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Effect of bottling and storage on the migration of plastic constituents in Spanish bottled waters

Albert Guart [a,b], Francisco Bono-Blay [a,b], Antonio Borrell [a], Silvia Lacorte [b,*]

[a] Laboratorio Dr. Oliver-Rodés S.A., Moreres, 21 (Polígon Estruc), 08820 El Prat de Llobregat, Spain
[b] Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, 08034 Barcelona, Catalonia, Spain

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ABSTRACT

Bottled water is packaged in either glass or, to a large extent, in plastic bottles with metallic or plastic caps of different material, shape and colour. Plastic materials are made of one or more monomers and several additives that can eventually migrate into water, either during bottle manufacturing, water filling or storage. The main objective of the present study was to carry out a comprehensive assessment of the quality of the Spanish bottled water market in terms of (i) migration of plastic components or additives during bottling and during storage and (ii) evaluation of the effect of the packaging material and bottle format on the migration potential. The compounds investigated were 5 phthalates, diethylhexyl adipate, alkylphenols and bisphenol A. A set of 362 bottled water samples corresponding to 131 natural mineral waters and spring waters sources and 3 treated waters of several commercial brands were analysed immediately after bottling and after one-year storage (a total of 724 samples). Target compounds were detected in 5.6% of the data values, with diethyl hexyl phthalate and bisphenol A being the most ubiquitous compounds detected. The total daily intake was estimated and a comparison with reference values was indicated.

1. Introduction

Bottled water has emerged as a drinking water, which preserves the original purity of natural mineral waters, and in many areas, where there is a lack of portable distribution water, is the only water available for human consumption. There are different categories of bottled water according to their origin: natural mineral water, spring water and bottled drinking water (so-called treated water). These bottled waters are regulated by Directive 2009/54/EC (EU, 2009) and Directive 98/83/EC (EU, 1998) for chemical analysis and microbiological tests.

The bottling industry pursues the production of high water quality. However, several factors can affect the water quality: (i) leaching of pollutants from unprotected agricultural and industrial areas, which can be avoided by establishing a protection perimeter in the sources of natural mineral water and spring water to preserve the original purity (Bono-Blay et al., 2012); (ii) the bottling process, where plastic components and additives can migrate into water from storage tanks and pipelines, and (iii) storage, where plastic components or additives can migrate into water depending on the packaging material and format (Diduch, Polkowska, & Namieśnik, 2011).

Bottle packaging is designed to act as a gas barrier to avoid interaction with the surrounding environment, but it does not have a functional barrier, as for example an aluminium layer (EU, 2011). The plastic material, used to manufacture bottles intended to contain water, consists of one or more monomers and several additives, such as accelerators, catalyzers, stabilizers, antioxidants, coupling agents and plasticizers (Bolgar, Hubball, Groeger, & Meronek, 2008). Bach, Dauchy, Chagnon, and Etienne (2012) reported that antioxidants, such as alkylphenols, can be in contact with water during polyethylene terephthalate (PET) manufacturing or during the washing steps of containers. High temperatures and the presence of oxygen in PET melt process can promote thermo-mechanical and thermo-oxidative reactions (Paci & La Mantia, 1998; Romão et al., 2009; Zhang & Ward, 1995), which enhances the migration of plastic material components. Phthalates may come from bottling lines (Higuchi et al., 2004), cap-sealing resins (Hirayama, Tanaka, Kawana, Tani, & Nakazawa, 2001), water treatment facilities (Leivadara, Nikolaou, & Lekkas, 2008; Montuori, Jover, Morgantini, Bayona, & Triassi, 2008) or migration during storage (Bach et al., 2012; Casajuana & Lacorte, 2003; Diduch et al., 2011). Several authors detected alkylphenols, such as nonylphenol (NP) and octylphenol (OP), in bottled water (Amiridou & Voutsa, 2011; Li, Ying, Su, Yang, & Wang, 2010) and after migration assays (Guart, Bono-Blay, Borrell, & Lacorte, 2011). Other studies indicate that polycarbonate (PC) plastic and epoxy resins can be

* Corresponding author. Tel.: +34 934006133.
E-mail address: slbqam@cid.csic.es (S. Lacorte).

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a source of bisphenol A (BPA) in water (Amiridou & Voutsa, 2011; Gallart-Ayala, Moyano, & Galceran, 2011; Le, Carlson, Chua, & Belcher, 2008; Nerín, Fernández, Domeño, & Salafranca, 2003).

The main objective of the present study was to carry out a comprehensive assessment on the quality of bottled water and to determine the effect of bottling, packaging type, format and storage time on water quality. To achieve this aim, 362 samples in different bottle types and formats corresponding to 131 sources (natural mineral waters and spring waters) and 3 treated waters were analysed: (i) in fresh samples immediately after bottling and (ii) in one-year stored samples. The analysed waters represent Spanish commercial brands. The studied compounds were 5 phthalates, bis(2-ethylhexyl) adipate, 2 alkylphenols and BPA. Association among target compounds detected and packaging material is presented and finally the total daily intake is calculated for the different compounds and compared to reference values.

