Antimony leaching from polyethylene terephthalate (PET) plastic used for bottled drinking water

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ARTICLE INFO

ABSTRACT

Antimony is a regulated contaminant that poses both acute and chronic health effects in drinking water. Previous reports suggest that polyethylene terephthalate (PET) plastics used for water bottles in Europe and Canada leach antimony, but no studies on bottled water in the United States have previously been conducted. Nine commercially available bottled waters in the southwestern US (Arizona) were purchased and tested for antimony concentrations as well as for potential antimony release by the plastics that compose the bottles. The southwestern US was chosen for the study because of its high consumption of bottled water and elevated temperatures, which could increase antimony leaching from PET plastics. Antimony concentrations in the bottled waters ranged from 0.095 to 0.521 ppb, well below the US Environmental Protection Agency (USEPA) maximum contaminant level (MCL) of 6 ppb. The average concentration was 0.195 ± 0.116 ppb at the beginning of the study and 0.226 ± 0.160 ppb 3 months later, with no statistical differences; samples were stored at 22 °C. However, storage at higher temperatures had a significant effect on the time-dependent release of antimony. The rate of antimony (Sb) release could be fit by a power function model ($Sb(t) = Sb_0 \times [Time, h]^k$; $k = 8.7 \times 10^{-6} \times [Temperature (°C)]^{2.55}$; Sb_0 is the initial antimony concentration). For exposure temperatures of 60, 65, 70, 75, 80, and 85 °C, the exposure durations necessary to exceed the 6 ppb MCL are 176, 38, 12, 4.7, 2.3, and 1.3 days, respectively. Summertime temperatures inside of cars, garages, and enclosed storage areas can exceed 65 °C in Arizona, and thus could promote antimony leaching from PET bottled waters. Microwave digestion revealed that the PET plastic used by one brand contained 213 ± 35 mgSb/kg plastic; leaching of all the antimony from this plastic into 0.5 L of water in a bottle could result in an antimony concentration of 376 ppb. Clearly, only a small fraction of the antimony in PET plastic bottles is released into the water. Still, the use of alternative types of plastics that do not leach antimony should be considered, especially for climates where exposure to extreme conditions can promote antimony release from PET plastics.

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1.   Introduction

The US Environmental Protection Agency (USEPA), the Ontario Ministry of Environment, and Health Canada regulate antimony in municipal drinking water at a maximum contaminant level (MCL) of 6 ppb (µg/L). The German Federal Ministry of Environment (5 ppb), European Union (5 ppb), Japan (2 ppb), and World Health Organization (20 ppb) also have drinking water standards for antimony. Antimony is regulated as a drinking water contaminant because it can cause health effects, such as nausea, vomiting, and diarrhea, when exposure exceeds the MCL for relatively short periods. Long-term exposure can lead to increased blood cholesterol and decreased blood sugar. The USEPA has not classified antimony as a human carcinogen in water due to lack of studies. However, research shows that antimony and arsenic, a proven carcinogen, are similarly toxic (Gebel, 1997).

Public safety perceptions and convenience trends have led to greater use of bottled water instead of tap water (Allen et al., 1989; Allen and Darby, 1994; Ikem et al., 2002; Innes and Cory, 2001). While several pollutants have been found in bottled waters, this paper focuses on antimony, which is associated with plastic bottles made of polyethylene terephthalate (PET) (Shotyk et al., 2006; Shotyk and Rachler, 2007; Suzuki et al., 2000). Earlier studies tested more than 100 brands of bottled water from Japan, Canada, and 28 countries in Europe, but not the United States. Observed antimony concentrations ranged from <0.005 to >0.5 ppb (Shotyk et al., 2006) and increased over time during storage.

