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Co-leaching of brominated compounds and antimony from bottled water

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ABSTRACT

A fast-growing bottled water market is occasionally challenged by reports calling for contaminant leaching from water-contact materials (plastics). Our focus was on leaching of antimony (Sb) and brominated compounds expressed by total soluble bromine (Br) measurements, including those of polybrominated diphenyl ethers (PBDE). Studies are lacking on concomitant leaching of two or more inorganic plastic constituents from the same bottle. A market-representative basket survey of bottled water was initiated in Boston, USA supermarkets. Bottled water classes sampled were: i) non-carbonated (NCR), ii) carbonated (CR), and iii) non-carbonated and enriched (NCRE). Plastic bottle materials sampled were: polyethylene terephthalate (PET), high-density polyethylene (HDPE), polystyrene (PS), and polycarbonate (PC). Storage conditions for the 31 bottled water samples were: 23 °C temperature, no-shaking and 12 h/12 h light/dark for 60 days of equilibration. Average Br and Sb concentrations after 60-days of storage followed the order of NCR < CR = NCRE, and NCR < CR < NCRE, respectively, suggesting that the presence of dissolved carbon dioxide in CR samples coupled to additions of flavors and color to NCRE could explain the elevated leaching of Br and Sb. Combining all bottled water classes and plastic material types, a highly significant ($p < 0.001$) correlation was observed between log-transformed soluble Br and Sb concentrations, suggesting similar leaching behavior. Among samples with the highest soluble Br concentrations, BDE-209 congener was qualitatively confirmed in three out of four bottled water samples. The PC, HDPE, and PS samples exhibited significantly ($p < 0.05$) lower Sb and Br leaching than PET. Upon quantitative validation of PBDE leaching from certain plastic bottles into water, a revisit to existing PBDE exposure assessment reports will be deemed necessary.

1. Introduction

Bottles for packaging drinking-water represent one of the most popular uses of plastic and polymer additives (Rodwan, 2010). Current estimates show that United States is the leading consumer of bottled water at about 33,100 million L contributing to 15.8% of global consumption, while Mexico tops the global per-capita annual bottled water consumption (234 L capita^{-1}) (Rodwan, 2010). It is noteworthy that 12 out of the top 20 countries leading the global per capita consumption list of bottled water come from the EU (Rodwan, 2010). Public concerns related to widespread consumption of bottled water stem from indictments on inadequate application of sustainability metrics and conformity to public health standards (Sax, 2010; Yang et al., 2011). It was only recently that the scientific community began to deal with the presence of toxic contaminants and bacteria in the finished water whether initially present in the raw water or as a result of leaching mechanisms from plastic walls. Water contact materials (primarily plastic) have been recently charged with the release of endocrine disrupting compounds into finished water, such as, bisphenol A (BPA) and other alkyl phenols like 4-nonylphenol, adipates, phthalates, and antimony (Sb) (Amiridou and Voutsa, 2011; Carwile et al., 2009; Muncke, 2009; Yang et al., 2011). Final rules of regulation exist for a small portion of the aforementioned contaminants in bottled water sold in the USA (FDA, 2010, 21 CFR Part 165.110), such as Sb, a catalyst used to speed up synthesis of polyethylene terephthalate (PET) (Pang et al., 2006) and di(2-ethylhexyl)adipate (DEHA) used as a plasticizer. The most stringent maximum contaminant level for Sb in drinking-water is observed in Japan (2 μg L^{-1}) (Shotyk and Krachler, 2007), while the MCL for Sb in EU, USA, and Canada remains at 5 μg L^{-1}, 6 μg L^{-1}, and 6 μg L^{-1}, respectively (EU 98/83; Health Canada, 1998; U.S. EPA,2002). Occurrence of Sb in bottled water has been reported in Japan (Suzuki et al., 2000), Greece (Hansen and Pergantis, 2006), Canada and Europe (Shotyk et al., 2006), USA (Westerhoff et al., 2008), Turkey (Guler and Alpaslan, 2009), Hungary (Keresztes et al., 2009),

