



## Alkylphenols and phthalates in bottled waters

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### ABSTRACT

The aim of this study was to investigate the occurrence of endocrine disrupting compounds (EDCs) in bottled waters. The examined compounds were bisphenol A (BPA), nonylphenol (NP), tert-octylphenol (tOP), dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), di(2-ethylhexyl)phthalate (DEHP) and di(n-octyl)phthalate (DNOP). The presence of EDCs in bottled waters under poor storage conditions was also investigated after exposure outdoors under realistic conditions for 15 and 30 days. EDCs were recovered after liquid–liquid extraction and determined by employing Gas Chromatography–Mass Spectrometry. Most of these compounds were detected in bottled water from different brands purchased from local market. Storage at outdoor conditions had no significant effect on the concentrations of the examined compounds. Only BPA occurred at higher concentrations in polycarbonate containers exhibited an increasing trend during exposure. The estimated exposure to EDCs via consumption of drinking water was very low.

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### 1. Introduction

The consumption of bottled water in Greece has been steadily growing up the last decades similarly to the trend observed worldwide. During the period 1998–2005 the consumption has tripled from 380 to 1000 millions liters that is about 100 L per capita per year. The main reasons for this increase are public concern about the quality of tap water, the presence of disinfection byproducts, the shortage of water in touristic areas, especially during warm period, in combination with the consistent quality of bottled water, efficient marketing and changes in consumer's habits last years. Current regulations for bottled water require the analysis for selected microbiological and physicochemical parameters [1–3]. However there is an anxiety about the quality of bottled water because it is stored for longer periods and not always preserved under the recommended conditions or because containers and bottles are reused without adequate cleaning or disinfection [4].

Moreover many questions have been raised about possible migration of chemicals from the bottles during long storage time especially under poor conditions (high temperatures, sun radiation, etc.). According to the European legislation any container used for packaging of natural mineral waters shall be fitted with closures designed to avoid any possibility of adulteration or contamination [1]. Therefore, the control of materials used in bottles and closures

for bottled water is of special concern [4]. Bottled water is usually available in two main sorts of packaging material; glass and plastic. About 80% of the plastic bottles used is of poly(ethylene terephthalate) (PET) owing to the desirability of its physical and chemical properties such as strength, transparency, light weight and easy recycling. Containers, mainly water carboys, made of polycarbonate (PC) are also used.

Many studies reported the presence of organic compounds in bottled water that may affect the organoleptic characteristics of the water, and pose health risk to consumers. Organic compounds could be source of carbon to inherent microorganisms which also have implications on odour and taste thresholds. The presence of xenobiotics in bottled waters represents a complex problem and the origin of several substances is not clearly established and still being debated. Bottled water can be contaminated in different phases of the production process, from supplying of the materials to handling, storing and distribution [5]. This includes contamination of water source in the field, during bottling process in the plant, migration from the material of the bottle or the caps to the water (monomers, catalysts, additives or degradation products) and formation of organic compounds under deficient storage conditions [5–10]. This study investigates the presence of compounds that can pose endocrine disruptions or are suspected for this in bottled waters. The examined compounds are bisphenol A, nonylphenol, octylphenol and phthalates.

Bisphenol A (BPA) is a monomer used in the production of polycarbonates and epoxy resins from which a variety of products are generated. Epoxy resins are used to lacquer-coat the interior of food cans, wine storage vats, water containers and water pipes. Polycarbonate plastics are used to manufacture water carboys, reusable

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**Table 1**  
Characteristics of the examined bottled waters.