PET is produced by the polymerization of the petroleum monomers terephthalic acid and ethylene glycol by antimony-, titanium- or germanium-based catalysts. Titanium catalysts may allow PET resin to be formed at higher temperatures, and no regulatory guidelines exist for titania in drinking water. No regulatory guidelines exist for germanium in water, and the metal has been used in some dietary supplements, although its overall human health effects are debatable (Tao and Bolger, 1997). But since germanium-based catalysts are more expensive than antimony-based catalysts, the latter account for more than 90% of the PET manufactured worldwide. Both private/publicly owned industry and municipal water agencies prefer to use PET plastics for bottled water because they are visibly clear. The authors believe, based upon informal surveys, that customers prefer the clear plastics because they emphasize the "clean" nature of the water.

Because PET plastic bottles are used for drinking water, it is important to understand the environmental factors that may influence the release of antimony from the catalysts into the water. Some industries or water agencies may use this information to decide to use PET bottles manufactured using germanium or other catalysts, or to switch to other types of plastic entirely. Thus, this paper compares the antimony content of several bottled waters purchased in the southwestern US and describes the effects of storage temperature and exposure to sunlight on antimony release from PET plastic bottles into water. Bottled water use is high in this area of the country, in part because the high calcium and total dissolved solids concentrations in tap water can cause unpleasant tastes (Allen and Darby, 1994; Innes and Cory,

2001). Furthermore, the hot southwestern climate affects water temperatures during bottled water storage and may lead to increased leaching of antimony from plastics.

2.   Methods

2.1.   Commercial bottled waters

Nine commercial brands (brand ID #) of bottled water were purchased in the summer of 2006 at stores in the southwestern US (Arizona): Tynant (1), Pure American (2), Aquafina (3), Refreshe (4), Smartwater (5), Hawaii Water (6), Albertsons Store Brand (7), Dasani (8), and Arrowhead (9). All bottles were labeled as being PET plastic. At least two bottles of each were purchased, sometimes from different store locations. A smaller number of samples were collected than in previous studies (Shotyk et al., 2006; Shotyk and Rachler, 2007) because those studies found relatively small variability among different brands, and because these were the major brands found at grocery and convenience stores in the central Arizona metropolitan area. All bottles were made of PET, although some were colorless and others had a blue tint. Local tap water (Tempe, Arizona) was also sampled. One set of samples was analyzed in July, and another set 3 months later after holding the samples at room temperature to examine how storage affected antimony levels. After the bottles were opened, water was transferred into 60 mL HNO_3-washed high-density polyethylene (HDPE) bottles, acidified with HNO_3 acid (Omni Trace Ultra™, EMD Chemicals, Gibbstown, NJ, USA), and spiked with indium (Spex CertiPrep®, Metuchen, NJ, USA) as an internal standard. Control samples using ultrapure water (NANOpure Infinity, IA, USA) handled in the same fashion contained less than 0.005 ppb of antimony.

2.2.   Experimental methods

Temperature-incubation experiments were conducted by placing the as-received bottles containing bottled water into ovens set at 40, 60 or 80 °C in a T12 Function Line Heraeus oven (Kendro Lab Products GmbH (now Thermo Fisher), Germany). Room-temperature incubation was conducted at 22 °C. After prescribed incubation times, water was removed from the bottles and transferred to clean HDPE bottles (prepared as described above).

Laboratory tests were conducted with one commercial bottled water (Brand 9). Three parameters were varied in a 3×4 experimental matrix: Three water pH levels were used with four experimental treatments. The pH was adjusted to 6.3, 7.3 or 8.3 with hydrochloric acid or sodium hydroxide. The four treatments were: (1) control sample held at room temperature; (2) sample frozen at -20 °C for 48 h; (3) sample heated to 80 °C for 48 h; (4) sample irradiated using a low-voltage UV-PEN (Fisher Scientific), which emits light at 254 nm; it operated inside the bottle for 6 h.

Sunlight exposure tests were conducted outdoors in Arizona (Tempe, AZ) on the roof of the laboratory building. Bottled waters, with labels removed, were exposed to sunlight for up to 7 days (August 9–16, 2006). Control samples wrapped in aluminum foil to prevent solar irradiation were placed on the roof to be exposed to the same air temperatures.

