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The screening of disinfection by-products in large and small water systems in Greece

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ABSTRACT

In this paper, we investigated the presence of twenty four disinfection by-products (DBPs) including four trihalomethanes, six haloacetonitriles, three haloketones, chloral hydrate, chloropicrin and nine haloacetic acids, in drinking water treatment plants (WTPs) and their distribution systems of Athens for a period of more than ten years (1993–2005). The detection of trihalomethanes was also conducted in two smaller water distribution systems in Greece for a period of six months to one year to evaluate the effect of different quality of raw water on the formation of these compounds. In all cases, the determination of DBPs was conducted monthly. The concentrations of DBPs were determined by a gas chromatography method, which included sample preparation with liquid–liquid extraction for volatile DBPs and acidic methanol esterification for haloacetic acids. The DBPs concentrations detected varied depending on the raw water qualities, in the WTPs after the point of prechlorination and in the distribution system, while their presence was not noticed in raw water. In any case, with little exceptions, the trihalomethanes and haloacetic acids concentrations were lower than the maximum contaminant level set by European Community and USA Environmental Protection Agency.

Keywords: Drinking water; Chlorination; Disinfection by-products; Trihalomethanes; Haloacetic acids; Volatile disinfection by-products

1. Introduction

Chlorination is the most widely used disinfection method and has been used for this purpose since the early years of the twentieth century. It is now still used because it removes or inactivates pathogenic organisms responsible for waterborne diseases. It is extremely efficient, cost effective and easy during application compared to other methods as chlorine dioxide and ultraviolet irradiation (UV). However, the chlorination of water leads to the production of a wide range of halogenated compounds, known as disinfection by products (DBPs). DBPs are formed because of the reaction of chlorine, bromine or iodine with naturally occurring organics in surface and groundwater, such as humic and fulvic acids. The chemistry of these reactions is complex and it is impossible to predict exactly the nature and quantities of the chemical products that may be formed [1].

Most of the DBPs have been proved to have toxic effects on living organisms and they pose risks to human health during the consumption of drinking water. The exposure to DBPs can also occur through dermal contact and inhalation during showering, bathing, cooking or other activities as swimming in pools where the chlorination for the water disinfection is applied [2]. According to toxicological studies, several DBPs are carcinogenic in laboratory animals, included chloroform, which is a suspected carcinogen [3–5], while a number of past studies has predicted cancer risks from exposure to DBPs in drinking water [2].

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Trihalomethanes (THMs) and haloacetic acids (HAAs) are the major DBPs categories reported to be formed during chlorination of drinking water. Haloketones (HKs), haloketonitriles (HANs), chloral hydrate (CH) and chloropicrin (CP) are also frequently detected but at lower concentrations. Iodinated THMs and 3-chloro-4-(dichloromethyl)-5-hydroxy-5H-furan-2-one (MX) and analogues are also being detected in drinking water in trace concentrations [6].

Much of the current research on drinking water DBPs is focused on newly discovered brominated and iodinated DBPs (I-DBPs) which are particularly problematic because they often are more toxic than their chlorinated analogues [7]. Iodo-trihalomethanes (I-THMs), especially iodoform (IF) formed during drinking water treatment processes when I^- (from natural sources, sea-water intrusion or brines) is present in raw water, are known to cause unpleasant medicinal and pharmaceutical taste and odor. Recent mammalian cell toxicity results demonstrated that IF was 60 times and 146 times more cytotoxic than bromoform (BF) and chloroform (CF), respectively [8]. Although more than 500 DBPs have been reported in the literature, only a small number have been addressed either in quantitative occurrence or health effects studies [9].

It is well known that the formation of these compounds is affected especially from the naturally organic material of raw water, the chlorine dose applied during the disinfection process, the contact time of chlorine with water, temperature, pH and the bromide concentrations of water [10]. In the recent past, the development of many models have been performed for the prediction of the DBPs formation using data from the raw and treated drinking water [11].

This paper was focused on the research of the occurrence of twenty four DBPs in drinking water for a period of thirteen years in Greece and especially in Athens, as with existing analytical techniques, it is no possible to detect all categories of DBPs [11]. This survey is one of the most extensive in Europe and in Greece and the total number of samples and analysis results are thousands. For the first time, there is a detailed picture of the variability of DBPs levels for a very long period of time, from 1993 to 2005. There is little information available on the occurrence of the most significant categories of DBPs in Europe for a long and continuous period of time. THMs and five HAAs are regulated by national and European institutions, while the rest are non-regulated. Especially the regulatory limit for total THMs (TTHMs) set by European Union (EU) is 100 μg/l [12], while the Maximum Contaminant Level (MCL) set by US Environmental Protection Agency (USEPA) is 80 μg/l for TTHMs and 60 μg/l for five HAAs (monochloro-, dichloro-, trichloro-, monobromo- and dibromoacetic acid) [13]. EU has not established any regulatory limit for other volatile DBPs and HAAs.

