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SEASONAL DETERMINATION AND INVESTIGATION OF DISINFECTION BY PRODUCT FORMATION POTENTIALS (DBPFPS) OF SURFACE WATERS, İSTANBUL ÖMERLİ AND BÜYÜKÇEKMECE CASE STUDY

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ABSTRACT

All surface and ground waters include natural organic matter (NOM). During the disinfection, NOM reacts with chlorine and forms various types of halogenated disinfection by-products (DBPs). There are some studies in the literature about possible carcinogenic effects of DBPs on human health. Trihalomethanes (THMs) and haloacetic acids (HAAs) are the most widely known and most produced DBPs. Also there are lots of different types of DBPs occurring after the chlorination and sometimes absorbable organic halogens (AOX) measurement can be used for determining the total amount of DBPs. In this study raw water samples were taken from Büyükçekmece (BC) and Ömerli (OM) surface water sources in the seasonal basis. At the first stage water quality parameters were analysed and then samples were chlorinated. After the 7 days of reaction period THMs, HAAs, haloacetonitrilles (HANs), haloketons (HK), chloral hydrate (CH), chloropicrin (CP) and AOX measurements were conducted and undefined DBPs percentage of AOX was calculated according to the results of the measurements. In terms of OM and BC raw water undefined portion of AOX was averagely calculated as 59.4% and 58% respectively.

Keywords: AOX, Chlorination, DBPs, Formation potential, NOM

İSTANBUL ÖMERLİ VE BÜYÜKÇEKMECE YÜZEYSEL SULARINDA DEZENFEKSİYON YAN ÜRÜN OLUŞUM POTANSİYELİNİN (DYÜOP) MEVSİMSEL DEĞİŞİMİNİN İNCELENMESİ

ÖZET

Tüm yüzey ve yeraltı suları doğal organik maddeleri (DOM'lar) içermektedir. Dezenfeksiyon sırasında DOM'lar klorla etkileşmekte ve birçok halojenli dezenfeksiyon yan ürününü (DYÜ) oluşturmaktadır. Literatürde bazı çalışmalar DYÜ'lerin insan sağlığı üzerindeki potansiyel kanserojen etkisini ortaya koymaktadır. Trihalometanlar (THM'ler) ve haloasetikasitler (HAA'lar) en fazla bilinen ve oluşumu en fazla olan DYÜ türleridir. Bununla birlikte klorlama sonrası oluşan birçok değişik DYÜ türü olup, bazı durumlarda toplam DYÜ oluşumunun belirlenmesi için absorplanabilir organik halojenler (AOX'ler) ölçülmektedir. Bu çalışmada Büyükçekmece (BC) ve Ömerli (OM) ham sularından mevsimsel bazda numune alınmıştır. İlk aşamada su kalite parametreleri analiz edilmiş ve takiben numuneler klorlanmıştır. 7 günlük reaksiyon süresi sonunda, THM'ler, HAA'lar, haloasetonitriller (HAN'lar) haloketonlar (HK'lar) kloral hidrat (KH), kloropikrin (KP) ve AOX ölçümleri yapılmış ve sonuçlara göre DYÜ'lerin tanımlanamayan kısmı yüzde bazında hesaplanmıştır. OM ve BC için AOX'in tanımlanamayan kısmı sırasıyla %59,4 ve %58 olarak hesaplanmıştır.

Anahtar Kelimeler: AOX, Klorlama, DYÜ'ler, Oluşum potansiyeli, DOM

1. INTRODUCTION

All active water resources contain natural organic matter (NOM) [1]. Dissolved organic matter (DOM) in the surface waters originates from vegetation, soil, domestic or industrial sources, and comes from humic and non-humic materials [2, 3]. DOM is an important organic pollutant for rivers and approximately 50% in rivers consists of humic substances [4, 5]. It is known that these organic substances affect the efficiency and design of a large number of drinking water treatment plants. In

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addition to causing color, taste and odor problems in the water, they also react with disinfectants during the treatment and cause disinfection by-products (DBPs) [6-11].

All chemical disinfectants (chlorine [Cl_2], monochloramine [NH_2Cl], ozone [O_3], chlorine dioxide [ClO_2]) cause DBPs formation via reacting with DBPs precursors such as DOM and bromide ion present in natural drinking water. pH, temperature, duration of disinfection and disinfectant doses affect this process [12]. Humic substances are the most important DOM components due to the fact that they form more than 300 different types of DBPs during disinfection. Therefore, the control of DBPs is usually based on DOM removal [13].

In addition to THMs and HAAs, lots of halogenated DBPs such as halocetons, haloacetonitriles (HANs), chloropicrin, cyanogen halides and chloral hydrate are also present in chlorinated drinking water with much lower concentrations than THMs and HAAs. For this reason, total organic halogen (TOX) parameter was defined to collectively measure all or nearly all of the halogenated DBPs at once in 1970s. TOX is a representative parameter that can be used to identify all species containing chlorine, bromine and iodine bound to the organic structure existing in the water [14].

