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FORMATION OF CHLORINATED ORGANICS IN DRINKING WATER OF ISTANBUL (TURKEY) AND SALERNO (ITALY)

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ABSTRACT
The occurrence of THMs and HAAs, and other volatile organics in Istanbul (Turkey) and Salerno (Italy) surface water resources was investigated by the previous and present data obtained on raw, coagulated, pre-chlorinated, pre-ozonated water samples. The present drinking water directives/regulations in developed countries set maximum contaminant level (MCL) for THMs at different levels. In Italy, where the 80-85% of water demand is supplied by groundwater, a relatively low THMs value of 30 µg l^{-1} was set, however there are no HAAs and bromate limits. On the other hand, there is still no regulation for the THMs in Turkey. The characterization of chlorinated by-products, particularly THMs, is detailed according to raw water origin and treatment technologies currently applied in both cities.

KEYWORDS: chlorinated by-products, TTHM formation potential, TTHMs and HAAs, surface water, pre-chlorination, pre-ozonation

1. INTRODUCTION
The interaction of chlorine with bromine and organics (e.g., humic and fulvic acids) naturally occurring in raw water, results in chlorinated or brominated disinfection by-products (DBPs) including trihalomethanes (THMs: chloroform-$CHCl_3$, dichlorobromomethane-$CHCl_2Br$, dibromochloromethane-$CHBr_2Cl$, bromofrom-$CHBr_3$), haloacetic acids (HAAs), haloacetonitriles (HANs) (Rook, 1974). Among these THMs are the most abundant compounds in chlorinated waters and HAAs concentrations are much lower (Palacios *et al.*, 2000; Villanueva *et al.*, 2003). The occurrence of THMs in finished drinking water is a matter of concern for human health because they are potentially carcinogen compounds (USEPA, 2002).

DBPs levels can vary greatly within a single water supply, depending on both water quality (e.g., total organic carbon (TOC), bromide, pH, temperature, ammonia, carbonate alkalinity) and treatment conditions (e.g., disinfectant dose, contact time, TOC removal before disinfection) (Amy *et al.*, 1987, USEPA, 1998). The THMs formation rate was

reported to increase with increasing pH (Krasner *et al.*, 1989) while that of HAAs and total organic halogen (TOX) decreases. Reckhow *et al.* (1990) showed a linear relationship between chlorine consumption and the activated aromatic content of the various humic and fulvic acids extracted from natural waters.

The control of THMs by reducing organic precursors, commonly expressed as NOM removal, using enhanced/optimized coagulation has a prime relevance (Bell-Ajy *et al.*, 2000, Rizzo *et al.*, 2004). The USEPA (1998) points out enhanced coagulation, joined to granular activated carbon (GAC) adsorption and precipitative softening among the best available technologies (BATs) for THMs control. Meanwhile photocatalysis (Bekbölet and Ozkosemen, 1996; Bekbolet *et al.*, 1996) and photoelectrocatalysis (Selcuk *et al.*, 2003) have become promising advanced oxidation technologies for NOM removal. Among many kinds of semiconductors, TiO_2 is the most widely employed catalyst due to its low cost, physical/chemical stability and its ability to mineralize chlorinated by-products precursors such as humic acids (HA) to CO_2.

The risks related to THMs formation force the community to look for alternative water sources, treatment methods or disinfectants. As an alternative disinfectant, chlorine dioxide (ClO_2) is commonly used in preoxidation and disinfection steps of surface water treatment due to low formation of THMs compared to chlorinated water (Li *et al.*, 1996; Chang *et al.*, 2000). However, disinfection with ClO_2 results in chlorite formation, disinfection by product not yet classifiable as to health effects and, namely, human carcinogenicity (USEPA, 2002). Although typically used as an oxidant, ozone is more effective than chlorine, chlorine dioxide, or chloramines for the inactivation of water-borne pathogens (von Gunten, 2003). Ozone has also some disadvantages which include; *(i)* increased biodegradable organic carbon (BDOC) *(ii)* formation of brominated disinfection by-products such as bromate; *(iii)* not stabile for the protection of the treated water in distribution system; (*iv*) more expensive and has more technological requirements than chlorination.