To determine antimony content in PET formed with antimony catalysts, a PET bottle (Brand 9) was digested using a CEM Mars5 microwave digestion system (CEM, Matthews, NC, USA). The bottle was cut into $\sim 8 \times 8\,mm^2$ pieces using an acid-cleaned ceramic blade, rinsed with de-ionized water and weighed to $0.25\,g \times 3$ replicates. Each replicate was mixed with $10\,mL$ of HNO_3 and $2\,mL$ of HCl (Omni Trace, EMD Chemicals, Gibbstown, NJ, USA) and digested in a Teflon closed vessel. The maximum temperature and pressure were $180\,°C$ and $\sim 250\,psi$ for 15 min using 50% of the digestion system's maximum power of 1200 W. The resulting solutions were diluted with de-ionized water and analyzed for antimony content.

To compare the leaching potential of two different colored PET bottles (from the nine brands sampled) and one HDPE plastic bottles, samples were cut into pieces with dimensions of $9.4\,cm \times 9.4\,cm$ ($88\,cm^2$; front and back surface area $= 176\,cm^2$). These samples were placed in 1-L glass bottles containing nanopure water and held at $80\,°C$ for up to 10 days.
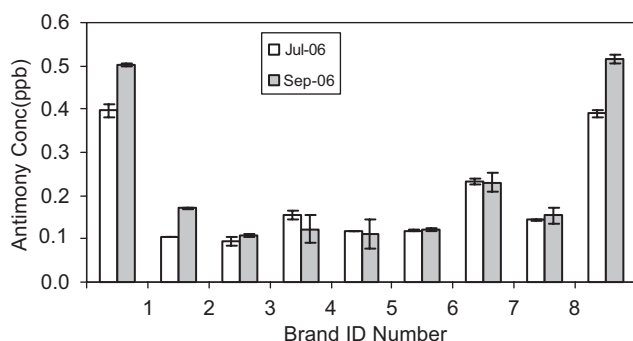
2.3. Analytical methods

Samples were analyzed for antimony using a Thermo Electron Element 2 single-collector double-focusing magnetic sector inductively coupled plasma mass spectrometer (ICP-MS) in low-resolution mode. Analytical accuracy and precision for the measurements were determined by analyses of river water standard reference materials NIST 1640, NIST 1643e, and NRC SRLS4. Precisions were within 3% (1σ). Measured and certified values for standards were within the quoted errors. The limit of detection and method reporting level are 0.004 and 0.028 ppb, respectively.

3. Results

3.1. Comparison of antimony in different brands of bottled water

Fig. 1 summarizes the antimony concentrations measured at the beginning and the end of the 3-month study period.
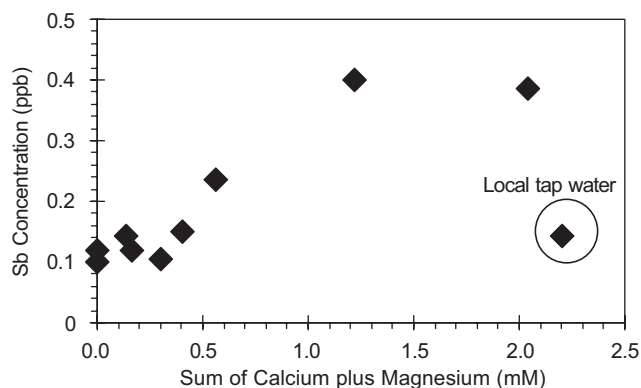
Overall, antimony concentrations ranged from 0.095 to 0.521 ppb (95 to 521 ppt). The average antimony concentration from the nine bottled waters was $0.195 \pm 0.116\,ppb$ at the beginning of the study and $0.226 \pm 0.160\,ppb$ after 3 months indoors at $22\,°C$. The two bottled waters with the highest initial antimony concentrations (samples 1 and 9) exhibited statistically significant increases of 25–35% over this holding time. However, student t-test statistical analysis of changes in antimony concentrations for the other seven bottles indicated no significant difference over the 3-month holding time. Furthermore, no relationship exists between the estimated internal surface area of the bottles (from which antimony could presumably leach) and the final antimony concentration. Brand 9 was used in subsequent work because it contained the highest initial antinomy and showed a propensity to release antimony over time.