In general, it is more accurate that the amount of organic halogen determined by pyrolysis of activated carbon is called as AOX instead of TOX. However, from the point of view of drinking water, it is considered that the difference between the TOX and AOX parameters are little if any and their expressions are nearly the same [15].

According to literature many DBPs are mutagens, carcinogens or toxicants characteristic. Because of this issue several DBPs species are regulated to limit their adverse effects to humans, for example THMs and HAA_5 limits are set by the US Environmental Protection Agency as 80 $\mu g\ L^{-1}$ and 60 $\mu g\ L^{-1}$ respectively; while the UK and Turkish limit for THM_4 is 100 $\mu g\ L^{-1}$. World health organization (WHO) implements limit values for THMs species separately as 60 μg/L for Bromodichloromethane, 100 μg/L for Bromoform, 300 μg/L for Chloroform and 100 μg/L for Dibromochloromethane. Also two haloacetonitrille species are limited by who as 70 μg/L for Dibromoacetonitrile and 20 μg/L for Dichloroacetonitrile [16, 17].

In the scope of this study, raw water samples were taken from Ömerli and Büyükçekmece Raw Water Sources located in İstanbul. At first step water quality parameters were investigated and then samples were chlorinated and DBPs measurements were conducted. In the context of DBPs analysis four types of haloacetonitriles (HANs), two types of haloketones (HK), chloral hydrate (CH) and chloropicrin (CP) analysis were made in addition to THMs and HAAs analysis. These components present in chlorinated water with lower concentrations than THMs and HAAs and they are considered as priority DBPs in the literature. Particularly in the United States, these DBPs are subjected to research about determining the potential toxicity and the quantities in water [18, 19].

There are very limited study in Turkey about the other DBPs formation potentials in the raw water sources except THMs and HAAs. The aim of this study is to fill this gap in the literature. DBPs analysis results were also compared with the AOX results so that identified and unidentified DBP species percentage in the water after chlorination were identified.

2. MATERIALS AND METHODS

2.1. Sampling Points

In this study samples were taken on the seasonal basis between 12.02.2010- 22.02.2011 from Ömerli and Büyükçekmece Lakes. These two water sources are the two big and important drinking water supplies of İstanbul and supply approximately 20% of the total daily drinking water requirement [7-9].

2.2. Chlorination Procedure

Standard Methods 5710 B method was applied for the chlorination procedure. According to method samples are placed in 125 mL glass bottles with screw caps and buffered at pH: 7.0 ± 0.2 and chlorinated with NaOCl dosing solution with the 5mg/mL concentration. After chlorination, all samples are placed into the incubator at 25 ^{0}C for 7 days of reaction time. At the end of the reaction time free chlorine residual between 3-5 mg Cl_2/L are expected in the sample. Experiments with the concentrations of four, five and six times Cl_2 of DOC concentration were conducted and by means of six times dosage free chlorine residual procedure was provided between 3-5 mg/L.

2.3. DBPFP Analysis

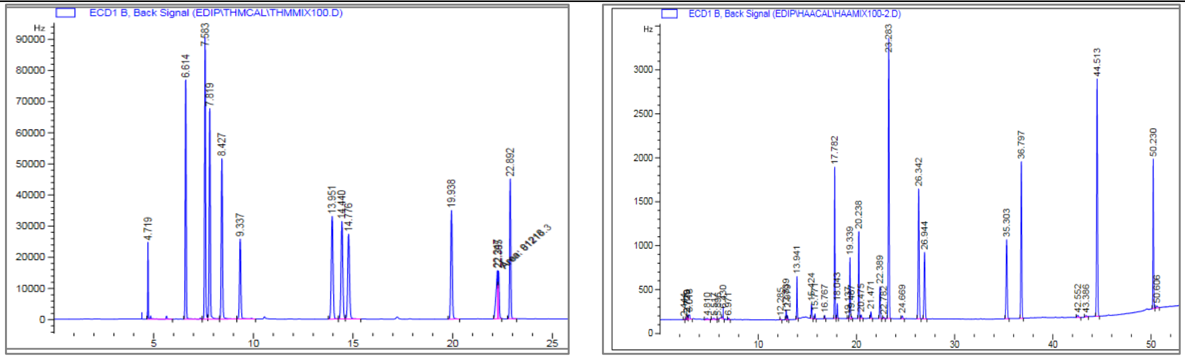
After seven days of reaction period samples were dechlorinated with 0.1 mL of 100 mg/mL sodium sulphide solution and then disinfection by product formation potential (THMFP, HAA_9FP, HANFP, HKFP, CHFP, CPFP) measurements were applied by means of GC-μECD (Agilent 6890). Also AOX measurement was applied by means of Behr Cl10 AOX Analyzer. The procedure was based on EPA 551.1 method in order to determine THMs, HANs, CP and CH. For HAAs and AOX, EPA 552.3 and ISO 9562:2004 methods were used respectively. DBP groups and types analyzed in this study were tabulated in Table 1. GC- μECD conditions utilized were tabulated in Table 2. Chromatograms related with EPA 551.1 method and EPA 552.3 method were given in Figure 1a and 1b respectively. For DBP groups' calibrations, all of the analytes were purchased from AccuStandard New Haven/USA.