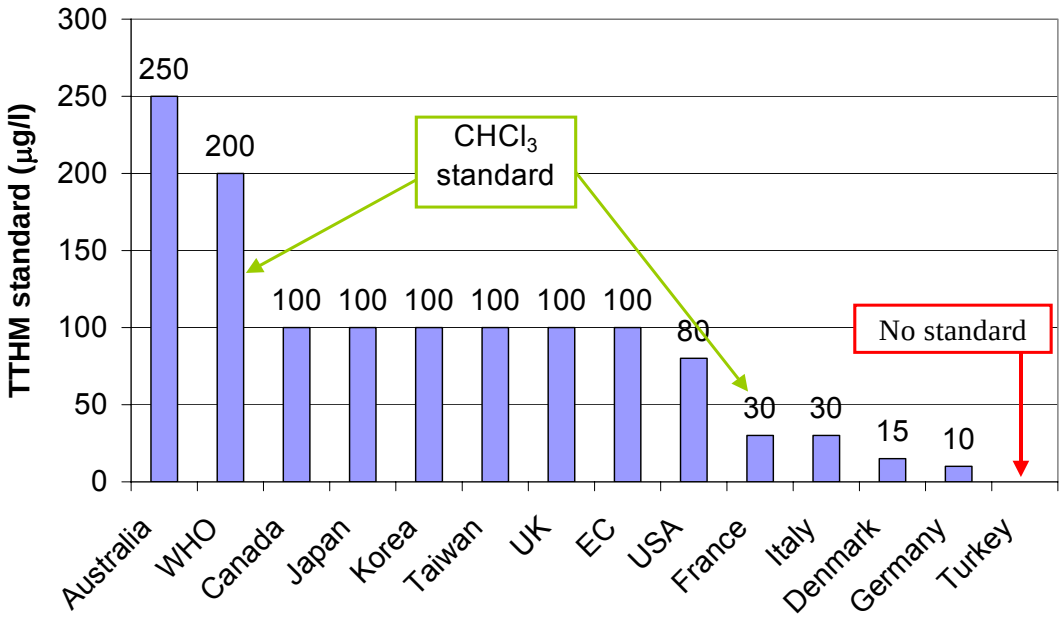

Figure 1. TTHMs standards in different countries

Standards and maximum contaminant level (MCL) for THMs were set at different levels in developed countries (Figure 1). In Italy, having 80-85% of water demand satisfied by groundwater, a relative lower THMs value of 30 µg l^{-1} was set (Official Journal of Italy, 2001). The drinking water treatment plants using chlorination are in Apulia region

(Souther Italy) and they asked the Italian Health Ministry for an extension of THMs limit to 60 μg l^{-1} (Official Journal of Italy, 2003). Other extensions were requested by Foggia and Brindisi provinces as 80 μg l^{-1} for Foggia and Brindisi provinces. However, in Turkey no regulation for THMs has been set yet.

This research focused on the evaluation of THMs formation in different water origin from Istanbul (Turkey) and Salerno (Italy). Treatment technologies currently applied and solutions to improve the efficiency in DBPs control are also detailed. Recent data on THMs, HAAs and other organics are presented for the same water resources.

2. MATERIALS AND METHODS

2.1. Sampling and conservation

The raw and finished samples were taken from Alento constructed basin and Basso Sele ground water resources in summer season (Salerno, Italy). The samples were delivered into the Environmental Analysis Laboratory of Salerno University within 1 h to be analysed or stored at 4 °C for further analyses. Previous THMs data for the raw and finished water for Istanbul's water resources were obtained from Istanbul Water and Sewage Works Administration Laboratory (www.ISKI.gov.tr).

The raw water samples taken in June 2004 were chlorinated and after 7 days of incubation, the free chlorine was blocked by thiopentasulpate, than they were transported as cooled to the Environmental Monitoring Laboratory of Aegean University, Greece for being analysed for THMs and HAAs formation potential.

2.2. Analytical measurements

Raw and finished samples were filtered through 0.45 μm GMF filter (25 mm GD/X, Whatman Inc, USA) for DOC and UV_{254} adsorbance measurements. TOC and DOC were measured by a SHIMADZU analyzer (model 5000A). UV-Vis spectrophotometer was used to measure UV_{254} absorbance (PerkinElmer, model Lambda12, USA). THMs were measured by GC-MS (ThermoFinnigan, USA) with column for organohalogenated compounds (Supelco, USA), according to 5710B method (AWWA-APHA-WEF, 1998). pH (Hach Ins, model 9024, USA) and turbidity (Hach Ins, model 2100N) were also monitored.