	Brands of bottled waters					
	A	B	C	D	E	G
<i>Bottle characteristics</i>						
Bottle type	PET	PET	PET	PET	PET	PC
Color <sup>a</sup>	CL	CL	CL	CL	LB	LB
Resin identification code	1	1	1	1	1	7
Volume (L)	1	1	1	1	1	18.9
Caps <sup>a</sup> (color/resin code)	DB (2)	–	LB (2)	W (13)	DB (PE)	LB
<i>Water characteristics</i>						
Water type <sup>b</sup>	NMW	NMW	NMW	NMW	BDW	NMW
EC (μS/cm)	392	448	472	671	665	408
pH	7.6	7.5	7.42	8.1	7.3	8.1
Hardness (mg/L)	183	228	250	330	313	210
CO <sub>3</sub> <sup>2-</sup> (mg/L)	ND	ND	ND	ND	ND	ND
SiO <sub>2</sub> (mg/L)	ND	ND	ND	ND	ND	ND
Fe <sup>2+</sup> · <sup>3+</sup> (mg/L)	ND	ND	ND	<0.10	ND	ND
NH <sub>4</sub> <sup>+</sup> (mg/L)	<0.26	<0.2	<0.26	<0.26	ND	ND
Cl <sup>-</sup> (mg/L)	8.8	6.91	9.42	39.7	24	4.0
Na <sup>+</sup> (mg/L)	9	6.56	6.9	17.1	21	2.4
K <sup>+</sup> (mg/L)	1.2	<2	0.78	0.8	1.4	1.2
Ca <sup>2+</sup> (mg/L)	64.6	66.33	95.07	11.3	45	78.6
Mg <sup>2+</sup> (mg/L)	5.3	21.3	0.92	73.4	49	3.4
HCO <sub>3</sub> <sup>-</sup> (mg/L)	223	262	290	383	372	ND
SO <sub>4</sub> <sup>2-</sup> (mg/L)	16.5	9.99	2	6.8	15	9.3
NO <sub>3</sub> <sup>-</sup> (mg/L)	<5	9.15	5	6.9	11	7.2
NO <sub>2</sub> <sup>-</sup> (mg/L)	<0.05	<0.05	<0.05	<0.05	ND	ND

ND, not detected.

<sup>a</sup> CL, clear; LB, light blue; DB, dark blue; W, white.

<sup>b</sup> NMW, natural mineral water; BDW, bottled drinking water.

milk containers, food storage vessels and baby bottles. It has been reported that incomplete polymerization of these products during manufacture and increased temperatures imposed during heating, can cause leaching of unreacted compounds into foods and beverages. BPA demonstrates estrogenic activity and is considered as important organic pollutant [11].

Nonylphenol (NP) is widely spread in the environment as a result of its use in industry as raw material, as additive in epoxy resins to enhance properties of polymerization, drying, plasticity, etc. Nonylphenol and octylphenol, that present endocrine response, are the main metabolites during degradation of alkylphenol ethoxylates (APEs), which are used as nonionic surfactants in cleaning agents, disinfectants and pesticides formulations. Since January 2005, there has been a restriction in Europe on the sale and use of products that contain more than 0.1% of 4-nonylphenol ethoxylates (NPEOs) or 4-nonylphenols (NPs) [12].

Phthalates (PEs) are ubiquitous pollutants in the environment, due to their widespread use for around 50 years. These compounds are used principally as plasticizers, to impact flexibility, workability and, durability to polymers but they can also be found in products such as paints, adhesives, inks and cosmetics. PEs are not chemically bounded to polymers; hence they are easily released and migrate into foods, beverages and drinking water from the packaging or bottling materials or manufacturing processes. This process accelerates as plastic products age and break down. With respect to their endocrine disrupting potential, phthalates such as BBP, DBP and DIBP have been found to elicit estrogenic responses in *in vitro* assays. It is possible that phthalates are a contributory factor to endocrine-mediated adverse effects observed in wildlife and humans over the past few decades [7,13,14].

The aim of this study was to investigate the occurrence of endocrine disrupting compounds; nonylphenol, tert-octylphenol, bisphenol A, and phthalates in bottled waters. Moreover the influence of storage of water bottles outdoors, under natural conditions, was also investigated. Finally, the exposure to EDCs via water consumption was estimated.

