



Effects of storage temperature and duration on release of antimony and bisphenol A from polyethylene terephthalate drinking water bottles of China



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ABSTRACT

We investigated effects of storage temperature and duration on release of antimony (Sb) and bisphenol A (BPA) from 16 brands of polyethylene terephthalate (PET) drinking water bottles in China. After 1-week storage, Sb release increased from 1.88–8.32 ng/L at 4 °C, to 2.10–18.4 ng/L at 25 °C and to 20.3–2604 ng/L at 70 °C. The corresponding releases for BPA were less at 0.26–18.7, 0.62–22.6, and 2.89–38.9 ng/L. Both Sb and BPA release increased with storage duration up to 4-week, but their releasing rates decreased with storage time, indicating that Sb and BPA release from PET bottles may become stable under long term storage. Human health risk was evaluated based on the worst case, i.e., storage at 70 °C for 4-week. Chronic daily intake (CDI) caused by BPA release was below USEPA regulation, Sb release in one brand exceeded USEPA regulated CDI (400 ng/kg bw/d) with values of 409 and 1430 ng/kg bw/d for adult and children.

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1. Introduction

Bottled water has become popular as it is perceived as source of clean water. China became the largest market in consumption of bottled water at 40 million tons in 2011 (Rani et al., 2012). Due to its low diffusivity and chemical inertness (Franz and Welle, 2002), polyethylene terephthalate (PET) is the most popular material for food or beverage packaging, accounting for >99% of all beverage bottles (ILSI-Europe, 2000). However, recent studies demonstrated that PET bottles can release harmful chemicals such as antimony (Sb) and bisphenol A (BPA) into water (Santhi et al., 2012; Westerhoff et al., 2008). Therefore, its safety becomes a controversial issue.

Antimony trioxide (Sb₂O₃) is one of the most important catalysts widely used for solid-phase poly-condensation of PET. It offers high catalytic activity, does not induce undesirable colors, and has a low tendency to catalyze side reactions (Duh, 2002). PET bottles typically contain 190–300 mg/kg Sb (Duh, 2002) with the highest Sb concentration being 353 mg/kg (Hureiki and Mouneimne, 2012).

Bottled waters become contaminated during storage due to Sb release from PET plastic (Shotyk and Krachler, 2007), which primarily attributes to PET degradation (Takahashi et al., 2008). Unlike Sb, BPA should not be present in PET bottles since BPA is not involved in PET manufacturing (Bach et al., 2012). However, detectable BPA in PET bottled water has been reported (Li et al., 2010; Toyo'oka and Oshige, 2000).

Sb is classified as a possible carcinogen to humans by the International Agency for Research on Cancer. Long-term exposure to elevated Sb can lead to increased blood cholesterol and decreased blood sugar (Westerhoff et al., 2008). BPA can cause immune disorders and affect nervous system (Vandenberg et al., 2007). Long term exposure to low levels (0.05 mg/kg bw) of BPA results in negative physiological consequences on human (Erler and Novak, 2010). Due to its estrogenic potency, BPA has been banned in children's products since 2008 (Erler and Novak, 2010). When considering the fact that one of the primary route for human exposure to contaminants is through drinking water, releasing of Sb and BPA from PET plastic is an important topic to investigate.

Factors affecting Sb release from PET bottles into water have been studied, including drink composition, property of PET bottles and storage conditions. For example, pH of bottled water at 6–8 poses no effect on Sb release (Hureiki and Mouneimne, 2012;

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Westerhoff et al., 2008). However, at pH of 4, Sb concentration increased from 0.46 to 4.61 $\mu\text{g/L}$ relative to controls (Cheng et al., 2010). Among all factors, storage temperature and duration are the most important (Greifenstein et al., 2013; Keresztes et al., 2009). Although Sb release from PET bottles stored at extreme conditions (i.e., high temperature) has been verified (Reimann et al., 2012; Rungchang et al., 2013), its release depends on the brands of PET bottles. For example, Reimann et al. (2012) found that, after 1 week storage, Sb concentration in bottled water reaches 5 $\mu\text{g/L}$ at 60 °C and 18 $\mu\text{g/L}$ at 80 °C. In contrast, Rungchang et al. (2013) reported that Sb concentration is <5 $\mu\text{g/L}$ when stored at 70 °C even for 600 d.

Compared to Sb, BPA release from PET bottles is rarely studied, and the source of BPA in bottled water is still unclear at present. For example, the detected BPA can be either from water resources before bottling (Wang et al., 2012, 2011) or from recycling of PET plastic (Franz and Welle, 2002). Inconsistent conclusions about BPA release have been reported (Casajuana and Lacorte, 2003; Toyo'oka and Oshige, 2000). Casajuana and Lacorte (2003) reported that BPA concentration in 3 out of 5 tested PET bottled water from Spain is elevated to 3–8 ng/L after 10 weeks storage at 30 °C (Casajuana and Lacorte, 2003). Whereas BPA concentration in PET bottled water from Japan remains the same after storing at 50 °C for 8 h (Toyo'oka and Oshige, 2000). The release of BPA into bottled water in China has rarely been reported. Li et al. (2010) measured BPA concentrations in 21 brands of bottled water from China with values ranging from 17.6 to 324 ng/L (detectable rate = 81%), but the source of BPA is not verified. People tend to store bottled water in cars for weeks or months. According to Manning and Ewing (2009), the temperature in car can reach to 75 °C at ambient temperature of 33 °C in summer. It can be expected that storage at high temperature may enhance contaminant release into water from PET bottles.

The objective of this study was to investigate the effects of storage temperature and duration on release of both inorganic (Sb) and organic (BPA) contaminants from PET water bottles. Sixteen brands of commercially available PET-bottled water were purchased from markets in China. Milli-Q water was used as aqueous stimulant to ensure that the contaminants were released from PET bottles not from drinking water before bottling.