The THMFP and HAAs-FP measurements of June 2004 samples were performed using a Hewlett Packard Gas Chromatograph (GC) 5890 Series II with a ^{63}Ni Electron Capture Detector (ECD). The carrier gas was He and the make-up gas N_2. The column used was fused silica DB-1, 30 m x 0.32 mm i.d. x 0.25 μm film thickness. The injection technique was split/splitless. The applied analytical methods as well as their evaluation have been reported elsewhere (Nikolaou et al, 2002a,b). Recoveries ranged from 87.6% to 112.8% for THMFP, from 60.4% to 144.5% for the other chlorinated by-products and from 78.1% to 123.7% for HAAs-FP. The DLs (estimated for signal-to-noise ratio 3:1) ranged from 0.005 μg l^{-1} to 0.070 μg l^{-1} for the volatile chlorinated by-products (CBPs) and from 0.01 μg l^{-1} to 0.2 μg l^{-1} for HAAs.

3. RESULTS AND DISCUSSION

3.1. Water resources and characteristics

Turkey

Istanbul is divided into two parts by the Bosphorus between the Black Sea and the Sea of Marmara. 65% of inhabitants of around 12 million lives on the European side while the rest is on the Asiatic side. Total water demand of Istanbul is supplied from Büyükçekmece, Sazlidere and Terkos Lakes in European and Ömerli, Darlik and Elmali reservoirs in Asian sides (Figure 2). Currently water demand is about $1.1*10^9$ $m^3 y^{-1}$ and it was estimated as 2.195 mil. $m^3 y^{-1}$ for 2020 (Selcuk *et al.*, 2004). Average water quality is classified slightly polluted in Darlik, polluted in Terkos, Buyukcekmece and Alibeykoy and

high polluted in Elmali reservoir (Table 1). Poor water quality in the most of reservoirs is attributed to the urban settlement, industries and farms in the catchment areas (Selcuk *et al.*, 2004) in the catchment areas.

Buyukcekmece treatment plant consists of pre-chlorination using chlorine gas while in Omerli treatment plant pre-ozonation is applied. Table 2 shows the chemicals used at the treatment plants.

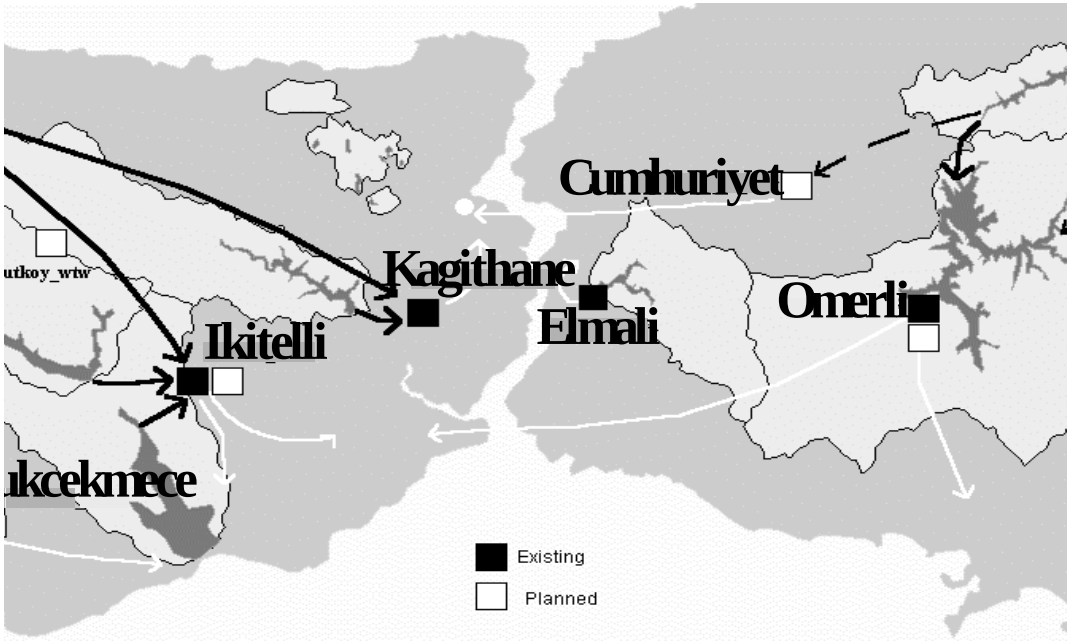

Figure 2. Location of the sampling point and water treatment plants in Istanbul, Turkey