2. Materials and methods

2.1. Chemical reagents

Phthalate Mix 525 (500 ng/μl each in methanol) containing dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), bis(2-ethylhexyl) adipate (DEHA) and bis(2-ethylhexyl) phthalate (DEHP) was from Supelco (Bellefonte, PA, USA). 4-nonylphenol (NP) was obtained from Riedel-de Häen (Seelze, Germany) as a solid technical mixture of isomers. BPA was purchased from Dr. Ehrenstorfer (Augsburg, Germany) as a solid and 4-tert-octylphenol from Supelco (Bellefonte, PA, USA) as a solid. The phthalates surrogate standard was dipropylphthalate-d_4 from Riedel-de Haën (Seelze, Germany), purchased as a solid. Alkylphenols surrogate standard was 4-n-nonylphenol-d_8 from Dr. Ehrenstorfer (Augsburg, Germany) as a solution at 100 ng/μl in acetone; BPA surrogate was BPA-d_{16} from Sigma Aldrich (St. Louis, MO, USA) as a solid; anthracene-d_{10} used as internal standard, was from Dr. Ehrenstrofer as a solution of 10 ng/μl in cyclohexane.

200 mg Oasis HLB solid phase extraction (SPE) cartridges were from Waters (Milford, MA, USA) and used with a Baker vacuum system (Product No. 7018-94; J.T. Baker, Deventer, the Netherlands). Chromatography-grade methanol, acetone, dichloromethane, n-hexane, ethyl acetate and HPLC water were purchased from Merck (Darmstadt, Germany). Nitrogen for drying with 99.995% of purity was from Air Liquid (Barcelona, Spain).

2.2. Samples

Spanish bottled waters of 0.1, 0.15, 0.2, 0.25, 0.33, 0.5, 0.75, 0.92, 1, 1.25, 1.5, 2, 5, 6.5, 8, 10, 11, 13, 18.9 and 20 l of 94 brands were analysed. The bottled water studied corresponded to: (i) glass bottles, 85 with metallic crown cap, 20 with metallic screw-cap and 4 with a high density polyethylene (HDPE) cap; (ii) 1 polypropylene (PP) bottle with HDPE cap; (iii) 20 PC bottles with LDPE cap; (iv) 224 PET bottles with HDPE cap; (v) 7 HDPE bottles with HDPE cap and (vi) 1 low density polyethylene (LDPE) bag (Table 1). All these waters were either natural mineral water, spring water or treated water. Samples were provided from the main Spanish bottling industry. Two samples of each material and volume were collected after filling in the bottling lines of each company (a total of 724 samples). One sample was analysed immediately after sampling (fresh sample) and the other was stored for 1 year and analysed (one-year stored). Fresh waters were stored at room temperature until analysis, which was performed within 15 days from the sampling date. On the other hand, waters stored for 1 year in its original bottle were placed in an exterior warehouse in the dependencies of the Laboratorio Dr. Oliver Rodés (El Prat del Llobregat, Barcelona, Spain), protected from rain and sunlight. The average monthly minimum and maximum temperatures were 14.7 and 28.0 °C, 12.4 and 28.9 °C, and 12.5 and 30.1 °C in years 2007, 2008 and 2009, respectively (Weather Online, 2013, Airport of Barcelona, El Prat del Llobregat, at 4 km from the Laboratory).

2.3. Instrumental analysis

Samples were analysed unfiltered and concentrated using SPE followed by gas chromatography coupled to a quadrupole mass spectrometer (GC–MS) in a Thermo Electron Corporation (San José, CA, USA) Trace GC 2000 instrument. Electron ionisation was

Table 1
Description of the several types of packaging, volumes and the respective number of samples for each type analysed in the study (Number inside brackets corresponds to the number of carbonated water).

Volume (L)	Glass[a] Metallic crown[b]	Glass[a] Metallic screw-cap[b]	Glass[a] HDPE[b]	PP[a] HDPE[b]	PC[a] LDPE[b]	PET[a] HDPE[b]	HDPE[a] HDPE[b]	LDPE[c] –
0.1	1	–	–	–	–	–	–	–
0.15	–	–	–	–	–	1(1)	–	–
0.2	–	–	–	–	–	1	–	–
0.25	18(9)	2(1)	–	–	–	3	–	–
0.33	13(7)	1(1)	–	–	–	34	–	–
0.5	23(4)	3(2)	–	–	–	39(2)	–	–
0.75	4(4)	4(2)	–	–	–	–	–	–
0.92	3(1)	–	–	–	–	–	–	–
1	23(6)	10(6)	1(0)	–	–	–	–	1
1.25	–	–	–	–	–	3(2)	–	–
1.5	–	–	–	–	–	61(3)	–	–
2	–	–	–	–	–	5	–	–
5	–	–	–	–	–	56	3	–
6.5	–	–	–	–	–	1	–	–
8	–	–	2	1	–	18	3	–
10	–	–	1	–	–	1	1	–
11	–	–	–	–	2	–	–	–
13	–	–	–	–	1	–	–	–
18.9	–	–	–	–	12	–	–	–
20	–	–	–	–	5	1	–	–
Total	85 (31)	20 (12)	4 (0)	1 (0)	20 (0)	224 (8)	7 (0)	1 (0)

[a] Material of the bottle.
[b] Material of the cap.
[c] Bag format.