Occurrence of disinfection by-products in low DOC surface waters in Turkey

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Abstract

A total of 29 surface waters from different regions of Turkey were sampled once a month during 2004. Filtered raw water samples were characterized, chlorinated and the concentrations of disinfection by-products (DBPs) were measured. All waters were low in DOC ranging from 0.91 to 4.42 mg/L. The range of annual average trihalomethanes (THMs) and haloacetic acids (HAAs) concentrations in all waters was 21–189 and 18–149 µg/L, respectively. Total mass contributions of halides in THMs and HAAs to absorbable organic halides (AOX) ranged between 10 and 56% in all waters on annual average basis, indicating that significant amounts of other DBPs are being formed in the majority of the tested waters. A strong linear correlation was obtained between the concentrations of THMs and HAAs. Rather poor correlations were found for THMs–AOX and HAAs–AOX levels. For both THMs and HAAs, chlorinated species dominated over brominated ones since the majority of water sources had very low bromide levels. While chloroform and trichloroacetic acid were the major THM and HAA compounds, respectively; the extent of formation and speciation of DBPs varied greatly by season and water source. No consistent general trends were observed in terms of seasonal variations in DBP levels, suggesting that the characteristics of NOM moieties and their chlorine reactivity vary by season in almost all waters tested.
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1. Introduction

Chlorination has been widely used as a disinfection method in drinking water treatment to eliminate pathogens and protect human health against waterborne diseases. However, it has an important drawback due to the formation of disinfection by-products (DBPs) from reactions of chlorine with natural organic matter (NOM) ubiquitously present in raw waters [1,2]. To date, more than 700 DBPs have been identified, including compounds such as chloroform and others [3]; haloacetic acids (HAAs) [4–6], haloacetonitriles (HANs) [5,7], haloketones (HKs) [4,5], short chain carboxylic acids, acetones, chlorinated phenols and phenolic acids [8], chlorinated quinones, benzoic acids and heterocyclic compounds [9].

All DBPs are suspected to be carcinogenic, mutagenic and teratogenic [10–12]. Among them, THMs and HAAs have been the center of particular attention because of their dominant occurrence in many chlorinated waters and potential carcinogenic effects. While these two groups contribute to about 50–75% of the total halogenated DBPs; they only account for 25–50% of the total organic halides (TOX) [13,14]. A major fraction of TOX is still unidentified in many chlorinated waters. The main factors affecting the DBP formation and speciation are pH, contact time, temperature, concentration and properties of NOM, chlorine dose, and bromide concentration [15–19].

Although there is yet no regulations on HAAs in Turkey, Turkish Ministry of Health has recently regulated total THMs at 150 µg/L in drinking waters. However, there is very limited research and information available on the occurrence and concentrations of various DBPs in Turkish drinking waters. In the past, THM levels in finished waters in Ankara [20,21] and Istanbul [22] cities were determined along with some cancer risk

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estimation for the City of Ankara [21]. Nevertheless, there is no study that has been done for HAAs so far.

The main aim of this work was to investigate the formation of THMs, HAAs and adsorbable organic halogens (AOX) in experimentally chlorinated drinking water sources in Turkey. A total of 29 major surface waters being drinking water sources to a population of about 20–25 million throughout different regions of the country were sampled once a month during 2004. Impacts of regional water quality on the formation and speciation of such DBPs were determined. Results obtained from this work are expected to be baseline for future national regulations on DBPs. It should, however, be noted that in this study DBPs were measured in chlorinated raw waters rather than in treated finished waters. Therefore, due to conventional treatment employed for the majority of the studied raw waters, tap water DBP levels are expected to be lower. However, the target of this work was to determine the general picture of Turkish water sources related to their DBP formation potentials. In the next phase of the project, formation and speciation of DBPs will be determined in finished waters after treatment plants.

2. Materials and methods

2.1. Water samples

Raw water samples were collected once a month from each water source by the personnel of Regional Directorate of State Hydraulic Works. A total of 29 drinking water sources were selected to represent a wide geography (Fig. 1). Fig. 1 shows the locations of sampled water sources throughout Turkey. All grab samples were collected headspace free in polyethylene 5 L bottles from the outlet part of the reservoirs and shipped overnight to our laboratories in cooled containers. All samples were kept in the dark at +4 °C until analysis. Analyses were

conducted within 7–10 days after the samples were received. After filtration through 0.45 μm cellulose acetate filters, samples were analyzed for dissolved organic carbon (DOC), UV$_{254}$ absorbance (UVA$_{254}$), specific UV absorbance (SUVA$_{254}$), bromide, pH and total hardness. Temperature was measured in situ during sample collection. Filtered raw waters were chlorinated and measured for THMs, HAAs and AOX.

2.2. Analytical methods

All samples were analyzed according to procedures described in standard methods (SM) [23]. All standard solutions were prepared in distilled and deionized water (DDW, Milli-Q plus, Millipore, France). Raw water samples were filtered using 0.45 μm cellulose acetate filters before analyses and chlorination. Filter papers were first pre-washed in filtration apparatus by passing 500 mL of DDW to prevent possible release of organic materials from the filters during sample filtration. DOC analysis was performed by the high temperature combustion method according to SM 5310B using a TOC-5000A TOC analyzer (Shimadzu Corp., Japan), which utilizes high purity oxygen as the carrier gas and for sample sparging. The minimum quantification limit of the analyzer was 0.1 mg/L. UV absorbance was measured using a Varian 100 UV/vis Spectrophotometer connected to a PC with a 1-cm quartz cell and at a wavelength of 254 nm. The concentration of bromide was measured using an ion chromatograph according to SM 4500C Br$^-$, with a quantification limit of 20 μg/L.