## 2. Experimental

### 2.1. Reagents and materials

EPA phthalate esters mix (DMP, DEP, DBP, BBP, DEHP, DNOP) were supplied from Supelco (Bellefonte, PA, USA). Bisphenol A was purchased from Cerilant (Austin, TX), 4-nonylphenol was obtained from Riedel de Haën (Seelze, Germany), 4-tert-octylphenol, 4-nonylphenol and N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) were supplied from Fluka (Buchs, Switzerland). Bisphenol A-d<sub>16</sub> and DNOP-d<sub>4</sub> were purchased from Aldrich (Dorset, UK).

### 2.2. Sample preparation

Commercially available bottled waters from randomly chosen brands of different price segments were purchased from local markets. Waters from ~20L reusable containers in water coolers were also used. Information on bottles and water characteristics as shown in their labels are presented in Table 1. Three bottles from each water brand, before the expiration dates, were obtained. The first was analyzed immediately upon purchase. The other two samples were stored outdoors and directly exposed to sunlight for 15 and 30 days respectively, during the period June–July 2008. The environmental conditions are described in Table 2. Replicate experiments for each sample were employed.

Water sample (1 L) was transferred from the bottle to a separating glass funnel. Liquid–liquid extraction with dichloromethane (3 × 50 mL) was employed for the isolation of target EDCs. The com-

**Table 2**  
Environmental conditions during outdoor exposure experiments.

Exposure (days)	Radiation (W/m <sup>2</sup> )	Sunshine (h)	Air temperature (min–max, °C)
15	9,780	180	15–38
30	20,070	365	18–40

**Table 3**  
Identification and quantification parameters of the studied compounds.

Compounds	Abbreviation	Chemical type	Target ions (abundance) ( <i>m/z</i> )	Quantitation ions ( <i>m/z</i> )
<i>Phenols</i>				
4- <i>t</i> -Octylphenol	tOP	C <sub>14</sub> H <sub>22</sub> O	207.2 (100), 208.2 (18.7)	207.2
4- <i>n</i> -Nonylphenol	NP	C <sub>15</sub> H <sub>24</sub> O	179.1 (41.6), 193.1 (48.2), 207.1 (100), 221.1 (47.8)	Sum of 8 peaks
Bisphenol A	BPA	C <sub>15</sub> H <sub>16</sub> O <sub>2</sub>	357.2 (100), 358.2 (33.3)	357.2
4- <i>n</i> -Nonylphenol <sup>a</sup>	nNP		179.2 (100), 180.2 (17.7), 292.2 (33.6)	179.2
Bisphenol A- <i>d</i> <sub>16</sub> <sup>a</sup>	BPA- <i>d</i> <sub>16</sub>		368.3 (100), 369.3 (32.8)	368.3
<i>Phthalates</i>				
Dimethyl phthalate	DMP	C <sub>10</sub> H <sub>10</sub> O <sub>4</sub>	135 (15.0), 163 (100), 194 (15.0)	163
Diethyl phthalate	DEP	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>	149 (100), 177 (28.0)	149
Di- <i>n</i> -butyl phthalate	DBP	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	149 (100), 205 (6.0), 223 (6.2)	149
Butylbenzyl phthalate	BBP	C <sub>19</sub> H <sub>20</sub> O <sub>4</sub>	91 (71.5), 149 (100), 205 (21.5)	149
Di-2-ethylhexyl phthalate	DEHP	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	149 (100), 167 (50.0), 279 (35.5)	149
Di( <i>n</i> -octyl)phthalate	DNOP	C <sub>24</sub> H <sub>38</sub> O <sub>4</sub>	149 (100), 279 (18.0)	149
Di( <i>n</i> -octyl)phthalate- <i>d</i> <sub>4</sub> <sup>a</sup>	DNOP- <i>d</i> <sub>4</sub>		153 (100), 283 (20.5)	153

<sup>a</sup> Internal standard.

bined extracts were poured through anhydrous sodium sulfate and concentrated in the evaporator and further under a gentle stream of nitrogen. Alkylphenols, after derivatization with BSTFA at 70 °C for 30 min, and phthalates were determined by employing GC–MS. Surrogate standards (nNP, BPA-*d*<sub>16</sub> and DNOP-*d*<sub>4</sub>) were added to all samples before extraction as well as in calibration standard solutions.