2. Material and methods

2.1. Chemicals and reagents

Sixteen commercial brands of PET bottled water were purchased in supermarkets of Nanjing, China. The detailed descriptions for the bottled water are listed in Supplementary information (SI) as Table S1. Standard of BPA (99%) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Stock solution of BPA was prepared at 1000 mg/L in methanol and stored in sealed amber glass bottles at –20 °C. All solvents and chemicals were of HPLC or analytical grade. Glassware used was heated at 450 °C for at least 4 h to prevent cross contamination.

2.2. Sb and BPA concentrations in PET bottles

The PET bottles were digested to determine total Sb in PET plastic according to Hureiki and Mouneimne (2012) and Westerhoff et al. (2008) with slight modification. Briefly, the PET bottles were cut into 3 × 3 mm² pieces using acid-cleaned scissors, and rinsed with Milli-Q water. After drying, 0.5 g of plastic samples were mixed with 8 mL HNO₃ and 2 mL H₂O₂, and digested on a Hotplate (LabTech, EG35B, China) for 4 h at 250 °C. Four replicates were digested for each brand of PET bottle. Sb in PET bottle was completely dissolved since only white powder residue remained in the digested solution. The digested solutions were diluted with Milli-Q water, filtered through a 0.45 μm PES filter (ANPEL, China), and determined for Sb by inductively coupled plasma mass spectrometry (ICP-MS; PerkinElmer, NexION 300, USA).

For determinations of total BPA content in PET plastic bottles, 0.5 g of plastic samples were soaked in ethanol for 72 h, and subject to ultrasound-assisted extraction for 1 h (Kim et al., 1990). Samples of 2 mL were taken for analysis after filtration through a 0.45 μm nylon filter (ANPEL, China). Four replicates were used for each brand.

2.3. Release of Sb and BPA from PET bottles

Effect of storage temperature on Sb and BPA release from PET bottles was investigated at 4, 25 and 70 °C, simulating three storage conditions, i.e., storage in refrigerator, room temperature, and extreme high temperature. Water in all bottles were emptied, and then filled with Milli-Q water (pH = 6.0 ± 0.2). The bottles containing Milli-Q water were stored for 7 d at 4, 25 and 70 °C, respectively. After 7 d, Milli-Q water in the bottles was sampled to determine Sb and BPA.

Effect of storage duration was tested by storing bottles at 70 °C for 1, 2, and 4 week. Milli-Q water was emptied from the bottles after 1 week of storage, and analyzed for Sb and BPA concentrations. Fresh Milli-Q water was added again to those bottles and stored for another week. The released concentration of Sb and BPA after 2 week of storage was accumulative of two weeks. Similarly, fresh Milli-Q water was refilled and stored for another 2 weeks, and accumulative Sb and BPA (week 1, 2, and 4) were calculated as release levels after storage for 4 weeks. Four replicates were used for each treatment and bottles were stored without direct light exposure.

The concentration of Sb in water was determined by ICP-MS. For BPA measurement, aliquots of 500–600 mL sampled Milli-Q water were concentrated by solid phase extraction (SPE) using 200 mg C18 SPE cartridges (ANPEL, China). To eliminate possible background contamination and enhance the binding between BPA and sorbent, C18 cartridges were conditioned with 6 mL of methanol and 6 mL of Milli-Q water before sample loading. Water samples were then loaded using Visiprep™ large volume sampler (Sigma–Aldrich Co. SUPELCO, Bellefonte, PA) at a flow rate of 5–6 mL/min and afterward the cartridges were dried under vacuum for 0.5 h. The dried cartridges were eluted using 4 × 3 mL of methanol. The eluent was condensed to near dryness in a rotary evaporator (IKA®RV10, Germany), and then reconstituted with 2 mL of methanol. The final extract was filtered through a 0.45 μm nylon filter (ANPEL, China) into a 2 mL amber vial and kept at –20 °C before analysis on high performance liquid chromatography (HPLC; Waters, e2695, Ireland).

2.4. Chemical and data analysis

Sb was determined by ICP-MS, with indium as internal standard to correct instrumental drifts. BPA was measured by using HPLC equipped with Waters XBridge™ C18 column (5 μm , 4.6 × 250 mm). Fluorescence detector (Waters, 2475, Ireland) was set with excitation at 278 nm and emission at 315 nm. The mobile phase was methanol–water (70:30, v:v) with a flow rate of 1 mL/min.

A simplified equation was adopted to construct release kinetic curves for Sb and BPA (Figs. S1 and S2).

$$C = C_{\max} \times (1 - e^{-bt}) \quad (1)$$

where C is the released contaminant concentration at time of t , C_{\max} is the maximum concentration of released contaminant (ng/L), t is storage duration (week), and b is kinetic constant (week⁻¹). Values of C_{\max} and b can be estimated by fitting data to Equation (1) (Table S2). Therefore, releasing rate (ng/week) at a particular time was derived from Equation (1) through differentiation as:

$$C_{\max} \times b \times e^{-bt} \quad (2)$$

2.5. Quality assurance and quality control

During Sb measurement using ICP-MS, certified water reference material SLRS-5 (National Research Council Canada, Ottawa, Canada) was measured at regular intervals. Excellent agreement between measured Sb concentration (289 ± 5 ng/L, $n = 5$) and certified value of 300 ng/L was obtained. Meanwhile, to ensure reliability of the SPE method for BPA extraction, recovery efficiency was tested by spiking BPA (10, 100, and 200 ng/L) into 500 mL Milli-Q water, and 105 ± 3.12, 89 ± 6.18, and 92 ± 0.87% of BPA was recovered. SPE procedural blanks were carried out by using Milli-Q water. Detection limit for BPA analysis on HPLC was 230 ng/L, and for Sb analysis on ICP-MS was <0.10 ng/L.