For comparison, analysis of a local tap water sample (Tempe, Arizona) showed it contained $0.146 \pm 0.002\,ppb$ of antimony. All samples were below the USEPA MCL of 6 ppb. The observed average antimony concentration of the nine US bottled water samples is comparable with that of 12 brands of bottled natural waters from Canada ($156 \pm 86\,ppt$) and 35 brands in Europe (343 ppt) (Shotyk et al., 2006; Shotyk and Rachler, 2007). As an indicator of other water quality in the bottled water, the sum of calcium plus magnesium concentrations were measured and related to the antinomy concentration in the as-received bottled water (Fig. 2). Higher salt content tended to result in higher antimony concentrations in the bottled waters.

3.2. Effect of pH, temperature, and irradiation of PET bottles on antimony leaching

Several experiments screened for factors that could potentially affect antimony leaching from PET bottles. Table 1 summarizes the results of control tests using Brand 9 plastic bottles filled with pH-adjusted nanopure water. The pH had no effect on antimony leaching over the range studied, suggesting that drinking waters, which are typically in the pH 6–8 range regardless of bottling location, will not be

Fig. 1 – Antimony concentrations in purchased bottled water over a 3-month holding period at room temperature ($22\,°C$). Averages of two water bottles are shown; error bars represent the difference between antimony analysis in the two water bottles.

Fig. 2 – Relationship between antimony concentrations in bottled waters and indicator of ionic composition in bottled waters (sum of divalent cations). Local tap water antimony concentration is shown for comparison.

Table 1 – Effect of pH, temperature, and UV-PEN irradiation of nanopure water inside Brand 9 PET bottles

Adjusted pH in Brand 9 bottles	Duplicate measurements of antimony concentration (ppb) at the end of treatment			
	Control (22 °C) for 48 h	Frozen (−20 °C) for 48 h	Heated (80 °C) for 48 h	UV irradiated for 6 h
6.3	0.64	0.57	8.3	3.0
	0.55	0.58	7.8	2.4
7.3	0.50	0.52	9.6	2.4
	–	0.53	8.5	2.5
8.3	0.52	0.54	8.9	3.1
	0.50	0.54	9.7	2.1

The UV-PEN-irradiated sample was heated to ∼45 °C. Measurements were precise to 3% (1σ).

impacted by solution pH. Freezing water inside a PET bottle did not change the antimony concentration relative to control samples. Heating the sample to 80 °C, however, increased the antimony concentration in the bottled water from ∼0.5 to >7 ppb, which is above the USEPA MCL. UV irradiation also increased the antimony concentration to a final range of 2–3 ppb. Since the lamp warmed the water to roughly 45 °C, separating the effects of irradiation from those of heating on antimony leaching from the plastic is difficult. Based on these screening experiments, more detailed studies were conducted on the effects of storage/exposure temperature and solar irradiation.
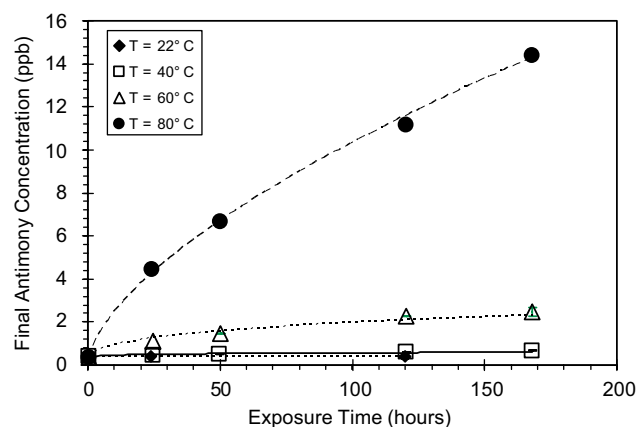
3.3. Effect of temperature on antimony leaching

