Migration of Bisphenol-A into the Natural Spring Water Packaged in Polycarbonate Carboys

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Abstract

Bisphenol-A is a widely used chemical in the structure of epoxy resins, polycarbonate packages, lacquer of metal food packages all over the world. Its weak estrogenic character and possible health effects are well known. For this reason the usage of the Bisphenol-A in food packages is limited and it's daily intake by human is restrictly under control. The declaration of specific migration limit is 0.6 ppm, the tolerable daily intake is 0.05mg/kg body weight per day by EFSA and other authorities. The EFSA and others prevent the manufacturing and using of Bisphenol-A in baby bottles in 2010. In Turkey, the 70% of the population are living in 5 metropolitan cities and the drinking water consumption is mostly supplied by packaged drinking water industry. The household and bulk usage is covered by natural spring and natural mineral water packaged in 19 liters polycarbonate carboys. That's why the possible migration of Bisphenol-A in drinking water packaged in polycarbonate carboys was decided to investigate. First of all, a screening test was carried out in the samples supplied by two main cities. And then 5 different trade mark packaged water samples was stored at 4, 25, and 35^{o}C for 60 days and Bisphenol-A content was determined in given intervals. It is found that the BPA migration was detected at least 450 times lower than the specific migration limit of EFSA during 60 days storage at these conditions.

Keywords: Water, PC carboys, BPA, Migration

1. Introduction

Bisphenol A (BPA) is the common name of 2,2-(4,4' dihydroxydiphenyl)propane, CAS Registry No. 80-05-7. It is used as an intermediate during the production of polycarbonate plastics and epoxy resins. Polycarbonate (PC) is a clear, strong, and rigid thermoplastic. Polycarbonate is used in food containers such as baby bottles, water carboys and bottles, and epoxy resins are used for the internal coating (lacquer) for food and beverage cans to protect the food from direct contact with the metal. During the manufacturing process, unreacted BPA will be present in the PC products and will be migrate from PC to the food (Grumetto et al., 2008). BPA has been known as a potential endocrine disrupter by positive in vitro test results for estrogen- like behavior (Krishnan et al., 1993, Biles et al., 1997). During past years endocrine disruptors (EDs) have been attracting the attention of the scientific world because of their possible negative effects on human health. This class includes many alkyl phenols, such as Bisphenol A (BPA), which has been recognized to be potent EDs (Kitamura et al.,2005, Wolff, 2006, Krishnan et al., 1993, Kim et al., 2001, Li et al., 2004, Suzuki et al., 2002, Palanza et al., 2002).

Because BPA is a potential endocrine disruptor that mimics the action of the hormone estrogen (Suzuki et al., 2002), the EC Directive reduced the previous specific migration limit for BPA at 3 mg kg-1 in food or food simulant (Palanza et al., 2002) to 0.6 mg/kg in an amending document relating to plastic materials and articles intended to come into contact with foodstuffs (Cao et al., 2008). The tolerable daily intake for BPA was established at 50 µg/kg bodyweight/day by the United States and the European Food Safety Authority (Stump et al., 2010, Ryan et al. 2010), while Health Canada established the provisional tolerable daily intake for BPA at 25 µg/kg bodyweight/day. Some dispute has been in the past about the actual levels of bisphenols able to cause toxic effects on humans; indeed, recent reports (Planza et al., 2002, Rajapakse et al., 2002, Vom Saal and Welshons, 2006) have indicated that health risks can result from exposure to doses much lower than the limit of 0.05 mg/kg body weight day, previously reported by chemical corporations and regulatory agencies (*EFSA*, *2006*). Therefore, to assess actual human health risks caused by BPA and BPB exposure, it is essential to achieve accurate data on their levels in foodstuffs even at very low concentrations. Currently, limited data are available in the literature on the removal of BPA from contaminated water.