2. Materials and methods

2.1. Sampling

In Greece, with the exception of Athens, a large proportion of all water supplied is drawn from groundwater. The disinfection of drinking water is mandatory for water supplied serving populations greater than 3,000 inhabitants. Little treatment is required for groundwater and in most cases only disinfection, especially chlorine, is applied. In Athens and Thessaloniki (the second larger city), there are public water companies, independent from municipality and functioning as private enterprises. The Athens Water Supply and Sewerage Company (EYDAP SA) supplies water abstracted from surface resources. In other places, serving populations from 10,000 to 200,000, there are municipal companies managing the sectors of water supply and serve as private companies. Twenty nine percent of the population is supplied from small plants (<5,000 inhabitants) [6].

In Athens, water treatment plants (WTPs) use mainly surface water as their raw water. Lakes Iliki, Mornos and Marathon (operates as an intermediate reservoir and supplied with water from Iliki lake) are the significant bodies of fresh water in Athens. Via Mornos, Iliki and other interconnecting aqueducts (total combined length of 500 km), raw water is transported from various sources to the four WTPs in the Athens area: Galatsi (GTP), Menidi (MTP), Polydendri (PTP) and Aspropirgos (ATP). These WTPs have a total capacity of 1.9 million cubic meters of water per day. First, raw water is pre-oxidized with chlorine and then the water treatment involves the processes of coagulation, sedimentation, sand filtration and finally disinfection with chlorination. Sometimes, the postchlorination is also applied before the input of finished water in the distribution network. From the finished storage reservoirs, water reaches the consumers through an extensive distribution network with an estimated total length of 7.55 million meters, which is constantly expanding and being refurbished [6]. Mytilene and Chalkida use groundwater mainly from local wells but and from boreholes and only chlorination is applied. In Mytilene, the total supply of water to 25,000 people was about 9,000 m^3/d, while in Chalkida the total supply of water to 52,000 people was about 3,000 m^3/d.

In Athens, chlorinated drinking water samples were collected from the different stages of water treatment and from representative points of distribution system (nine points). Samples including raw water were also collected from the WTPs influents. In Mytilene and Chalkida water supply systems, samples were collected from the distribution system and from the water sources (raw water), from September 1993–March 1994 and from November 1993–October 1994, respectively. In these regions, only THMs were studied.

Duplicate samples for THMs measurement were collected from each sampling location in 40-ml glass bottles and were capped with PTFE-faced silica septum (Pierce 13075), including samples containing raw water. Sample bottles were carefully filled just to overflowing, without passing air bubbles through sample or trapping air bubbles in sealed bottle. The bottles were prepared according to the standard methods as described elsewhere [1,14]. Samples were sent in cool boxes in the dark to the Water Quality Laboratory (WQL) for analysis at the Department of Environmental Studies of the University of the Aegean, in Mytilene. The water samples were collected on a monthly basis and in some cases (THMs detection) for four consecutive days. Because of the huge number of samples and the different analytical methods for each DBPs category, the samples collection does not refer to the same places at the same time for these thirteen years survey.

2.2. Analytical procedure

At first, liquid–liquid extraction (LLE) and Gas Chromatography (GC) were used to measure only the concentrations of THMs in the water samples

(Golfinopoulos et al., 1996), while later a modification of EPA Method 551.1 was also performed for analysis of volatile DBPs (VDBPs) including THMs, HKs, HANs, CH and CP. Acidic methanol esterification followed by GC with Electron Capture Detector (ECD) was applied for the determination of nine HAAs. A gas chromatography-mass spectrometry method (GC–MS) was also used for confirmatory purposes. All these methods that have been optimised by the authors have been described with details elsewhere [14].

