Antimony release in PET bottled natural water in Lebanon
Lina Hureiki and Youssef Mouneimne

ABSTRACT
Antimony (Sb) leaching from polyethylene terephthalate (PET) bottling material was assessed in eight registered Lebanese brands of bottled natural water as a function of contact time. The study was performed indoors at 22 °C in the dark and outdoors at a maximum temperature of 45 °C under sunlight. The leached antimony concentration increased with contact time for all of the studied brands except one. The antimony concentration reached 5.5 μg/L after 544 days of contact time with PET packaging. Small bottles with large contact surface area had higher antimony concentration. However, outdoor storage under sunlight at temperatures below 45 °C did not reveal a significant effect on antimony release. Among some physico-chemical parameters studied (pH, calcium, magnesium and bicarbonate), only calcium concentration showed a significant effect on antimony release. The rate of antimony leaching, normalized to the surface to volume ratio of the water bottle, fits the exponential model $\frac{Sb}{S/V} = 0.562e^{0.0047t}$, with $R^2 = 0.87$. Atomic absorption spectroscopy analysis of the different PET packaging material showed an antimony concentration between 80.6 and 352.7 mg Sb/kg PET.

Key words | antimony, bottled natural water, leaching, PET

INTRODUCTION
Over the last 20 years, bottled water from diverse natural and industrial sources has gained popularity and sales volume has risen rapidly worldwide. Of the top 10 per capita consumers of bottled water Lebanon ranks eighth. Bottled water consumption per person increased by 62.8% between 1996 and 2007 (Beverage Marketing Corporation 2003, 2008). The presence of hazardous metal contaminants in bottled water raises serious public health concerns in the water industry. The most widespread material used for bottling is polyethylene terephthalate (PET) with antimony trioxide as the catalyst in the manufacturing process (Pang et al. 2006). The antimony (Sb) concentration of the commercialized PET resin is between 150 and 300 mg/kg (Westerhoff et al. 2008; Keresztes et al. 2009). The leach of antimony from PET bottles into mineral water represents a possible risk to human health, and little is known about the acute and chronic health effects. The environmental protection agency of the USA (EPA) and the Council of the European Communities (CEC) classify antimony as a serious contaminant, with 6 μg/l (USEPA 1994) and 5 μg/L (European Union Council 1998) as the maximum contaminant level in drinking water. In Japan the threshold is lower still at 2 μg/l (Shotyk et al. 2006; Westerhoff et al. 2008). However, no guideline value currently exists for antimony in the Lebanese Standard Institution (LIBNOR 1999).

To satisfy the domestic Lebanese need for bottled water, numerous suppliers have proliferated in the market, many of which do not have approved licenses from the public health authorities. As a result, it is difficult to estimate the exact number of bottled water brands in Lebanon. The objective of this study was to assess antimony contamination leaching from eight registered Lebanese brands of natural water bottled in PET. This paper compares the antimony content of bottled water purchased in Lebanon and describes the effects of contact time, temperature, sunlight and physico-chemical water composition on antimony release from PET bottles.

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MATERIALS AND METHODS

Bottled water from Lebanon in PET

Eight registered Lebanese brands of bottled natural water were chosen for this study. Water samples were acquired from each brand before and after bottling with the same bottling date. Container sizes chosen were 0.5, 1.5 and 2 L. All bottled water samples remained sealed in their original PET containers until analysis. Though all bottles were made of PET, one was colorless and others had a blue tint. All bottles of the same brand were studied in duplicate. To experiment under realistic storage conditions, the bottled waters were kept indoors at room temperature (22 °C) and in the dark. Other bottles were kept outdoors and exposed to sunlight.

Analytical procedures

Antimony was determined in all water samples and their PET containers using a Thermo Lab Systems Solar atomic absorption spectrometer. Deionized water was used for standards preparation (concentrated 1,000 ppm, Romil pure chemistry, UK). Calibration solutions were prepared fresh and validated to previous calibrations. All antimony measurements were carried out using furnace atomic absorption. The detection limit was 0.2 μg/L and the mean and standard deviation were determined from duplicate measurements of each sample. Duplicate water bottles were used for Sb analysis.