### 2.3. Analytical determination

The analysis was performed using a gas chromatograph (Trace GC ultra, Thermo Finnigan Electron Corporation) coupled with an ion trap mass spectrometer (Polaris Q, Thermo Finnigan) and an autosampler (AI 3000, Thermo Finnigan Electron Corporation). Compounds were separated on a Rtx–5MS Crossbond 5% diphenyl–95% dimethyl polysiloxane capillary column (30 m length, 0.25 mm i.d., 0.25 mm film thickness) from Thames Restek UK Ltd.

The compounds were separated using the following oven program: the column temperature was initially set at 60 °C for 1.5 min, then increased at a rate of 20 °C/min up to 180 °C, 5 °C/min up to 230 °C, 20 °C/min up to 310 °C, which was maintained for 5 min. Helium carrier gas (99.99% purity) was maintained at a constant rate of 1.5 mL/min. The temperature at the injector was 280 °C. The ion source and transfer line temperature was set at 200 °C and at 300 °C, respectively. Mass spectra were obtained using electron impact ionization (70 eV). Under these condi-

tions, the following compounds were detected: 4-*tert*-octylphenol (tOP), 4-*nonylphenol* (NP), bisphenol A (BPA), dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*n*-butyl phthalate (DBP), butyl benzyl phthalate (BBP), di(2-ethylhexyl)phthalate (DEHP) and di(*n*-octyl)phthalate (DNOP).

The identification of target compounds was based on the relative retention time, the presence of target ions and their relative abundance according to Commission Decision 2002/657/EC. Two to four ions were monitored in MS–SIM mode (Table 3). The quantification of phthalate esters was carried out by calculating the relative response factors based on the area of surrogate internal standard DNOP-*d*<sub>4</sub>. BPA was quantified by the relative response factor to surrogate internal standard BPA-*d*<sub>16</sub>. NP and tOP were quantified using the surrogate internal standard nNP. For NP the integrated peak area of the summed selected ions within a retention time window (8 peaks) was used [15].

The linearity of the method was tested with calibration standards at seven concentration levels (10–200 ng). A linear fit of the ratios of the studied compounds over internal standards peak areas was obtained with high correlation coefficients ( $R^2 > 0.993$ ). Bottled water spiked with target compounds at three concentration levels (20, 50, 100 ng) was employed for the recovery tests. The recoveries were in the range of 77–92% for alkylphenols and 70–94% for phthalates. The detection limits, calculated from the standard deviation of seven replicates of the lowest working standard (US EPA, code 40), ranged from 2 ng/L for tOP up to 30 ng/L for DMP.

