Original article

The effect of temperature and storage time on the migration of antimony from polyethylene terephthalate (PET) into commercial bottled water in Kuwait

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Summary. Polyethylene terephthalate (PET) is a safe material used widely in manufacturing plastic water bottles. However, recent studies have linked PET with Antimony which poses both acute and chronic health effects. The objective of this study was to investigate the effect of storage and temperature on the amount of antimony leached to the bottled water. Three brands of bottled water were used for this analysis. Samples were stored at 25°C for three months to examine the storage duration on antimony levels. To examine the effect of temperature on antimony levels, samples were stored at -5°C, 25°C and 50°C for 24 hours, respectively. To investigate the duel effect of both temperature and time on antimony levels, samples from one brand were heated at 50°C for 7 days. Antimony analysis was conducted using a Thermo Electron Element 2 single-collector double-focusing magnetic sector inductively coupled plasma mass spectrometer (ICP-MS). Results showed that there were no statistical differences of antimony concentrations before and after storage at room temperature. Heating samples to 50°C increased the antimony concentrations to 8.530 ppb and 16.8 ppb in 24 hours and 7 days, respectively. Although the range of Antimony concentrations in the bottled waters is well below WHO maximum contaminant level if stored at room temperature, inappropriate and prolonged storage of plastic bottles may lead to exceed the maximum contaminant level of 6 ppb. The data collected from this study can be useful to plastic bottle manufacturers for setting a safe storage temperature for PET bottles. (www.actabiomedica.it)

Key words: antimony, PET, bottled water, Kuwait

Introduction

A polymer is a substance composed of molecules with large molecular mass and having repeating structures (also called monomers) connected by covalent chemical bonds. Many examples of polymers can be found in common households items. These include grocery plastic bags, blends with fabric in clothing, automotive parts and components, flatware, eating utensils, building materials and water bottles. A polymer can be classified depending on the source from which it is made. One type of polymers is made from renewable resources such as starches and proteins that originate from plants and bacteria. Other types of polymers are made from hydrocarbon sources such as crude oil. Examples of these are polyethylene (PE), polypropylene (PP) and Polyethylene terephthalate (PET) (1).

Polyethylene terephthalate (PET) is a thermoplastic polymer that belongs to the polyester family. PET accounts for 18% of the world polymer production and is the third-most-produced polymer after polyethylene (PE) and polypropylene (PP), respectively (2). The majority of the world's PET production goes for synthetic fibers and plastic bottle production

(3). PET offers very good alcohol and hydrophobic barrier properties, good chemical resistance and a high degree of impact resistance and tensile strength (4). PET is synthesized by the polymerization reaction of terephthalic acid and ethylene glycol by antimony (Sb), titanium or germanium catalysts. But since antimony catalysts are the cheapest, they account for more than 90% of the global PET production (5).

Uncharged antimony is a white and brittle metal that infrequently occurs in nature. Since antimony metal is too brittle when used alone, it is used in alloys to increase metal characteristics such as hardness, mechanical strength, corrosion resistance and electrochemical stability. Metallic antimony is used as grid metal in lead storage batteries, solder metal, sheet metal, pipe metal, and type metal (6).

Another, most popular, form of antimony is antimony trioxide. Antimony trioxide is a stable, nonvolatile white powder that dissolves in water slightly and is used for its fire retardation properties in many materials such as plastics, rubber, adhesives, textiles, paper and pigments (6).

The maximum contaminant level (MCL) of antimony in municipal drinking water is 6 ppb (mg/L) based on the US Environmental Protection Agency (USEPA), the Ontario Ministry of Environment, and Health Canada. The German Federal Ministry of Environment and European Union set the MCL of antimony at 5 ppb. Moreover, Japan and the World Health Organization set the antimony levels at 2 and 20 ppb, respectively. Acute antimony exposure can cause serious health effects such as nausea, vomiting, and diarrhea while chronic exposure can increase low density lipoprotein (LDL) and decrease blood sugar. Moreover, research shows that antimony and arsenic are similarly carcinogenic (7).

Several papers have studied the effect of different environmental parameters on the release of antimony from PET plastic water bottles. Chapa-Martínez et al. (8) found that factors such as temperature, pH and storage duration can affect the amount of antimony leached into water and the MCL of antimony was surpassed under the highest conditions. Qiao et al. (9) found that storing plastic water bottles in a car trunk at temperatures higher than 40 °C increased the release of antimony from these bottles and the amount of antimony released had a direct relationship with temperatures. In Iran, a study by Faraji et al. (10) found that antimony levels from plastic water bottles were within limits under storage conditions of 45°C for 45 days. However, temperatures above 45°C may easily increase antimony level exponentially.