Table 1. DBP groups and types analyzed in this study.

Disinfection By Products		**Types**		
Group	**Abbreviation**	**Name**	**Abbreviation**	**Cas Number**
Trihalomethanes	THMs	Chloroform	TCM	67-66-3
		Bromodichloromethane	BDCM	75-27-4
		Dibromochloromethane	DBCM	124-48-1
		Bromoform	TBM	75-25-2
Haloacetonitrilles	HANs	Trichloroacetonitrille	TCAN	545-06-2
		Dichloroacetonitrille	DCAN	3018-12-0
		Bromochloroacetonitrille	BCAN	83463-62-1
		Dibromoacetonitrille	DBAN	3252-43-5
Haloketons	HKs	1,1,1- trichloropropanone	TCP	918-00-3
		1,1-dichloropropanone	DCP	513-88-2
Haloacetic acids	HAAs	Monochloroacetic acid	MCAA	79-11-8
		Dichloroacetic acid	DCAA	79-43-6
		Trichloroacetic acid	TCAA	76-03-9
		Monobromoacetic acid	MBAA	79-08-3
		Dibromoacetic acid	DBAA	631-64-1
		Tribromoacetic acid	TBAA	75-96-7
		Bromochloroacetic acid	BCAA	5589-96-8
		Bromodichloroacetic acid	BDCAA	71133-14-7
		Dibromochloroacetic acid	DBCAA	5278-95-5
-	-	Chloral hydrate	CH	302-17-0
-	-	Chloropicrin	CP	76-06-2

Table 2. GC-µECD conditions [7-9]

Parameters	**Methods**							
	EPA 551.1				**EPA 552.3**			
Analitical Column								
Model	DB 1							
Manufacturer	J&W Scientific Folsom CA							
Type	fused silica capiler							
Lenght (m)	30							
Internal diameter (mm)	0.32							
Film tickness (µm)	1							
Injector								
Injeection Volume (µL)	2							
Temperature (°C)	200				180			
Dedector								
Type	µECD							
Temperature (°C)	300				280			
Oven Program								
	^{0}C/min	Next ^{0}C	Hold min	Run Time (min)	^{0}C/min	Next ^{0}C	Hold min	Run Time (min)
Initial	-	35	9	9	-	35	10	10
Ramp1	1	40	3	17	5	75	15	33
Ramp 2	6	150	1	36.22	5	100	5	43
Ramp 3					5	135	10	60
Carrier gas								
Type	Helium							
Carrier flow (mL/min)	1.3				13.9			
Makeup gas								
Type	Nitrogen							
Makeup flow (mL/min)	58.7				40			
Detection limit (µg/L)	0.1				0.1			



Retention time	Component	LOD* (µg/L)	LOQ* (µg/L)	Mean Recovery (%)
4.719	TCM	0.055	0.075	99.4
6.614	TCAN	0.002	0.004	100.6
7.583	DCAN	0.006	0.010	94.4
7.819	BDCM	0.003	0.005	98.7
8.427	CH	0.005	0.011	100.8
9.337	DCP	0.002	0.007	101.9
13.951	CP	0.002	0.014	102.1
14.440	DBCM	0.001	0.007	99.8
14.776	BCAN	0.002	0.009	106.2
19.938	TCP	0.016	0.016	101.6
22.305	TBM	0.004	0.006	100.2
22.892	DBAN	0.006	0.010	100.6

Retention time	Component	LOD*	LOQ*	Mean Recovery (%)
15.771	MCAA	0.17	1.00	119.8
19.339	MBAA	0.027	0.5	102.4
20.238	DCAA	0.020	0.5	101.9
22.389	Dalapon acid	0.024	0.5	100.6
26.342	BCAA	0.016	0.50	101.1
26.944	TCAA	0.019	0.50	100.4
35.303	DBAA	0.012	0.50	101.7
36.797	BDCAA	0.034	0.50	95.7
44.513	CDBAA	0.054	0.50	95.8
50.230	TBAA	0.11	0.50	96.6

(a) **(b)**

Figure 1. Chromatograms related with EPA 551.1 method (a) and EPA 552.3 method (b)
(*Limit of detection (LOD) and limit of quantification (LOQ) values were taken from EPA 551.1 and EPA 552.3 methods.)

3. EXPERIMENTAL RESULTS

3.1. Raw Water Quality

Within the scope of the experimental studies, raw water samples were analyzed in terms of quality parameters. During the sampling period; pH, chloride, bromide, sulphate, hardness, alkalinity, conductivity, salinity, and TDS parameter concentrations were higher for BC than OM (Table 3). This difference was a consequence of Marmara Sea water intrusion to BC water supply.