3. Results and discussions

3.1. Total Sb and BPA in PET bottles

Total concentrations of Sb (by ICP-MS after HNO₃-digestion) and BPA (by HPLC after extraction of ethanol with ultrasonication) in PET bottles are listed in Table 1. The Sb concentrations ranged from 104 ± 8.81 to 166 ± 3.30 mg/kg with the median value of 113 ± 2.75 mg/kg (Table 1), which were lower than those in previous studies (Keresztes et al., 2009; Tukur et al., 2012). For example, Sb concentrations in PET bottles from Hungarian, Nigeria, and Britain were 210–290 (Keresztes et al., 2009), 178–287, and 195–242 mg/kg (Tukur et al., 2012), indicating variable quality of PET plastics in different countries. The total Sb released from PET

Table 1
Total antimony (Sb) and bisphenol A (BPA) in polyethylene terephthalate (PET) bottles based on four replicates.

Sample ID	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
[Sb] ^a (mg/kg)	113 ± 2.75	113 ± 12.5	104 ± 1.85	104 ± 8.81	121 ± 7.63	116 ± 5.19	113 ± 3.29	112 ± 5.14	130 ± 2.27	126 ± 7.46	108 ± 6.11	118 ± 25.1	127 ± 27.2	166 ± 3.30	125 ± 7.20	126 ± 4.84
[Sb] _{max} ^b (mg/L)	2.40 ± 0.06	3.34 ± 0.37	3.31 ± 0.06	2.30 ± 0.19	2.60 ± 0.16	5.67 ± 0.25	4.48 ± 0.13	4.64 ± 0.21	5.11 ± 0.09	5.00 ± 0.30	2.68 ± 0.15	4.87 ± 1.03	5.43 ± 1.16	4.01 ± 0.08	3.86 ± 0.22	4.85 ± 0.18
[BPA] ^c (mg/L)	48.8 ± 7.18	58.2 ± 8.78	53.1 ± 2.65	64.1 ± 5.82	49.7 ± 1.44	57.0 ± 2.68	37.7 ± 5.73	39.1 ± 3.76	51.3 ± 1.07	58.1 ± 10.3	40.5 ± 3.03	38.7 ± 4.67	42.3 ± 1.43	50.0 ± 2.76	43.1 ± 4.39	58.9 ± 11.1
[BPA] _{max} ^d (μg/kg)	1.03 ± 0.15	1.68 ± 0.30	1.73 ± 0.04	1.42 ± 0.13	1.04 ± 0.03	2.78 ± 0.13	1.46 ± 0.23	1.62 ± 0.16	2.01 ± 0.04	2.30 ± 0.41	0.96 ± 0.11	1.67 ± 0.13	1.80 ± 0.13	1.20 ± 0.07	1.33 ± 0.13	2.26 ± 0.43

^a [Sb] (mg/kg) means total Sb contents in PET bottles.
^b [Sb]_{max} (mg/L) means the maximum Sb concentrations in water if all Sb in PET were released into bottled water.
^c BPA (μg/kg) means total BPA contents in PET bottles.
^d [BPA]_{max} (μg/L) means the maximum BPA concentrations if all BPA in PET were released into bottled water.

bottle can be calculated by multiplying total Sb concentrations in PET bottle (mg/kg) with the mass of PET bottle (kg) and divided by the volume of drinking water (L) (Table S1). The calculated Sb concentrations in water ranged from 2.30 ± 0.19 to 5.67 ± 0.25 mg/L with median value of 4.01 ± 0.05 mg/L (Table 1), which is ~800 higher than the MCL of 5 μg/L of Sb in China (Ministry of Health, 2006).

For all 16 brands, total contents of BPA in PET bottles ranged from 37.7 ± 5.73 to 64.1 ± 5.82 μg/kg with median value of 50.0 ± 2.76 μg/kg. About 0.96 ± 0.11–2.78 ± 0.13 μg/L were expected in bottled water if all BPA were released into water (Table 1). Clearly, it is unlikely that all Sb or BPA in PET bottles will be released into water. Therefore, releasing tests under various storage conditions are necessary to better understand release behaviors of Sb and BPA from PET bottles.

3.2. Effect of storage temperature on Sb and BPA release from PET bottles

Effect of storage temperature on Sb and BPA release from PET bottles were investigated by storing bottles at 4, 25, and 70 °C for 7 d. Sb concentrations ranged from 1.88 ± 0.05 to 8.32 ± 0.70 ng/L with the median at 3.18 ± 0.54 ng/L at 4 °C. Temperature increase to 25 °C enhanced Sb release from PET bottle, which ranged from 2.10 ± 0.09 to 18.4 ± 3.82 ng/L with the median at 6.88 ± 2.50 ng/L (Fig. 1). When comparison was based on single brand, Sb release increased by 1.2–2.2 times if temperature increased to 25 °C, which is consistent with Reimann et al. (2012). For instance, for European PET bottles, 2.76–23.3 ng/L Sb was released after stored at 2 °C for 7 d, and 11.7–54.1 ng/L Sb was released at 22 °C (Reimann et al., 2012). However, much higher Sb concentration (8.90–2570 ng/L) was reported by Shotyk and Krachler (2007) based on 69 brands of PET bottles, which were stored at room temperature for 6 months. Higher Sb levels reported by Shotyk and Krachler (2007) can be attributed to longer storage time (six months) compared with the current study and Reimann et al. (2012) (1 week).