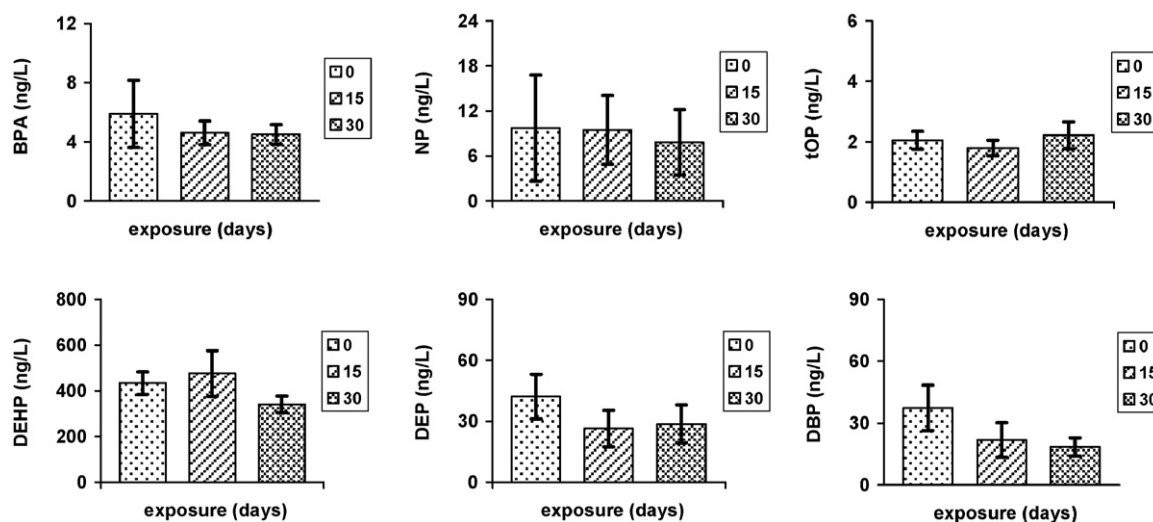


Fig. 1. Concentrations of studied compounds in water from PET bottles after exposure outdoors ( $n = 10$ ).

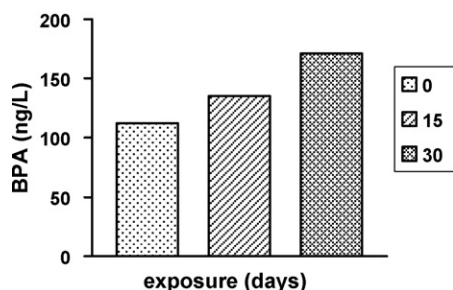


Fig. 2. Concentrations of BPA in water from polycarbonate container after exposure outdoors ( $n=2$ ).

All the glassware equipment was carefully cleaned by hexane, acetone and dichloromethane and left in a furnace at 500 °C for 3 h. Glassware, solvents and samples were carefully handled to avoid contamination [16]. Reagent procedural blanks were regularly analyzed and all data presented in this study were corrected for blank values.

#### 2.4. Statistical treatment

The SPSS (version 16.0) was employed for statistical treatment of the results. The Kruskal–Wallis test was used for comparison of results among different groups. A  $P < 0.05$  was considered to indicate statistical significance.

### 3. Results and discussion

#### 3.1. Concentrations of EDCs

The median concentrations of alkylphenols determined in bottled waters purchased from the market were 4.6 ng/L for BPA, 7.9 ng/L for NP and <2 ng/L for tOP. The lower concentrations were observed in water from PET bottles (samples A–E) (Fig. 1). The sample G, bottled in polycarbonate container, exhibited relatively higher concentrations of BPA (112 ng/L) (Fig. 2).

BPA is a key building block of polycarbonate materials. Kawamura et al. [17] reported that BPA on the surface or near the surface of polycarbonate products is easily eluted. Le et al. [18] found that BPA migrate from polycarbonate bottles into water and elevated temperatures greatly increased the rate of BPA migration. Toyooka and Oshige [19] measured BPA in several brands of mineral water from PET bottles at concentrations ranged from 3 to 10 ng/L, whereas Shao et al. [20] did not detect BPA in different beverages from plastic bottles including mineral water. However, both studies confirmed the occurrence of nonylphenols at concentrations ranging from 16 up to 465 ng/L. The migration of nonylphenol from plastic containers filled with distilled water was also investigated by Loyo-Rosales et al. [21] that measured NP in water from HDPE, PVC and PET containers at concentrations of 180, 300 and <8 ng/L, respectively. Kawamura et al. [22] who reported NP in different food contact materials (PVC, PS, PC, PP, etc.) presumed that this could be attributed to degradation of TNPP antioxidant.