The compounds studied were the following VDBPs: THMs including chloroform (CF), dichlorobromomethane (DCBM), dibromochloromethane (DBCM), bromoform (BF), HANs including monochloroacetonitrile (MCAN), trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), monobromoacetonitrile (MBAN), dibromoacetonitrile (DBAN), bromochloroacetonitrile (BCAN), HKs including 1,1- dichloropropanone (1,1-DCP), 1,1,1-trichloropropanone (1,1,1-TCP), 1,3-dichloropropanone (1,3-DCP). Chloral hydrate (CH) and chloropicrin (CP) were also determined. Apart from these compounds, a category of non-volatile DBPs including HAAs was also investigated. Monochloroacetic (MCAA), monobromoacetic (MBAA), dichloroacetic (DCAA), bromochloroacetic (BCAA), trichloroacetic (TCAA), dibromoacetic (DBAA), bromodichloroacetic (BDCA), dibromochloroacetic (DBCA) and tribromoacetic (TBAA) acid were investigated in this study. The detection limits of the compounds (estimated for signal-to-noise ratio 3/1) ranged from 0.005 to 0.20 μg/l and are presented in Table 1.

Table 1
Detection limits for DBPs concentrations

DBPs	Detection limits (μg/l)
CF	0.010
DCBM	0.005
DBCM	0.007
BM	0.010
MCAN	0.040
TCAN	0.070
DCAN	0.007
MBAN	0.040
DBAN	0.070
BCAN	0.040
1,1-DCP	0.040
1,1,1-TCP	0.040
1,3-DCP	0.070
CH	0.007
CP	0.040
MCAA	0.20
MBAA	0.05
DCAA	0.02
BCAA	0.02
TCAA	0.01
DBAA	0.02
BDCA	0.10
DBCA	0.20
TBAA	0.20

3. Results and discussion

The results of this survey show the occurrence of a large category of DBPs in water samples from Greece and especially in Athens drinking water. These compounds were detected only in water samples after the point of chlorination in the different stages of water treatment plant as well as in the distribution system, while no compound was found in raw water. This fact proves that the formation of the compounds studied results from the disinfection of water.

All DBPs were detected except MCAN and MBAN. Especially CF, DCBM, DBCM, BF (in some cases), CH, 1,1-DCP, 1,1,1-TCP, MCAA, DCAA, TCAA, DBAA, BCAA are the most frequently compounds that were detected during this large period of sampling. The other DBPs including DCAN, TCAN, DBAN, CP, BCAN, 1-3-DCP and the HAAs as MBAA, BDCA, DBCA and TBAA were detected in very low levels (less than 0.5 μg/l) in a small percentage of samples. According to the levels of concentrations and the frequency of detection, for better analysis of data, the results were divided in three main groups: group I involved only THMs, group II involved HAAs and group III consisted of VDBPs. Last group includes only three compounds CH, 1,1-DCP and 1,1,1-TCP. The rest of the DBPs were measured in very low concentrations or were not detectable.

Significant differences were observed between the WTPs in Athens and from region to region. The changes in DBPs concentrations can be attributed to the different organic content of raw water as the water treatment processes are similar. The surface waters and the boreholes, in case of city of Athens and city of Chalkida, produced larger levels of THMs than the groundwater in case of town of Mytilene.

Fig. 1 presents the annual mean concentrations of DBPs that were detected in finished water reservoirs of Athens WTPs. In GTP the THMs, HAAs, and other VDBPs ranged from 11.2 to 63.6 μg/l, from 16.3 to 70.2 μg/l and from 1.3 to 7.5 μg/l, respectively. In MTP (old unit) the THMs, HAAs, and VDBPs ranged from 11.6 to 34.5 μg/l, from 8.1 to 29.7 μg/l and from 1.1 to 6.8 μg/l, respectively. In PTP, THMs concentrations were similar to the levels measured in GTP and ranged from 15.7 to 62.6 μg/l, while HAAs concentrations were a little higher as during 2002 the mean annual concentration was 107.2 μg/l (11.2 μg/l was the lower annual value). VDBPs concentrations ranged from 0.8 to 13.1 μg/l. In ATP, the THMs, HAAs, and VDBPs ranged from 22.7 to 66.1 μg/l, from 10.5 to 24.4 μg/l and from 0.8 to 9.2 μg/l, respectively.

Fig. 2 presents the speciation of DBPs during the sampling period of 2001 in the finished water reservoir of GTP. During this period, CF was the predominant DBP compound represents about 32% of the total DBPs studied and follow TCAA and DCAA, that represents about 20% and 11% of DBPs, respectively. Similar results are obtained during the distribution of DBPs in other WTPs during this survey, with the exception of period 1993–1995 where the predominant species were brominated, due to the high levels of bromides (0.31–1.30 mg/l) [15].

