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Analytical Methods

Determination of organic compounds in bottled waters

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Abstract

The presence of organic compounds in bottled waters available in the Greek market and their fate when the representative samples exposed at different conditions were the main purposes of this study. The determination of the organic compounds was performed by gas chromatography–mass spectrometry techniques. Disinfection by-products compounds, such as trihalomethanes (THMs) and haloacetic acids (HAAs), were detected at low concentrations in bottled waters. As far as it concerns other organic substances, Greek bottled drinking waters did not contain volatile organic compounds (VOCs), and carbonyl compounds as well as other carcinogen and hormone disrupter phthalates were not identified, except for the plasticiser phthalate, diethylhexyl phthalate (DEHP). Moreover, samples contained other organic chemicals, whose identity has not yet been confirmed. The behavior of organic compounds was influenced by parameters such as conditions of storage, type of water. Finally, a comparison has been performed between the analysis of bottled and local tap waters.

Keywords: Organic compounds; THMs; DEHP; Bottled drinking water

1. Introduction

Bottled water consumption has been steadily growing up the last three decades in a global level (Ferrier, 2001). The main reasons for this rapid consumption are the lack of safe and accessible drinking water and the taste of chemicals, particularly chlorine, used to purify tap water. Furthermore, the efficient marketing and advertising strategies followed by the bottled water producers enhanced this consumption. An evidence is the fact that especially consumers who live in developed countries buy bottled water as a healthy alternative to other beverages, to improve their diet and health. Bottled water is called the packaged water that is commercially available for human consumption.

Bottled water is perceived as pure and safe, although this is not necessarily the case regarding the presence of organic compounds, as its quality can often be questionable. According to the Natural Resources Defense Council, a four-year American research revealed that one third of the bottled water samples analyzed contained bacteria or other chemical pollutants in levels that exceeded the regulatory limits.

Organic compounds such as chloroform or other disinfection by-products (DBPs) have been detected in bottled waters (Gibbons & Laha, 1999) in several countries all over the world. In Canada, Page et al. (1993) reported the occurrence of the volatile organic compounds (VOCs), toluene, benzene, chloroform and dichloromethane in the bottled waters. Moreover, the Kansas Department of Health and Environment tested 80 samples of bottled water coming from retail stores and manufacturers. According to the results, chloroform was detected in 53 of the 80 samples and bromodichloromethane in 33. Traces of some form of carcinogen and hormone disrupter phthalate were detected in 46 samples, while 12 of those exceeded federa safety levels for that chemical (Natural Resources Defense Council, 1999b). In China, in 2003, HAAs, especially dichloroacetic acid (DCA), were investigated in bottled

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drinking water. The concentration of DCA decreased significantly when storage time was increased. Other HAAs were not detected in the samples (Liu & Mou, 2004). In Poland, carbonyl compounds, particularly formaldehyde, acetaldehyde and acetone, were investigated in bottled waters. The storage conditions enhanced the process of migration from PET bottles or the formation of aldehydes into water (Nawrocki, Dabrowska, & Borcz, 2002). In addition, in Swedish laboratories the migration of organic compounds from the PET bottles into water was confirmed as low concentrations of di(2-ethylhexyl)phthalate (DEHP) while di(2-ethyl-hexyl)adipate (DEHA) was detected in their samples (Kohler & Wolfensberger, 2003). In Italy, Biscardi et al. (2003) identified low concentrations of DEHP in their sample after 9–10 months of storage. Studies in Spain showed that not only in plastic but also in glass packages of bottled waters the quality of water can be distorted. The analysis of glass bottled water revealed traces of 4-nonylphenol (4-NP) before and after the storage whereas the plastic samples contained low concentrations of DEHP and diethylphthalate (DEP) (Casajuana & Lacorte, 2003).

Deductively, there are three potential sources of organic pollutants in bottled water: (i) compounds which are initially present in the aquifer as contaminants; (ii) external contamination from bottling plant and (iii) migration from containers, especially during the storage (Casajuana & Lacorte, 2003; Nawrocki et al., 2002). Organic compounds such as chloroform and other THMs might originate from more than one source, e.g. natural or anthropogenic (Hoekstra, De-Leer, & Brinkman, 1998).

Due to health concern, there is an increasing attention on the quality of bottled drinking water (Liu & Mou, 2004). Epidemiological studies in test animals have indicated an increase in some kinds of cancer, behavior changes, anomalies in the reproductive and immunologic functions of some species, and damages of the central nervous system. Therefore both in America and in European Union, strict regulations have been set for the concentrations of organic compounds in drinking water. The FDA is responsible for the restrictions and regulations particularly as it concerns the bottled water. In Greece, there is no specific regulation related to organic compounds except for THMs at 0.1 $\mu g\, l^{-1}$.

