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Recycling plastics containing decabromodiphenyl ether into new consumer products including children’s toys purchased in Japan and seventeen other countries purchased in Japan and seventeen other countries

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Abstract

Polybrominated diphenyl ethers (PBDEs) are flame retardants widely used to manufacture several commercial plastic products. The major congeners in commercial PBDE mixtures are listed in the Stockholm Convention on Persistent Organic Pollutants and are scheduled for global elimination. Hence, to understand more about unintentional contamination of plastic recycling stream by restricted PBDEs, we examined 540 small plastic consumer products (1139 components after dismantling), including children’s toys, purchased in 18 countries (mainly Japan) between 2015 and 2019. Handheld X-ray fluorescence analysis revealed that only 219 plastic components (19% of the total samples) contained bromine at a concentration of ≥30 mg kg\(^{-1}\). Chemical analysis of these bromine-positive components revealed that 109 pieces (9.6% of the total), mainly those made of black-colored plastic, contained PBDEs at concentrations ranging between 35–10,000 mg kg\(^{-1}\), with the maximum contribution from decabromodiphenyl ether (decaBDE). These PBDE concentrations were insufficient to impart flame retardancy, suggesting that the recycled plastic used to manufacture these consumer products originated from electronic waste, the manufacture of which was the primary use of commercial decaBDE mixtures. PBDEs were also found in secondary raw plastic materials and their final products obtained in India in 2019, demonstrating that plastics containing decaBDE end up in products where they serve no functional purpose. To contribute to the circular economy, the recycling of plastic waste in end-of-life products should be promoted. However, urgent action is needed to prevent plastic additives of concern, including PBDEs, from entering new products used in daily lives, particularly those used by children.

Keywords: brominated flame retardants (BFRs); polybrominated diphenyl ethers (PBDEs); decaBDE; e-waste; circular economy; black plastic
Graphical abstract
1. Introduction

Polybrominated diphenyl ethers (PBDEs) are brominated flame retardants (BFRs) that were widely used in the manufacture of plastics, textile coatings, and electronic appliances (de Wit, 2002). There are three types of commercial PBDE mixtures (c-pentaBDE, c-octa BDE, and c-decaBDE), each containing a different major congener (pentabromodiphenyl ether, octabromodiphenyl ether, and decabromodiphenyl ether, respectively). Despite the beneficial uses of PBDEs, their persistence, bioaccumulation, and possible adverse effects on wildlife and humans are causes for concern (Norén and Meironyté, 2000; Darnerud et al., 2001; de Wit, 2002; Birnbaum and Staskal, 2004). To address these concerns, the use of commercial PBDE mixtures is being phased out under international restrictions such as the European Directive on the Restriction of the Use of Certain Hazardous Substances in Electrical Equipment (RoHS), which sets a maximum allowable total PBDE concentration of 1000 mg/kg in electrical equipment (The European Parliament and the Council of the European Union, 2011), and the Stockholm Convention on Persistent Organic Pollutants (POPs) (Annex A), which specifies that tetra- to heptaBDEs (present in c-pentaBDE and c-octaBDE), and decaBDE (BDE-209; present in c-decaBDE), are to be eliminated (UNEP, 2009a; 2009b; 2017).

There is a growing body of research showing the presence of PBDEs in a range of products where they are neither needed, nor expected, yet being an unnecessary hazard to the consumer (Ionas et al., 2016; Miller et al., 2016; Pivnenko et al., 2017). Uncontrolled recycling of electronic waste (e-waste) polymers containing BFRs has led to the contamination of several banned BFRs in recycled plastic products, including children’s toys and kitchen utensils, with consequent health and exposure implications (Ionas et al., 2014; Guzzonato et al., 2017; Kuang et al., 2018; Fatunsin et al., 2020). Particular attention has been drawn to the presence of decaBDE in consumer products due to recycling of e-waste (Li et al., 2020). These findings indicate that strategies and approaches for the sound management of PBDE-containing wastes are needed. To remove plastics containing tetra- to heptaBDE
and decaBDE (hereafter referred to collectively as POP-BDEs) from the recycling stream, the Parties of the Basel Convention have proposed several low POP content (LPC) limits for total POP-BDE content (tentatively proposed as 50, 500, or 1000 mg kg$^{-1}$ as of 2019). These limits would be used to identify wastes that must be destroyed or irreversibly transformed in an environmentally sound manner to render them unavailable for material recycling (UNEP, 2019). However, as there is currently no international agreement on the LPC limit for POP-BDEs under the Basel Convention, the international circulation of waste plastics containing PBDEs and the recycled products continues.