In most cases, the concentrations of DBPs were higher in the finished water reservoirs (Fig. 3) as well as in the distribution system (Fig. 4) than in the effluents of sedimentation tank (first point of chlorination). This was expected as the reaction of chlorine with natural organic material (NOM) requires

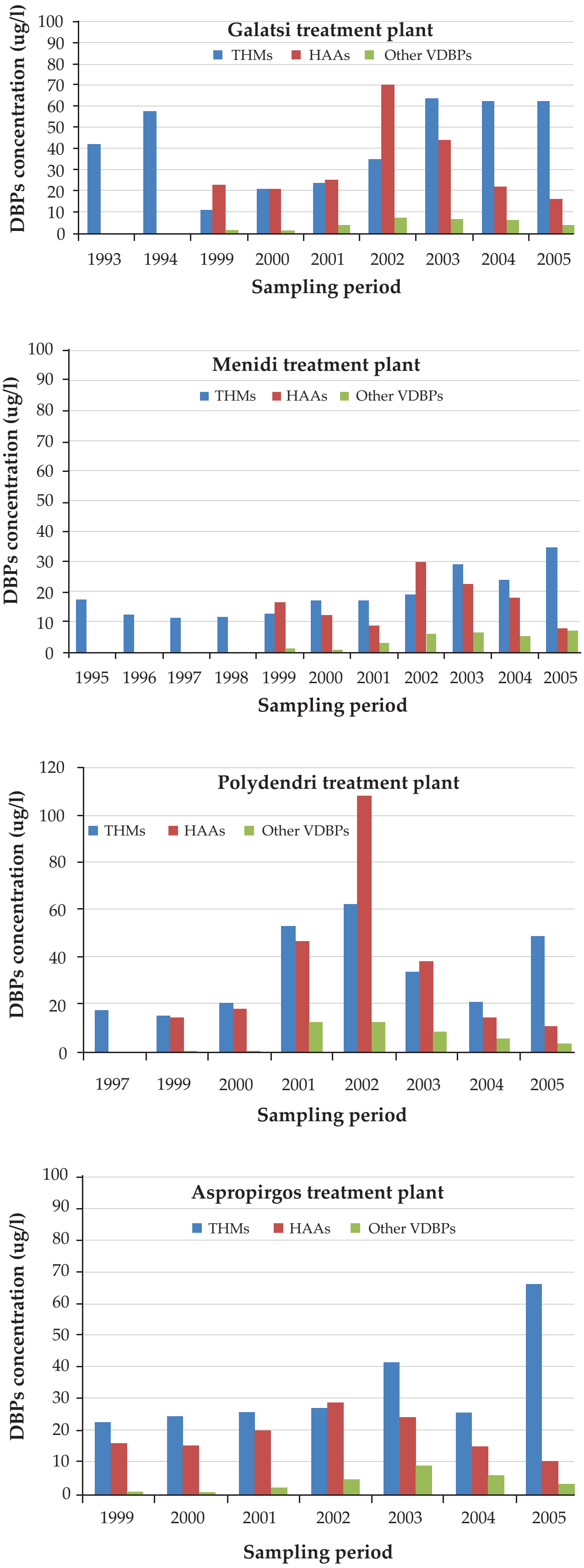

Fig. 1. Annual mean DBPs concentrations in finished water reservoirs of Athens WTPs during April 1993 to August 2005.

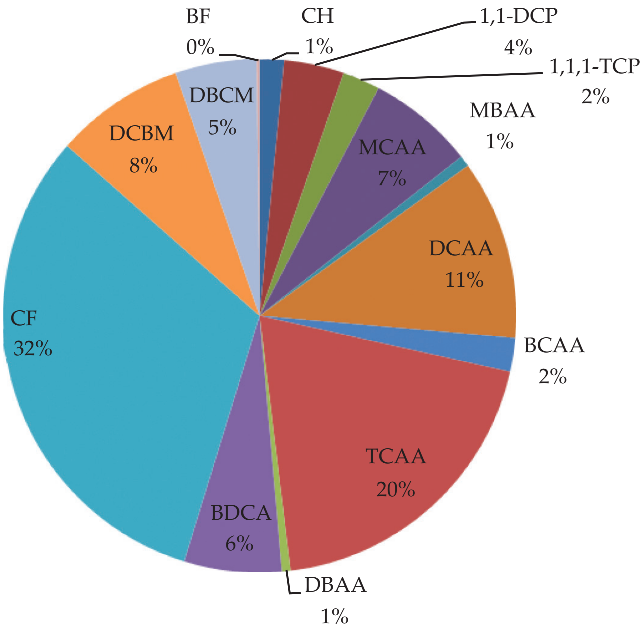

Fig. 2. Distribution of DBPs in finished water reservoir of GTP during 2001.