The aim of this study was the investigation of the quality of bottled waters commercially available in Greece, before the Olympic games, regarding the presence of DBPs, DEHP, VOCs and base-extractable organic compounds. Furthermore, there is an attempt to estimate any potential degradation of bottled water quality due to the migration of pollutants from the bottling material or due to the formation of organic compounds through other pathways, before and after storage under varying environmental conditions. These conditions were selected according to the peak consumption of bottled waters in Greece and the usual method of storage. Moreover, a comparison between tap and bottled waters was performed.

2. Materials and methods

2.1. Glassware

The glassware used for the analysis was washed with detergent, rinsed with tap water, ultrapure water (Millipore: Milli-Ro 5 plus and Milli Q plus 185), acetone (Mallinckrodt Chemical Works, St. Louis) and dried in an oven at 150 °C for 2 h.

2.2. Reagents and standards

Methanol (Purge and Trap grade) was purchased from Sigma–Aldrich, methyl-tert-butyl ether (MTBE) suprasolv grade, sodium sulfate, copper (II) sulfate pentahydrate and sulfuric acid concentrated ISO for analysis from Merck. Ultrapure water came from a Milli-Q water purification system (Millipore: Milli-Ro 5 plus and Milli Q plus 185).

Stock solutions of volatile DBPs were prepared in methanol after adding certified DBPs standards (Chemservice, purity > 99%). Stock solutions of the nine HAAs and their methyl esters in MTBE, as well as DEHP, were purchased from Supelco and were accompanied by certificates of analysis (purity > 99%). All stock solutions were stored at 4 °C.

From the stock solutions, standard solutions of DBPs 100 $mg\, l^{-1}$ in MTBE were prepared, known volumes of which were injected into ultrapure water, giving standard solutions for system calibration.

The same process was followed in the case of HAAs and DEHP. The analysis of both blank and standard solutions in water, subjected to the same analytical procedure as real samples, was included in the daily analytical control protocol to reassure the quality of analytical results.

2.3. Sample collection and storage

Thirteen typical brands of bottled drinking water samples consisting of natural mineral and carbonized water types were purchased from retail stores in Mytilene in May 2004. All bottled waters were in either plastic or glass containers with plastic screw caps. The results of their physicochemical parameters as reported in their labels are presented in Table 1. These waters were analyzed twice: (i) immediately after purchase and (ii) after 3 months. To prevent any losses or transformations of the compounds contained in the water after opening of the bottle, different bottles of the same company were initially obtained, stored and used for each sampling. During 3 months, samples were stored up in two different conditions: (i) external (out-doors) exposed to sun and temperatures up to 30 °C and (ii) room storage conditions recommended by the container labels. In addition, bottles from different brands of bottled water were filled up with ultrapure water and exposed at external conditions, to determine the potential influence of the bottling material on the water quality. Moreover, tap waters from the local distribution network

Table 1
Physicochemical analyzes results reported on the bottled waters

Water samples	pH	Conductivity	Solid residue	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NH_4^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3 (N)	NO_2^-
1	na	na	na	100	130	410	20	na	1810	80	100	na	na
2	7.3	490	na	54	31.5	8.2	0.8	0.1	267.5	15	13.5	6.2	<0.05
3	8.2	650	na	12	73.7	19,2	0.8	<0.26	368	6.4	34.5	6.8	<0.05
4	6.5	1254	720	244	29.2	5.6	1.1	<0.26	885.5	5.7	<5	<5	<0.05
5	na	na	na	149	7	11.5	na	na	420	42	23	na	na
6	na	na	na	360	11.8	22	2.8	<0.26	na	na	10.2	<5	<0.05
7	7.6	396	na	68	8.2	9.2	1.3	<0.26	215.6	15.5	9.1	<5	<0.05
8	na	na	na	486	84	9.1	3.2	na	403	1187	10	na	na
9	8.2	652	370	12	73.3	20.9	0.8	<0.26	367.4	6.7	34.7	6.7	<0.05
10	7.3	509	291	101	2.1	4.7	0.8	na	na	4.3	10.2	4.3	0.0
11	6	na	na	4.5	1.3	3	0.5	na	15	4	5	1.9	na
12	7.62	472	na	102	0.7	2.1	0.8	<0.26	297.6	2.4	8.5	2.5	<0.05
13	7.75	406	260	78	3.2	3.5	1.5	<0.26	165	15	4.7	3.9	<0.05

na = not-reported.

(Mytilene) were collected in plastic bottles and analyzed to compare with the above samples.

Mytilene tap water sample was stored in two plastic bottles of the same brand, exposed to out-door conditions similar to bottled waters and the average of the replicates analysis was measured.