The prevailing compound among phthalates measured in bottled water was DEHP with median concentration 350 ng/L. DBP and DEP were found at lower concentrations, 44 and 33 ng/L respectively. The other phthalates DMP, BBP and DNOP were not found at detectable concentrations.

Similarly, many studies reported the presence of plasticizer residues in bottled water that can be attributed to (a) water contamination in the bottling plant, (b) migration of plasticizers from the bottle material to the water since quality may vary depending on the raw material as well as the technology used in bottle production, and (c) cross-contamination during analytical proce-

dures due to the wide use of plasticizers. Kim et al. [23] reported the presence of phthalates (DEHP, DBP, DEP) among organic compounds extracted from PET bottles that was attributed to color resin. Casajuana and Lacorte [24] found increased concentrations of DMP, DEP, DBP and DEHP in mineral water after storing in PET bottles for 10 weeks. Montuori et al. [25] reported the presence of phthalates in water bottled in PET (phthalic acid 1.28, DMP 0.07, DEP 0.17, DiBP 0.20, DBP 0.21, and DEHP 0.02  $\mu\text{g/L}$ ); significantly higher (nearly 20 times) compared to glass bottles. Cao [26] reported the presence of DEP, DiBP, DBP, and DEHP in water from PETE bottles (80, 223, 138, and 118 ng/L, respectively), although they did not find considerable differences in phthalate levels between PETE and PC containers, or between carbonated and non carbonated water samples. The presence of DEHP in mineral water was also reported by other investigators [5,27]. Criado et al. [28] reported high DBP concentrations in water from PET bottles (2  $\mu\text{g/L}$ ) with a 20% increase after 5-month storage. Serôdio and Nogueira [7] found that DBP was the most abundant phthalate in mineral water (0.95  $\mu\text{g/L}$ ). Finally, Bošnjir et al. [29] reported high levels of phthalates in mineral water (20.22  $\mu\text{g/L}$ ) with DBP and DEHP showing the highest migration rate (56.04 and 43.42%, respectively).

#### 3.2. Storage at outdoor conditions

Bottled waters have to be kept in a cool place (<18 °C) and away from sun and odours. However these recommendations are not always followed by consumers. In order to investigate the influence of storage conditions, bottled waters were exposed outdoors in summer period for 15 and 30 days. As day, a period of 24 h was considered under natural conditions, including hours without sun radiation. The hours of sunshine were 180 and 365, respectively (Table 2). Temperatures up to 40 °C were measured in the exposed waters.

The concentrations of the examined EDCs in water from PET bottles under different exposure periods (15 and 30 days) with respect to sample analyzed immediately after the purchase from local market (0 days of exposure, although previous poor storage and exposure of these samples from production up to purchasing cannot be excluded) are illustrated in Fig. 1. The concentrations of alkylphenols and phthalates after different exposure periods (0, 15 and 30 days) were not statistically significant ( $P < 0.05$ ). However, bottled water from polycarbonate container (sample E) exhibited an increased trend of BPA concentrations during the exposure outdoors (Fig. 2).

Various processes such as leaching from containers, photolytic formation or degradation of organic compounds could take place during the storage of bottled waters. Le et al. [18] reported that the concentration of BPA released from polycarbonate bottles into water at room temperature increased with time and under elevated temperatures (up to 55-folds at 100 °C). Solar irradiation can also cause degradation of organic pollutants via direct or indirect photoreactions. Mezcuca et al. [30] reported that during the photolysis of BPA in deionized water under natural sun irradiation, the concentration of BPA remained at 80% of the initial concentration during the first 5 days of exposure followed by a decreased trend. After 14 days of exposure the half concentration was remained. Zhan et al. [31] reported that BPA presents slow direct photolysis in neutral pure water under simulated solar irradiation, but rapid process in the presence of humic substances. Neamtu and Frimmel [32] also reported photodegradation of nonylphenol in water by simulated solar UV-irradiation.