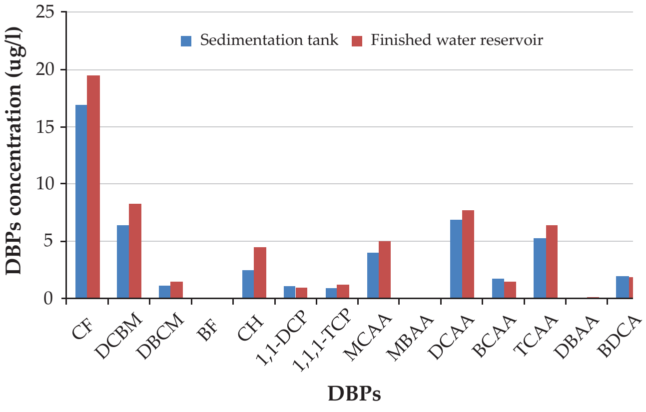

Fig. 3. DBPs concentration in the different phases of the MTP during 2003.

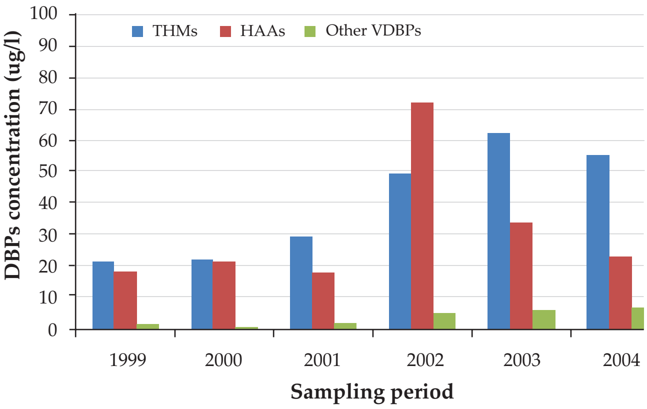

Fig. 4. Annual mean DBPs concentrations in distribution system of Athens (sampling point Piraeus) during January 1999 to December 2004.

time to be completed. It is obvious that in the finished water reservoir, the levels of THMs and HAAs concentrations were slightly higher or ranged in similar levels compared to the concentrations that detected in the effluent of sedimentation tank of WTPs, due to the longer reaction time. This trend did not appear for some other compounds as HKs and HANs where the concentrations levels were lower in the distribution system due to the decomposition with time.

As it concerns the levels of DBPs in the distribution system, recent research has demonstrated that their concentrations can also increase considerably between water distribution systems and the consumer's tap. This is due to stagnation in the plumbing pipes and hot water tanks and it is possible to increase risks to human health [2].

In the distribution system of Mytilene, the TTHMs mean concentrations ranged from 7.0 to 17.5 μg/l, while in Chalkida they ranged from 9.5 to 51 μg/l. The low levels in Mytilene is due to the lack of NOM in groundwater, as this type of water is poor in NOM which affects DBPs formation, in contrast with some sampling points of Chalkida that used boreholes and the levels of bromides were high. It is well known that the presence of bromides increases the yield of THMs and influences their distribution.

The DBPs results showed also some seasonal variation in agreement with many studies reported higher levels of DBPs in summer in contrast to winter (Fig. 5).

It is well known that the formation of DBPs influenced from the quality of raw water, the processes of treatment and the conditions of environment, especially the parameters NOM, chlorine dose, temperature, pH, bromides and reaction time of chlorine with the organic material. These parameters affect the formation of each category of DBPs in a different way. For example, increased pH values enhance THMs formation and limit HAAs formation and favor the HKs decomposition. Increased reaction time results in the formation of THMs and some species of HAAs in higher levels. On the contrary, long reaction time leads to the decomposition of HANs, HKs and other species of HAAs.

During this period of study (1993–2005), the levels of DBPs were generally low with the major categories to be THMs and HAAs. In all cases, TTHMs concentrations were lower than the EU limit of 100 μg/l. As it concerns VDBPs, their concentration ranged from no detectable to very low levels. In contrast, HAAs sometimes were detected in significant levels.