Table 1. Capacities and basic characteristics of water treatment plants in Istanbul

Plant	Symbol	Treated water in 2000 (m^3)	Turbidity (NTU)		TOC ($mg\ l^{-1}$)
			Raw water	Treated water	Raw water
Ömerli	WTP1	301 541 881	3.1 (1.2 – 5.51)[1]	0.5 (0.3 – 0.6)	3.0-3.5
Kağıthane	WTP2	158 091 572	11.6 (6.9 – 20)	0.8 (0.6 – 1.1)	2.8-4.2
Ikitelli	WTP3	83 582 300	3 (2.6 – 3.8)	0.3 (0..3 – 0.5)	3.0-4.2
B. Cekmece	WTP4	67 260 287	3 (2 – 4.5)	0.4 (0.27 – 0.6)	2.7-4.4
Elmalı	WTP5	4 702 352	6.9 (2 – 20.9)	0.9 (0.5 – 1.3)	3.5-5.5
TOTAL		615 178 392			

[1] minimum and maximum values measured.

Table 2. Chemicals used in water treatment plants in Istanbul for the year 2000.

Plant	Alum		Cl_2		Poly	PAC	O_3		Hypoch.
	($kg\ y^{-1}$)	($mg\ l^{-1}$)	($kg\ y^{-1}$)	($mg\ l^{-1}$)	($kg\ y^{-1}$)	($kg\ y^{-1}$)	($kg\ y^{-1}$)	($mg\ l^{-1}$)	($kg\ y^{-1}$)
WTP1	9 107 380	27	2025208	6.7	45 400				
WTP2	4 385 114	26	627042	4	--		In part		1785
WTP3	2 600 726	30	212165	2.5	8 361		12374 0	1.4	
WTP4	1 833 945	23	343235	5.1	3 813				
WTP5	349 750	71	26068	5.5	--	3 275	1 996	0.4	

Italy

The annual report of the Italian Environmental Protection Agency (APAT, 2003) shows that the use of groundwater resources increased from 80% to 85% between the years 1993-1998.

Particularly, in several coastal areas with great tourist vocation the population can increase from 3 to 10 times mainly in southern Italy, thus water requirement can be only satisfied by integrative treated surface water. Figure 3 shows the location of the water treatment plant constructed in Alento basin which was main concern of this study. In Figure 3, the schematic presentation of the existing treatment plant is also shown. The Alento constructed basin has a capacity of $26*10^6$ m^3 y^{-1} and its $7.3 \cdot 10^6$ m^3 y^{-1} part can be used to produce drinking water in summer season. The treatment plant consists of pre-oxidation with ClO_2, on line coagulation with polyaluminium chloride (PACl) addition, filtration and final disinfection with the use of ClO_2 (Figure 3).