Kuwait is a country located in the Middle East that has a dry hot long summer and short winter. The temperature in the summer can reach 50°C under shadow. On the other hand, the temperature in the winter can reach 0°C. The dramatic fluctuations in temperature may lead to increased leaching of antimony from plastics to bottled water. Therefore, the objective of this study is to investigate the effect of long storage duration and temperature on the amount of antimony leached to bottled water.

Methods

Nine clear PET plastic noncarbonated water bottles from three commercial brands were purchased in the summer of 2018 at stores in Kuwait City, Kuwait. The sampled bottles had volumes of 330 mL. Bottles were checked for the global identification resin number to make sure that all studied water bottles were made of PET.

One set of all brands was stored at 25°C for three months to examine the storage duration on antimony levels. To examine the effect of temperature on antimony levels, three sets of plastic water bottles were stored at -5°C, 25°C and 50°C for 24 hours, respectively. Stored bottles at 50°C were kept warm using Heraeus oven UT5200 (Kendro Lab Products GmbH, Germany).

After prescribed incubation temperatures, water from the bottles was transferred to 60 mL high density polyethylene (HDPE) bottles and acidified with HNO3 acid. Reverse osmosis water (Pure Aqua, CA, USA) which contained less than 0.005 ppb of antimony was used as the control.

Antimony analysis was conducted using a Thermo Electron Element 2 single-collector double-focusing magnetic sector inductively coupled plasma mass spectrometer (ICP-MS). Reagents used in all experiments were of analytical grade and ultra-clean water was used to prepare all solutions. Standard solution of antimony was arranged using the technique described by Chapa-Martínez et al. (8). The antimony concentration in the samples was mesured in triplicate for each brand.

Statistical analysis

Paired t-test was used to compare antimony concentrations in purchased bottled water before and after a 3-month holding period at room temperature. To determine the impact of three set temperatures on antimony levels, analysis of variance (ANOVA) for three factors was conducted. Statistical significance level was set at $p<0.05$. Data were analyzed using the SPSS statistical software package version 24.0.

Results and discussion

Figure 1 shows the antimony concentrations over the 3-month study period. Generally, concentrations of antimony ranged from 0.247 to 0.511 ppb. The average antimony concentrations from the three brands were 0.390±0.133 ppb and 0.384±0.124 ppb at the beginning and at the end of the study, respectively. Student t-test statistical analysis showed that there were no significant changes in antimony concentrations for all bottles over the 3-month holding time.

Overall, all test samples exhibited an initial antimony concentration less than the maximum allowable level set by the EU (5 ppb) and USA (6 ppb). These results are consistent with the results reported by Chapa-Martínez et al. for 12 water bottles tested in Mexico which ranged from 0.28 to 2.30 ppb and 23 water bottles in the Serbian market which ranged from 0.3 to 1.81 ppb (8), but higher than the results reported by Qiao et al. (9) in China that had antimony concentrations less than 0.02 ppb at 25°C. The wide range of antimony concentrations on previous studies is possibly a result of the different quality and manufacturing procedures of PET plastics in different countries and the conditions during transportation and storage (8, 9, 10).

Figure 2 shows the effect of three main set temperatures (-5, 25 and 50°C) on the amount of antimony leached to the bottled water. There were no significant changes in antimony concentrations after freezing water inside the bottles. However, heating the sample to 50°C increased the antimony concentrations from 0.532 to 8.530 ppb in 24 hours, which is well above the USEPA MCL. These results are consistent with the results reported by Chapa-Martínez et al. and Westerhoff et al. (8,11) which showed that temperature has significantly influence antimony leaching from PET bottles. According to Takahashi et al. (12), the source of leached antimony from PET plastic bottles to water is caused by high temperature during storage and transportation and it is not linked to antimony chemi-