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a group of 28 countries (Krachler and Shotyk, 2009), and a group of EU countries (Reimann et al., 2010). These studies related the nature of container material, such as PET or glass, to Sb levels; but did not consider differences among bottled water classes, such as carbonated versus non-carbonated, except for Keresztes et al. (2009). At ambient temperature, Sb concentrations in bottled water were well below the MCL, but bottled water exposure to various environmental stressors, such as, temperature, UV exposure, etc., promoted Sb leaching into finished water (Keresztes et al., 2009; Shotyk et al., 2006; Shotyk and Krachler, 2007) and at harsh environments (>60 °C temperature) leached Sb concentrations exceeded the MCL value (6 μg L^{-1}) (Westerhoff et al., 2008).

While much attention has been drawn upon single contaminant leaching into plastic bottled water, the majority of relevant studies fail to address concomitant leaching of two or more contaminants within the same bottle; the study of DEHA and DEHP leaching from PET bottles was an exception (Schmid et al., 2008). Our focus was on Sb and brominated compounds, as expressed by total soluble Br measurements, including those for polybrominated diphenyl ethers (PBDE). Organo-brominated compounds, in particular decabromodiphenyl oxide (BDE-209), are used as flame retardants in the preparation of both PET and PC plastics (Albemarle, 2011), while tetrabromobisphenol A (TBBPA) is also used in epoxy and PC resins (Talsness et al., 2009). However, no study has ever attempted to monitor PBDE concentrations in bottled water (Talsness et al., 2009; USEPA, 2010; Covaci et al., 2011). Analytical reports on the presence of certain PBDE congeners in plastics, such as BDE-153, 183, 196, 197, 203, 206, 207, and 209, were reported in high density polyethylene (HDPE), polystyrene (PS), polypropylene (PS) (Mingwu et al., 2010), and BDE-47 in PET by CDS Analytical (2010), but no data exist for organo-brominated compounds, i.e., PBDE leaching into bottled water. Inorganic brominated compounds may also occur in drinking water from water treatment processes, such as, bromate — the toxic form (WHO, 2009), and brominated acetic acids or brominated di/tri halomethanes which are common disinfection byproducts (WHO, 2004). Guler and Alpaslan (2009) reported high levels of total bromine (mean 20 μg L^{-1} which range from 0.6 to 108 μg L^{-1}) in 70 bottled water brands from Turkey.

However, bromate and brominated haloacetic acids primarily occur in raw water prior to bottling. Leaching of brominated compounds from plastic containers, such as PBDE in conjunction with monitoring of other inorganic leachants, such as, Sb has never been simultaneously studied before. This study was based upon a representative basket survey sampling of bottled water in randomly selected Boston, MA, USA supermarkets. Different bottled water classes were sampled ranging from: i) non-carbonated (NCR), ii) carbonated (CR), and iii) non-carbonated and enriched (NCRE). The objectives of this study were: i) determine the effects of plastic material (PET, HDPE, PC, and PS), bottled water classes (non-carbonated, carbonated, and non-carbonated and enriched), and storage time on the simultaneous co-leaching patterns of antimony and brominated compounds from bottled water, and ii) qualitatively characterize the type of brominated compounds leaching from plastic bottled water.

2. Materials and methods

2.1. Market survey of bottled water

Plastic-based bottled water from various brands, classes (non-carbonated-NCR, carbonated-CR, and non-carbonated and enriched-NCRE), container volumes, and plastic materials, covering the majority of market share were purchased from major supermarkets in the wide Boston area, MA, USA, covering >90% of all available bottled water brands in the market (Table 1). The selection of bottled water samples for this basket survey study was based upon the major bottled water classes that are widely sold in the USA market. These bottled water classes were: 1) non-carbonated (NCR), 2) carbonated (CR), and 3) non-carbonated and enriched (NCRE). The third bottled water class, i.e., NCRE represents bottled water that has been typically enriched with various flavors, including, vitamins, nutrients, minerals, and/or electrolytes. In addition to the elevated dissolved carbon dioxide content, the CR bottled water class differed from NCRE in the addition of lime and lemon to almost all of the CR bottled waters. NCR class represents the conventional spring, mineral bottled water brands. Variable plastic bottle volumes were sampled ranging from 0.25 L to 18.9 L. Nation-wide, local, and imported brands of bottled water were included in this representative basket survey study. A suite of different plastic materials identified by the global resin identification number shown in the bottom or side of each bottle was collected, including polyethylene terephthalate (PET), high-density polyethylene (HDPE), polystyrene (PS), and polycarbonate (PC). Collectively, a total of 31 bottled water independent samples were included in this study (11 NCR, 11 CR, and 9 NCRE samples).