Chlorination of the filtered natural waters was performed according to the uniform formation condition (UFC) protocol [24] with minor modifications. This protocol simulates the average chlorination conditions in drinking water distribution systems in the USA and requires a free chlorine residual of 1.0 ± 0.4 mg/L be maintained after 1 day of contact time. In
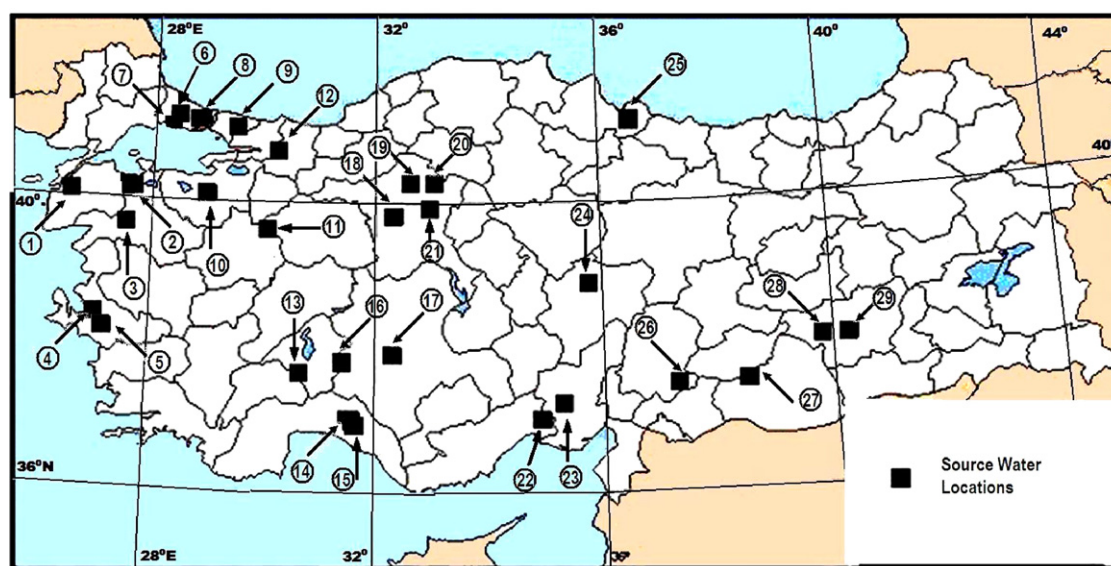

Fig. 1. Sampled drinking water sources (all surface water) throughout Turkey: (1) Atikhisar, (2) Gonen, (3) İkizcetepeler, (4) Tahtali, (5) Balcova, (6) Alibeykoy, (7)Terkos, (8) B.Cekmece, (9) Omerli, (10) Doganci, (11) Porsuk, (12) Sapanca, (13) Karacaoren, (14) Manavgat, (15) Oymapinar, (16) Beysehir, (17) Altinapa, (18) Kurtbogazi, (19) Camlidere, (20) Cubuk-2, (21) Kayas, (22) Berdan, (23) Catalan, (24) Sarimsakli, (25) Cakmak, (26) Kartalkaya, (27) Ataturk, (28) Devegecidi, (29) Dicle.

order to determine the Cl_2 dose/DOC ratio (mg/mg) that would provide the above range of chlorine residuals after 1 day of contact time, preliminary chlorination experiments with varying Cl_2/DOC ratios were performed for all samples. This was necessary because natural waters have different chlorine demands depending on the nature of organic and inorganic chlorine consumers. After determining the proper ratio for each sample, actual chlorinations were performed for DBP analysis. Residual chlorine concentrations also measured after actual chlorination experiments indicated that samples were not chlorine limited. Chlorination was accomplished head-space free in 60 mL or 100 mL amber serum bottles with teflon-lined screw caps. Chlorine was spiked in each bottle using gas-tight glass syringes from a stock solution prepared from sodium hypochlorite solution (13% available free chlorine). The free available residual chlorine concentration was measured according to the colorimetric DPD method using a HACH DR/2000 spectrophotometer. The residual chlorine remaining in the bottles was quenched with sodium sulfite (Na_2SO_3) prior to analysis for DBPs and UV absorbance.

THMs (chloroform, bromodichloroform, dibromochloroform, and bromoform) were measured according to SM 6232 employing liquid–liquid extraction (with pentane) and gas chromatography (GC) measurement. Calibration standards were prepared using the standard mixture purchased from Supelco (Sigma–Aldrich Co., USA) Calibration curves had at least

eight points, and calibration standards were also extracted with the same protocol as samples in order to compensate for the extraction efficiency effects. Nine haloacetic acids (monochloro-, dichloro-, trichloro-, monobromo-, dibromo-, tribromo-, bromochloro-, bromodichloro-, dibromochloro acetic acid) were analyzed employing liquid–liquid extraction and further derivatization with acidic methanol according to USEPA 552.3 method. Calibration standards were prepared using the standard mixture purchased from Supelco (Sigma–Aldrich Co., USA). A Varian CP3380 model gas chromatograph with an electron capture detector was used for both THM and HAA measurements. Calibration standards for THM and HAA measurements were prepared using the test mix produced by Supelco at concentrations ranging from 2.5 to 250 μg/L ($r^2 = 0.99$) and 0.1 to 600 μg/L ($r^2 = 0.99$), respectively. The capillary column used for both measurements have the following characteristics: CP-Sil8 column, length: 24 m, i.d.: 0.32 mm, film thickness: 0.25 μm (Varian MD-21-10-1). Ultra high purity helium (1.8 mL/min) and nitrogen (25 mL/min) were used as the carrier and make-up gas, respectively. The detection limits for THM and HAA species were about 0.5–1.5 μg/L. GC operating conditions for HAA measurements were as following: injector temperature: 200 °C, detector temperature: 290 °C, injection volume: 1 μL, temperature program: 40 °C for 20 min, 5 °C/min ramp to 120 °C, 3-min hold, 10 °C/min ramp to 150 °C, total run time: 42 min. GC operating conditions for THM measurements

Table 1
Annual average values of typical quality parameters of raw waters for the year 2004