DOC and SUVA distribution of OM and BC waters were given in Figure 2. According to the figure BC water DOC concentrations were generally higher than (except May and August) OM water. DOC concentrations varied seasonally and it was understood that increment and decrement trends were similar with the long term air temperature variations. Generally highest DOC levels were determined in the rainy seasons. Both of the water showed low $SUVA_{254}$ ($SUVA_{254}$<3 L/ mg.m) water characteristic. This finding is similar to the literature and indicated that OM and BC waters contained low molecular weight, hydrophobic and aromatic DOMs [7, 8, 9, 20].

Table 3. Raw water quality characterization of OM and BC for sampling period [7]

Parameter	Unit	OM		BC	
		Average	Std. Dev.	Average	Std. Dev.
pH	-	7.73	0.22	8.23	0.08
Cl -	mg/L	18.2	3.3	36.7	8.5
Br -	mg/L	0.038	0.024	0.104	0.053
SO_4^{2-}	mg/L	22	9	55	3
Hardness	$mgCaCO_3/L$	98	19	200	14
TKN	mgN/L	0.7	0.3	0.7	0.4
NH_3	mgN/L	0.155	0.164	0.244	0.223
Alkalinity	$mgCaCO_3/L$	78	23	161	30
Conductivity	µS/cm	238	19	505	37
Salinity	%	0.011	0.001	0.023	0.001
TDS	mg/L	116	11	249	21
DOC	mg/L	3.595	0.325	3.765	0.411
UV_{254}	1/cm	0.093	0.015	0.083	0.020

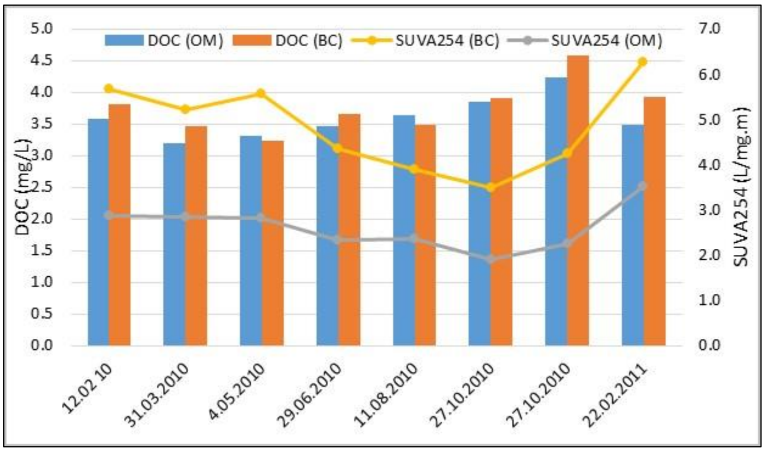


Figure 2. OM and BC waters DOC and SUVA variations in the sampling period

When average DOC (BC:3.765 and OM:3.595 mg/L according to SM 5310 D) and UV_{254} (BC: 0.083 cm^{-1}; OM:0.093 cm^{-1}) values of this study were compared with literature [18] (DOC; BC:4,08 and

OM:3.90 mg/L according to SM 5310 B; UV_{254}; BC: 0.072 cm^{-1}; OM:0.066 cm^{-1}), it was seen that there was no significant variation between this study DOC results and concentrations given in the literature. The difference between the DOC concentrations were thought to be caused by the difference of the DOC measurement methods. UV_{254} values showed an increase in the both of the waters but increment level of OM was more significant than that of BC. This indicated that aromatic content of OM increased significantly in years. Difference between SUVA values of this study (BC: 2.224; OM: 2.613 L/mg.m) and literature [20] (BC:1.785; OM:1.732 L/mg.m) also supported to this idea.

3.2. THMs Formation Potential (THMFP) Analysis

According to Figure 3, THMFP levels of both waters varied seasonally. Generally the highest THMFP concentrations in both waters were determined in autumn, winter and the lowest concentrations were determined in spring and summer seasons. OM THMFP values (min: 150; max: 374; avg: 233 µg/L) were higher than BC (min: 122; max: 406; avg: 205 µg/L). This commonly indicated that THMs were higher in rainy seasons and that DOM entering the water in that season was important precursor in terms of formation potential.