In Japan, national limits for PBDE content and regulations for managing PBDE-containing wastes remain under discussion. One factor complicating the debate is that it is difficult to immediately identify products containing POP-BDEs. Moreover, the fact that recycled products present on the Japanese market are made not only from domestic materials, but also from imported materials that contain waste plastics derived from various countries, probably including waste plastics exported from Japan to other countries for recycling. This problem is compounded by a lack of information on international material flows, such as the origin and destination of waste plastics containing PBDEs. It is usually difficult to trace the origins of recycled plastic products in the Japanese market and probably the same situation exists in other countries.

Gas chromatography-mass spectrometry (GC-MS) is a common means of determining PBDE concentrations in plastics (e.g., Eguchi et al., 2021). Although GC-MS is a sensitive technique, sample preparation, which involves extraction of PBDEs from the item with a suitable solvent, can be both time- and resource-consuming. To address this issue, energy-dispersive X-ray fluorescence (XRF) spectrometry is being increasingly used for the screening analysis of plastics by using bromine (Br) content as a proxy for BFRs (e.g., Turner and Filella, 2017; Turner, 2018; Drage et al., 2018; Sharkey et al., 2018). Although XRF spectrometry cannot discriminate between different brominated compounds, and the lower detection limits are in the order of tens of mg kg$^{-1}$, this technique has the advantage of
being rapid, non-destructive, and suitable X-ray shielding, portable hand-held devices. In the context of using portable XRF analyzers as a tool for testing compliance with PBDE LPC limits, more research to determine the lower detection limit for Br concentration and the incidence of false positive or false negative results is needed.

Therefore, to examine the current status of the international circulation of PBDE-containing waste plastics, we determined the concentrations of Br and PBDEs in a wide range of small plastic items, including children’s toys, purchased in Japan and 17 other countries in Asia, Europe and Canada. In addition, we conducted a case study in which we examined the current situation regarding the recycling of PBDE-containing waste plastics in India by determining the concentrations of Br and PBDEs in secondary raw plastic materials (flakes and pellets) and their final products. Such samples with known secondary raw material and the final product pairs were available only in India.

**2. Materials and Methods**

**2.1 Sample collection**

A total of 540 commonly available small plastic items (e.g., toys, stationery, cutlery, photo frames, calculators, flashlights, hair accessories, clothes hangers) were purchased from Japan (n = 279), India (64), Belgium (47), Serbia (28), Taiwan (21), Thailand (21), Vietnam (20), Canada (11), Brazil (8), Myanmar (8), Cameroon (6), Korea (6), Argentina (5), Hong Kong (5), Sri Lanka (5), Kenya (3), Indonesia (2), and Malaysia (1) between 2015 and 2019. Because it is usually impossible to distinguish from the product label alone between recycled and non-recycled products, cheap and low-quality products were considered to contain a high percentage of recycled materials in this study. So, we selectively bought the cheapest product when there were different prices for the same product. These products were collected randomly and without regard for color or polymer type. The plastic items were classified into three categories: giveaway toys and 100-yen shop products purchased from the Japanese
market, and cheap products purchased from outside of Japan (hereafter “overseas products”). All purchased items were dismantled manually and 1139 plastic components were prepared for the analysis. A summary of the items collected is shown in Table 1.

In addition, five different types of secondary raw materials from plastic waste were collected from recycling facilities in India in 2019 (Recyclates 1–5, Table 2). Recyclates 1–4 were shredded plastic wastes (approx. 2 cm square), and Recyclylate 5 was granulated pellets (approx. 5 mm diameter, 5 mm length). Recycle 1 was the raw material for the manufacture of plastic pencil shafts. Recycle 4 was the raw material for the manufacture of wooden-looking photo frames.