Even though higher median concentration (6.88 ± 2.50 ng/L) of Sb in the Milli-Q water from the PET bottled was measured at 25 °C than those at 4 °C (3.18 ± 0.54 ng/L), the enhancement by temperature was not conclusive. When subject to ANOVA analysis (Fig. 1), increase from 4 °C to 25 °C induced significant (p < 0.05) enhancement of Sb release in only 6 out of 16 brands. When stored at 70 °C, substantially higher Sb was observed across all PET bottles,

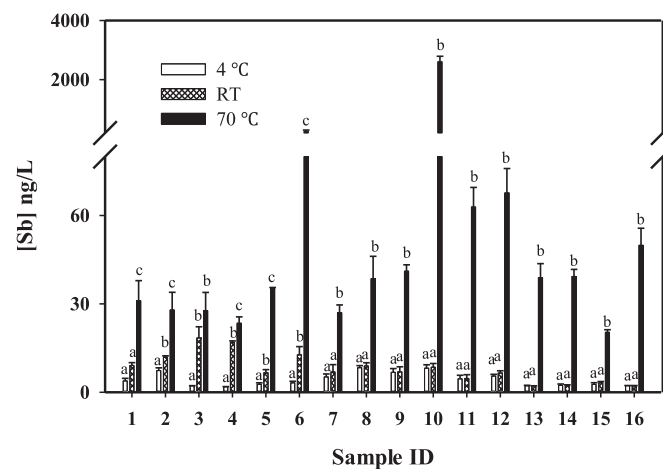


Fig. 1. Antimony (Sb) concentrations released into bottled Milli-Q water when stored at 4, 25, and 70 °C for 7 days. Different letters mean significant difference at p < 0.05 among three storage temperatures with four replicates.

ranging from 20.3 ± 0.90 to 2604 ± 185 ng/L with the median value of 38.5 ± 7.68 ng/L. When compared among the three temperatures, Sb concentrations increased by 4.4–319 times when temperature increased from 4 to 70 °C, and 1.2–4.7 times when temperature increased from 25 to 70 °C. Consistent with our study, a slight increase in Sb concentration in bottled water was reported when storage temperature increased from 2 °C to 22 °C (2.76 to 11.7 ng/L), and much higher Sb (1240 ng/L) was observed when temperature increased to 45 °C by Reimann et al. (2012).

When considering Sb release into water under 70 °C, the highest Sb at 2604 ng/L was observed for brand 10. When looking at the other two temperature (4 and 25 °C), Sb release for brand 10 was not significantly higher than other brands (Fig. 1). Since Sb release was mainly controlled by degradation of PET plastics (Takahashi et al., 2008), it was expected that PET of brand 10 was easier to be degraded under high temperature. The relatively low Sb release observed for other 15 brands (<500 ng/L) is comparable with the result of Greifenstein et al. (2013) who reported that Sb concentrations in most PET bottles were <1 µg/L after 70 d storage at 60 °C. Nevertheless, higher concentrations were reported in other studies. For example, Sb concentrations ranged from 3.5 to 10.9 µg/L after storing PET bottles at 60–80 °C for 1 week (Bach et al., 2013; Reimann et al., 2012; Westerhoff et al., 2008). The variable Sb release levels among different studies can be attributed to different quality of PET materials, which may vary depending on raw materials as well as technology used for PET production (Sax, 2010). Although Sb release levels varied with different studies, the fact that elevated temperatures (e.g., 70 °C) significantly increased Sb release into water was confirmed.

BPA release from PET bottles under different storage temperatures are shown in Fig. 2. ANOVA statistical analysis showed no significant differences in BPA concentrations at 4 and 25 °C except for 3 brands (Fig. 2). The BPA concentrations in all brands ranged from 0.26 ± 0.07 to 18.7 ± 2.58 ng/L (the median value was 7.27 ± 1.95 ng/L) and 0.62 ± 0.10 to 22.6 ± 4.97 ng/L (the median value was 10.44 ± 2.21 ng/L) for storage at 4 and 25 °C. When stored at 70 °C, BPA concentrations ranged from 2.89 to 38.9 ng/L with the median at 23.4 ± 3.51 ng/L. Unlike Sb, the increase of BPA release when temperature increased from 4 or 25 °C to 70 °C was not that significant, which was by 1.01–2.90 and 1.12–13.8 times.

BPA has been reported to be released from polycarbonate bottles and its release becomes significant with increase of temperature (Nam et al., 2010). Unlike polycarbonate bottles, there should no

BPA in PET bottles since BPA is not involved in manufacture of PET (Bach et al., 2012). However, a number of studies including the current study reported detectable BPA in PET bottled water: 17.6–324 ng/L (Li et al., 2010), 2–10 ng/L (Toyo'oka and Oshige, 2000), and 200–300 ng/L (Wu et al., 2010). According to previous studies, BPA detected in PET bottled water may come from various sources, including caps of PET bottles, background contamination, recycling of PET plastics, or water sources before bottling (Guart et al., 2011; Li et al., 2010; Sax, 2010). Since Milli-Q water was used in this study and no BPA was detected in Milli-Q water, BPA in the current study most likely came from PET bottles. As shown in Fig. 2, high temperature induced BPA release from PET bottles, even though the enhancement was not as remarkable as Sb. Santhi et al. (2012) reported that BPA levels in PET bottled water from Malaysia increased from 3.30 to 11.3 ng/L over 3 d storage at 50 °C, which is lower than the current result, probably due to lower storage temperature (50 °C vs. 70 °C).

3.3. Effect of storage duration on Sb and BPA release from PET bottles

To evaluate the effect of storage duration on Sb release, Sb concentrations released from PET bottles were measured after 1, 2, and 4 week storage at 70 °C. The Sb levels increased with storage duration with median values being 211, 316, and 448 ng/L (Table 2). Our data showed that Sb concentrations increased significantly ($p < 0.05$) with storage duration for 13 out of 16 brand PET bottles. After 4 weeks storage, brand 10 showed Sb release level at 5.44 ± 0.68 µg/L, which is comparable to the Sb MCL (5.0 µg/L) in drinking water of China (Ministry of Health, 2006).