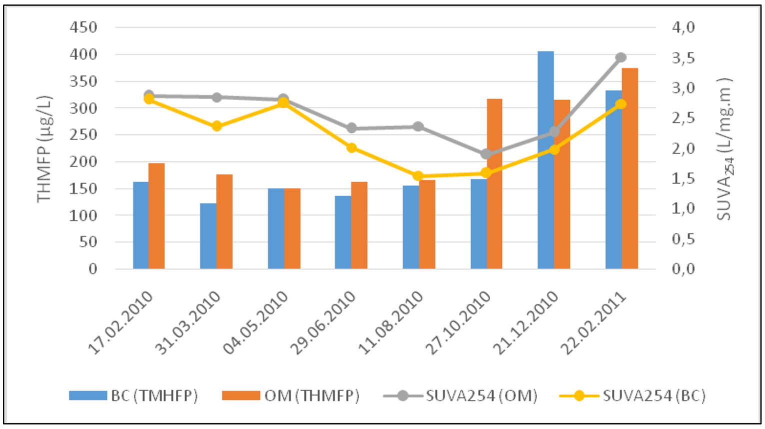


Figure 3. OM and BC waters THMFP variations in the sampling period

In both waters, the dominant THMs species was TCM and it accounted for more than 80% and 45% of THMFP in OM and BC respectively during the sampling period. Similar results were determined in the literature [18, 19]. This is related to the low bromide content of raw waters in Turkey. In both waters, BDCM and DBCM are the most common species following TCM formation. According to one study, the average sampling period THMFP was determined as 164 and 126 µg/L for OM and BC respectively [18]. According to another study, average raw water THMFP was determined as 213 and 237 µg/L for OM and BC respectively [20]. The increase in THMFP concentrations over the years coincides with the increase in SUVA value of raw waters. This situation originated from the increase of DBPFP due to the increase of aromatic structure in water [20]. In addition, as different from other studies in the literature OM raw water THMFP was determined as higher than BC. This situation was due to the increment of the waters aromaticity characteristics by years. Concentrations of brominated THM species (BDCM, DBCM, TBM) were higher in BC due to higher bromide concentration than OM.

3.3. HAA_9 Formation Potential (HAA_9FP) Analysis

As can be seen from Figure 4, HAA_9FP levels were similar to THMFP levels and varies during the sampling period in both waters. Unlike THMFP, BC raw water HAA_9FP level was generally higher than OM. During the sampling period, the HAA_9FP concentrations of OM and BC raw waters varied between 170 to 355 µg/L (average: 271 µg/L) and 200-337 µg/L (average: 257 µg/L). This suggested that the HAA_9FP levels of both waters were generally higher than THMFP levels. The predominant HAAs species were determined as DCAA and TCAA which produce more than 65% of HAA_9FP in OM and more than 40% of HAA_9FP in BC. Due to the higher bromide concentration of BC water, the concentrations of brominated HAAs species (TBAA, DBAA, MBAA) were higher in BC. According to literature, BC and OM sampling period average HAA_9FP were reported as 105 µg/L and 80 µg/L, respectively [18]. It was believed that the increase in SUVA over the years had led to an increase in the amount of HAAs like THMs. It was seen that dominant species forming HAAFP in both raw waters have not changed. HAA_9FP and $SUVA_{254}$ alteration trends in the sampling period were more compatible in BC than OM raw water.

3.4. HANs Formation Potential (HANFP) Analysis

HANFP distributions of both waters are considerably lower than THMs and HAAs (Figure 5). The highest HANFP level in OM and BC waters were determined in March (OM: 9.1 µg/L, BC: 16.5 µg/L), and the lowest concentrations in June (OM: 4.3 µg/L, BC: 3.7 µg/L). The average HANFP concentrations of the sampling period were determined as 6.8 µg/L for OM and 7.2 µg/L for BC. In both water sources firstly DCAN and then DBAN species were formed more than other species. BCAN and TCAN were not detected in some samples that were formed at lower concentrations. Similar to the findings in literature, the concentrations of brominated HAN species were detected as lower than chlorinated species [21, 23]. This was due to the lower bromide content of both waters than the chloride content.

3.5. HKs Formation Potential (HKFP) Analysis

It was determined that the HKFP levels of the sampling period were lower than THMFP, HAAFP and HANFP levels (Figure 6**Hata! Başvuru kaynağı bulunamadı.**). It was generally observed that HKFP levels were higher in BC raw water than OM except for the summer season. During the sampling period, the average HKFP concentration was found as 4.58 µg/L and 5.10 µg/L respectively for OM and BC. In terms of HK species in both waters, TCP levels were higher than DCP. According to literature, it was seen that the highest HKFP concentrations were obtained by the chlorination of groundwater and varied between 0.24-10.4 µg/L in İzmir drinking water network [19]. HKFP values obtained for OM and BC were close to the values obtained in the literature [21].

3.6. CH Formation Potential (CHFP) Analysis

The concentrations of CHFP measured in the sampling period were lower than THMFP and HAAFP but higher than HANFP and HKFP concentrations (Figure 7**Hata! Başvuru kaynağı bulunamadı.**). Average CHFP concentration was determined as 20.68 µg/L and 33.99 µg/L respectively for OM and BC in the sampling period.