2.4. Sample preparation

For volatile DBPs, a modification of EPA Method 551.1 was performed, which includes Liquid–Liquid-Extraction (LLE) with MTBE, after adding anhydrous sodium sulfate (Nikolaou, Lekkas, Golfinopoulos, & Kostopoulou, 2002). For HAAs, acidic methanol esterification was used, which includes acidification to $pH < 0.5$, addition of anhydrous sodium sulfate and copper sulfate pentahydrate, LLE with MTBE and derivatization with solution of sulfuric acid in methanol (Nikolaou et al., 2002).

Volatile organic compounds (VOCs) were analyzed with a modification of the Purge and Trap–GC–MS method, which has been previously described (Golfinopoulos, Lekkas, & Nikolaou, 2001), without any sample preparation.

As regards DEHP and other organic compounds, sample preparation includes LLE of 1 L sample with 20 ml dichloromethane and 20 ml pentane, consecutively, after adding 5 g anhydrous sodium sulfate. The extracts are combined, dried with sodium sulfate, concentrated to dryness in a water bath, and redissolved in 1 ml dichloromethane (Kanaki, Nikolaou, Makri, & Lekkas, 2007; Nikolaou, Kanaki, & Lekkas, 2004). The validation data for all analytical methods mentioned above (recoveries, %RSD and detection limits for the particular compounds) have been reported in detail by Golfinopoulos et al. (2001), Kanaki et al. (2007), Nikolaou et al. (2004, 2002).

2.5. Instrumentation and analytical conditions

For the determination of DBPs, a Hewlett Packard gas chromatograph (GC) 5890 Series II with a ^{63}Ni electron capture detector (ECD) was used. The analytical conditions of GC for this method are presented in Table 2.

For the determination of volatile and semi-volatile organic compounds and for the investigation of the potential presence of other organic compounds, a Hewlett Packard gas chromatogragh (GC) 5890 Series II with mass selective detector 5971 was used. In the case of volatile compounds, the Hewlett Packard Purge and Trap concentrator 7695 was used. The analytical conditions are presented in Table 2 for the determination of VOCs and DEHP.

During the analysis of VOCs, the samples were analyzed both in selected ion monitoring (SIM) and in scan mode, to determine the presence of any of the 43 VOCs mentioned in the first case or any other organic compounds such as carbonyl compounds (acetaldehyde or acetone) in the second case. The SIM mode masses for the 43 VOCs were those reported by Golfinopoulos et al. (2001).

During the analysis of DEHP and other base-extractable organic compounds, the samples were also analyzed both in SIM (Kanaki et al., 2007; Nikolaou et al., 2004) and scan mode, to quantify DEHP in the first case and determine the presence of any other base-extractable organic compounds, according to EPA method 1625.

The recoveries and detection limits of the analytical methods used have been previously reported (Golfinopoulos et al., 2001; Kanaki et al., 2007; Nikolaou et al., 2004; Nikolaou et al., 2002). The detection limits ranged from 0.005 to 0.070 $\mu g\, l^{-1}$ for the volatile DBPs, from 0.01 to 0.2 $\mu g\, l^{-1}$ for HAAs and from 0.01 to 0.5 $\mu g\, l^{-1}$ for VOCs. For DEHP the detection limit was 0.02 $\mu g\, l^{-1}$.

3. Results and discussion

3.1. Results

The concentrations of THMs, HAAs and DEHP in bottled waters are summarized in Table 3. The first two categories might exist naturally in the environment or be

Table 2
Analytical conditions for the determination of DBPs, VOCs, DEHP and screening of other organic compounds

Compounds determined	DBPs	VOCs	DEHP and other organic compounds
Instrumentation used	GC–ECD	Purge and Trap–GC–MS	GC–MS
Carrier gas	He	He	He
Makeup gas	N_2	n/a	n/a
Injection technique	Split/splitless	Split/splitless	Split/splitless
Column	Fused silica DB-1, 30 m × 0.32 mm i.d. × 0.25 μm film thickness	Fused silica DB-5 MS, 30 m × 0.32 mm × 1.8 μm	Fused silica DB-5 MS, 30 m × 0.32 mm × 1.8 μm
Carrier gas flow	1.3 ml min^{-1}	1 ml min^{-1}	1.2 ml min^{-1}
Oven temperature	35 °C for 9 min, 1 °C min^{-1} to 40 °C for 3 min, 6 °C min^{-1} to 220 °C for 10 min	35 °C for 3 min, 10 °C min^{-1} to 23 °C	50 °C for 4 min, 20 °C min^{-1} to 170 °C, 8 °C min^{-1} to 270 °C for 10 min
Injector temperature	175 °C	200 °C	200 °C
Detector temperature	300 °C	280 °C	280 °C
Split ratio	1:25	1:25	1:25
Purge valve on	1 min	1 min	1 min
Solvent delay	n/a	0	9 min
Mass range (amu)	n/a	35–250	50–550, scan mode
Scan/sec	n/a	1.9	1.9

n/a: not applicable.

formed during the storage. The concentrations of THMs increase with temperature, pH, time and concentrations of precursors substances. According to Serodes, Rodriguez, Li, and Bouchard (2003), the concentrations of TOC have an important role in waters, because their variability influences the speciation of HAAs and THMs that are formed. The majority of samples consisted of natural mineral waters; therefore, they contain organic matter which might be dissolved in the samples and react in variable conditions.