Antimony analysis

Antimony in water

Water samples and deionized water were directly measured according to the manufacturer's protocol.

Antimony in PET

PET samples were digested by the microwave digestion system, Ethos Plus, from Milestone, Shelton, USA, according to a standard digestion protocol provided by the manufacturer. About 0.1 g of PET was cut from each bottle, weighed and added to the microwave vessels with 6 mL nitric acid (65%) and 1 mL hydrogen peroxide (30%). Digested samples were diluted to fit the furnace detectable range.

RESULTS AND DISCUSSION

Previous studies reported the increase of the concentration of released antimony in PET bottled water with the increase of storage time (Shotyk et al. 2006; Westerhoff et al. 2008; Keresztes et al. 2009). This release is related to the contact time between water and PET bottle and is commonly fixed while testing other parameters' effects on Sb leaching. The objective of this study was to determine the concentration of antimony in eight commercially bottled natural waters under different conditions (storage time, exposure to sunlight, water composition and the PET material used). The results showed the presence of antimony in Lebanese bottled natural water contained in PET (0.2 to 5.5 μg/L). These values were similar to results obtained for different international brands (Shotyk et al. 2006; Guler 2007; Westerhoff et al. 2008; Keresztes et al. 2009; Smedley 2010).

It was possible to visit six of the eight bottling plants in Lebanon, where samples of water prior to bottling were collected and considered the reference with zero PET contact time. These samples were conserved in brown glass bottles to prevent antimony migration prior to Sb analysis (Shotyk & Krachler 2007). The data indicated an Sb concentration less than 0.2 μg/L (detection limit of the experimental method used). The antimony leaching increased for all studied brands according to the contact time, except for brand number 8. The Sb concentrations detected in the other seven brands, stored indoors, in the dark at room temperature, ranged from 0.2 to 5.1 μg/L, according to contact time and brand. The highest significant Sb release was detected in brand 2 with 565 days of contact time at a concentration of 5.1 μg/L. Figure 1 summarizes the Sb concentrations measured for the eight brands studied during the period of March to September 2010. Error bars represent the standard deviation of duplicate measurements and experiments. Errors below 0.2 μg/L are not shown in figures.

The related contact times $t_0, t_1, t_2, t_3, t_4, t_5$ for each brand are detailed in Table 1.
To investigate the effect of storage at higher temperatures under sunlight exposure, and to simulate the case of improper storage (inside cars, outdoors storage), especially during the summer time, the bottled waters for the eight brands were exposed to sunlight and air temperature during the period of March to September 2010. The temperature in the summer reached 45 °C.

For each brand, duplicate bottles were placed outdoors on 11/3/2010 (t1: time zero for exposure) maintaining the same bottling date as those stored indoors. Figure 2 summarizes the concentration of Sb released from the eight brands at different exposure time to sunlight.

Over the 200 days of outdoors exposure to sunlight (including summer season), Sb concentrations increased differently according to the brand and contact time with PET package. Specifically, brand 2 reached the highest concentration of Sb (5.5 ng/L) after 544 days of contact time with PET package and 200 days exposure time to sunlight. No significant increase was observed for brand 8 during the 310 days of contact time with PET.

For the same contact time, no significant difference was found in the antimony release between bottled water stored indoors at room temperature and the same brand exposed to sunlight and air temperature. Therefore no significant effect was found for UV exposure and temperatures up to 45 °C. This finding is consistent with results from other studies in the literature; however the migration of antimony was notably observed for temperatures above 60 °C (Westerhoff et al. 2008; Keresztes et al. 2009). Figures 3 and 4 compare the antimony released in bottled waters stored indoors and those exposed to sunlight for different bottle volumes.

Within the 2 years’ expiration limit for the bottled water, the highest antimony concentration measured after 544 days was 5.5 μg/L, close to the limits set by the EPA (6 μg/L) and the CEC (5 μg/L), and well above the 2 μg/L tolerated by Japan.

According to these results shown in Figures 3 and 4, the second main parameter affecting the leaching of antimony
Figure 2 | Antimony concentrations in Lebanese bottled water contained in PET, stored outdoors, in sunlight with different contact times.