Air temperatures in the southwestern US can exceed 45 °C. Temperatures inside cars, garages, and storage areas can exceed 60 °C. Therefore, tests were conducted from 22 to 80 °C to develop a temperature- and time-related relationship for antimony leaching; Fig. 3 presents the results. Increasing storage temperatures led to faster rates of antimony leaching into the as-received bottled water. After 7 days at 80 °C, for example, the antimony concentration reached 14.4 ppb, more than twice the USEPA MCL.

The rate of change in antimony leaching was best fit by a power function at 60 and 80 °C, rather than by first- or second-order reaction kinetics with respect to antimony concentration. The equation to fit these data was

$$C = a \times [time]^k, \quad (1)$$

where a is the fitted initial antimony concentration (C, ppb) at time zero and k is a temperature-dependent power function constant. Time is in hours. Table 2 summarizes the fitted values of a and k and statistical goodness of fit (R^2) values for the different temperatures. The exponential model fit 60 and 80 °C data well, as high R^2 values show. The average a concentration (0.47 ppb) fitted by the models closely approximated the measured time zero antimony concentration. While experiments at 22 and 40 °C were fit by the power function model, they had higher R^2 values for linear rather than power function model fits. At 22 °C no statistical change in antimony concentration actually occurred over time, so the

Fig. 3 – Effect of exposure temperature and time on antimony leaching into bottled water (Brand 9). Symbols are measured data, and lines are power function model fits using the parameters in Table 2. Error bars represent one standard deviation on triplicate experiments; in most cases the error bars are smaller than the symbols.
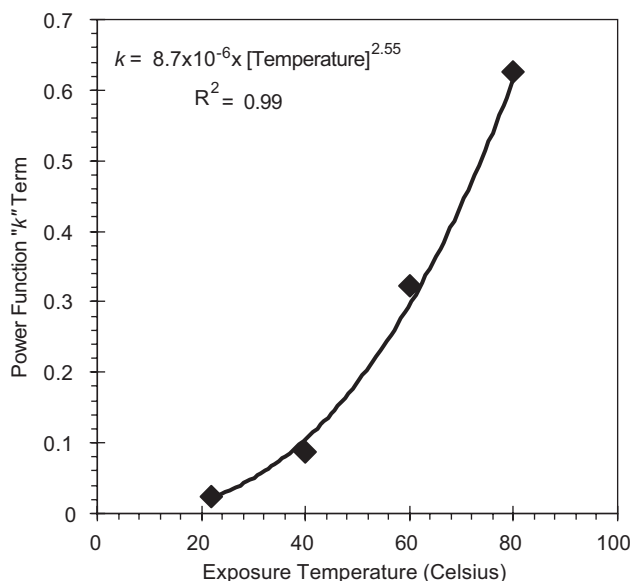
Table 2 – Effect of temperature on fitted parameters for a time-dependent power function (i.e., Eq. (1))

Exposure temperature (°C)	a	k	R^2
22	0.37	0.0248	0.89*
40	0.38	0.0878	0.78*
60	0.45	0.3237	0.99
80	0.58	0.6249	0.99

* Experiments at 22 and 40 °C had higher R^2 values for linear rather than power function model fits.

slope was zero. At 40 °C the linear model fit is Sb (ppb) = 0.0017 × (time, h)+0.39; R^2 = 0.99.

Although the R^2 values of the lower temperature exposure tests were higher for linear than power function model fits, overall the power function model trended the observed data well (Fig. 3). The power function exponent, k, was plotted against temperature to obtain a temperature- and

Fig. 4 – Relationship between the power function k term (Table 2) and exposure temperature.