Clearly, the type of bottled drinking water might cause a potential variability at the presence or the level of concentration of organic compounds. An example of this is chloroform. Despite the fact that this compound was not detectable during the first sampling, it is remarkable that chloroform was traced at four samples which had been exposed to out-door conditions, mostly in carbonized water. A main factor that affected chloroform formation, except for the type of water, was temperature. Studies had shown that chloroform and other chlorinated and brominated substances could be formed abiotically or produced by microorganisms that grow in water due to temperature and sunlight (Gribble, 1998; Hoekstra et al., 1998; McCulloch, 2003). Furthermore, chloroform might be formed as a result of decomposition of trichloroacetic acid (TCA), which initially occurred to the samples, and then decreased or disappeared (Fig. 1). TCA and trichloropropanone (TCP) had been detected at low concentrations in the natural mineral waters in Florida by Gibbons and Laha (1999), McCulloch (2003) confirmed their results.

A similar fluctuation was observed for dichlorobromomethane ($CHCl_2Br$). This compound was detected only after storage in four samples. The main reason for its formation was the duration of storage, as conditions did not lead to different results. The high temperature during out-doors conditions enhanced the formation of $CHCl_2Br$ only in carbonized water. Despite this variety of results in the type of bottled water, no significant difference was observed between samples stored in room conditions and those in out-doors.

HAAs are the second most important category of the DBPs, after THMs. It would be difficult to form a general picture for their fluctuations in this study, unless they were examined separately.

The initial concentrations of compounds, such as DCA and TCA, declined a lot during the storage (Fig. 1) in both types of bottled waters. The same note had been reported by Liu and Mou (2004), where the concentrations were almost eliminated after 20 day storage. It has been reported that TCA decomposes to chloroform, while the exact mechanisms are not known yet.

However, other HAAs substances, like BCA and DBA, appeared only after storage for the majority of samples. BCA was initially detected only in one sample. Nevertheless, after storage it was also detected in other bottled waters. The storage conditions did not have significant effects on BCA concentrations, which were mostly detected in carbonized waters. The average final concentration of DBA was 0.7 μg l^{-1} and the main factor affecting its formation was time.

1,1,1-Trichloropropanone (TCP) was detected in 11 samples, and it was also formed during the storage without having appeared initially. These results suggest the possible decomposition of TCA or DCA to chloroform and then to

Table 3
Concentrations of organic compounds detected in the bottled water samples

Samples	Compounds-sampling number																	
	THMs-volatile DBPs (μg l^{-1})																	
	$CHCl_3$		$CHCl_2Br$		$CHClBr_2$		$CHBr_3$		CH		TCP		DCAN		MCAN		DCP	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
1-a	nd	nd	nd	1.8	nd	nd	nd	nd	Nd	nd	nd	0.6	nd	nd	nd	nd	nd	nd
1-b	NA	nd	NA	1.8	NA	nd	NA	nd	NA	nd	NA	0.6	NA	nd	NA	nd	NA	nd
1-c	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
2-a	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.5	nd	nd	nd	nd	nd	nd
2-b	NA	0.5	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
2-c	NA	nd	NA	nd	NA	nd	NA	nd	NA	0.4	NA	nd	NA	nd	NA	nd	NA	nd
3-a	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
3-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	0.9	NA	nd	NA	nd	NA	nd	NA	nd
3-c	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
4-a	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.6	nd	nd	nd	nd	nd	nd
4-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	1	NA	nd	NA	nd	NA	nd	NA	nd
4-c	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
5-a	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	0.7	NA	nd	NA	nd	NA	nd
5-b	NA	21.7	NA	2.6	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
6-a	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
6-b	NA	0.3	NA	nd	NA	nd	NA	nd	NA	nd	NA	0.4	NA	nd	NA	nd	NA	nd
7-a	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
7-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	0.5	NA	nd	NA	nd	NA	nd
8-a	nd	nd	nd	1.7	nd	nd	nd	nd	nd	nd	nd	0.6	0.12	nd	nd	nd	nd	nd
8-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
9-a	nd	nd	Nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
9-b	NA	nd	NA	nd	NA	nd	NA	Nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
9-c	NA	nd	NA	nd	NA	0.5	NA	0.9	NA	0.6	NA	nd	NA	nd	NA	nd	NA	nd
10-a	nd	nd	Nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.22	nd	nd	nd	nd	nd
10-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
11-a	nd	nd	Nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
11-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	0.5	NA	nd	NA	nd	NA	nd
12-a	nd	nd	Nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
12-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
13-a	nd	nd	Nd	nd	nd	nd	nd	nd	nd	nd	nd	0.6	nd	nd	nd	nd	nd	nd
13-b	NA	0.2	NA	nd	NA	nd	NA	nd	NA	Nd	NA	nd	NA	nd	NA	nd	NA	nd