2.2 **Determination of Br content by portable XRF**

The elemental Br content in each component was determined as a surrogate for BFR content by using a handheld XRF analyzer (DELTA Premium DP-6500, Olympus Corporation, Japan). Before use, the handheld XRF analyzer was calibrated by using the peak positions of iron and molybdenum, the peak width at half height of manganese, and the total count of SUS316 stainless steel. The screening survey was conducted in RoHS/WEEE mode, and the reading time was set at 30 s. Components containing ≥30 mg kg\(^{-1}\) by weight of Br were considered Br-positives and selected for further chemical analysis.

2.3 **Determination of Br content by combustion-ion chromatography**

Before chemical analysis, the selected components by the XRF screening were crushed into small, homogeneous pieces and then pulverized to a fine powder (approx. particle size <300 μm) with a freezer mill (SPEX Freezer/Mill 6750, SPEX SamplePrep, Metuchen, NJ). Recyclates 1–4 were very heterogeneous, so each recyclate was mixed well and divided into three equal portions before being pulverized so that three samples each were obtained for chemical analysis. Recyclate 5 was very homogenous, so only one sample was prepared.
To confirm the Br concentrations obtained by XRF analysis, the organobromine concentrations in the
pulverized samples were determined by combustion-ion chromatography (C-IC) according to Japanese
Industrial Standard (JIS) K 7392 (Japanese Standard Association, 2009). Briefly, after combustion of
the samples (approx. 1.5–40 mg depending on the Br concentration obtained by XRF analysis) in an
AQF-2100H Automatic Quick Furnace (Nittoseiko Analytech, Kanagawa, Japan; inlet temperature,
900°C; outlet temperature, 1000°C), the bromide ions were collected in 30 ppm H$_2$O$_2$, and bromide ion
concentrations in the solution were quantified with a Dionex ICS-1600 ion chromatograph (Thermo
Fisher Scientific, MA, US) under the following conditions: column, Dionex IonPac AS12A (4 mm id,
200 mm length); mobile phase, 2.7 mM Na$_2$CO$_3$/0.3 mM NaHCO$_3$; flow rate, 1.0 mL min$^{-1}$; suppressor,
ASRA (in recycle mode, 50 mA); detection, conductivity.

2.4 Determination of PBDE content by gas chromatography-mass spectrometry

To determine the concentrations of PBDEs, approximately 0.30 g of each sample was ultrasonically
extracted with 20 mL of toluene. During ultrasonic extraction, ice was put in the water bath to prevent
a temperature increase. Next, a 200 μL aliquot of the toluene extract was added dropwise to 20 mL of
hexane to precipitate the dissolved polymer matrix. After the precipitate was removed, a 100-μL aliquot
of the supernatant was mixed with 100-μL of internal standard (13C$_{12}$-labeled BDE 138, 20 ng mL$^{-1}$ in
nonane) in a brown glass vial and concentrated to approximately 100 μL under a gentle nitrogen stream.
The resulting solution was used for the PBDE analysis, which was conducted on a GC coupled with an
electron ionization-triple-quadrupole mass spectrometry (MS/MS) system (Agilent 7000C Triple
Quadrupole GC/MS system, Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a DB-
5MS capillary column (15 m × 0.25 mm, i.d., 0.1 mm film thickness; Agilent Technologies Inc.). The
GC oven temperature program was as follows: initial 100°C, hold for 1 min, ramp to 310°C at 10°C
min$^{-1}$, hold for 10 min. The cool-on-column injector temperature program was as follows: initial 100°C,
hold for 0.1 min, ramp to 300°C at 100°C min⁻¹, hold for 15 min. Helium was used as the carrier gas at a column flow rate of 1 mL min⁻¹. The GC injection volume was 2 μL. Twenty-seven congeners of PBDEs (BDE 3, 7, 15, 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, and 209) were identified and quantified by the isotope dilution method by using the response factor of each congener to the internal standard. The detection limit of PBDEs in the samples was set at 30 mg/kg.