No.	Raw water	pH	UVA$_{254}$	DOC (mg/L)	SUVA$_{254}$ (L/mg m)	Bromide (μg/L)	Total hardness (mg/L as CaCO$_3$)
1	Atikhisar	7.9 (0.2)	0.099 (0.019)	4.42 (0.80)	2.234 (0.270)	<20	65 (8)
2	İkizcetepeler	8.1 (0.1)	0.063 (0.011)	3.16 (0.92)	2.019 (0.382)	<20	79 (8)
3	Gonen	8.0 (0.2)	0.059 (0.020)	2.48 (1.35)	2.493 (0.770)	<20	64 (15)
4	Tahtali	8.0 (0.2)	0.049 (0.007)	3.06 (0.59)	1.613 (0.242)	80 (0.005)	68 (17)
5	Balcova	8.1 ((0.2)	0.033 (0.007)	1.80 (0.68)	1.950 (0.772)	<20	98 (8)
6	Alibeykoy	7.7 (0.2)	0.089 (0.010)	3.85 (0.86)	2.326 (0.342)	120 (0.007)	95 (13)
7	Terkos	8.0 (0.2)	0.102 (0.015)	4.29 (1.02)	2.399 (0.337)	94 (0.006)	65 (19)
8	B.Cekmece	8.1 (0.1)	0.072 (0.014)	4.08 (0.92)	1.785 (0.238)	70 (0.009)	89 (8)
9	Omerli	7.8 (0.3)	0.066 (0.008)	3.90 (0.83)	1.732 (0.277)	70 (0.004)	39 (8)
10	Doganci	8.2 (0.2)	0.031 (0.011)	1.99 (1.16)	1.749 (0.866)	<20	87 (14)
11	Porsuk	8.1 (0.1)	0.065 (0.013)	3.58 (0.61)	1.834 (0.365)	<20	129 (28)
12	Sapanca	7.0 (0.2)	0.025 (0.006)	2.10 (0.65)	1.208 (0.422)	<20	56 (4)
13	Karacaoren	8.2 (0.2)	0.021 (0.007)	1.53 (0.88)	1.540 (0.938)	<20	85 (16)
14	Manavgat	7.9 (0.1)	0.009 (0.002)	0.91 (1.16)	1.033 (0.537)	<20	71 (15)
15	Oymapinar	8.1 (0.1)	0.009 (0.004)	1.26 (0.96)	1.058 (0.975)	<20	72 (16)
16	Beysehir	8.5 (0.5)	0.033 (0.006)	3.52 (1.12)	0.974 (0.299)	<20	75 (14)
17	Altinapa	8.1 (0.2)	0.033 (0.007)	2.24 (1.15)	1.546 (0.487)	<20	100 (10)
18	Kurtbogazi	7.9 (0.1)	0.101 (0.016)	3.51 (0.60)	2.893 (0.516)	<20	46 (15)
19	Camlidere	8.1 (0.3)	0.078 (0.010)	3.58 (0.53)	2.206 (0.420)	<20	42 (7)
20	Cubuk-2	8.0 (0.1)	0.060 (0.011)	2.36 (0.46)	2.714 (0.598)	<20	71 (12)
21	Kayas	7.9 (0.2)	0.041 (0.006)	2.59 (0.92)	1.641 (0.446)	<20	83 (20)
22	Berdan	8.0 (0.1)	0.012 (0.006)	1.00 (0.40)	1.349 (0.742)	<20	82 (19)
23	Catalan	8.2 (0.1)	0.013 (0.006)	1.33 (0.59)	1.110 (0.606)	<20	83 (15)
24	Sarimsakli	8.0 (0.2)	0.026 (0.013)	1.88 (1.17)	1.548 (0.764)	<20	131 (44)
25	Cakmak	8.2 (0.1)	0.032 (0.009)	2.33 (1.20)	1.431 (0.482)	<20	85 (14)
26	Kartalkaya	8.1 (0.1)	0.022 (0.006)	1.44 (0.48)	1.594 (0.666)	<20	95 (16)
27	Ataturk	8.1 (0.2)	0.013 (0.006)	1.62 (0.76)	0.934 (0.549)	<20	72 (13)
28	Devegecidi	7.9 (0.2)	0.050 (0.016)	3.43 (1.43)	1.548 (0.640)	<20	74 (16)
29	Dicle	8.1 (0.2)	0.015 (0.005)	1.41 (0.84)	1.477 (0.894)	<20	82 (17)

Values in the brackets indicate ±standard deviation of each datum.

were as following: injector temperature: 280 °C, detector temperature: 290 °C, injection volume: 1 μL, temperature program: 40 °C for 2 min, 4 °C/min ramp to 80 °C, 20 °C/min ramp to 110 °C, total run time: 13.5 min. AOX measurements were performed according to ISO9562 method using an Euroglass AOX Analyzer. Operating conditions for AOX measurements were as following: drying at 200 °C for 1 min, combustion at 1000 °C for 4 min and cooling for 5 min.

3. Results and discussion

3.1. Characterization of raw waters

Table 1 summarizes the annual average of the measured water quality characteristics in 29 raw waters throughout Turkey, along with $SUVA_{254}$ which represents the ratio UV_{254}/DOC and constitutes an indicator of carbon aromaticity in water. In general, the results showed that, humic material content of raw waters in Turkey range from low to medium as indicated by DOC content ranging from 0.91 to 4.42 mg/L (average 2.58 mg/L) with a UVA_{254} from 0.009 to 0.102 (average 0.046). The highest UVA_{254} and DOC were observed in B.Cekmece, Terkos and Atikhisar reservoirs, which are located nearby urban areas. On the other hand, in Manavgat, Oymapinar, Karacaoren and Berdan raw waters, DOC was below 2 mg/L throughout the year. In parallel, $SUVA_{254}$ values in all samples were also in the low to medium range indicating that NOM in raw waters in Turkey is of low molecular weight with hydrophobic and aromatic characteristics. The annual average $SUVA_{254}$ for 29 waters was 1.722 L/mg m, while the maximum and the minimum were in Kurtbogazi (2.893 L/mg m) and Ataturk (0.934 L/mg m) raw waters, respectively. Natural waters with high $SUVA_{254}$ values (e.g., >4 L/mg-C m) have been shown to have relatively high hydrophobic and aromatic content with high molecular weight DOM fractions, such as humic and fulvic acids [25,26].