The highest concentration value was detected for BC water in May sample, which had a possibility of measurement error. However it was reported in the literature that the THMFP and N-Nitrosodimethylamine formation potential (NDMAFP) values obtained in BC water varied. Point or diffuse anthropogenic pollution sources (domestic or industrial discharges, agricultural pollution) had this variation [24]. In this context, it was necessary to investigate this subject in more detailed. In the US, the average CH concentration in water resources was found as 5 µg/L, and concentration varied between 0.5 µg/L to 92 µg/L in the network. The CH content in the surface waters (median 4 µg/L) was higher than groundwater (median 0.5 µg/L) [25] When the results of the study were compared with the literature, it was seen that CHFP in the waters were generally similar with the literature, except for the value obtained in May for BC. It was reported in the literature that by using of alternative disinfectants (chloramines and ozone) instead of chlorine the occurrence of DBPs was reduced, but that of CHFP was increased [26].

3.7. CP Formation Potential (CPFP) Analysis

The CPFP levels measured in the sampling period were determined as the lowest occurrence potential in the by-products measured. As can be seen in Figure 8, the CP concentration in both waters was remained below the detection limit for several months. Due to the higher aromaticity content of OM raw water (average 2.32 µg/L) CPFP was higher than BC water (average 1.81 µg/L). The lowest concentrations were determined in summer seasons in both waters. These results were similar with THMFP results on the seasonal basis. Chloropicrin is formed during the reaction of chlorine with humic acids, amino acids and nitrophenols in water. Nitrate content in the water increases the formation. It is present in drinking water and transformed into chloroform in the presence of reducing substances. In the literature, the average and maximum concentrations were found as 0.6 µg/L and 5.6 µg/L respectively [27].

3.8. AOX Formation Potential (AOXFP) Analysis

After chlorination, AOXFP was measured to represent the sum of all halogenated DBPs in both water sources (Figure 9). As can be seen, the AOXFP values of both waters varied on a seasonal basis. In general, except for the samples of June and December 2010, it was determined that the OM water AOXFP was higher than BC.