Fig. 5 – Exposure of Brand 9 water bottle to outdoor sunlight. Error bar represents one standard deviation based on triplicate experiments.

time-dependent relationship for antimony leaching (Fig. 4). The final power function relationship from Fig. 4

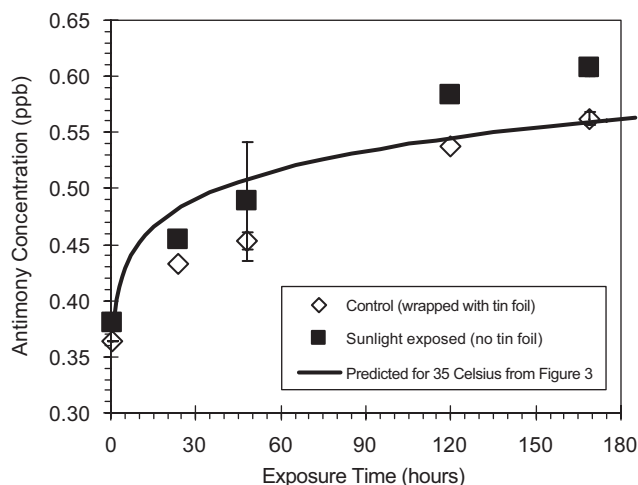$$k = 8.7 \times 10^{-6} \times [\text{Temperature (°C)}]^{2.55}, \qquad (2)$$

where k is used in Eq. (1)) can be used to estimate the exposure time required for a bottled water with an initial concentration of 0.5 ppb ($Sb_0 = 0.5$ ppb) to reach the USEPA MCL of 6 ppb

$$\text{Time (days)} = ([6\,\text{ppb}]/Sb_0)^{1/k}. \qquad (3)$$

For exposure temperatures of less than 58 °C, exposure durations of greater than 1 year are required to reach the MCL. For exposure temperatures of 60, 65, 70, 75, 80, and 85 °C, however, the exposure durations decrease rapidly to 176, 38, 12, 4.7, 2.3, and 1.3 days, respectively. While these temperatures may seem extremely high, it is possible to approach these conditions in the southwestern US. Thus, short-duration exposure to elevated temperatures during transit or storage by the seller or consumer could yield antimony concentrations that approach or exceed the 6 ppb MCL.

3.4. Effect of outdoor sunlight on antimony leaching

Preliminary experiments suggested that UV irradiation may increase antimony leaching from PET plastic bottles, but the experiments were confounded by simultaneous irradiation and temperature differences relative to the control. Therefore, natural sunlight experiments were conducted in which the control was held at the same air temperature, but wrapped in aluminum foil to reduce the influence of sunlight irradiation. The average water temperature was 35 °C at morning and afternoon sample collection times over the 7-day exposure test. Over the 7 days, antimony concentrations increased from 0.37 to only 0.61 ppb for samples exposed to sunlight, and from 0.37 to 0.56 ppb for controls (Fig. 5). As such, after 7 days the antimony concentration in the sunlight-exposed sample was only 5–10% higher than the control sample, which is not statistically significant.
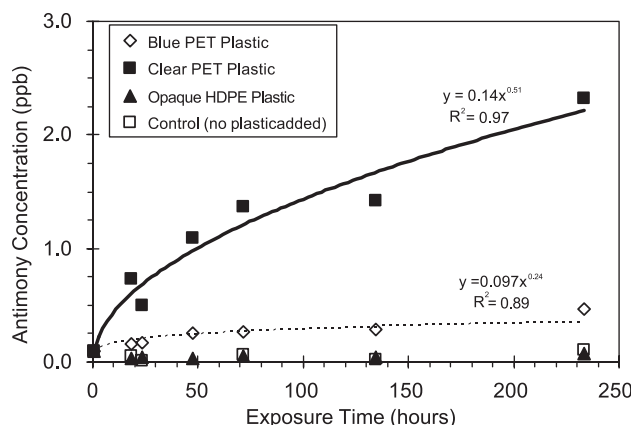
These results suggest that sunlight irradiation has only a small effect on antimony leaching. Fig. 5 includes a trend line predicted using Eq. (1) for the average observed water temperature of 35 °C, that tracks the actual antimony concentration reasonably well. Both control and sunlight-exposed samples experienced diurnal temperature variations, but the sunlight-exposed bottle likely warmed slightly more than the aluminum foil wrapped control sample. As such, temperature, rather than sunlight exposure, appears to control antimony leaching from PET water bottles.