2. Material and Methods

HPLC-grade Acetonitrile, methanol, toluene, BPA (99%) were purchased from Sigma-Aldrich (Germany). Experiments were carried out in our “plastic (BPA)-free” laboratory, all laboratory-wares were glass. To minimize losses of BPA onto glass surfaces, all glassware was cleaned in detailed. Briefly, glassware was heated in an oven at 200 °C to remove any water adsorbed on the glass surfaces, and the heated glassware was soaked overnight in a 5% trimethylchlorosilane solution in toluene. The glassware was rinsed with toluene and methanol and then dried in an oven at 100 °C for 1 h. Individual standard solutions of BPA were prepared in methanol.
In this study, samples of 42 different natural spring and natural mineral water marketed under 42 different brands were purchased in local store in Ankara and Istanbul in June 2010 for screening survey. After the screening survey, the samples of 45 natural spring and natural mineral water marketed under 5 different brands by 5 different companies were purchased for systematic specific migration study for BPA. All the samples came in the same type of containers, which were the 19 liters polycarbonate carboys. 5 different PC plastic companies produced all carboys at different age (the date of production). PC carboy water samples were tested as consumed, they purchased to the laboratory in 2 days of packaging. 3 carboys of each brand were stored at 4^{o}C in a room-type refrigerator, 3 carboys at 25^{o}C and 3 carboys at 35^{o}C for each of 5 different brands of packaged natural spring water manufacturer.

The sampling process was carried out by taking of 1 mL of water sample by glass pipette for 30-times with mixing of the carboy every time. The collected 30 mL of water sample mixed well in a Pyrex bottle and then put into the amber glass vials and used for BPA analysis. Remained samples after the analyses were stored in freezer at -70^{o}C for any problem. The Agilent 1100 series HPLC system (Agilent Technologies Inc., CA, USA) equipped with a quaternary pump (Agilent, G1311A), a manual injection block (Agilent, G1328B), a fluorescence detector (Agilent, G1321A), a column thermostat (Agilent, G1316A) and a degasser (Agilent, G1379A) was used for BPA analyses. The equipment controlled by a software (Agilent Chemstation) for the solvent gradient, data acquisition and data processing. Silica based C-18 RP-HPLC column (250mm length x 4.6mm i.d., Thermo Hypersil ODS, particle size 5µm, pore size 120˚A) was used for analyses. Isocratic acetonitrile: water elution (70:30) was used. Total run time: 5 min. Column temperature: 20˚C. Flow rate: 1.0 mL/min. Detection wavelengths: λ_{ex}=275 nm, λ_{em}=300 nm. Injection volume of final sample solution: 20 µL. BPA standard were prepared in methanol at the concentration between 0.001- 1 ppm (w/v).

3. Results and Discussion

42 samples of natural spring and natural mineral water packaged in PC carboy of different brands, supplied from Ankara and Istanbul markets for screening work of BPA. Given 45 samples of natural spring and natural mineral water packaged in PC carboy of 5 different companies were used for specific migration investigation of BPA during 60 days of storage at 3 different temperatures. BPA concentration was determined by RP-HPLC as explained above. The typical chromatograms of the standards were given in Figure 2. The standard curve and the trend line (dashed) used for calculation of BPA from the peak areas obtained from RP-HPLC chromatograms were given in Figure 3. It was observed that the all PC carboys, which were used for the water samples in this study, had been produced by 9 different carboy manufacturers in Turkey. It is found that at least 85% of the carboys have been produced between 2008-2010 (Figure 1). It is possibly means that, the reusage probability of the PC carboys for natural spring water packaging is 3 years.

It was observed that PC carboys, which were used for packaging of natural spring and mineral waters, have been used for three years with reused manner. Less than 2 % of them aged more than three years (Figure 3). The correlation between the production date (age) of the PC carboys and BPA migration was found to be insignificant ($p<0.01$) (Figure 5). It means that “the age” of PC carboy do not affect the BPA migration into the drinking water. The possible reason of this observation was suggested as the carboys have been washed and disinfected strongly in the plants before reloaded. So, possible migrated BPA has been washed out before reusage. There was no BPA migration was observed in natural spring and mineral waters packaged in PC carboys, which were stored at 4^{o}C for 60 days. On the other hand, it was determined that BPA has migrated up to the concentration of 0.001 mg/kg in the PC carboys stored at 20^{o}C, and 0.003 mg/kg at 35^{o}C. It means that, BPA migration levels were lower than 450 times than that of EFSA’s specific migration limit at 20^{o}C, and lower than 200 times at 35^{o}C during the storage for 60 days (Figure 4).It was assumed that the function of BPA migration during the storage time was linear (r=0.999).