As presented in Table 1, in most of the raw waters; bromide levels were also very low. In 24 of the raw waters, bromide concentration was detected to be below 20 μg/L; while it was over 100 μg/L in only once raw water (Alibeyköy), which is nearby the coastline. The other four raw waters with relatively high bromide content (70–94 μg/L) are also from the reservoirs, which are located in the coastline.

3.2. DBP levels

Annual average total THM, HAA and AOX concentrations of the chlorinated drinking water sources are shown in Fig. 2(a)–(c). The water sources shown on the x-axis of these figures are presented based on their locations, i.e., from west to east Turkey (right direction on the x-axis). The distance between the water sources at the farthest west and east is approximately 1800 km. In addition, the annual climate and geographical properties also vary significantly for these water sources distributed in Turkey. The annual average concentrations of all three DBP groups varied widely among the 29 raw waters, suggesting significant differences between NOM properties of raw waters. The ranges of annual average total THM and HAA concen-
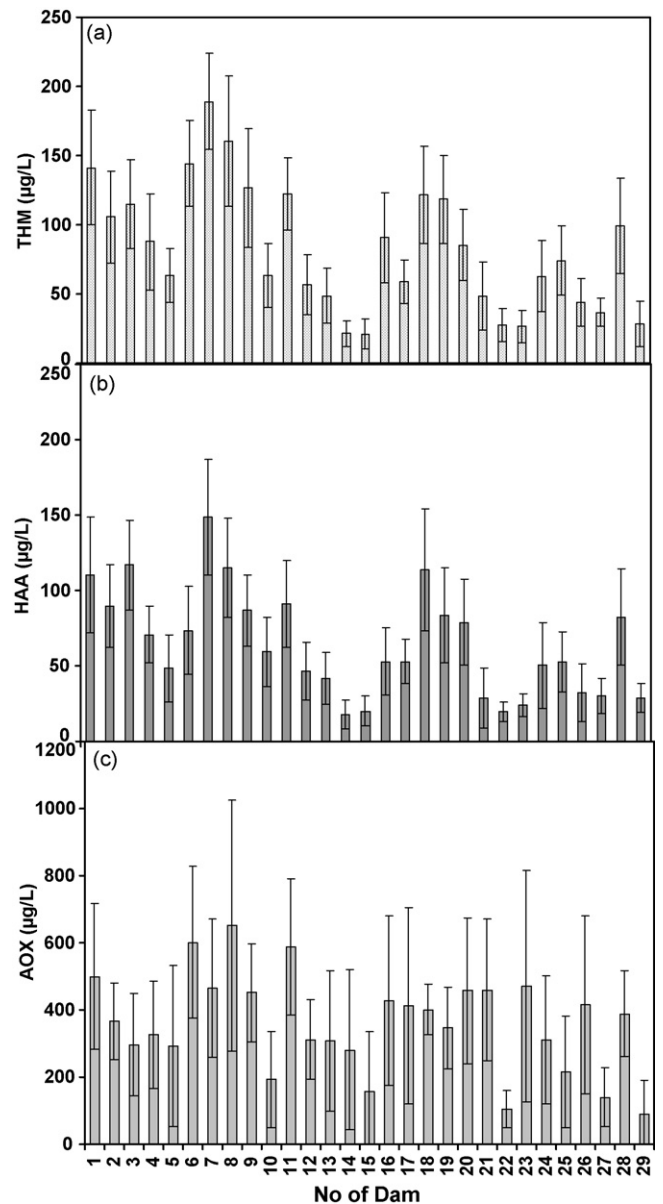

Fig. 2. Annual average DBPs formation in chlorinated raw waters. (a) Total THM concentrations, (b) total HAA concentrations, and (c) AOX concentrations. Error bars indicate the standard deviations calculated for annual data.

trations were 21–189 and 18–149 μg/L, respectively. While the highest average THM concentration (189 μg/L) was found in Terkos water (in metropolitan area of the City of Istanbul), the lowest (21 μg/L) was measured in Manavgat water, south-west Turkey in Antalya region. THM concentration in Terkos water was followed by B.Cekmece and Alibeykoy reservoir waters in decreasing order. All these three reservoirs supply a major portion of the drinking water demand of the City of Istanbul. As with THMs, the highest and the lowest HAA concentrations were measured in Terkos (149 μg/L) and Manavgat (18 μg/L) waters, respectively. Furthermore, other waters in Istanbul also had relatively higher HAA concentrations. For AOX, the highest and the lowest concentrations were measured in B.Cekmece (652 μg/L) and Dicle (89 μg/L) raw waters, respectively, supporting the trends found for THMs and HAAs.

As can be noted from Fig. 2, a general decreasing trend was found for THM (a) and HAA (b) levels in waters from west to east Turkey. Surface water reservoirs in west Turkey are mostly located in highly populated and industrialized areas. Such water sources have also been subject to illegal and uncontrolled discharge of raw and/or insufficiently treated domestic and industrial wastewaters for years. Therefore, in addition to the presence of aquatic or pedogenic NOM, other types of organic materials may also be present in reservoirs, especially in industrial Marmara Region and metropolitan areas including the City of Istanbul, Ankara and Izmir. Some exceptions to this trend included Cakmak, Sarimsakli and Devegecidi waters in rural areas of east Turkey with relatively higher THM and HAA concentrations. However, such trend was not observed for AOX levels (Fig. 2(c)), indicating that THM and HAA precursors in waters are different compared to those of AOX. On the other hand, similar concentration levels and the regional trend found suggest that THM and HAA precursors in NOM have similar characteristics. It is indicated in the literature that the amount of total halides (chlorine and bromine) in THMs and HAAs contribute about 50–75% to TOX. However, in source waters, the contribution of halides in THMs and HAAs to TOX on a mass basis ranged between 6–36% and 4–20%, respectively. When the total contribution of halides in both THMs and HAAs considered, such range is 10–56%. This range is significantly lower than those typically reported in the literature, supporting the previous observation that NOM precursors for THMs–HAAs and AOX are different in the majority of raw waters. In addition, the significant differences between the amount of halides in THMs–HAAs and AOX suggest that halogenated DBPs other than THMs and HAAs should be of important concern to regulators in Turkey. Although not measured in this study, such DBPs may be HANs, HKs, chlorinated phenolic compounds, or most probably, other DBPs unidentifiable with the current available analytical techniques.