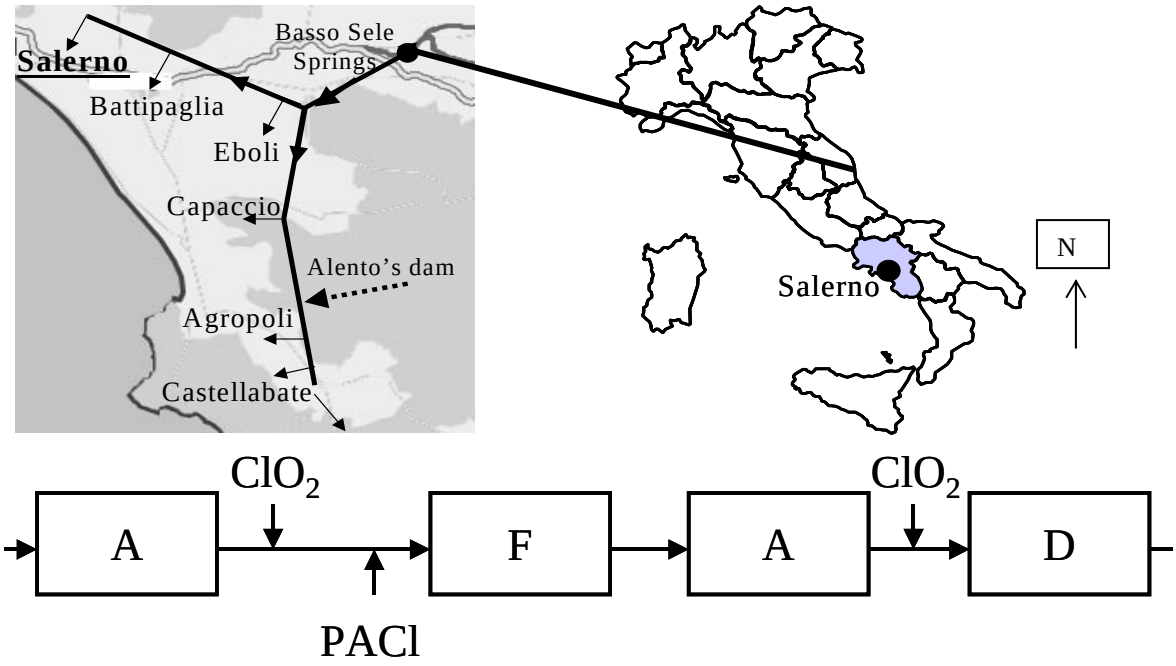

Figure 3. Schematic representation of the water system in the province of Salerno, Italy

The characteristics of some water resources used in the province of Salerno are presented in Table 3.

Table 3. Water characteristic of some drinking water sources in Salerno province

Resource	Type	T (°C)	pH	Alk (mg l^{-1})*	Br^{-1} (mg l^{-1})	NO_3^- (mg l^{-1})	TOC (mg l^{-1})	DOC (mg l^{-1})	UV_{254} (1 cm^{-1})
Alento (SA)	CB	18.6	7.66	192.5	-	-	2.8-4	2.96	-
Basso Sele	SW	13.7	7.14	303.3	0.19	0.9	0.20		0.002
W1 (Eboli)	GW	14.2			0.06	2.62			0.079
W2 (Eboli)	WW	16.7	7.13		0.016	6			0.011
W3 (Eboli)	WW	11.6	6.3		0.12	0.59			0.001
W4 (Eboli)	WW	15.2	7.17		0.06	19.2			0.010
W5 (Eboli)	WW	15.2	7.01		0.07	8.38			0.004

*as mg $CaCO_3$ l^{-1}; CB: constructed basin; SW: spring water; GW: groundwater; WW: well water

The Basso Sele (SA) springs have a flow rate of 1,600 l s^{-1} and continuously being used to supply water to 50 municipalities in Salerno province. Due to high water quality only disinfection with sodium hypochlorite (0.2-0.4 mg Cl_2 l^{-1}) is applied as treatment.

3.2. THMs in raw and finished water

Turkey

The THMs concentrations detected in November 1999 in finished water of some Istanbul water treatment plants are shown in Figure 4. The use of pre-ozonation in Elmali treatment plant (WTP5b) resulted in the average 65% reduction of THMs formation. The average TTHMs concentration in finished water from Buyukcekmece plant (WTP4) was above USEPA limit (80 µg l^{-1}). The formation of TTHMFPs varied depending on the nature of the water and treatment process efficiency; i.e. in the case of chlorine pre-oxidation in Elmali, chloroform ($CHCl_3$) was the dominant specie while the percent of brominated species in total TTHMFPs increased in the case of ozone pre-oxidation although their concentrations were lower than the case of chlorine pre-oxidation. Although no pre-ozonation is used, by the fact that its bromide concentration is high (> 275 µg l^{-1}), $CHBr_2Cl$ was the major THMs specie followed by $CHBrCl_2$ and $CHCl_3$ in Buyukcekmece plant.