Sb releasing rate was calculated (Equation 2) and decreased with storage duration for all brands (Table 2). It is expected that limited Sb was released from PET bottles over long storage duration as Sb release rate may gradually decreased to zero. This is consistent with Rungchang et al. (2013) who showed that Sb concentration increase with storage duration gradually decreases under different temperatures. However, it is notable that the release rates of Sb at 4 weeks were still significantly ($p < 0.05$) higher than zero (Table 2) in the current study. Therefore, longer storage duration should be employed to reach the maximum release concentration of Sb in PET bottled water.

BPA release from PET bottle increases with temperature, however, the effect of storage duration on BPA release is unknown. We

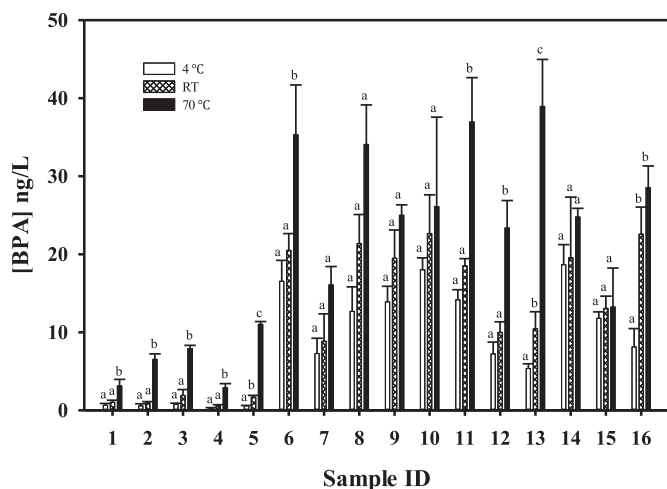


Fig. 2. Bisphenol A (BPA) concentrations released in bottled Milli-Q water when stored at 4, 25, and 70 °C for 7 days. Different letters mean significant difference at $p < 0.05$ among three storage temperatures with four replicates.

Table 2

Antimony (Sb) concentrations and release rates after storing at 70 °C for different durations based on four replicates.

Sample ID	Sb concentrations (ng/L)			Sb releasing rates (ng/week)		
	1 week	2 weeks	4 weeks	1 week	2 weeks	4 weeks
1	31.0 ± 6.84	60.5 ± 10.1	94.0 ± 11.1	29.1	22.7	13.8
2	27.9 ± 6.00	56.3 ± 12.2	84.6 ± 11.6	26.6	20.3	11.8
3	27.6 ± 6.22	55.6 ± 12.3	98.2 ± 20.2	27.3	24.4	19.6
4	23.4 ± 2.17	47.4 ± 4.35	71.0 ± 4.78	22.4	17.0	9.86
5	35.4 ± 0.12	72.0 ± 0.16	117 ± 24.7	34.7	28.7	19.7
6	244 ± 55.1	297 ± 49.9	383 ± 51.8	140	56.7	9.29
7	27.0 ± 2.68	43.9 ± 4.75	64.2 ± 5.89	21.6	14.4	6.46
8	38.5 ± 7.68	90.3 ± 16.4	116 ± 12.0	39.5	27.1	12.7
9	41.1 ± 2.13	67.2 ± 8.95	88.8 ± 11.3	31.7	18.5	6.33
10	2604 ± 185	3829 ± 375	5436 ± 678	1899	1141	412
11	62.9 ± 6.63	85.7 ± 11.3	117 ± 7.77	42.2	22.2	6.19
12	67.6 ± 8.32	102 ± 7.82	140 ± 18.3	49.6	28.9	9.79
13	38.8 ± 4.78	62.7 ± 4.99	102 ± 13.0	31.8	24.0	13.6
14	39.3 ± 2.39	65.8 ± 5.88	97.6 ± 5.91	32.3	22.3	10.7
15	20.3 ± 0.90	48.5 ± 19.0	65.4 ± 20.1	21.5	15.5	8.10
16	49.8 ± 5.80	75.4 ± 8.19	96.0 ± 7.85	35.2	18.3	4.94

studied BPA release by storing PET bottles at 70 °C for 1, 2, and 4 weeks (Table 3). BPA concentrations increased with storage duration. After 1 week storage, BPA concentrations ranged from 2.89 ± 0.52 to 38.9 ± 6.03 ng/L (median concentration was 23.4 ± 3.51 ng/L), and increased to 7.23 ± 3.77 – 78.2 ± 11.0 ng/L (44.5 ± 2.23 ng/L) when storage duration extended to 2 weeks. The Sb concentration increased to 14.4 ± 4.93 – 119 ± 9.71 ng/L (59.4 ± 7.10 ng/L) when storage duration was prolonged to 4 weeks. Casajuana and Lacorte (2003) investigated the effect of storage duration on BPA release from PET bottles in Spain, and BPA concentrations were 3, 4, and 8 ng/L after 10 weeks storage at 30 °C for three brands, which was lower than the current study, probably due to lower storage temperature (30 °C vs. 70 °C). The maximum BPA concentrations measured in the current study was 119 ± 9.71 ng/L, which is well below the MCL of BPA at 10 µg/L according to drinking water regulation in China (Ministry of Health, 2006). Therefore, BPA released from PET bottles after storage at 70 °C for 4 weeks may not pose notable negative effect on human health.

Similar to Sb, BPA releasing rates (Table 3) also decreased with storage duration for 14 out of 16 brands of PET bottles, suggesting that BPA levels may become stable over long storage duration. However, BPA release rate in two brands (brands 1, and 4) showed no notable change with storage duration, indicating that BPA concentrations in these two PET bottled waters increased linearly during 4-week storage. Longer storage duration for these two bottles may be interesting, since either high BPA release is expected due to the constant release rate or constant concentration will be achieved like the other 14 brands over long storage duration. Similarly, BPA levels in water released from polycarbonate baby bottles became constant after several cycles of heating in water bath (Coensel et al., 2009). As a result, the human health risk caused by BPA release needs to be assessed based on prolonged storage duration (e.g., shelf life), even though no notable risk was expected after 4 week storage in the current study.