	HAAs (μg l^{-1})												Diethylhexylphthalate	
	MCA		DCA		BCA		TCA		DBA		DCA		DEHP	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
1-a	nd	nd	4	nd	2.2	1.8	1.3	nd	nd	0.9	Nd	nd	0.2	1.5
1-b	NA	nd	NA	nd	NA	1.6	NA	nd	NA	0.6	NA	nd	NA	0.1
1-c	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	0.06
2-a	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.7	Nd	nd	nd	nd
2-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
2-c	NA	nd	NA	nd	NA	nd	NA	nd	NA	0.6	NA	nd	NA	nd
3-a	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	Nd	nd	0.2	nd
3-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
3-c	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
4-a	nd	nd	nd	nd	nd	nd	nd	Nd	nd	nd	nd	nd	nd	nd
4-b	NA	nd	NA	nd	NA	1.6	NA	Nd	NA	0.6	NA	1	NA	nd
4-c	NA	nd	NA	nd	NA	nd	NA	Nd	NA	0.6	NA	nd	NA	nd
5-a	NA	nd	NA	nd	NA	1.6	NA	Nd	NA	0.6	NA	nd	NA	nd
5-b	NA	nd	NA	nd	NA	1.6	NA	Nd	NA	0.7	NA	nd	NA	nd
6-a	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	6.8
6-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
7-a	nd	nd	nd	nd	nd	1.6	nd	nd	nd	0.7	nd	nd	nd	0.2
7-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
8-a	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.2	0.15
8-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
9-a	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.04	nd
9-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd

(*continued on next page*)

Table 3 (*continued*)

	HAAs ($\mu g\ l^{-1}$)												Diethylhexylphthalate	
	MCA		DCA		BCA		TCA		DBA		DCA		DEHP	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
9-c	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
10-a	nd	nd	2.7	nd	nd	nd	1.1	0.2	nd	nd	nd	nd	nd	nd
10-b	NA	nd	NA	nd	NA	nd	NA	0.1	NA	0.6	NA	nd	NA	nd
11-a	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.6	nd	1	nd	nd
11-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
12-a	nd	nd	5.2	nd	nd	nd	1.5	nd	nd	nd	nd	nd	nd	nd
12-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd
13-a	nd	nd	nd	nd	nd	nd	1	nd	nd	nd	nd	nd	nd	nd
13-b	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd	NA	nd

Sampling 1: May 2004 and Sampling 2: August 2004.
nd = not-detected; NA = not-analyzed; a = recommended conditions; b = out-doors conditions; c = bottle with deionized water; 1–6: carbonated water; 7–13: natural mineral water; 1–5: glass containers; 6–13: plastic containers; CH: chloral-hydrate; TCP: trichloropropanone; DCP: dichloropropanone; DCAN: dichloroacetonitrile; MCAN: monochloroacetonitrile; MCA: monochloroacetic acid; DCA: dichloroacetic acid; TCA: trichloroacetic-acid; BCA: bromochloroacetic acid; DBA: dibromoacetic acid; and BDCA: bromo-dichloroacetic acid.

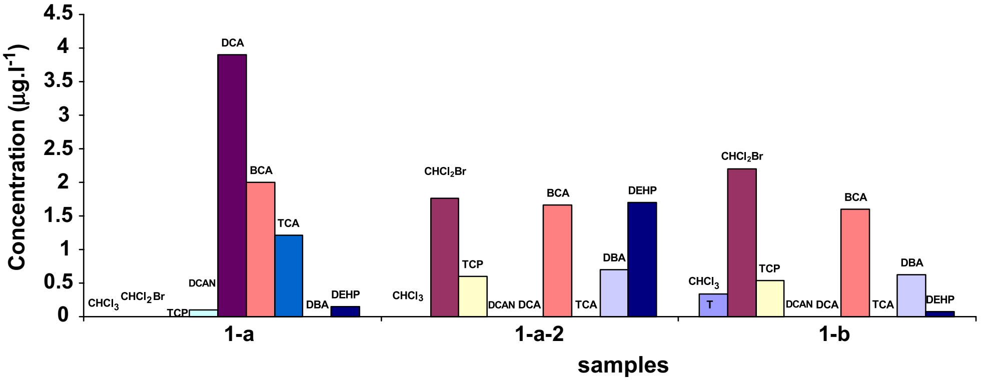

Fig. 1. Organic compounds detected in bottled water (1-a-1: 1st sampling, 1-a-2: 2nd sampling, after storage under recommended conditions, and 1-b: 2nd sampling, after storage under out-door conditions).