The estimated time-dependant level of BPA migration would take 1200 days (32 years) at 35°C for reaching the BPA level to the EFSA's SML (0.6 mg/kg). The TDI value of BPA was recalculated by EFSA as 0.05 mg/kg bw/d in November 2010. Additionally two different toxicological experiments which were evaluated by German Federal Risk Assessment Institute (BFR) showed that there is no negative health effect in rats where oral BPA intake has loaded up to 200 mg/kg bw/d (Stump et al., 2010, Ryan et al. 2010). It is possible evaluated, as a healthy consumer would be intake 200 mg BPA per day per kg of body weight without any defect. In this study the maximum BPA migration has detected as 0.003 mg/kg in natural spring and mineral water samples packaged in PC carboys. According to the estimations above mentioned, it is meant that a healthy person have to drink 4500 liters of PC-packaged water for health risk caused by migrated BPA (estimated due to BFRI data). This estimation was 1200 liters per day that was calculated according to the TDI value of EFSA (0.005 mg/kg). So, it means that it has to be drink 60 carboys of water per day for any defect.

4. Conclusion

The results of this survey clearly indicate that exposure of BPA thru the consumption of bottled water would be extremely low. The low levels of BPA found in polycarbonate bottled water products available for sale in conclusion that the current dietary exposure to BPA through food packaging uses is not expected to pose a health risk to the general population.

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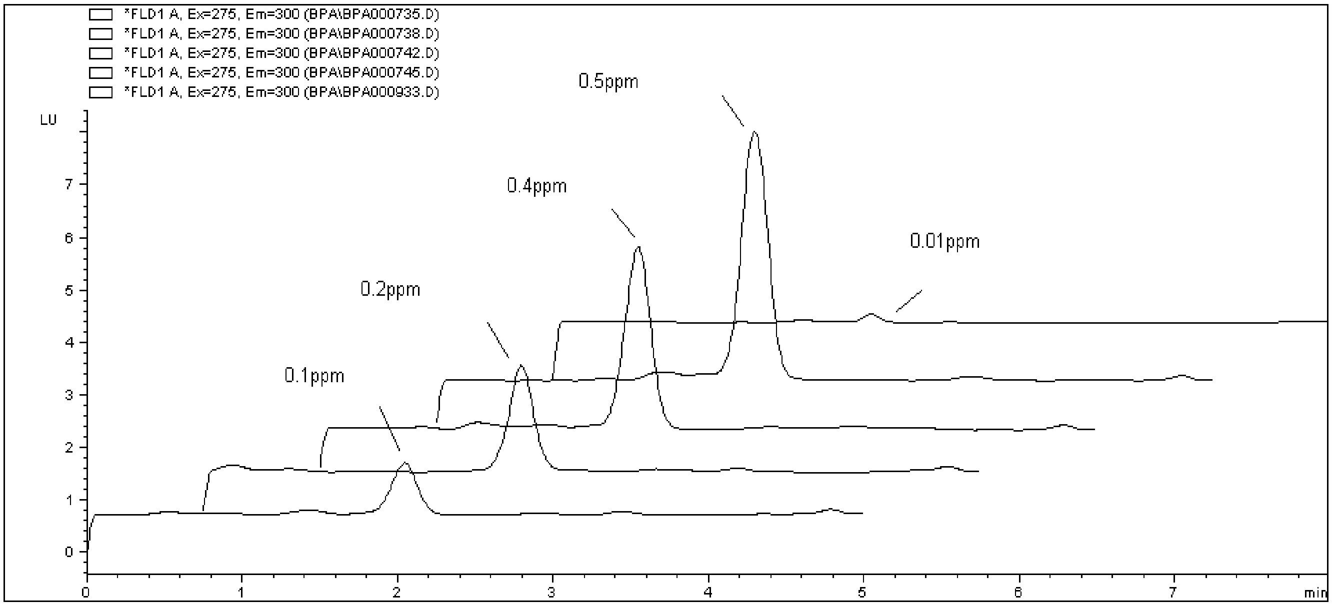
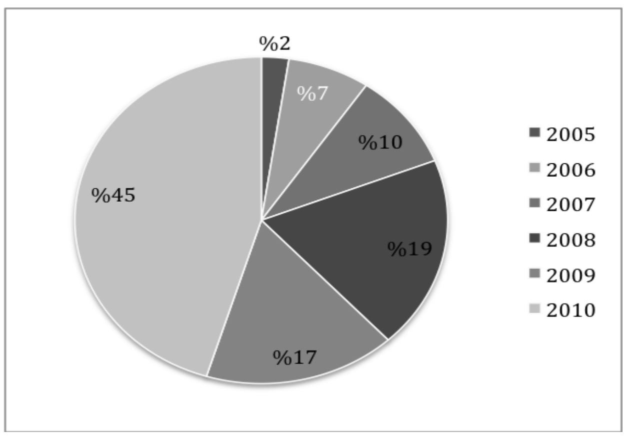
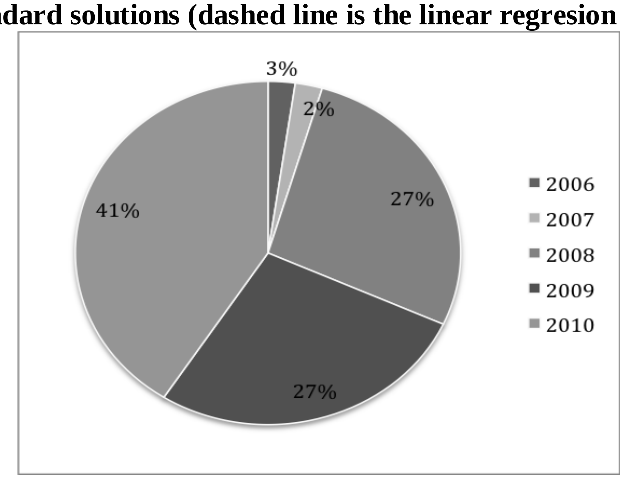