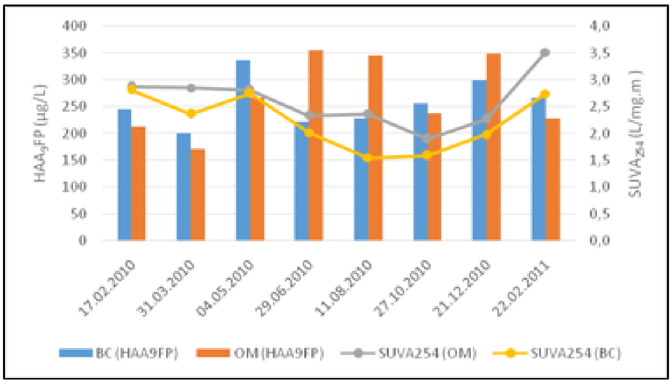


Figure 4. OM and BC waters HAA9FP variations in the sampling period

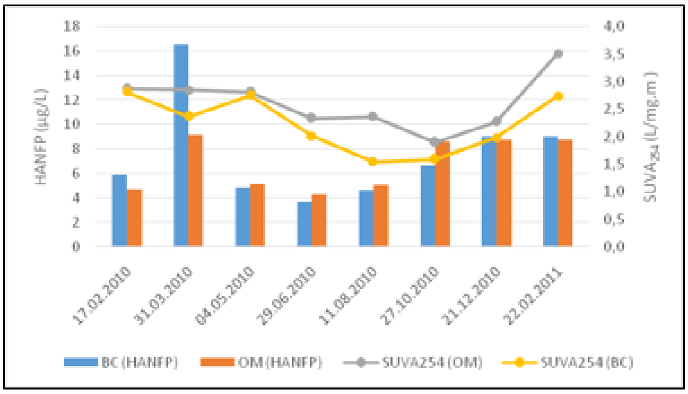


Figure 5. OM and BC waters HANFP variations in the sampling period

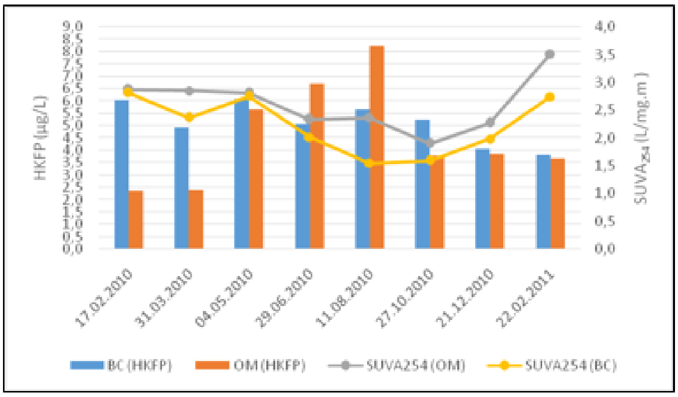


Figure 6. OM and BC waters HKFP variations in the sampling period

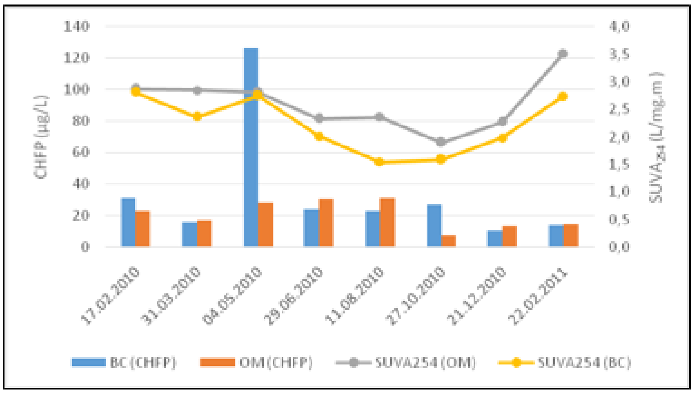


Figure 7. OM and BC waters CHFP variations in the sampling period

This situation was similar with other DBPFPs and due to the high aromaticity of OM compared with BC. Sampling period average AOXFPs were 1048.39 µg/L and 992.05 µg/L for OM and BC respectively. In the study, the concentration of each of the DBPs formed after chlorination was calculated in terms of chlorine equivalent, and the values obtained for each sample were added and the sum was compared with the AOXFP of that sample. Thus it was determined how much of the measured AOXFP could be identified and how much was not. Figure 10 and Figure 11 showed the percentages of the species identified and unidentified fraction of the AOXFP in the OM and BC raw waters during the sampling period.

In terms of OM raw water the most important contribution to AOX on the species basis was seen by the THMs and HAAs. The contribution of THMFP to AOXFP varied between 10.1% (May) to 34.9% (December) and the average contribution in the monitoring period was determined as 21%. The second most important contribution to AOXFP was provided by HAAFP. Generally, contribution to AOXFP during the sampling period varied between 7.8% (February 2011) to 27.4% (December) and the average contribution in the monitoring period was determined as 17.3%. The contribution of other species to AOXFP varied between 1.1% (February 2011) to 3.3% (August) and the average of the monitoring period was 2.3%. The unidentified part in OM varied between 35.3% (December) to 75.3% (May) in the sampling period and the average was 59.4%. These results showed that, despite the species being measured, there was an important byproduct potential in the water that could not be identified on the species basis.

In terms of BC, the most important contribution to AOXFP on the species basis was seen by the THMs and HAAs similar to the OM. The contribution of THMFP to AOXFP generally varied between 7.7% (June) to 41% (December) and the average contribution in the sampling period was determined as 20.4%. The second most important contribution to AOXFP was provided by HAAFP. Generally, contribution to AOXFP during the sampling period varied between 9% (June) to 25.9% (October) and the average contribution in the monitoring period was determined as 18.2%. The contribution of other species to AOXFP varied between 1.4% (June) to 6.7% (May) and the average of the monitoring period was 3.3%. The unidentified part in BC varied between 36% to 81.9% (May) in the sampling period and the average was 58%.

These results showed that unidentified species constituted larger percentage of AOXFP in the BC compared to the OM. According to literature the use of alternative disinfectants instead of chlorine reduces THMFP, HAAFP and TOXFP. Previous studies in the literature have shown that 30-60% of TOXFP can be determined on the species [24]. The relationship between the occurrences of DBPs species was statistically analyzed by SPSS program (Pearson correlation). When the obtained data were evaluated, It was determined that, there wasn't any linear relationship between DBP species and AOXFP. In this context, the unidentified part of AOX formation is thought to be more effective in increasing or decreasing of AOX.

According to Kristina et. al., (2009) it was determined that THMFP after chlorination constitutes up to 47 % of TOXFP. Considering the different studies in the literature, it has been stated that only 50% of TOXFP can be determined in species basis. Krasner et al. (2006) reported that using alternative disinfectants instead of chlorine reduced THMFP, HAAFP and TOXFP. It has been determined that 30-60% of TOXFP can be determined on species basis according to previous studies in the literature, and in that study, the measured DBPs were constituted 30-39% of TOXFP.

Kim and Yu, (2005) conducted chlorination study on highly hydrophilic water. According to results 26% of measured TOXFP was THMs and, 43% of HAAs, and 31% could not be identified. In the study conducted by Ateş et al., (2007), DBPFP of 29 different surface water sources in Turkey was investigated. According to results THMs and HAAs formation potentials varied between 10% to 56% f AOXFP. It had been reported that investigation of other DBPs were required. The highest AOXFP measured in the study was reported to be 652 µg / L measured in Büyükçekmece water.

