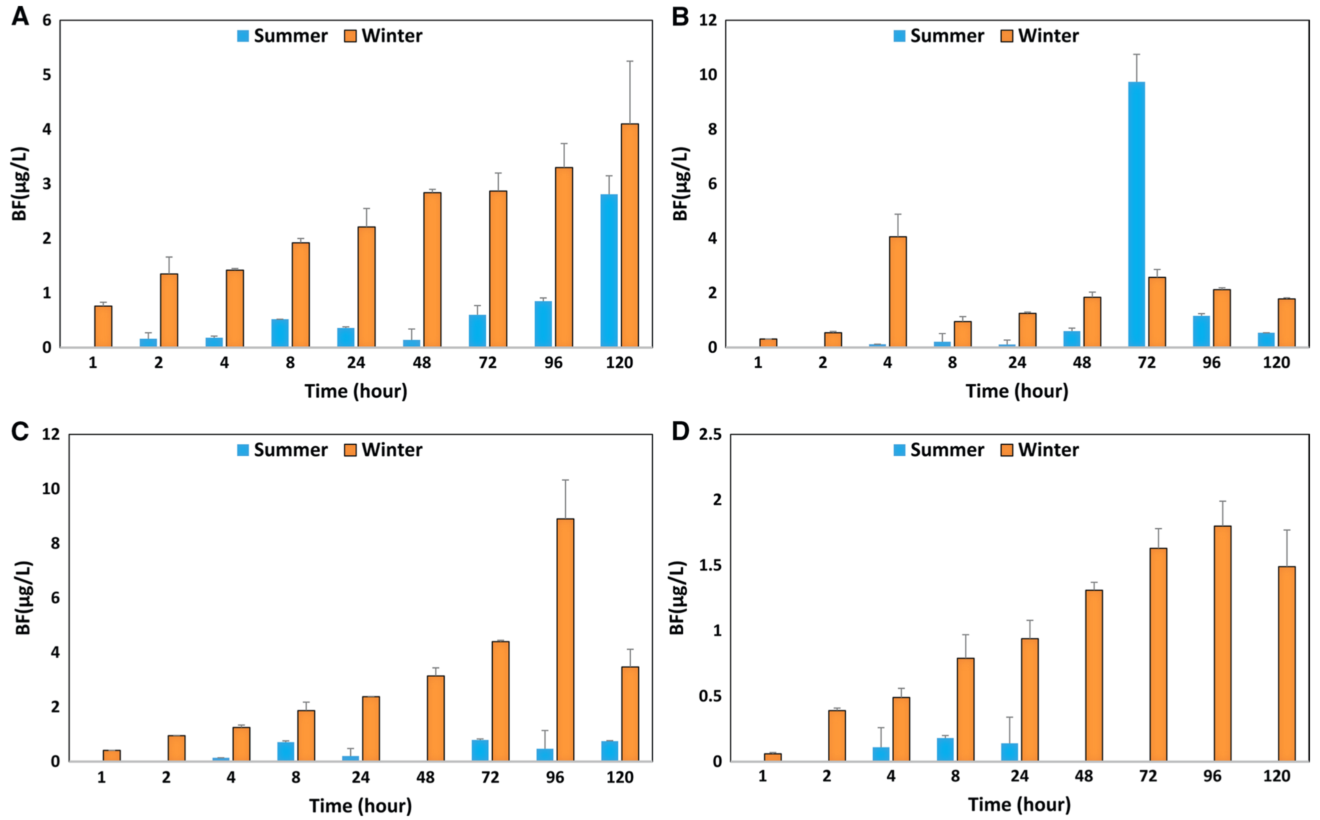

Fig. 4 Bromoform (BF) formation in groundwater samples from **a** the Anabta (2) well during the winter and the summer, **b** the Anabta (3) well during the winter and the summer, **c** the Al Fawar well during the winter and the summer, and **d** the Rehya well during the winter and the summer. Each error bar shows the standard deviation of replicate measurements

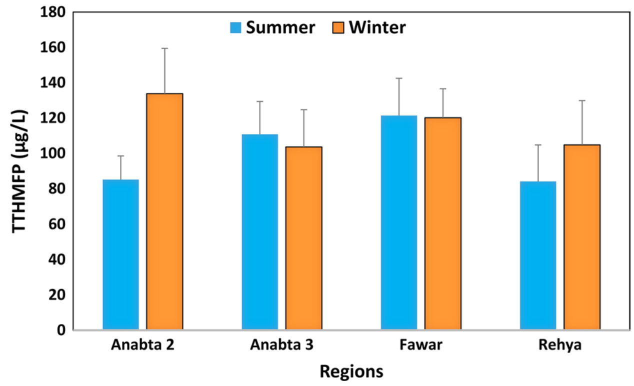

Fig. 5 TTHMPs in groundwater samples from wells in the north (Anabta (2) and (3)) and the south (Al Fawar and Al Rehya) during the summer and winter. Each error bar shows the standard deviation of replicate measurements

be due to differences between the regions in meteorological and hydrological characteristics (temperature, rainfall, etc.), land use, geological structure, and well depths. It should be emphasized that all of the comparisons performed in this work were based on the measurement of formation potential, which usually yields the maximum possible concentration of trihalomethanes, allowing for seasonal and spatial comparisons. To retrieve more plausible data and obtain a better understanding of the occurrence of trihalomethanes and how their levels vary seasonally and spatially in Palestine, a comprehensive survey of trihalomethane occurrence in chlorinated drinking water is needed.

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Compliance with ethical standards

Conflict of interest The authors declare that there is no conflict of interest.

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