Casajuana and Lacorte [24] determined EDCs (BPA, NP, DEHP, DEP, DBP, DMP, and BBP) in water samples from PET and PE bottles after exposure outdoors for 10 weeks at temperatures up to

**Table 4**  
Estimation of exposure of EDCs via consumption of drinking water.

	DEHP	DEP	BPA	NP
Max concentration ( $\mu\text{g/L}$ )	0.580	0.070	0.170	0.150
Daily intake via drinking water ( $\mu\text{g/kg bw/day}$ )	0.019	0.002	0.006	0.005
Drinking water guidelines ( $\mu\text{g/L}$ )	8/6 <sup>a</sup>		100 <sup>b</sup>	0.5 <sup>c</sup>
Calculated safety factor	13.7/10.3		588	3.3
Tolerable daily intake (TDI, $\mu\text{g/kg bw}$ )	50 <sup>d</sup>		50 <sup>e</sup>	5 <sup>e</sup>
Contribution via drinking water (%)	0.038		0.012	0.1
Reference dose (RfD, $\text{mg/kg bw/day}$ ) <sup>f</sup>	$2 \times 10^{-2}$	$8 \times 10^{-1}$	$5 \times 10^{-2}$	
Calculated safety factor	$10.5 \times 10^2$	$4.0 \times 10^5$	$8.3 \times 10^3$	
Drinking water unit risk (per $\mu\text{g/L}$ ) <sup>f</sup>	$4.0 \times 10^{-7}$			
Calculated carcinogenic risk	$2.3 \times 10^{-7}$			

<sup>a</sup> Ref. [4]/Ref. [37].<sup>b</sup> Ref. [39].<sup>c</sup> Ref. [40].<sup>d</sup> Ref. [44].<sup>e</sup> Ref. [43].<sup>f</sup> Ref. [41].

30 °C. Similarly, Schmid et al. [33] reported concentrations of DEHP from 0.10 to 0.71  $\mu\text{g/L}$  in water from PET bottles during solar water disinfection process at different exposure conditions (ambient sun, shade, sun and 60 °C); being at the same range to those found in commercial bottled water. Leivadara et al. [27] reported that DEHP was not observed in bottled waters stored at outdoor conditions for 3 months although this compound was initially present in water. Photolysis may be a significant pathway for abiotic degradation of phthalates in waters [34].

### 3.3. Exposure

Food packaging could be a source of xenobiotics, especially those with endocrine disrupting properties. Chemical leaching from food packaging into food contribute to human EDCs exposure and might lead to chronic disease in the light of the current knowledge. Even at low concentrations chronic exposure to EDCs is toxicologically relevant. Concern increases when humans are exposed to mixtures of similar acting EDCs and/or during sensitive windows of development [35].

According to recent legislation (Directive 2008/105/EC, Annex II) DEHP, NP and OP are listed as priority substances in the field of water policy. NP and OP are identified as priority hazardous substances and environmental quality criteria for surface waters have been set. BPA is in the list of substances subject to review for identification as possible priority substances in the field of water policy [36]. In the field of drinking water WHO proposed a guideline value of 0.008  $\text{mg/L}$  for DEHP [4]. The US EPA under the Safe Drinking Water Act, also regulate DEHP and bis(2-ethylhexyl) adipate by means of National Primary Drinking Water Regulations. DEHP is in the list of drinking water contaminants and a maximum concentration limit of 0.006  $\text{mg/L}$  has been set [37]. Simultaneously, US EPA advises closely screening of phthalate in drinking water at concentrations above this limit. Moreover, other compounds such as BBP, DBP, DEP, DINP, NP, NPEs, OP, OPEs and BPA are nominated in the third contaminant candidate list for compounds that may require regulations under the Safe Drinking Water Act [38]. For BPA a total allowable concentration of 100  $\mu\text{g/L}$  in drinking water has been set in a study from Willhite et al. [39]. For NP the limit value of 0.5  $\mu\text{g/L}$  proposed for phenols in drinking water offers adequate protection against adverse health effects induced by NP or NPE [40].