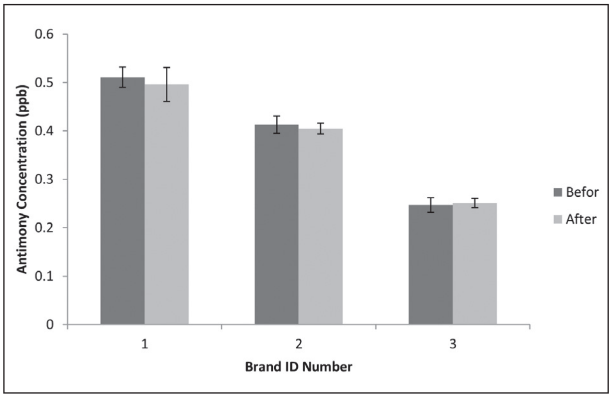

Figure 1. Antimony concentrations in purchased bottled water over a 3-month holding period at room temperature (22°C). Averages of three water bottles are shown; error bars represent the difference between antimony analyses in the three water bottles

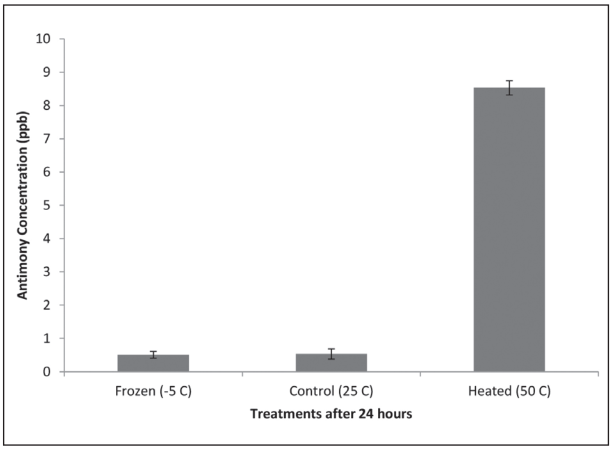

Figure 2. Effect of low and high temperatures on antimony concentrations of bottled water

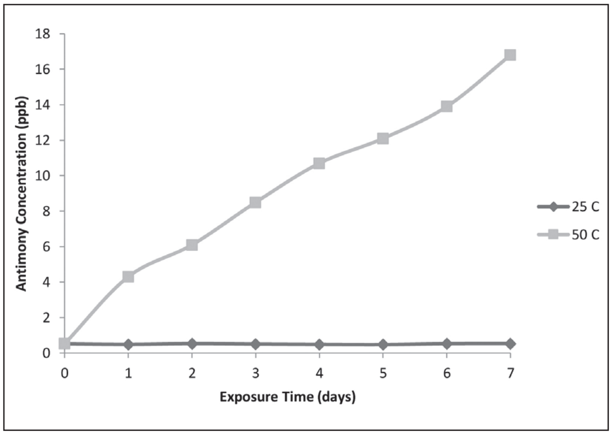

Figure 3. Effect of exposure temperature and time on antimony leaching into bottled water

cal components during manufacturing of the PET bottles. Furthermore, Carrieri et al. (13) indicated a high leaching effect at temperatures of 45-60°C. The authors also reported a value 18 ppb of antimony at 80°C.

Figure 3 represents the effect of both temperature and time on antimony leaching into bottled water. Storage temperatures had a positive relationship with rates of antimony leaching into bottled water. After only 5 days at 50°C, the antimony concentration reached more than twice the USEPA MCL of 6 ppb. Several studies are consistent with the current results (8, 9). However, Holland and Hay (14) reported different results when PET bottles were subjected to a temperature above 75°C and in longer storage times. At those conditions, low amounts of antimony were observed. The authors attributed that to the likelihood of having distinct functional groups resulting from the disruption of the PET at high temperature. These functional groups are believed to absorb the antimony released in.

Conclusions

Antimony can be leached from water bottles made of PET plastics. The rate of leaching is low at a storage temperature of 25°C. However, at temperatures of 50°C and above, antimony release can occur very rapidly. It is likely to approach these temperatures in the Middle East generally and in Kuwait specifically. Therefore, exposure to high temperatures in short period of time during packaging, transportation or storage could produce antimony concentrations that exceed the USEPA MCL of 6 ppb. Based on the results of this study, all brands of bottled water sold in Kuwait must be checked for their quality. The good manufacturing practice for the ideal storage condition should be compulsory by the public authority for food and nutrition. Also, exporting water companies should be required to provide a specification of their PET bottles. Future studies should concentrate on finding the best quality PET so antimony levels will be minimized.

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Conflict of interest: Each author declares that he or she has no commercial associations (e.g. consultancies, stock ownership, equity interest, patent/licensing arrangement etc.) that might pose a conflict of interest in connection with the submitted article

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