2.5 Quality assurance and quality control

Samples were analyzed by using established laboratory quality assurance and quality control procedures. The glassware was cleaned before use by rinsing three times each with acetone, hexane, and toluene. Sample processing container or solvents were tested separately for background levels of PBDE contamination. None of the target congeners was present in the containers above the detection limit of this study. For every six to ten samples, nonane was injected to GC/MS as a solvent blank to check for carryover. All analytical processes for PBDEs were conducted under UV-cutoff conditions.

3. Results and Discussion

3.1 Br concentrations determined by XRF

First, we used XRF to determine the Br concentrations in the 1139 plastic components (Figure 1). Overall, around 70% of plastic components had a Br concentration that was below the limit of detection (<30 mg kg⁻¹). Among the three categories of items, 49–87% of plastic components had a Br concentration below the detection limit. Although polymer-type identification was not performed, a relatively high proportion of components with a low Br concentration (<30 mg kg⁻¹) was found in giveaway toys purchased in Japan. This may be because many of them were manufactured from polymers that usually did not contain Br (e.g., polyethylene, polyethylene terephthalate, and polyvinyl
chloride). Only 10 components had a Br concentration >10,000 mg kg\(^{-1}\). The maximum concentration detected was 54,000 mg kg\(^{-1}\). Components with a Br concentration >10,000 mg kg\(^{-1}\) were most frequently detected in products from 100-yen shops. Components with a Br concentration <30 mg kg\(^{-1}\) were considered unlikely to contain PBDEs above the tentative Basel LPC limits and were excluded from the subsequent chemical analysis. As a result, 219 components (19% of the original total number of components) with Br concentrations ≥30 mg kg\(^{-1}\) were used in the subsequent chemical analysis. Also, for most plastic items, the country of purchase did not match the country of manufacture. Although the country of manufacture was not specified for some of the products, most of them were manufactured in East Asia, principally in China. Therefore, in the subsequent analysis, the three categories of items were treated together without distinction.

### 3.2 Comparison of Br concentrations measured by XRF and C-IC

After pulverizing the 219 selected samples, their Br concentrations were confirmed by C-IC (Figure 2). Although it was not always possible to pulverize the exactly same part of the sample where the XRF measurements were actually made, and there was a possibility that the Br concentration in each component was not evenly distributed, a clear positive relationship (Pearson’s \(r = 0.87, p < 0.001\)) was found between Br concentrations determined by XRF, a non-destructive technique, and those measured by C-IC, which is more sensitive than XRF but also destructive.

The Br (atomic weight, 79.9) content in tetraBDE (molecular weight, 485.8) and decaBDE (molecular weight, 959.2) is 66% and 83%, respectively. Therefore, if the Br concentration in a sample is below 1000 mg kg\(^{-1}\), theoretically, the total POP-BDE content cannot exceed the Basel LPC limit of 1000 mg kg\(^{-1}\), even if all the Br is derived from POP-BDEs. The same reasoning can be applied to the tentative LPC limits of 50 or 500 mg kg\(^{-1}\). However, if such limits are brought into practice, it will be important to understand the frequency at which false results (negative and positive) arise when a handheld XRF
analyzer is used to determine Br concentrations. From a conservative perspective, false positives may
be acceptable, but false negatives should be as infrequent as possible. Therefore, we examined the
number of false results that arose when applying the tentative Basel LPC limits and assuming that data
obtained by C-IC were the true values (Figure 2). When a Br concentration of 1000 mg kg\(^{-1}\) was used
as the upper limit, there was only one false-positive result (0.1% of the total number of components)
and no false-negative results among the 1139 results obtained by XRF analysis (Figure 2b). When a Br
conscentration of 500 mg kg\(^{-1}\) was used as the upper limit, there were 8 false-positive results (0.7% of
the total number of components) and one false-negative result (0.1% of the total number of components)
(Figure 2c). When a Br concentration of 50 mg kg\(^{-1}\) was used as the upper limit, there were 8 false-
positive results (0.7% of the total number of components) and 6 false-negative results (0.5% of the total
number of components) (Figure 2d). Together, these results show that a handheld XRF analyzer is an
effective and reliable tool for identifying plastics containing Br at a concentration >50 mg kg\(^{-1}\). This
approach provides a frequency of false negatives of ≤0.5%.