TCP. Most samples had the initially appeared TCA concentration. The final concentrations were similar for both in-door and out-door conditions (0.4–0.6 $\mu g\ l^{-1}$). It is worth mentioning that both types of waters and brands present an increase in TCP.

In contrast to TCP, the haloacetonitriles occurred in the samples before storage, but they were not detected after storage, due to decomposition (Nikolaou, Golfinopoulos, Kostopoulou, & Lekkas, 2000).

Generally, the growth of microorganisms in waters seems to be the reason for the presence of these compounds, because they produce halogenated species in the presence of chloride and bromide ions (Gribble, 1998; Hoekstra et al., 1998; McCulloch, 2003). The initial concentration of bromide ions in the samples, which consists an important factor for the formation of brominated products (DBA, BCA, brominated THMs), is not known.

The third category was plasticizers compounds, mainly DEHP. According to measurements, DEHP was detected in a number of samples, mostly after storage and also surprisingly in samples in glass containers. This compound could have migrated from the pipes supplying the water at the bottling process. Biscardi et al. (2003) had also suggested this source when they detected DEHP in natural mineral water. During the present study, the type of bottled water did not affect the presence of DEHP. After storage, the following picture was reported in the majority of samples: DEHP was not detected when bottled waters were stored in out-door conditions. Nevertheless, in room conditions where the temperature was at 24 °C, DEHP concentration increased or remained at similar levels. Studies have shown that biodegradation of DEHP is influenced by temperature and its half-life is longer at low temperature. The highest DEHP concentrations in the samples were found at lower temperature (below 20 °C), and lower DEHP concentrations were found at high temperature (over 20 °C) (Jie, Guo-Lan, Xin, De-Gang, & Yuan, 2003). DEHP was detected at low concentrations, after the storage in plastic bottled waters of Spain, by Casajuana and Lacorte (2003).

Two samples have given interesting results. In one sample, DEHP was detected, despite the material of container, which is glass. In this sample, the initial DEHP concentration increased significantly after storage in ambient conditions. DEHP was detected after storage also in the corresponding brand filled with ultrapure water. A possible explanation concerns that the material of this brand might be a mixture of plastic and glass to improve its resistance during the transformation. The second sample involved carbonized bottled water at plastic container. During the second sampling, the DEHP concentration exceeded the legal level of EPA (6 μg l^{-1}) but not of WHO (8 μg l^{-1}). This is the only sample with such a high concentration of DEHP, taking into account also that its expiration date had been concurred within the storage time (EPA, 2002).

Contrary to studies in bottled waters from Poland, carbonyl compounds were not identified in the Greek bottled drinking waters analyzed, according to the screening GC–MS analysis. The Purge and Trap–GC–MS analytical method used was capable of detection of carbonyl compounds, although analytical standards of these compounds were not available. Similar method had been applied by Fernandez-Garcia, Gaya, Medina, and Nunez (2004) Mamede, Cardello, and Pastore (2005) for the determination of carbonyl compounds in wine and milk/cheese, respectively.

Evandri, Tucci, and Bolle (2000) had mentioned that results of classical analytical methods of determination, such as GC–MS, showed that, besides the presence of known compounds, there are also chemicals whose identity has yet to be confirmed. It is remarkable that the results of Greek bottled waters do include unknown organic compounds. An unknown compound, which was detected in two samples, might be a derivative of benzene, according to its mass spectrum. In Figs. 2, the peaks and the spectra of unknown substances detected are given. In addition, two other unknown organic compounds have been detected, which our MS database could not correlate with high probability to recorded compounds, possibly due to their low concentration. During GC–ECD analysis, three unknown compounds also occurred in containers with ultrapure water and in some samples, which were exposed to out-door conditions. Concretely, almost all containers of ultrapure water presented a characteristic unknown peak. Furthermore, in the majority of carbonized waters exposed to out-door conditions two other unknown substances appeared.