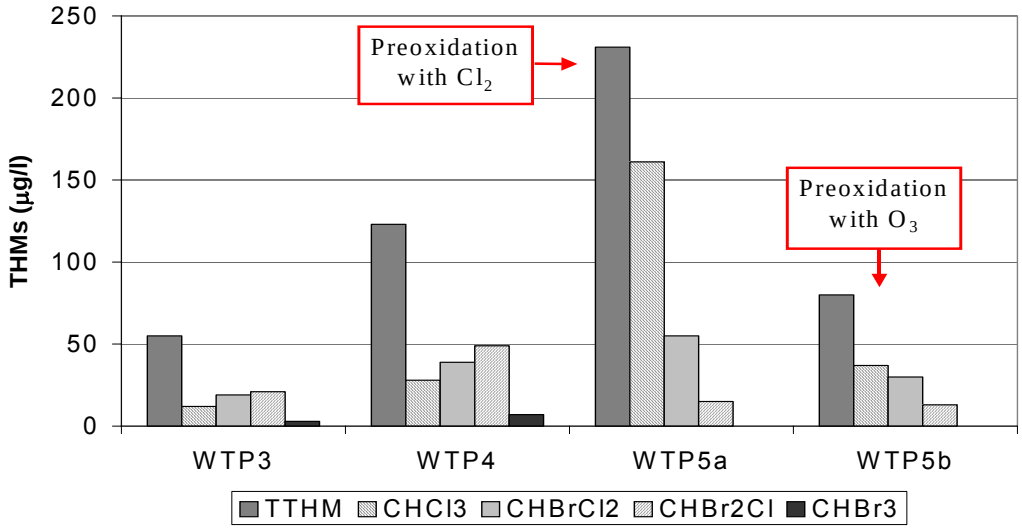

Figure 4. TTHMs in Istanbul water treatment plants

Figure 5 shows the monthly average variations in TTHMs in finished water of the treatment plants of Istanbul for the period of March 2002-Febrauary 2004. According to those results, TTHMs level in Buyukcekmece and Elmali (ozone pre-oxidation) finished water decreased approximately 50% due to improvements in coagulation process and decreased final chlorine dose used. The highest levels of TTHMs were observed in Buyukcekmece and Kagithane finished water. There was around 50% of difference in TTHMs of the treatment plants between winter and summer seasons. These results were in accordance with the previous studies (Gallard and Gunten, 2002).

Italy

The average TTHMFPs of raw water of Alento basin were measured as 234 µg l^{-1} for water characteristics varied from 3-4 mg $l^{-1}$of TOC, 2.7-2.9 mg $l^{-1}$of DOC, 2-3 l $(mg\text{-}m)^{-1}$ of specific UV_{254} absorbance ($SUVA_{254}$) and 190 mg as $CaCO_3$ l^{-1} of alkalinity. Bromide concentration was below detection limit. As well as the high level of TTHMFPs (>150 µg l^{-1}) in raw water, ratios of the dominant species in total amount was more interesting because the brominated species are still under suspicions of the carcinogenicity studies (Lily *et al.*, 1994; USEPA, 2002). The water treatment decreased TOC and TTHMFPs

levels at 20 and 35%, respectively. However, due to high chlorite formation in the effluent, the improvement of organic THMs precursors removal by jar test was evaluated with the aim of replacing ClO_2 with Cl_2. By using PACl dose up to 30-35 mg Al_2O_3 l^{-1} TOC removal was enhanced at 20% and TTHMFPs was reduced to less than 30 μg l^{-1} (Rizzo *et al.*, 2004).