3.3. Seasonal variations in DBPs

Seasonal variations in the concentrations of total THMs, HAAs and AOX are summarized in Table 2. Spring, summer, autumn and winter seasons represent the months of March–May, June–August, September–November, and December–February, respectively. It should be noted that all chlorination experiments were performed at room temperature ($20 \pm 2\,^{\circ}C$) in this study. Therefore, seasonal variations in DBP levels are considered in terms of changes in NOM characteristics of water sources seasonally rather than water temperature. As may be expected the extent of formation and speciation of DBPs varied greatly by

Table 2
Seasonal variations in the concentrations of THMs, HAAs and AOX for the year 2004

No.	Surface waters	HAA (µg/L)				THM (µg/L)				AOX (µg/L)[a]			
		Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn	Winter
1	Atikhisar	98	73	142	92	154	130	151	135	347	290	491	871
2	İkizcetepeler	99	90	138	102	110	94	117	131	386	375	394	312
3	Gonen	79	53	98	100	80	85	103	146	243	235	420	287
4	Tahtali	58	52	79	71	89	94	66	102	325	154	499	NA
5	Balcova	65	39	47	44	64	56	47	87	222	40	304	603
6	Alibeykoy	58	58	94	60	115	135	146	172	434	386	573	1010
7	Terkos	116	103	150	177	181	183	181	160	320	294	549	691
8	B.Cekmece	71	114	107	129	165	143	158	191	492	301	474	1341
9	Omerli	72	57	94	95	115	155	109	124	430	290	378	705
10	Doganci	75	28	68	66	61	44	58	91	204	7	280	279
11	Porsuk	109	56	121	78	99	115	141	134	384	470	560	933
12	Sapanca	32	32	68	35	53	66	55	51	307	231	331	378
13	Karacaoren	30	26	56	42	63	39	47	51	241	209	396	382
14	Manavgat	19	7	22	17	15	15	26	28	70	276	323	456
15	Oymapinar	19	6	25	23	15	13	28	26	193	7	217	206
16	Beysehir	54	28	80	50	64	86	117	97	272	81	556	801
17	Altinapa	66	33	61	52	49	48	71	69	162	209	470	808
18	Kurtbogazi	124	81	160	89	95	121	158	110	410	290	391	514
19	Camlidere	78	63	120	73	82	128	147	116	356	235	397	397
20	Cubuk-2	105	60	80	72	96	72	80	92	338	243	562	687
21	Kayas	51	25	8	32	59	41	19	76	252	287	450	849
22	Berdan	21	12	21	24	22	26	27	36	130	59	145	85
23	Catalan	25	17	23	31	29	21	20	37	130	254	414	1084
24	Sarimsakli	48	30	75	49	55	63	66	68	233	316	463	231
25	Cakmak	66	23	57	65	60	74	75	93	224	99	383	154
26	Kartalkaya	31	14	54	29	35	32	56	53	213	125	473	849
27	Ataturk	33	19	39	29	33	31	38	45	138	7	140	272
28	Devegecidi	90	37	111	92	91	72	101	131	287	489	435	345
29	Dicle	36	18	35	26	22	16	43	37	145	22	140	48

Values are averages of 3 months from each season.

[a] Data of summer and winter only belong to June and December, respectively. NA: data not available.

season and water source, as suggested by the literature [14,27]. For some waters, the highest average HAA concentrations were observed in spring and autumn; the lowest HAA concentrations were obtained in summer. Although the seasonal variations in THM concentrations depended on source water, some surface waters produced the highest and the lowest average THM concentrations in winter and summer, respectively. Similar to THM trends, highest average AOX concentrations were found in winter for a few water source. In spring months in general, AOX formed in lowest quantities. Relatively close AOX concentrations were found in summer and autumn months. In particular, formations of AOX in the surface waters of metropolitan cities (Istanbul, Ankara, Eskisehir, Adana, and Konya) were quite higher in winter compared to other seasons. Overall, no consistent general trends were observed in terms of seasonal variations in DBP levels. Furthermore, no correlations between THM, HAA and AOX concentrations were found with respect to their seasonal dependence for all waters. These results suggest that the characteristics of NOM moieties and their chlorine reactivity vary by season in almost all waters tested, significantly affecting DBP formations. Given the complex nature of NOM depending upon the water source and the number of water sources tested in wide geographical locations, it may be expected to observe no consistent trends for DBP levels seasonally. Furthermore, in addition to water temperature, characteristics of NOM fractions in surface waters are also known to vary seasonally, especially in smaller and unprotected watersheds. Reservoir stratification, NOM input and output from reservoirs and NOM decay by various means are also affected by seasonal changes. All these complex and water-specific interactions appear to affect DBP formations seasonally.

3.4. Speciation of THMs and HAAs

Fig. 3 shows the annual average concentrations of THM (a) and HAA (b) species, respectively. Consistent for both THMs and HAAs, chlorinated species dominated over brominated ones for all waters. Chloroform (TCM) was found to be the major THM compound (77.9%), followed by bromodichloromethane (BDCM, 16.4%), dibromochloromethane (DBCM, 4.9%), and bromoform (TBM, 0.9%), on annual average for all waters chlorinated. Similarly, the major HAA species were dichloroacetic acid (DCAA, 31.3%) and trichloroacetic acid (TCAA, 47.6%). These di- and tri-chlorinated HAA species were followed by bromodichloroacetic acid (BDCAA, 8.7%), bromochloroacetic acid (BCAA, 6.7%) and monochloroacetic acid (MCAA, 3.1%). For all waters, concentrations of dibromoacetic acid (DBAA), dibromochloroacetic acid (DBCAA), monobromoacetic acid(MBAA) and tribromoacetic acid (TBAA) were near detection limits (<2 µg/L for all THM and HAA species).