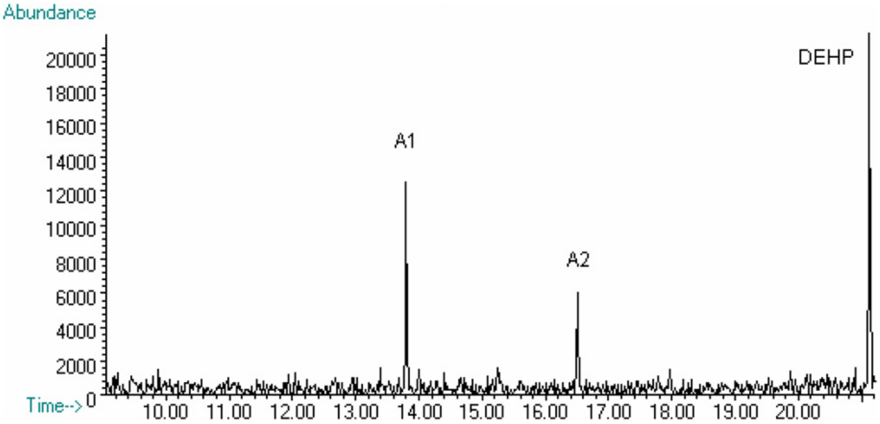

Fig. 2a. Chromatogram (GC–MS) of the sample 1α: A1 = unknown peak with retention time 13.79 min, A2 = unknown peak with retention time 16.50 min, and DEHP = diethylhexylpthalate, with retention time 21.11 min.

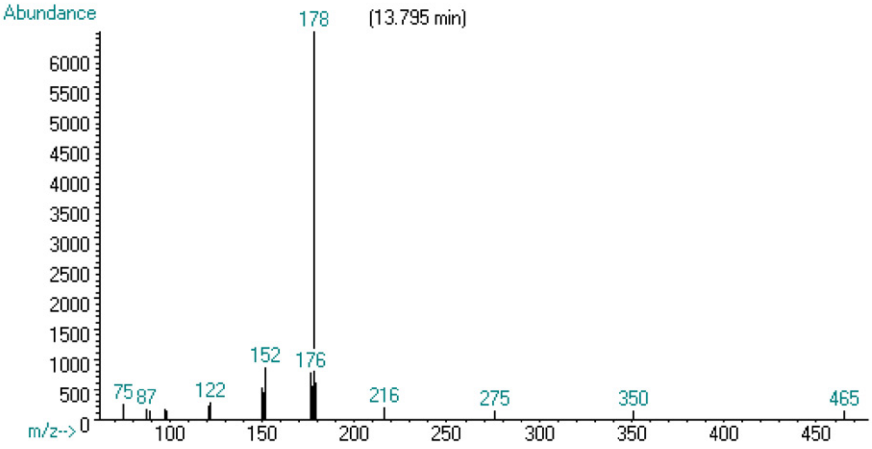

Fig. 2b. Mass spectrum that corresponds to the unknown peak A1 of Fig. 2a.

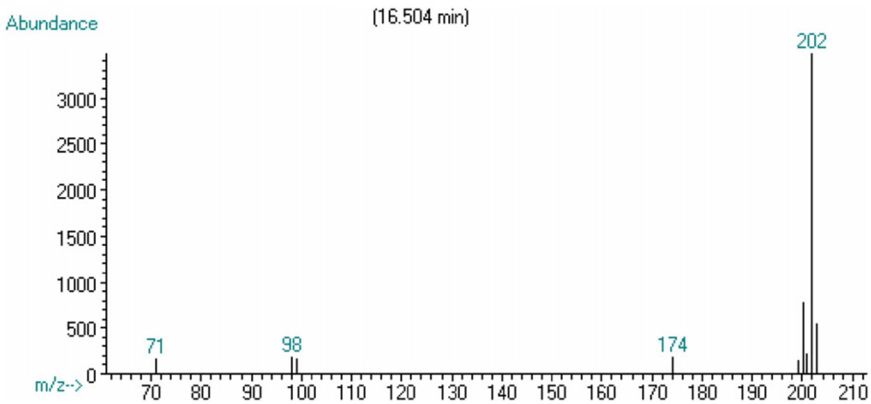

Fig. 2c. Mass spectrum that corresponds to the unknown peak A2 of Fig. 2a.

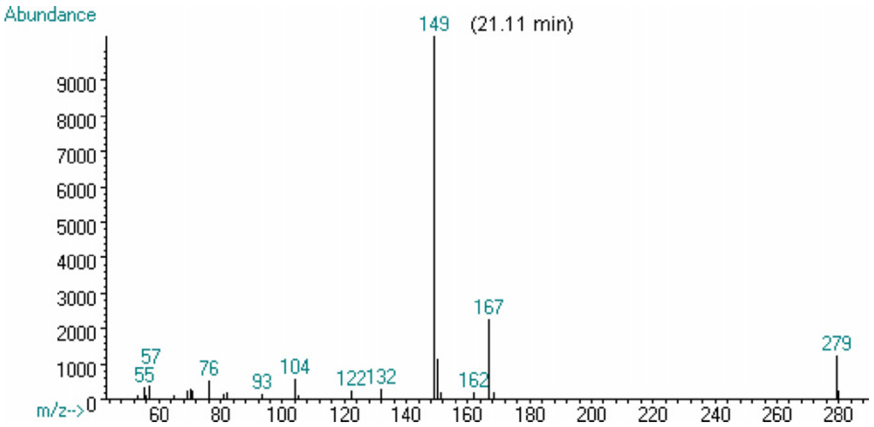

Fig. 2d. Mass spectrum that corresponds to DEHP.