Figure 1. The typical chromatograms of the BPA standard solutions.



(a)

Figure 2. The estimation of BPA concentrations via peak area of the RP-HPLC chromatograms of the BPA standard solutions (dashed line is the linear regresion line).



(b)

Figure 3. The percentage of the production years of PC carboys used for the packaging of the natural spring and natural mineral waters in the study; screening survey samples (a), specific migration test samples (b)

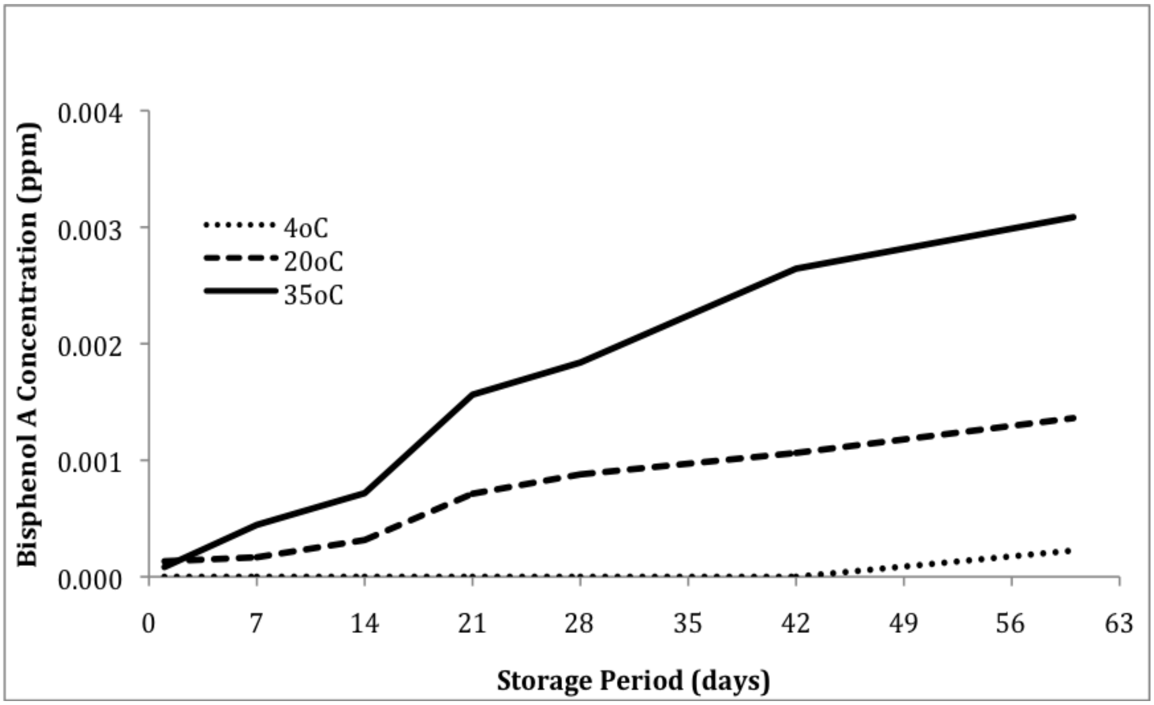


Figure 4. The effect of storage temperature on the BPA migration.

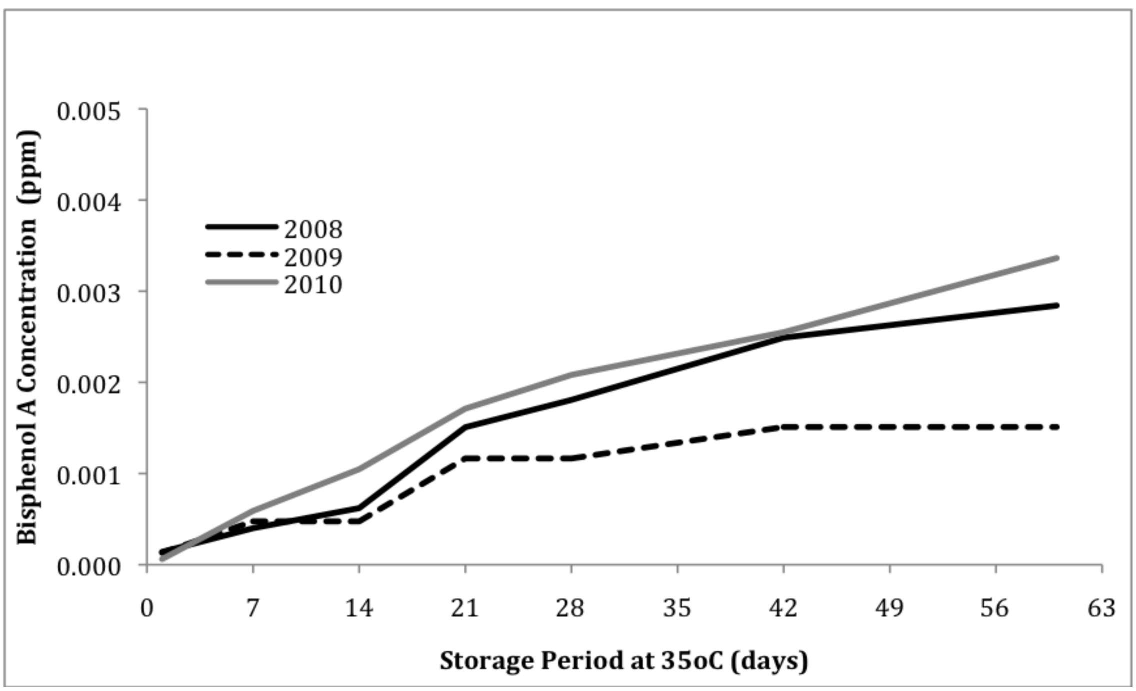


Figure 5. The effect of carboy's age on the BPA migration.