Besides storage duration and temperature, contaminant release from PET bottles may also be influenced by other factors, such as color and the ratio of contact area to bottle volume, sunlight, and contaminant speciation. Inconsistent results have been reported in previous studies. For example, Sb release is negatively correlated with the ratio of contact area to water volume (Hureiki and

Mouneimne, 2012), which is also confirmed by Tukur et al. (2012) who showed that Sb release decreased from about 5.2 to 2.3 µg/L when the ratio decreased from 0.29 to 0.45 cm⁻¹. Sunlight causes no significant difference on Sb release, and Sb in sunlight-exposed water was only 5–10% higher than that in control (Westerhoff et al., 2008). They also detected 4 times more Sb release from clear PET bottles than that from blue-colored ones, while Reimann et al. (2012) obtained the opposite result. In the current study, correlation analysis was conducted between Sb/BPA release rates (Tables 2 and 3) and PET bottle properties (thickness, color, and weight, Table S1). No significant correlation was established between Sb release rates and PET bottle properties. For BPA, there was a significant positive correlation ($p < 0.02$) between PET bottle thickness and releasing rates at 1 and 2 weeks, but not for 4 weeks (Fig. 3). Similar correlation was also found for PET bottle mass (Fig. 4). However, the mechanism regarding how the thickness and mass of PET bottle impacts the release rates of Sb or BPA was unclear, which deserve much more attention in the future study.

3.4. Environmental implications

In order to estimate the risk caused by long time exposure to low levels of Sb and BPA, chronic daily intake (CDI) was calculated according to Kavcar et al. (2009) (Table 4):

$$CDI = \frac{C \times DI}{BW} \quad (3)$$

where C is the contaminant level in drinking water (ng/L), DI is the average daily intake of drinking water (L/d), and BW is body weight (kg). For an adult, the average BW and DI are 70 kg and 2 L water per day (10 kg and 1 L for children) (USEPA, 2012). A reference dose (RfD) means the daily oral exposure to human population is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA, 2012). The RfD of Sb is recommended by USEPA as 400 ng/kg/d (USEPA, 2012). Since about 38% of the total Sb intake by human comes from drinking water (Keresztes et al., 2009), the total CDIs of Sb by human was calculated by dividing CDI from Equation (3) by 38% (i.e., total CDI = CDI/38%).

The worst case, i.e., storage for 4 weeks at 70 °C, was used for total CDI calculation. As shown in Table 4, the total CDI of Sb for adult (409 ± 50.9 ng/kg/d) by human through drinking Sb contaminated water of brand 10 was close to USEPA RfD of 400 ng/kg/d (USEPA, 2012), which may cause health risk, especially for children (1430 ± 178 ng/kg/d). Sb released from the other 15 brands of PET bottles may not cause health risk since their total CDIs are <110 ng/kg/d. However, this result needs to be interpreted with caution. Sb release has been reported to increase with the concentration of calcium (Ca) in water though no mechanism was provided (Hureiki and Mouneimne, 2012; Westerhoff et al., 2008). For example, positive correlation was observed between Ca concentrations (21–65.5 mg/L) and Sb release for 8 brands PET bottles in Lebanon with the lowest Sb release being associated with the lowest Ca concentration (Hureiki and Mouneimne, 2012). Calcium levels in the current study are nearly zero since Milli Q water was used as aqueous stimulant. However, some bottled waters, especially mineral water, may contain elevated Ca. Therefore, the health risk caused by Sb release from PET bottles in this study may be underestimated to some extents. Furthermore, speciation of Sb should be considered due to the fact that Sb(III) is more toxic than Sb(V) (Stemmer, 1976). Studies about Sb speciation in PET bottles showed large variance among different bottles, i.e., only Sb(III) is detected in some bottles whereas Sb(III) oxidation is observed as up to 50% Sb(V) is detected in some samples (Martin et al., 2010; Takahashi et al., 2008). In the current study, Sb speciation was

Table 3

Bisphenol A (BPA) concentrations and releasing rates after storage at 70 °C for different durations based on four replicates.

Sample ID	BPA concentrations (ng/L)			BPA leaching rate (ng/week)		
	1 week	2 weeks	4 weeks	1 week	2 weeks	4 weeks
1	3.12 ± 0.83	7.23 ± 3.77	14.4 ± 4.93	3.70	3.70	3.69
2	6.52 ± 0.72	9.07 ± 0.58	19.0 ± 2.82	5.04	4.69	4.05
3	7.90 ± 0.43	11.3 ± 0.04	23.1 ± 0.99	6.22	5.70	4.78
4	2.89 ± 0.52	7.87 ± 1.37	14.8 ± 2.54	3.68	3.68	3.67
5	11.0 ± 0.37	19.4 ± 1.44	35.2 ± 3.41	9.86	8.68	6.72
6	35.3 ± 6.40	66.0 ± 9.48	119 ± 9.71	33.0	29.4	23.4
7	16.1 ± 2.36	39.6 ± 3.49	59.4 ± 7.09	18.0	14.6	9.65
8	34.1 ± 5.08	74.6 ± 6.26	97.6 ± 8.84	33.2	22.5	10.3
9	25.0 ± 1.33	56.8 ± 6.88	71.2 ± 7.86	24.8	16.2	6.93
10	26.1 ± 11.5	55.0 ± 8.23	72.4 ± 9.39	24.7	16.6	7.43
11	37.0 ± 5.68	69.7 ± 14.8	89.1 ± 15.2	31.6	19.3	7.24
12	23.4 ± 3.51	76.4 ± 16.4	90.4 ± 24.2	30.9	21.5	10.5
13	38.9 ± 6.03	78.2 ± 11.0	90.2 ± 11.4	33.4	18.6	5.74
14	24.8 ± 1.11	61.1 ± 11.8	77.0 ± 14.6	26.3	17.9	8.28
15	13.2 ± 4.99	44.5 ± 2.23	58.9 ± 12.8	18.6	14.5	8.86
16	28.5 ± 2.79	— ^a	50.0 ± 3.77	18.7	8.48	1.74

^a limited samples.