The speciation of DBPs may depend on several factors: the nature and concentrations of NOM, the bromide ion concentration, chlorine/DOC ratio, bromide/DOC ratio, background water chemistry, and chlorination conditions [28–32]. Hypochlorous acid (HOCl) or other oxidants can oxidize bromide to hypobromous acid (HOBr). HOBr is not only a stronger oxidant but also a stronger halogenating agent than chlorine species. A mixture
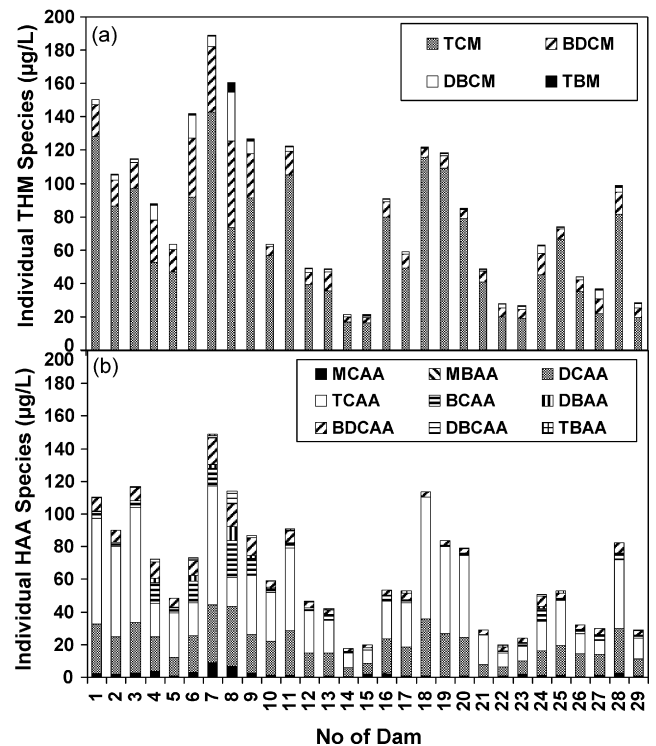

Fig. 3. Annual average concentrations of THM (a) and HAA (b) species in chlorinated raw waters.

of HOCl/HOBr leads to the formation of various brominated and chlorinated DBP species. As the amount of bromide increases in waters, a shift toward brominated DBP species over chlorinated ones generally occurs, with all other factors held constant. The majority of water sources studied had very low bromide levels such as almost for all months 24 waters out of 29 had bromide concentrations less than the detection limit (20 µg/L). The maximum bromide concentration found in all waters was 150 µg/L. Therefore, for these low-bromide containing surface waters, chlorinated DBP species dominated over brominated ones, a trend consistent with the literature [28,33,34]. Furthermore, within chlorinated species, di- and tri-chlorinated ones (i.e., DCAA and TCAA) exhibited higher concentrations than those of mono-chlorinated species. The dominance of multi-chlorine substituted species within DBPs is a commonly observed trend in literature for natural waters having low bromide levels.

3.5. Correlations between DBPs

Correlation between the annual average concentrations of THMs and HAAs in all waters is shown in Fig. 4. A strong linear correlation (regression coefficient of 0.92) indicates that the levels of THMs and HAAs formed after chlorination of filtered raw waters are closely related. This finding further supports the previous observation that THM and HAA precursors in NOM are similar for the majority of the waters in terms of reactivity with chlorine. A slope of 1.27 obtained from the linear correlation shows that under same chlorination conditions about 1.27 µg/L of total THMs is formed per 1 µg/L of total HAAs, on an annual average concentration basis. Although using annual
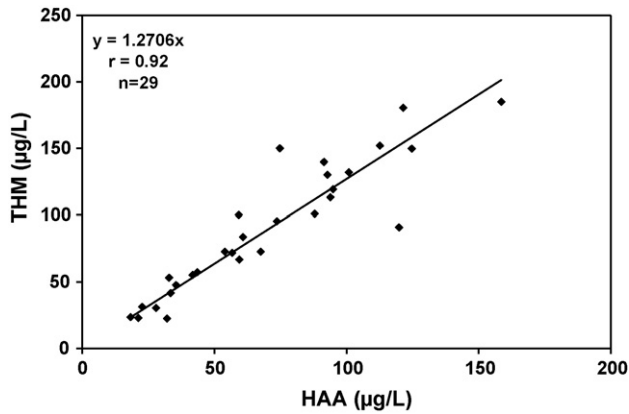
Fig. 4. Correlation between the annual average concentrations of THMs and HAAs.

average data for each water and correlating the data of all 29 waters probably with different NOM characteristics is not an absolute mechanistic approach in understanding DBP reactivity, the strong correlation obtained is still a good indication of close relation between THM and HAA precursors in Turkish waters. Similarly, Villanuevaa et al. [12] showed a strong correlation between total THM and HAA concentrations in a subset of 18 samples (HAA (μg/L) = 2.643 + 0.526 THM (μg/L), r = 0.85). Furthermore, Sérodes et al. [3] found a quite good correlation between THM and HAA concentrations at different incubation temperatures (r = 0.75). On the contrary, Malliarou et al. [35] indicated that THM levels are not considered to be a good indicator of HAA levels in drinking waters in the UK.