The handheld XRF analyzer is an effective tool for primary determination of BFR content, but judging
the acceptability of material for recycling solely based on Br concentration would mean the exclusion
of products containing unregulated BFRs due to false positive results.

3.3 PBDE concentrations in the selected plastic components

GC-MS/MS analysis of the 219 Br-positive components revealed that only 109 plastic components
contained PBDEs (9.6% of the total number of pieces). The PBDE concentrations ranged from 35 to
10,000 mg kg\(^{-1}\) (Figure 3, detailed data for the individual components are available in the Supporting
Information). Thus, almost half of the Br-positive samples must have been false positives regarding
identifying products containing PBDEs, which in turn suggests that they contained other Br-based
compounds, presumably other unrestricted BFRs. BDE-209 was the predominant congener in all
samples, accounting for >90% of the PBDEs detected in 80% of the components (Tables S1 and S2). In addition, only BDE-209 was detected in 40% of the components. Together, these findings indicate that the PBDEs found in the components were mostly derived from c-decaBDE.

The 109 PBDE-containing components were taken originally from 84 of the 540 items collected for the study. PBDE concentrations above 1000 mg kg\(^{-1}\) were found in 34 black plastic components from a variety of cheap toys (e.g., toy cars, a toy guitar, a game, water guns, children’s accessories) and cheap consumer products (e.g., flashlights, calculators, hair accessories, binoculars). The highest concentration (10,000 mg kg\(^{-1}\); 1 wt%) was detected in black clothes hanger from Hong Kong in 2019. A minimum of 3% to 5% by weight of BFR is required in most plastics to achieve adequate flame retardancy, which is equivalent to a Br content of at least around 20,000 mg kg\(^{-1}\) (Papazoglou, 2004). The PBDE concentrations found in the present study were too low to be considered as intentional additions, and instead were considered to be the result of material recycling of e-waste plastics containing decaBDE, as observed in previous studies (Ionas et al., 2014; Miller et al., 2016; Pivnenko et al., 2017). These findings suggest that PBDE-containing plastics are being recycled as a wide range of consumer products that do not inherently require flame retardancy, such as toys and everyday items. These products are being distributed worldwide.

Figure 4 shows the relationship between PBDE concentration and Br concentration for the Br-positive samples. If the detected Br concentration in a component originated solely from decaBDE, the plot would appear on the dashed line in the figure. However, all plots were below the dashed line, indicating that none of the Br detected in the samples could be explained solely by the presence of decaBDE. This finding was attributed to the presence of other currently non-regulated Br-containing compounds found in e-waste plastics, such as decabromodiphenyl ethane and tetrabromobisphenol A (Stubbings et al., 2019; Suzuki et al., 2021). The presence of multiple BFRs in individual samples is considered the direct result of polymer mixing and contamination during plastic recycling (Pivnenko et al., 2017).
Seventy-five percent of the Br-positive samples were made of black-colored plastics, and the Br concentration in non-black samples was generally low, except in printed circuit boards. Those black components may be manufactured entirely from black e-waste plastic or by adding black pigment when waste plastics are mixed and recycled without sorting by color (Turner, 2018). It is noteworthy that relatively high PBDE concentrations (710–3900 mg kg\(^{-1}\)) were detected in silver-painted beaded bracelets for children, but when the paint was removed, it was found to be black plastic inside. Similarly, black plastic containing PBDE was also found in the body of a miniature car (950 mg kg\(^{-1}\)) and in toy handcuffs (190 mg kg\(^{-1}\)), which were both painted silvers. Based on these observations, to avoid having consumer products containing PBDEs, especially products for children, it may be necessary to pay attention not only to black plastic products, but also to painted plastic products.