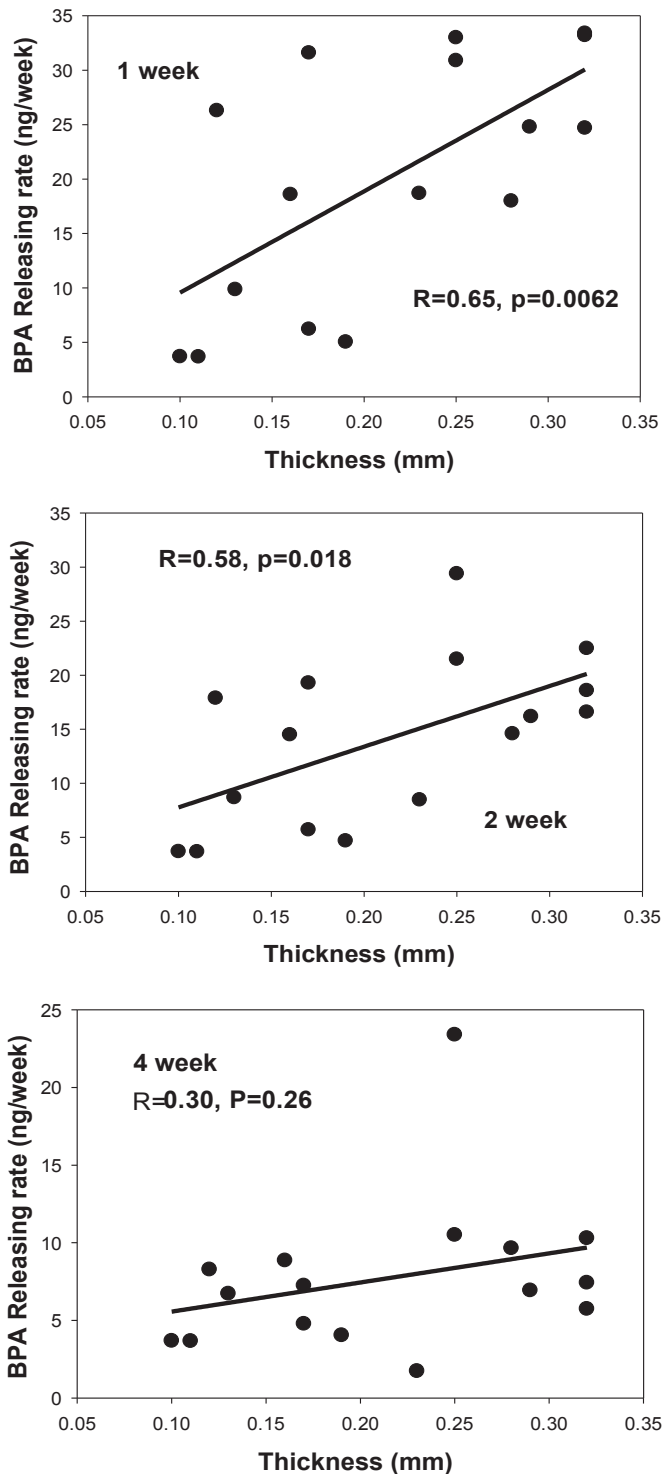


Fig. 3. Correlation between PET bottle thickness and release rates of bisphenol A after 1, 2, and 4 weeks.

investigated for brand 10 (under 70 °C for 4 weeks), and only Sb(V) was observed (Fig. S3).

As for BPA, the highest total CDIs in the current study were 8.94 ± 0.73 and 31.3 ± 5.55 ng/kg/d (Table 4) for adult and child, respectively, which are well below the RfD of 5000 ng/kg/d recommended by USEPA and European Food Safety Authority (Krishnan et al., 2010). However, we need to bear in mind that health risk assessment with a single compound (i.e., BPA) may not