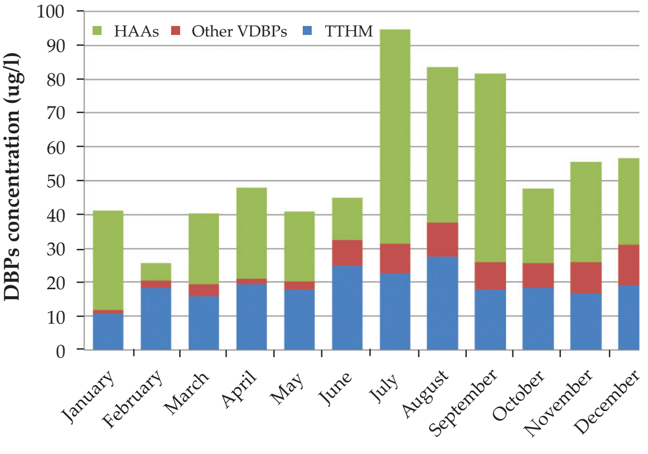

Fig. 5. Seasonal variation of DBPs in finished water reservoir of MTP during 2002.

Many studies have been conducted all over the world for the determination of these DBPs, with similar results. Some of them have shown that THMs and HAAs differ in spatial behaviour. The first studies were carried out in the 1990s, using chlorination and ozonation. It was noticed that the addition of chlorine caused the formation of halogenated species of DBPs. HAAs had a different behavior than THMs, while HKs and CH were detected at very low concentrations (below 1 μg/l) and no CP was detected [16]. An investigation of HAAs was also performed from 2008–2009 in Tunisia (Bizerte) and the analysis showed the detection of DBPs in all chlorinated samples. The most dominated species were TCAA, DCAA and MCAA while the other DBPs were detected at low levels. The TCAA, DCAA and, MCAA concentrations ranged from 3.9 to 26.25 μg/l, from 2.76 to 23.19 μg /l, and from 6.65 to 34.07 μg/, respectively. Seasonal variations in HAAs were observed and mainly linked with changes in water temperature and variations of natural organic materials. The highest HAA levels occurred in summer [17]. In North China, during one year survey for the determination of THMs and HAAs, their concentrations were almost 50 μg/l and detected in autumn. In contrast, the lowest levels of DBPs were found in spring and they did not exceed 10 μg/l. As it concerns the dynamic along the process, a continuously increase of THMs concentration was noticed while HAAs increased before the process of filtration and decreased significantly in the filtration tank [18]. In the past, in Finland, the results from an investigation of DBPs from 35 waterworks showed their detection in all chlorinated samples. Seasonal variations were also noticed in agreement with many studies reporting higher concentrations of DBPs in summer compared with winter. DCAA, TCAA and CF were the major DBPs while the concentration levels (108 μg/l) of six HAAs were higher than THMs concentrations (26 μg/l) [19].

4. Conclusions

In this work, the presence of 24 DBPs, including THMs, HAAs, HANs, HKs, CP and CH in four WTPs and in representative sampling points of distribution system in the area of Athens as well as in two other smaller water supply systems in Chalkida and Mytilene, was studied for a long time (about 13 years).

The results indicate the presence of all of them in the WTPs after the point of prechlorination, while their detection was not noticed in raw water. DBPs concentrations differed in the WTPs and from region to region. The groundwater showed little DBPs formation in contrast to surface water where the concentration levels were higher. The differences that were observed between the WTPs are due to the origin of water. A significant factor that affected the formation of DBPs was the natural organic material (NOM) of raw water.

Another significant factor was the reaction time of chlorine with the water as it affects THMs and HAAs formation in a different way compared to the other DBPs. In the samples from the distribution network, the concentrations of THMs and HAAs generally ranged in similar or slightly higher levels than within the WTPs, because their formation continues as water passes through the distribution network. On the contrary, the HKs and HANs in most cases showed decreasing trends due to decomposition in time.

The results showed that in most cases, the DBPs levels were low. The highest DBPs concentrations were detected in summer due to the high temperature and the increased dose of chlorine. THMs and HAAs were the most abundant DBPs.

The distribution of individual DBPs was affected from the bromides. In the case of high bromide levels, the predominant species were the brominated DBPs while the bromides ranged in very low levels and the chlorinated DBPs were the most abundant.

TTHMs and five HAAs are the only regulated DBPs. In any case, with little exceptions, the TTHMs and HAAs concentrations were lower than the MCL set by EU and USEPA.

For the detection of new unregulated DBPs in drinking water, more detailed surveys need to be conducted.

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