Currently, in Japan, when small plastic items, including toys covered in this study, are disposed of, they are incinerated rather than collected as a resource. Therefore, even if these items contain PBDEs over the tentative Basel LPC limits, it can be assumed that these items do not end up in the recycling stream under the current Japanese waste management system, and PBDEs in the products are sufficiently decomposed during incineration (Kajiwara et al., 2021). However, to contribute to the circular economy and enhance resource efficiency, attempts to collect and recycle such non-electronic plastic products will likely be accelerated in the near future. Therefore, it will become necessary to establish an efficient system to exclude PBDE-containing products, not only for electronic appliances but also for those shown in this study, from the recycling stream.

3.4 Secondary raw materials and their final products

In 2019, we conducted an on-site investigation of the recycling of e-waste and other plastic-containing wastes in India. At that time, we collected samples of secondary raw materials and some of their recycled products (Table 2). Br was detected in all recyclates examined (Table 3), implying certain BFR-
containing plastics. Unexpectedly, Br was detected in the flakes of food container plastic waste (Recyclate 1) at more than 1000 mg kg\(^{-1}\), although flame retardancy is not normally required for food containers. PBDEs (250–1400 mg kg\(^{-1}\)) were found only in the recyclates containing black plastic (Recyclates 2, 4, and 5). Because the contribution of BDE-209 to the total PBDEs in the Recyclates was more than 90% (Table S3), they were considered to be derived from decaBDE contained in e-waste plastic. Consistent with these findings, the PBDE concentration was lower than the detection limit in the shafts of plastic pencils manufactured from food container plastic waste (Recyclate 1) in which PBDEs were not detected (<30 mg kg\(^{-1}\)). In photo frames made from Recyclate 4, which had an average PBDE concentration of 340 mg kg\(^{-1}\), 7 out of 10 photo frames were found to be contaminated with up to 160 mg kg\(^{-1}\) of decaBDE. These results provide a glimpse into the recycling of PBDE-containing plastics in India.

4. Conclusions

This study reveals that about 10% of the analyzed consumer products, including toys, are unintentionally contaminated with PBDEs at concentrations insufficient to impart flame retardancy (35–10,000 mg kg\(^{-1}\)). The health risks of using products with such concentrations of PBDEs are not known, but it is clear that PBDEs have been transferred from electronic appliances such as television housings to products to which humans have daily exposure. Because plastic resources circulate internationally, a situation where different countries take different actions should be avoided. Given the different circumstances in each country, we suggest that it may be necessary to set national standards (even tentatively) for the POP content of circulating resources and products as soon as possible, without waiting for an international agreement, to prevent POP-containing waste from being unintentionally mixed with waste plastic resources intended for domestic use or export. Furthermore, a system to ensure that recycled plastic products do not contain more than the permitted amount of POPs is needed.
Acknowledgements

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 References


UNEP (2019), General technical guidelines on the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants. Available at:
Table 1. Summary of the plastic items examined in the present study.

<table>
<thead>
<tr>
<th>Category</th>
<th>No. of items</th>
<th>No. of components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Giveaway toys</td>
<td>187</td>
<td>393</td>
</tr>
<tr>
<td>100-yen shop products</td>
<td>92</td>
<td>228</td>
</tr>
<tr>
<td>Inexpensive overseas products</td>
<td>261</td>
<td>518</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>540</strong></td>
<td><strong>1139</strong></td>
</tr>
</tbody>
</table>
Table 2. Summary of the secondary raw materials from plastic waste collected in India.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Description</th>
<th>Color</th>
<th>Final product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recyclate 1</td>
<td>Flakes of food-container plastic waste</td>
<td>White</td>
<td>Plastic pencils (shaft)</td>
</tr>
<tr>
<td>Recyclate 2</td>
<td>Flakes of mixed e-waste plastics</td>
<td>Mixed, including black</td>
<td>-a</td>
</tr>
<tr>
<td>Recyclate 3</td>
<td>Flakes of mixed plastic waste</td>
<td>Mixed, without black</td>
<td>-</td>
</tr>
<tr>
<td>Recyclate 4</td>
<td>Flakes of mixed plastic waste</td>
<td>Mixed, including black</td>
<td>Photo frames</td>
</tr>
<tr>
<td>Recyclate 5</td>
<td>Pellets of high-impact polystyrene</td>
<td>Black</td>
<td>-</td>
</tr>
</tbody>
</table>