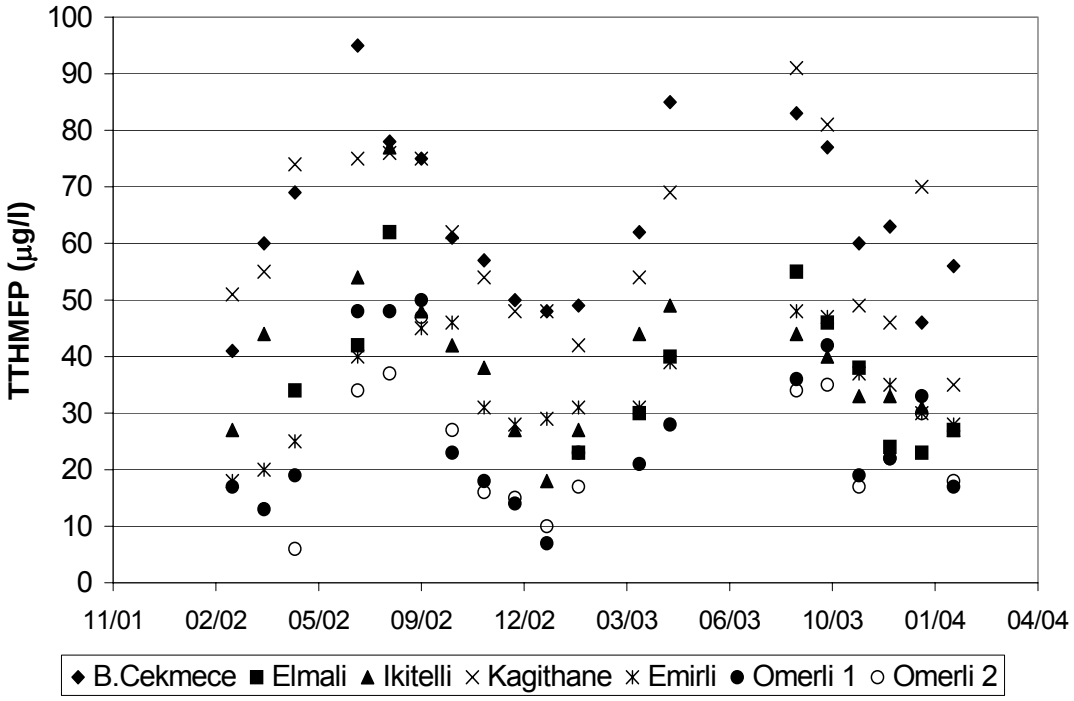

Figure 5. THMFPs of TTHMs in water resources of Istanbul between 2002 and 2004

TTHMFPs, (SP) level of Basso Sele springs (SPW) and the water from wells were measured much lower (25-109 μg l^{-1}) than Alento basin. The groundwater with too low NOM content, measured as TOC and UV_{254} (Table 3), contributed to hold low TTHMs formation risk. However, the groundwater yielded the highest concentrations of brominated species, particularly $CHBr_3$, and almost no chloroform formation (SPW, WW3, WW4). The spectra of the species formed are to be studied by integrating with the toxicological studies (Teuschler and Simmons, 2003).

3.3. TTHMFPs and HAA-FPs and other volatile organics measurements in raw water samples

The raw water characteristics of the June 2004 samples taken from Omerli and Buyukcekmece (Istanbul) and Alento (Salerno) water resources are given in Table 4. Buyukcekmece and Alento basin characteristics seemed to be similar in terms of UV_{254} and alkalinity with the exception of bromide concentration which was high in the Buyukcekmece water sample.

In chlorinated raw water samples by 20 mg l^{-1} of Cl_2, many chlorinated and other volatile organics were detected as presented in Table 5. THMs and HAAs were the most abundant substances, while the other CBPs (haloacetonitriles, haloketones) except chloral hydrate occurred at much lower concentrations. In terms of THMs, the order of the magnitude among the water samples was Buyukcekmece (159.4 μg l^{-1}) > Omerli (128.5 μg l^{-1}) > Alento (75.6 μg l^{-1}).

Table 4. Water characteristics of June 2004 samples

Parameter	Unit	Omerli	Buyukcekmece	Alento
Alkalinity	(mg l^{-1})	70	150	194.4
Turbidity	(NTU)	2.7	3.2	2.5
UV_{254}	(1 m^{-1})	0.97	0.1	0.1
TOC	(mg l^{-1})	3.05	3.61	Nm
Bromide	(μg l^{-1})	95	274	Nd
Chloride	(mg l^{-1})	45	98	14
Alluminum	(mg l^{-1})	Nm	Nm	0.025
Iron	(mg l^{-1})	Nm	Nm	0.172
pH	--	7.18	7.65	7.33

Nm: not measured

For the present water characteristics the distribution of the species changed with respect to the previous findings. For instance, in Omerli $CHCl_3$ was detected at higher level than brominated species while dibromochloromethane was the dominant specie and the brominated species were formed at considerable levels in Buyukcekmece water which has the highest level of bromide (0.274 mg l^{-1}). Neither Omerli nor Alento samples yielded bromoform at detectable level.