Figure 3 | Comparison of the antimony concentrations for bottled waters of 0.5 L volume stored indoors, in darkness and those exposed to sunlight.

Figure 4 | Comparison of the antimony concentrations for bottled waters of 1.5 and 2 L volumes stored indoors, in darkness and those exposed to sunlight.
from PET packaging into bottled water was the bottle volume. Consequently, the bottle volume is related to the contact surface area between water and PET material, as shown in Table 2.

Figure 5 represents the effect of bottle volume on Sb concentration for brands 1 to 7 stored indoors and outdoors combined.

The above results show that the leaching rate of antimony is proportional to the ratio of contact surface area to water volume (S/V). Smaller bottles have a larger S/V ratio and therefore a higher antimony concentration for similar contact time between water and PET material. Considering this information, Figure 6 presents the normalization of results with respect to different surface to volume ratios.

Table 2  | Ratio of contact surface area to water volume for studied bottles

<table>
<thead>
<tr>
<th>Bottle volume</th>
<th>0.5 L</th>
<th>1.5 L</th>
<th>2 L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio of contact surface area to water volume; S/V (cm²/ml)</td>
<td>0.83</td>
<td>0.58</td>
<td>0.54</td>
</tr>
</tbody>
</table>

At temperatures below 45 °C the rate of antimony leaching, regardless of the bottle volume, will best fit the exponential model $Sb/S/V = 0.562e^{0.0043t}$ with $R^2 = 0.87$, which is a first order kinetic with rate constant of 0.0041 per day.

Several experiments were performed to study the effect of some parameters related to water composition that could potentially affect antimony leaching from PET bottles. The effects of pH (7–8), total dissolved solids (TDS) (130–260 mg/L), and some major ions (calcium: 21–65.5 mg/L, magnesium: 5–20 mg/L and bicarbonate: 80–293 mg/L) on Sb release in water were studied for almost similar contact time (300 days) between water and PET bottle for both samples (indoors and outdoors). The values of the physico-chemical parameters considered were those indicated on the water bottles. The study showed a correlation between TDS and the release of Sb in bottled water. Upon further analysis of individual TDS constituents (calcium, magnesium, bicarbonate), only calcium revealed a significant effect. The pH results were similar to the literature (Westerhoff et al. 2008) with no effect on antimony leaching within
the pH range (6–8) of drinking water. Figure 7 shows the correlation between the calcium concentration and the release of antimony, normalized to S/V, for both indoors and outdoors samples. Lower calcium concentration yielded less leaching.

The Sb concentration in the bottling material was determined following microwave digestion of PET material of the 8 brands. Figure 8 represents the Sb concentration measured in PET bottling material.

The results showed the presence of Sb in all analyzed PET samples with the highest concentration found for brand 8, which had no Sb release over 310 days contact time. However, this brand presented the lowest calcium concentration. Antimony concentrations were between 80.6 and 352.7 mg Sb/kg PET, nearly in the same range mentioned by the literature (Westerhoff et al. 2008; Keresztes et al. 2009).
CONCLUSIONS

The results of this study confirm that antimony release is correlated to the bottled water contact time with PET material and not storage conditions such as UV exposure and temperatures up to 45 °C. The antimony level found in Lebanese bottled natural water was 5.5 µg/L following 544 days of contact time with PET bottle, close to the 2 years’ expiry date. This Sb concentration is very close to the guidelines set by the US EPA and exceeds the level set by the CEC and Japan. In addition, the results show that water bottle volume affects the rate of Sb release and that the antimony release is proportional to the ratio of contact area to water volume. Accordingly, smaller volume bottles should have shorter expiry dates.

Regarding the physico-chemical effect, the results indicate that antimony leaching increased with the calcium concentration (from 21 to 65.5 Ca mg/L) in bottled water; however, no correlation was found with the pH (from 7 to 8), magnesium (5–20 mg/L) and bicarbonate (80–293 mg/L) concentrations. As previously mentioned, brand 8, which had the lowest calcium concentration, showed the lowest release of antimony despite having the highest concentration of Sb in the PET packaging material. Consequently, the expiry date should also consider the calcium level in bottled water.

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REFERENCES