2.2. Screening storage study

A single day was used to purchase all bottled water samples and it was denoted as time-zero. All samples were placed in a laboratory bench with a 12 h/12 h light/dark set up and room air temperature set at 23 °C. Leaching of Sb and Br from plastic bottles was monitored as a function of storage time at 1, 7, 30 and 60-days of equilibration. Care was taken to avoid any sort of contamination or damage during storage. Bottled water subsampling was carefully handled to avoid external contamination within a Class 100 particle-, and metal-free clean room within the Aquatic Biogeochemistry laboratory at Harvard

Table 1
General characteristics of the various bottled water samples collected from Boston, MA, USA.

Non-carbonated (NCR)	Carbonated (CR)	Non-carbonated and enriched (NCRE)
[Brand number, Material type[a], Volume, Initial pH (Mean ± SD)]		
1. Brand #1, HDPE, 9.46 L, 6.77 ± 0.08	1. Brand #1, PET, 1.00 L, 3.65 ± 0.08 (no flavor)	1. Brand #2, PET, 1.00 L, 5.99 ± 0.05
2. Brand #1, HDPE, 3.79 L, 6.82 ± 0.04	2. Brand #1, PET, 1.00 L, 3.85 ± 0.02 (flavor)	2. Brand #9, PET, 0.59 L, 6.22 ± 0.01
3. Brand #1, PET, 0.70 L, 6.70 ± 0.03	3. Brand #2, PET, 2.00 L, 3.59 ± 0.05 (flavor 1)	3. Brand #10, PET, 0.59 L, 5.69 ± 0.16
4. Brand #1, PC, 18.9 L, 6.70 ± 0.07	4. Brand #2, PET, 1.00 L, 3.03 ± 0.11 (flavor 2)	4. Brand #11, PET, 0.53 L, 6.00 ± 0.07
5. Brand #1, PC, 18.9 L, 6.73 ± 0.01	5. Brand #2, PET, 1.00 L, 3.60 ± 0.10 (flavor 3)	5. Brand #12, PET, 0.47 L, 6.14 ± 0.04
6. Brand #2, HDPE, 9.46 L, 6.35 ± 0.08	6. Brand #2, PET, 1.00 L, 3.53 ± 0.08 (flavor 4)	6. Brand #13, PET, 0.71 L, 6.38 ± 0.04
7. Brand #2, HDPE, 3.00 L, 6.21 ± 0.03	7. Brand #2, PET, 1.00 L, 3.64 ± 0.04 (flavor 5)	7. Brand #15, PET, 0.95 L, 6.15 ± 0.10
8. Brand #3, PET, 0.50 L, 6.79 ± 0.02	8. Brand #7, PET, 2.00 L, 3.86 ± 0.03 (no flavor)	8. Brand #16, PET, 0.59 L, 5.52 ± 0.13
9. Brand #4, PET, 1.50 L, 6.92 ± 0.01	9. Brand #8, PET, 2.00 L, 4.06 ± 0.11 (no flavor)	9. Brand #16, PET, 0.59 L, 6.00 ± 0.13
10. Brand #5, PC, 0.25 L, 6.89 ± 0.05	10. Brand #14, PET, 1.00 L, 3.37 ± 0.03 (flavor 1)	
11. Brand #6, PS, 0.25 L, 6.86 ± 0.04	11. Brand #14, PET, 1.00 L, 3.72 ± 0.01 (flavor 2)	

[a] Polyethylene terephthalate (PET), high-density polyethylene (HDPE), polystyrene (PS), and polycarbonate (PC).