The Integrated Risk Information System (IRIS) of US EPA proposed values of reference dose for chronic oral exposure (RfD) based on chronic health hazard assessment for non-carcinogenic effects for the following compounds: BPA  $5 \times 10^{-2}$   $\text{mg/kg bw/day}$ , DEP  $8 \times 10^{-1}$ , DBP  $1 \times 10^{-1}$ , BBP  $2 \times 10^{-1}$ , DEHP  $2 \times 10^{-2}$  [41]. According to IARC, DEHP has been placed in group 3 “not classifiable as to its carcinogenicity to humans” [42]. However, at

IRIS list, DEHP is characterized as B2, compound that is probable human carcinogen. The proposed carcinogenic risk from drinking water is  $4.0 \times 10^{-7}$  per  $\mu\text{g/L}$  [41]. Finally, the European Food Safety Authority established a Tolerable daily intake (TDI) for BPA of 0.050  $\text{mg/kg bw}$ , which represents a safe level for daily exposure over a lifetime [43]. For DEHP and DBP the TDI values are 0.050 and 0.010  $\text{mg/kg bw}$ , whereas lower preventing limit values proposed for the most susceptible population groups (infants, newborns) [44,45].

The exposure to EDCs due to the consumption of bottled water was estimated. For this purpose the worst case scenario of consumption drinking water exhibited maximum concentration of EDCs measured in this study was employed. A daily consumption of 2 L of drinking water per capita by an adult of 60 kg body weight was considered [4]. Results concerning the estimation of exposure to DEHP, DEP, BPA and NP via consumption of drinking water are shown in Table 4. DEHP, BPA and NP maximum concentrations in bottled waters are well below the guideline values for drinking water. The daily intake of these compounds via consumption of drinking water is low, contributing <0.1% to respective tolerable intakes. Compared to IRIS reference doses for chronic oral exposure (RfD), daily intake of maximum detected DEHP, DEP and BPA levels in water is far below maximum safe doses, as indicated by the calculated safe factors. Finally, the carcinogenic risk posed by the more critical concentration of DEHP is below the accepted risk level of  $10^{-6}$ .

Similar estimations have been done from Schmid et al. [33] for DEHP during solar water disinfection process. Clark et al. [46] in an assessment of exposure pathways reported that drinking water represent less than 0.2% of exposure to phthalates (i.e. DEP, DBP, and DEHP), except for the formula-fed infants where ingestion of drinking water accounts higher contribution (i.e. 0.7% for DEHP, 2.9% for DBP and 21.4% for DEP). Finally, Loyo-Rosales et al. [21] reported that consumption of water from HDPE and PVC containers represent 4.8 and 8% the daily intake of NP.

## 4. Conclusions

The aim of this study was to investigate the occurrence of selected EDCs (NP, OP, BPA, DMP, DEP, DBP, BBP, DEHP, DNOP) in bottled waters. The influence of environmental factors and storage time on the occurrence of chemical substances was also studied after exposure at outdoor conditions for 15 and 30 days.

The examined compounds were detected at low levels in bottled water purchased from local market. The results are within the concentration range observed by other investigators. BPA exhibited higher concentrations in water from polycarbonate containers. Exposure of bottled water outdoors did not result in signifi-

cant different concentrations of examined compounds, except the increased trend of BPA in polycarbonate containers. The daily intake of DEHP, BPA and NP via consumption of drinking water was low, contributing <0.1% to respective tolerable intakes. The daily intake calculated from the DEHP, DEP and BPA concentrations in drinking water is below the maximum safe doses for chronic oral exposure.

Scientific studies on EDCs have triggered public concern about their possible occurrence in drinking water. This issue is still under discussion and currently there is no European legislation specific to EDCs in drinking water. Further research in this field is necessary.

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