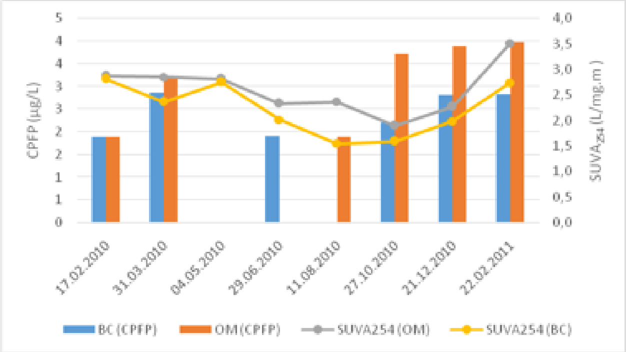


Figure 8. OM and BC waters CPFP variations in the sampling period

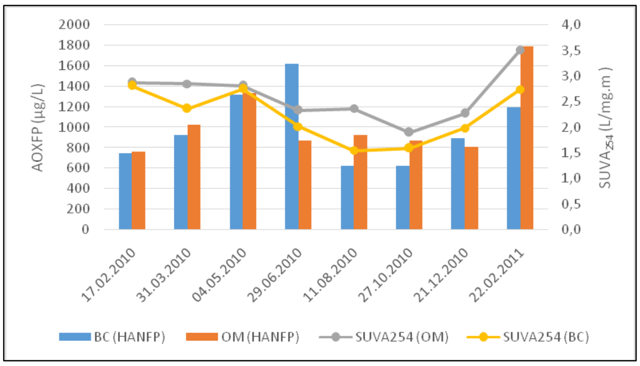


Figure 9. OM and BC waters AOXFP variations in the sampling period

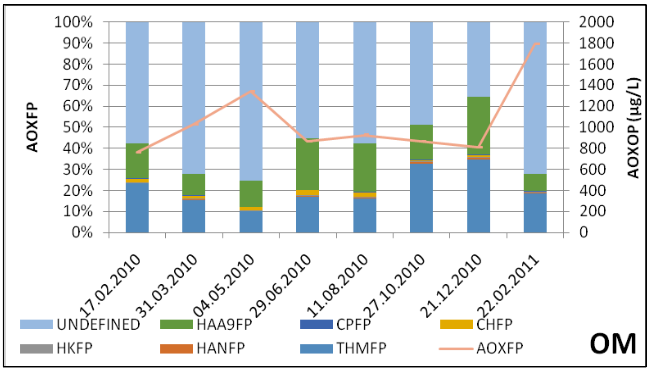


Figure 10. Percentage distributions of species forming AOXFP in OM raw water

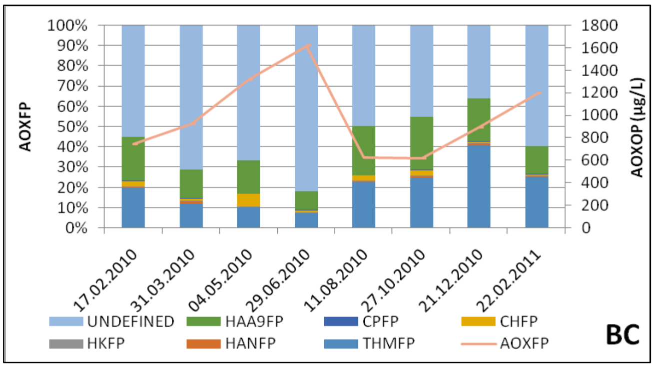


Figure 11. Percentage distributions of species forming AOXFP in BC raw water

In this study, it was observed that the proportion of species identified in AOX were sometimes lower than the literature and could be reduced to about 18%. Different from the observations by Kim and Yu (2005), in this study THMs appeared to have a higher percent than HAAs in terms of AOXFP distribution. It has been observed that the AOXFP distribution varies seasonally in both the OM and BC, and the unidentifed portion was highest in the spring season.

As reported in Ateş et al., (2007) and further developed in this study, species that can not be identified in water vary in a wide range on a seasonal basis and this issue needs to be further investigated. Similar to the mentioned study, no significant statistical relationship was found between DBP species and AOX formation, this indicated that the different precursor compounds affect the formation of THM, HAA and highest portion of AOX in water.

4. CONCLUSIONS

Within the scope of the study, raw water samples were taken from Ömerli and Büyükçekmece which are the most important drinking water sources of Istanbul, in 8 different months between February 2010 and February 2011. Water quality parameter analyses were carried out at the first stage in the receiving samples. Experimental studies were then carried out to determine the DBPFPs of the waters. In the monitoring period, the DOC concentrations of both waters generally remained below 4 mg/L. In general, BC raw water DOC concentration was little bit higher than OM. When the other quality parameters were examined; pH, chlorine, bromide, sulphate, conductivity, alkalinity, conductivity, salinity, and TDS parameters were higher in BC raw water than OM water. This was the result of Marmara Sea water intrusion to BC. In terms of Ömerli raw water, most important DBPs were THMs (sampling period average was 21%) and HAAs (sampling period average was 17.3%) respectively. Undefined portion of

AOX was averagely calculated as 59.4% for the sampling period. Similar to the Ömerli, in terms of Büyükçekmece raw water most important DBPs were THMs (sampling period average was 20.4%) and HAAs (sampling period average was 18.2%) respectively. Undefined portion of AOX was averagely calculated as 58% for the sampling period. According to this finding significant portion of AOXFP was not detectable on a species basis for both of the waters.

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