3.2. Comparison between tap and bottled waters in Greece

One of the main reasons for huge consumption of bottled waters is the “bad” quality of tap water. To justify this tendency, samples from tap water of Mytilene Island in Greece were collected in corresponding containers to those of the bottled waters and analyzed. Furthermore, samples had been exposed to out-door conditions for 3 months, so that there should be a comparison with bottled waters.

Although chlorination by-products occur in natural waters after an oxidation/disinfection treatment by chlorine (Rook, 1974), drinking water samples from the distribution network of Mytilene contain higher bromide species concentrations (Table 4). Mytilene is a coastal region, where the marine water influences the quality of drinking

Table 4
Concentrations of organic compounds detected in Mytilene tap water samples

Samples	Compounds-sampling number																	
	THMs-volatile DBPs (μg l^{-1})																	
	$CHCl_3$		$CHCl_2Br$		$CHClBr_2$		$CHBr_3$		CH		TCP		DCAN		MCAN		DCP	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Mytilene	nd	nd	5.3	3.7	16.4	14.6	20.2	17.4	0.5	Nd	0.7	nd	nd	nd	nd	nd	nd	nd

	HAAs (μg l^{-1})				Diethylhexylphthalate									
	MCA		DCA		BCA		TCA		DBA		BDCA		DEHP	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Mytilene	4.3	3.2	3.5	2.6	2.1	1.7	0.6	0.1	1.3	0.8	nd	nd	nd	nd

Sampling 1: May 2004; Sampling 2: August 2004 – out-doors conditions.
nd = not-detected and NA = not-analyzed.

water regarding bromide (Golfinopoulos, 2002; Tyrovola & Diamadopoulos, 2005). The detected concentrations of THMs and HAAs do not exceed the legislative levels, but are still higher than in bottled waters.

Both in bottled and tap waters, almost the same organic compounds such as DCA, DBA, THMs were identified. Opposed to tap water, where chloroform was not detected, some of bottled waters contained low concentrations of chloroform after the process of storage. MCA occurred only to tap water, whereas DCA was detected both in bottled and tap waters. A decreasing tendency of TCA and BCA was observed in both types of waters after the storage. It is worth mentioning that the TCP seems to degrade in tap water, instead of bottled waters. Furthermore, BDCA and DBA appeared in tap water of Mytilene, and also in bottled waters after storage. Finally, a compound detected only in some bottled waters is the DEHP. The plasticizer was not detected in the tap waters which had been stored in certain plastic bottles.

As regards duration and conditions of storage, sunlight and temperature seem to accelerate the degradation of organic compounds more in tap than in bottled water.

3.3. Conclusions

It is difficult to give a clear answer to the most common question, what type of bottled water is the best for consumption. Carbonized waters seem slightly safer for consumption than mineral, considering the results of first sampling. However, the quality of carbonized waters degrades more easily, especially regarding HAAs than in the case of mineral waters, throughout the time. The differences between glass and plastic brands were negligible, maybe due to the limited time. Compared to the water from local distribution network, tap drinking water presents higher concentrations of DBPs than bottled waters, due to chlorine that is used as disinfectant. Bottled waters contain not only low DBPs concentrations, but also DEHP and some unknown organic substances for which their characteristics and effects on human organism are not known. It is remarkable that the majority of THMs were formed after the 3 months storage, while the concentrations of HAAs mainly decreased in bottled waters. Furthermore, the plasticizer DEHP was detected only at bottled waters and its highest concentrations presented at the recommended conditions, with temperature at 24 °C. In addition, it was detected in a sample of bottled water exceeding the legal level of the EPA ($6\ \mu g\ l^{-1}$) but not of the WHO ($8\ \mu g\ l^{-1}$).

Conclusively, the fate of organic compounds depends on the storage conditions – mainly time and temperature – before the consumption and the type of waters and brands. Organic compounds co-exist and interact by their environment, which includes the action of microorganisms as well. A microbiological approach and determination could, probably, explain in a better way the formation and the behavior of certain organic compounds in bottled waters. Furthermore, further research on the recommended conditions of storage is needed as well as frequent monitoring of bottled waters.

Overall, it could be stated that both tap and bottled waters, available in Greece, are safe for the human consumption, as regards their organic compounds levels.

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