On the other hand, rather poor correlations were found for THMs–AOX and HAAs–AOX levels for all waters (Fig. 5). This result also supports the previous observation that formation mechanisms of AOX are different than those of THMs or HAAs. In addition to THMs and HAAs, it is clear that significant amounts of other DBPs, either identifiable or unidentifiable with the available analytical techniques, are being formed in the majority of the tested Turkish waters, as reflected by AOX measurements. Based on mass balance calculations given in previous discussions, total contributions of halides in THMs and HAAs to AOX ranged between 10 and 56% in all waters on annual
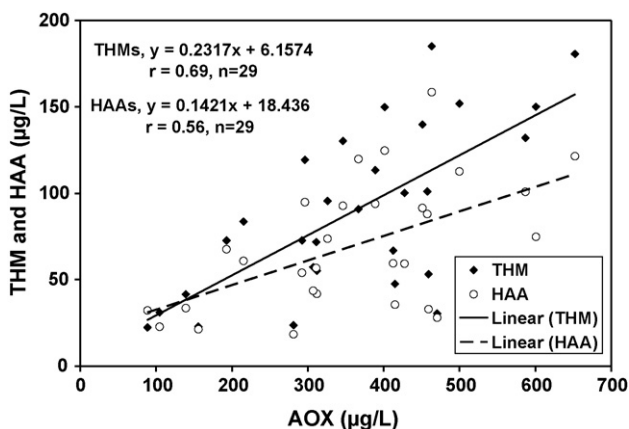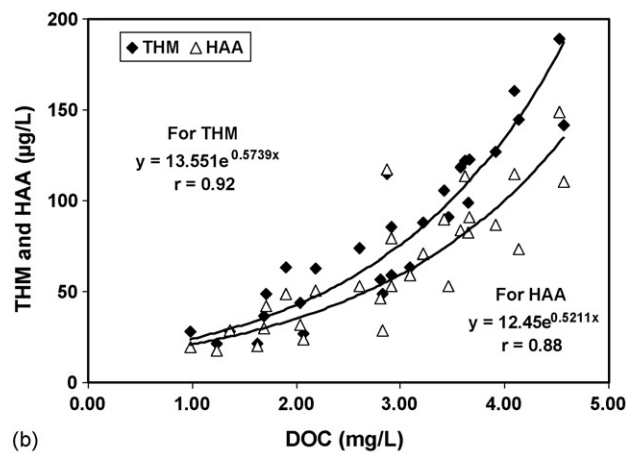
average basis, highlighting the significant amounts of unknown halogenated organic compounds formed after chlorination.

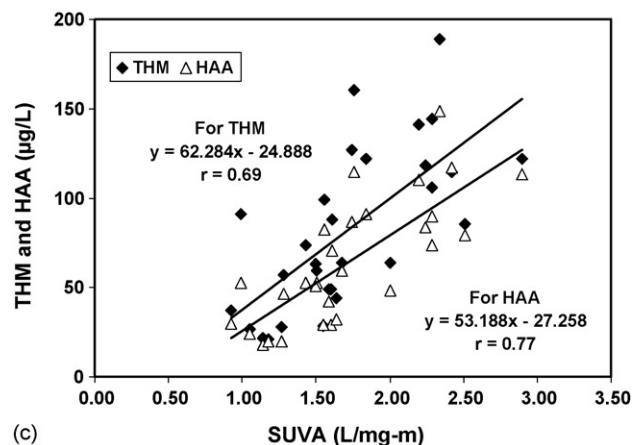### 3.6. Correlations between DOC, UVA and SUVA with DBPs

In many research, DBPs formations have been correlated with some surrogate parameters for predicting of DBPs. It is known that DBPs measurements are very tedious and time-consuming analysis. The relationships between UVA$_{254}$ (a), DOC (b) and
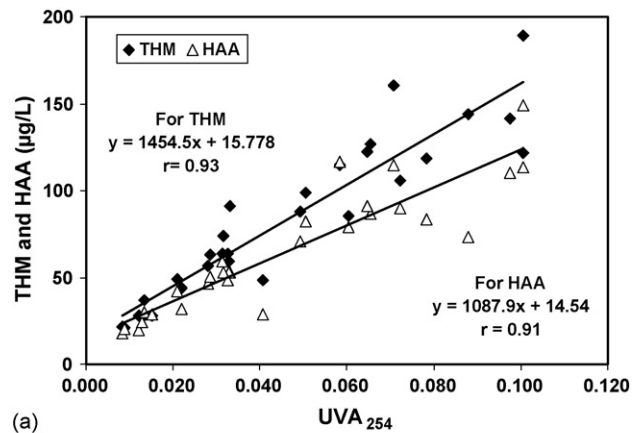
(a)

(b)

(c)

Fig. 6. Relationships between UVA$_{254}$ (a), DOC (b) and SUVA (c) with THM and HAA.

Fig. 5. Correlation between the annual average concentrations of THMs–AOX and HAAs–AOX.

SUVA (c) with THM and HAA levels in studied waters are shown in Fig. 6. THM and HAA formations well correlated with UVA$_{254}$ and DOC with high regression coefficients. While THM and HAA linearly correlated with UVA$_{254}$, correlations with DOC were generally exponential. Furthermore, rather poor correlations were found between SUVA and THM and HAA concentrations, which can be attributed to the presence of NOM with low molecular weight, less hydrophobicity and aromaticity in the studied raw waters. Similarly, poor correlations were found between AOX concentrations and DOC, UVA$_{254}$ and SUVA (data not shown).

4. Conclusions

The annual average concentrations of THMs, HAAs and AOX varied widely (21–189, 18–149 and 89–652 µg/L, respectively) among the 29 raw waters with DOC ranging from 0.91 to 4.42 mg/L. For both THMs and HAAs, chlorinated species dominated over brominated ones since the majority of water sources had very low bromide levels (<20 µg/L). Total mass contributions of halides in THMs and HAAs to AOX were low (between 10 and 56%), indicating that significant amounts of other DBPs, are being formed in the majority source waters. A strong linear correlation between the concentrations of THMs and HAAs indicated that their precursors in NOM are similar for the majority of the waters in terms of reactivity with chlorine. Rather poor correlations were found for THMs–AOX and HAAs–AOX levels suggesting that formation mechanisms of AOX are different than those of THMs or HAAs.

Acknowledgements

References

[1] J.J. Rook, Formation of haloforms during chlorination of natural waters, Water Treat. Exam. 23 (1974) 234–243.

[2] J.M. Symons, T.A. Bellar, J.K. Carswell, J. DeMarco, K.L. Krapp, A.A. Steevens, National organics reconnaissance survey for halogenated organics, J. AWWA 67 (1975) 634–648.

[3] J.-B. Sérodes, M.J. Rodriguez, H. Li, C. Bouchard, Occurence of THMs and HAAs in experimental chlorinated waters of the Quebec City Area (Canada), Chemosphere 51 (2003) 253–263.

[4] B. Koch, S.W. Krasner, M.J. Sclimenti, W.K. Schimpff, Predicting the formation of DBPs by the simulated distribution system, J. AWWA 83 (1991) 62–69.