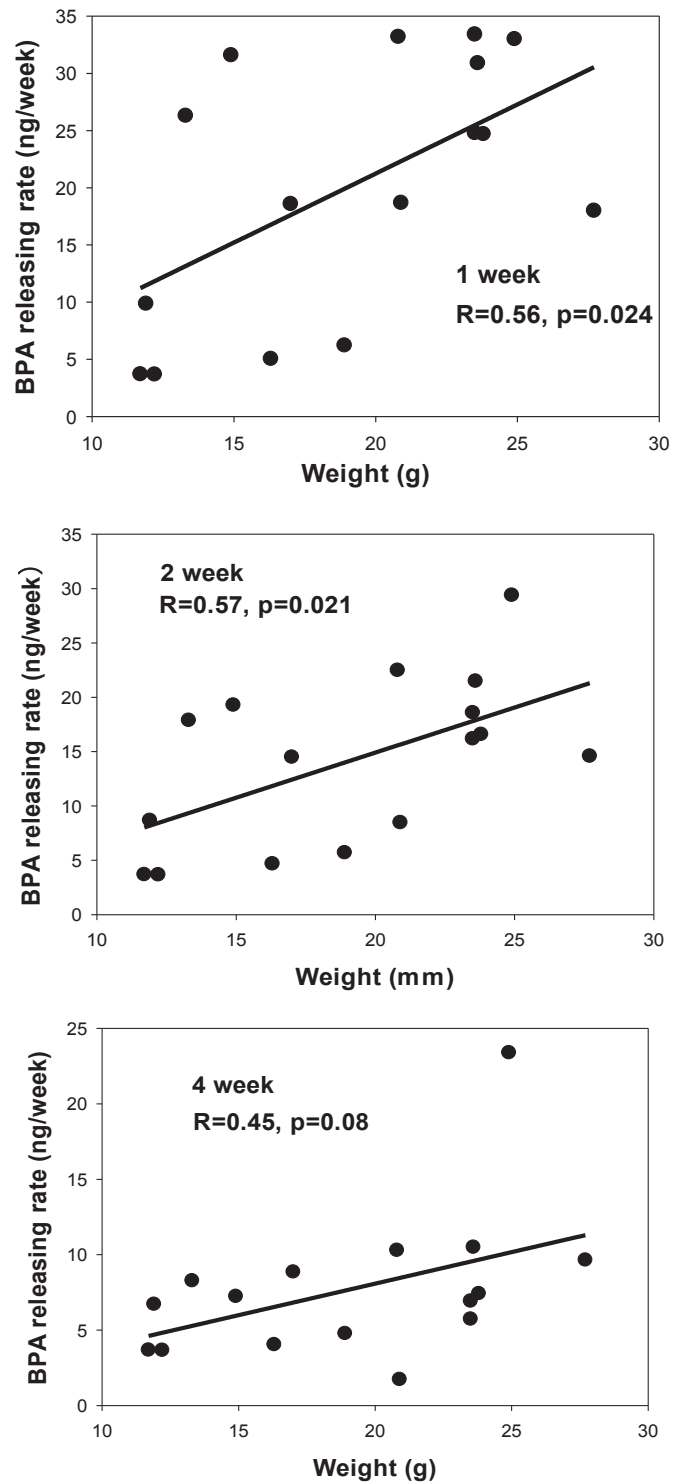


Fig. 4. Correlation between PET bottle mass and release rates of bisphenol A after 1, 2, and 4 weeks.

fully reflect the effects of exposures to endocrine disruptor compounds (EDC) mixture, which can be released from PET bottle. For instance, Greifenstein et al. (2013) reported that total organic carbon contents in bottled water increased from 0.25 mg/L to 2 mg/L after exposure at 60 °C for 70 d, which is likely due to release of mixture of organic compounds from PET bottles. Therefore, monitoring organic EDCs migrating from PET bottles should be extended to more compounds in future study.

Table 4
Total chronic daily intake (CDI, ng/kg/d) of antimony (Sb) and bisphenol A (BPA) by human based on Sb and BPA levels released from PET bottles that stored at 70 °C for 4 week based on four replicates.

ID	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Adult Sb	7.07 ± 0.84	6.36 ± 0.87	7.39 ± 1.52	5.34 ± 0.36	8.80 ± 1.86	28.8 ± 3.90	4.83 ± 0.44	8.75 ± 0.90	6.68 ± 0.85	409 ± 50.9 ^a	8.78 ± 0.58	10.5 ± 1.38	7.64 ± 0.98	7.34 ± 0.44	4.92 ± 1.51	7.22 ± 0.59
BPA	1.08 ± 0.37	1.43 ± 0.21	1.74 ± 0.07	1.11 ± 0.19	2.64 ± 0.26	8.94 ± 0.73	4.47 ± 0.61	7.34 ± 0.66	5.35 ± 0.59	5.44 ± 0.71	6.70 ± 1.14	6.80 ± 1.82	6.78 ± 0.85	5.79 ± 1.10	4.43 ± 0.96	3.76 ± 0.28
Child Sb	24.7 ± 2.92	22.3 ± 3.05	25.9 ± 5.32	18.7 ± 1.26	30.8 ± 6.50	101 ± 13.6	16.9 ± 1.55	30.6 ± 3.16	23.4 ± 2.98	1430 ± 178 ^a	30.7 ± 2.04	36.8 ± 4.81	26.7 ± 3.42	25.7 ± 1.56	17.2 ± 5.30	25.3 ± 2.07
BPA	3.79 ± 1.30	5.00 ± 0.74	6.09 ± 0.26	3.90 ± 0.67	9.26 ± 0.90	31.3 ± 2.55	15.6 ± 2.12	25.7 ± 2.33	18.7 ± 2.07	19.0 ± 2.47	23.5 ± 4.00	23.8 ± 6.37	23.7 ± 3.00	20.3 ± 3.84	15.5 ± 3.36	13.1 ± 0.99

^a CDI values exceed reference CDI regulated by USEPA.

4. Conclusions

Sb and BPA release from 16 brands of PET drinking water bottles in China was investigated by storing bottles under different temperatures and durations. Release of Sb and BPA increased with storage temperature, especially at 70 °C, hence storing PET bottles under high temperature is not recommended. The daily intake (409 ± 50.9 ng/kg/d for adult and 1430 ± 178 ng/kg/d for children) caused by Sb releasing in one brand of PET bottle after one month storage at 70 °C was higher than USEPA RfD of 400 ng/kg/d (USEPA, 2012). However, risk caused by contaminant release from PET bottles need to be considered with caution as 4-week storage was used in the current study. Longer storage duration is necessary for future study. Meanwhile, more attention should be given to other drinks packaged using PET plastic, such as milk, coffee, and acidic juice, and other types of food containers. This is because the ingredient of these drinks and food are more complex compared to drinking water, thus may induce more contaminants release and also more complicated speciation from the containers. For example, Sb concentrations in commercial juices are detected up to 2.7-fold above the EU limit for drinking water (5 µg/L). The more toxic inorganic Sb(III) (44%) and an Sb(V)–citrate complex with unknown toxicity (41%) are the main species in the juices (Hansen et al., 2010; Hansen and Pergantis, 2006). The results about Sb speciation reported in literature are somehow inconsistent, which may be depend on the nature of PET materials, the type of food and the experimental condition selected.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2014.05.012>.

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