On the contrary, Alento sample exhibited the highest total HAAs concentrations, especially trichloroacetic acid (TCA, 137.7 μg l^{-1}), followed by dichloroacetic acid (DCA, 72.9 μg l^{-1}). TCA and DCA were the most dominant HAAs species for other resources as well (TCA: 19.7 μg l^{-1} and 41.4 μg l^{-1} for Buyukcekmece and Omerli, respectively, DCA: 23.1 μg l^{-1} and 36.6 μg l^{-1} for Buyukcekmece and Omerli, respectively).

Among other volatile DBPs, the major specie was chloral hydrate (CH) which was formed at levels comparable to or higher than THMs species (range 61.3-78.1 µg l^{-1}), while among haloacetonitriles monochloroacetonitrile (MCAN) and dichloroacetonitrile (DCAN) occurred at much lower concentrations. 1,1 Dichloroproponanone and 1,1,1-trichloropropanone were at detectable levels after 7 days of retention, although they have been reported to decompose in short time (Nikolaou *et al.*, 2001), which is an implication that their concentrations could have been higher just after chlorination, and then decreasing during the 7-d period due to their decomposition to chloroform. This could be also an explanation for the occurrence of relatively high chloroform concentrations even in samples from Omerli and Buyukcekmece waters with high bromide concentration.

4. CONCLUSIONS

The TTHMFPs varied seasonally in surface water resources for Istanbul. Due to relatively high TTHMs concentrations in the water treatment plant effluent attention must be paid to TTHMs concentration in the distribution network. The pre-oxidation with ozone as substitute to chlorine in Elmali water treatment plant significantly decreased TTHMs concentration in the effluent. Thus the upgrading of the Istanbul water treatment plants in terms of both ozone in place of chlorine (in preoxidation) and enhancing coagulation can improve TTHMs control.

The results obtained from Italian water resources showed that the level of TTHMFPs in raw water was high in the case of surface water, and after treatment it decreased by 35%. The raw groundwater yielded much more lower TTHMFPs (<100 μg l^{-1}) while the distribution of the species was different from surface to groundwater depending on raw water characteristics, in particular, TOC and bromide concentrations.

Table 5. TTHMFPs and HAAs-FPs and chlorinated compounds detected in the chlorinated Istanbul and Salerno's raw water samples

Concentration ($\mu g\ l^{-1}$)	Buyukcekmece	Omerli	Alento
THMs			
Chloroform	42.1	62.4	57.5
Dichlorobromomethane	49.3	42.5	15.9
Dibromochloromethane	65.8	23.6	2.2
Bromoform	2.2	Nd	nd
Total	159.4	128.5	75.6
HAAs			
Monochloroacetic acid	13.3	7.9	2.8
Monobromoacetic acid	2.5	2.7	2.4
Dichloroacetic acid	23.1	36.6	72.9
Bromochloroacetic acid	8.1	7.4	5.2
Trichloroacetic acid	19.7	41.4	137.7
Dibromoacetic acid	2.4	1.2	0.8
Bromodichloroacetic acid	8.7	9.3	3.6
Dibromochloroacetic acid	12.1	10.6	9.2
Tribromoacetic acid	nd	nd	8.4
Total	89.9	117.1	243
Other volatile DBPs			
Monochloroacetonitrile	2.4	2.0	2.0
Dichloroacetonitrile	3.5	3.4	3.9
Trichloroacetonitrile	nd	nd	nd
Chloral hydrate	69.2	78.1	61.3
1,1-Dichloropropanone	0.6	0.4	1.2
1,3-Dichloropropanone	nd	nd	nd
1,1,1-Trichloropropanone	0.7	0.7	0.9
Monobromoacetonitrile	1.6	0.6	2.6
Dibromoacetonitrile	1.1	0.9	nd
Bromochloroacetonitrile	nd	nd	3.2
Chloropicrin	nd	nd	nd

n.d. not detected

The recent water samples taken from Omerli and Buyukcekmece (Istanbul) and Alento (Salerno) showed different THMs characteristics from the previous results. The measurement of HAAs and other volatile chlorinated compounds enhanced the basic knowledge to evaluate the water quality and the water treatment systems for the particular water resources. However, detailed measurements are necessary, in more samples from both present and other water resources as well as toxicity studies conducted in parallel, to evaluate the effect of raw water characteristics on the DBPs formation and their control.

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