[5] L. Tan, G.L. Amy, Comparing ozonation and membrane separation for color removal and disinfection by-product control, J. AWWA 83 (1991) 74–79.

[6] T.K. Nissinen, I.T. Miettinen, P.J. Martikainen, T. Vartiainen, Disinfection by-products in Finnish drinking waters, Chemosphere 48 (2002) 9–20.

[7] J. Kim, Y. Chung, D. Shin, M. Kim, Y. Lee, Y. Lim, D. Lee, Chlorination by-products in surface water treatment process, Desalination 151 (2002) 1–9.

[8] L. Kronberg, Water treatment practice and the formation of genotoxic chlorohyroxyfuranones, Water Sci. Technol. 40 (1999) 31–36.

[9] E.R. Blatchley, D. Margetas, R. Duggirala, Copper catalysis in chloroform formation during water chlorination, Water Res. 37 (2003) 4385–4394.

[10] B.D. Black, G.W. Harrington, P.C. Singer, Reducing cancer risks by improving organic carbon removal, J. AWWA 88 (1996) 40–52.

[11] P.C. Singer, Humic substances as precursors for potentially harmful disinfection by-products, Water Sci. Technol. 40 (1999) 25–30.

[12] C.M. Villanuevaa, M. Kogevinasa, J.O. Grimaltb, Haloacetic acids and trihalomethanes in finished drinking waters from heterogeneous sources, Research note, Water Res. 37 (2003) 953–958.

[13] S.W. Krasner, M. McGuire, J.G. Jacangelo, N.L. Patania, K.M. Reagen, E.M. Aieta, Occurrence of disinfection by-products in US drinking water, J. AWWA 81 (1989) 41–53.

[14] E.C. Nieminski, S. Chaudhuri, T. Lamoreaux, The occurrence of DBPs in Utah drinking waters, J. AWWA 85 (1993) 98–105.

[15] P.C. Singer, Formation and characterization of disinfection by-products, in: G.F. Craun (Ed.), Safety of Water Disinfection: Balancing Chemical and Microbial Risks, ILSI Press, Washington, DC, USA, 1993, pp. 201–219.

[16] P.C. Singer, Control of disinfection by-products in drinking water, J. Environ. Eng. 120 (1994) 727–744.

[17] H. Pourmoghaddas, A.A. Stevens, Relationship between trihalomethanes and haloacetic acids with total organic halogen during chlorination, Water Res. 29 (1995) 2059–2062.

[18] A.D. Nikolaou, M.N. Kostopoulou, T.D. Lekkas, Organic by-products of drinking water chlorination, Global Nest: Int. J. 1 (1999) 143–156.

[19] M. Kitis, T. Karanfil, A. Wigton, J.E. Kilduff, Probing reactivity of dissolved organic matter for disinfection by-product formation using XAD-8 resin adsorption and ultrafiltration fractionation, Water Res. 36 (2002) 3834–3848.

[20] G. Capar, U. Yetis, Removal of THM precursors by GAC: Ankara case study, Water Res. 36 (2002) 1379–1384.

[21] B. Tokmak, G. Capar, F.B. Dilek, U. Yetis, Trihalomethanes and associated potential cancer risks in the water supply in Ankara, Turkey, Environ. Res. 96 (2004) 345–352.

[22] I. Toroz, V. Uyak, Seasonal variations of trihalomethanes (THMs) in water distribution networks of Istanbul City, Desalination 176 (2005) 27–141.

[23] APHA, AWWA, WEF. Standard Methods for the Examination of Water and Wastewater. 20th ed. Washington, DC, 1998.

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

[25] J.K. Edzwald, J.E. Van Benschoten, Aluminum coagulation of natural organic matter, in: H.H. Hahn, R. Klute (Eds.), Chemical Water and Wastewater Treatment, Springer–Verlag, Berlin, 1996, 1990, pp. 341–359.

[26] M.C. White, J.D. Thompson, G.W. Harrington, P.C. Singer, Evaluating criteria for enhanced coagulation compliance, J. AWWA 89 (1997) 64–77.

[27] K.J. Lee, B.H. Kim, J.E. Hong, H.S. Pyo, S.-J. Park, D.W. Lee, A study on the distribution of chlorination by-products (CBPs) in treated water in Korea, Water Res. 35 (2001) 2861–2872.

[28] J.M. Symons, S.W. Krasner, L.A. Simms, M. Sclimenti, Measurement of THM and precursor concentrations revisited: the effect of bromide ion, J. AWWA 85 (1993) 51–62.

[29] J.M. Symons, S.W. Krasner, M.J. Sclimenti, L.A. Simms, H.W. Sorensen Jr., G.E. Spietel Jr., A.C. Diehl, Influence of bromide ion on trihalomethane and haloacetic acid formation, in: R.A. Minear, G.L. Amy (Eds.), Disinfection By-products in Water Treatment: The Chemistry of Their Formation and Control, Lewis Publishers, FL, 1996, pp. 91–130.

[30] G.A. Cowman, P.C. Singer, Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances, Environ. Sci. Technol. 30 (1996) 16–24.

[31] B. Panyapinyopol, T.F. Marhaba, V. Kanokkantapong, P. Pavasant, Characterization of precursors to trihalomethanes formation in Bangkok source water, J. Hazard. Mater. 120 (2005) 229–236.

[32] Z. Zhao, J.D. Gu, X.J. Fan, H. Li, Molecular size distribution of dissolved organic matter in water of the Pearl River and trihalomethane formation characteristics with chlorine and chlorine dioxide treatments, J. Hazard. Mater. 134 (2006) 60–66.

[33] S.W. Krasner, M.J. Sclimenti, E.G. Means, Quality degradation: implications for DBP formation, J. AWWA 86 (1994) 34–47.

[34] S.K. Golfinopoulos, A.D. Nikolaou, Survey of disinfection by-products in drinking water in Athens, Greece, Desalination 176 (2005) 13–24.

[35] E. Malliarou, C. Collins, N. Graham, M.J. Nieuwenhuijsen, Haloacetic acids in drinking water in the United Kingdom, Water Res. 39 (2005) 2722–2730.