* a not identified
Table 3. Concentrations (mg kg\(^{-1}\)) of bromine (Br) and polybrominated diphenyl ethers (PBDEs) found in the secondary raw materials and their recycled products in India\(^a\).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>n</th>
<th>Br(^b)</th>
<th>PBDEs</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recyclate 1</td>
<td>3</td>
<td>1700 (1100–2300)</td>
<td>&lt;30</td>
<td></td>
</tr>
<tr>
<td>Recyclate 2</td>
<td>3</td>
<td>2100 (1700–2500)</td>
<td>950 (540–1400)</td>
<td></td>
</tr>
<tr>
<td>Recyclate 3</td>
<td>3</td>
<td>1000 (140–2700)</td>
<td>&lt;30</td>
<td></td>
</tr>
<tr>
<td>Recyclate 4</td>
<td>3</td>
<td>1200 (1100–1400)</td>
<td>340 (250–390)</td>
<td></td>
</tr>
<tr>
<td>Recyclate 5</td>
<td>1</td>
<td>950</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>Plastic pencils</td>
<td>1</td>
<td>100</td>
<td>&lt;30</td>
<td>Made from Recyclate 1</td>
</tr>
<tr>
<td>Photo frames</td>
<td>10</td>
<td>470 (210–740)</td>
<td>66 (&lt;30–160)</td>
<td>Made from Recyclate 4</td>
</tr>
</tbody>
</table>

\(^a\) figures in parentheses indicate the range
\(^b\) measured by combustion-ion chromatography
**Figure legends**

**Figure 1.** Bromine concentrations in the 1139 components examined in the present study, as determined by energy-dispersive X-ray fluorescence spectrometry.

**Figure 2.** Comparison of bromine (Br) concentrations in the components determined by energy-dispersive X-ray fluorescence spectrometry (XRF) or by combustion-ion chromatography (C-IC) before and after pulverizing the samples. The dashed line indicates a concentration ratio of 1:1. Data are shown for all components (a) and for components with a Br concentration of <10,000 mg kg\(^{-1}\) (b), <1000 mg kg\(^{-1}\) (c), or <500 mg kg\(^{-1}\) (d). Also shown in (b–d) are the false positive and false negative XRF results obtained when a tentatively proposed Basel LPC limit of 1000 mg kg\(^{-1}\), 500 mg kg\(^{-1}\), or 50 mg kg\(^{-1}\) was applied.

**Figure 3.** Polybrominated diphenyl ether (PBDE) concentration in the components with a bromine concentration ≥30 mg kg\(^{-1}\). The dashed lines indicate PBDE concentration boundaries.

**Figure 4.** Comparison of total polybrominated diphenyl ether (PBDE) concentration and bromine (Br) concentration measured by combustion-ion chromatography in components with a Br concentration of >30 mg kg\(^{-1}\) as determined by energy-dispersive X-ray fluorescence spectrometry. The dashed line indicates the concentration when all the detected Br is derived from decaBDE.
Figure 1

Giveaway toys (n=393)

100-yen shop products (n=228)

Cheap overseas products (n=518)

- <30 mg/kg
- 30–100 mg/kg
- 100–1000 mg/kg
- 1000–10,000 mg/kg
- >10,000 mg/kg
Figure 2

(a) All samples

(b) <10,000 mg/kg

(c) <1000 mg/kg

(d) <500 mg/kg

Br conc. (mg/kg) determined by C-IC

Br conc. (mg/kg) determined by XRF

False negative
False positive
Figure 3

PBDE concentration (mg/kg)

- Toys
- Other items

- >1000 mg/kg: 34 samples
- 500–1000 mg/kg: 14 samples
- 50–500 mg/kg: 55 samples
- <50 mg/kg: 6 samples
Figure 4