3.5. Effect of different plastic materials on antimony leaching

Microwave digestion determined that Brand 9 plastic (five replicates) contained 213 ± 35 mgSb/kg plastic (equivalent to $4.3 \pm 0.7\,\mu\text{gSb/cm}^2$). Leaching of all the antimony in a plastic water bottle with an internal surface area of $174\,\text{cm}^2$ into 0.5 L of water could result in an antimony concentration of 376 ppb. This is improbable, of course, and indicates that a very small percentage of the antimony in the plastic bottles actually leaches into the water. Of the 23 other metals analyzed by ICP-MS simultaneously with antimony, noticeable levels of Co (27 mg/kg), Cr (0.11 mg/kg), Fe (1.3 mg/kg), Mn (0.34 mg/kg), and P (19 mg/kg) were also released after digestion. The type of plastic used for bottled water affects the potential for antimony release into the water, however, and the potential for leaching of other metals appears to be lower than that for antimony.

The observations above implicate antimony in plastic bottles as a source of the metal in bottled waters. To evaluate the leaching potential of two different PET bottles (clear and blue-colored) plus one opaque HDPE bottle, equal dimensions of plastic were submerged in nanopure water in 1 L glass bottles. These samples were incubated at 80 °C, and over a

Fig. 6 – Comparison of antimony leaching based on type of plastic (80 °C; 88 cm^2 plastic samples incubated in 1 L nanopure water in glass bottles).

germanium rather than antimony-based catalysts (Shotyk and Rachler, 2007; Thiele, 2004)). Future tests should determine if relationships exist between the quality of water in the bottles (e.g., conductivity, major ion composition) and antimony leaching rates. Antimony leaching should be of concern to private manufacturers, wholesalers, and retail stores, as well as to public water utilities that often bottle water for public events, disasters, or even resale. Because antimony causes both acute and chronic health issues, conditions, such as types of plastic or storage temperature, that promote deterioration of water quality (i.e., increasing antimony concentrations over time) should be avoided.

Acknowledgments

10-day period the samples were withdrawn for antimony analysis (Fig. 6). Antimony concentrations for the opaque HDPE bottle were not statistically different from the control (no plastic added). Both PET plastics released antimony over time, however. The clear plastic PET released four times more antimony than the blue-colored PET plastic. The ratio of water-exposed surface area of clear PET (176 cm^2) to water (1 L) in this experiment is 0.176 cm^2/cm^3. In comparison, the samples used to obtain the results in Fig. 3 have a surface area to water ratio of ~0.78 cm^2/cm^3. The amount of antimony in these 1 L tests (Fig. 6) is approximately 2.2 ppb, or 16% of the maximum antimony concentration (13.9 ppb) in Fig. 3. This value of 16% is very close to the ratio of surface area to volume (22%) between the two tests. It follows that antimony release is probably proportional to contact area to liquid volume ratio.

4. Conclusions

Antimony can be released (i.e., leached) from the PET plastic used to make commercial and municipal water bottles. While the rate of leaching is low below storage temperatures of 60 °C, above this temperature antimony release can occur rapidly. From personal experience, in the southwestern US the temperatures inside automobiles and garages, where bottled water is often stored, can exceed 60 °C. Bottled water manufacturers should consider the shipping/storage conditions of the bottled waters, and possibly select plastics that do not leach antimony (e.g., PET made with titanium or

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