BFRs IN CONSUMER PRODUCTS MADE OF RECYCLED PLASTIC FROM SEVEN AFRICAN COUNTRIES - STOCKHOLM CONVENTION CONSEQUENCES

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Introduction

Brominated flame retardants (BFRs) have for a long time been widely used in plastic and foam products, including furniture upholstery, car seats, electronics, and building insulation[1-3]. Their purpose was to increase the fire safety of the highly flammable plastic materials used. However, progress in scientific knowledge, efforts to protect consumers, as well as public pressure, have contributed to a gradual ban of the most toxic BFRs. Polybrominated diphenyl ethers (PBDEs: penta-, octa-, and decaBDE), and hexabromocyclododecane (HBCD) were listed under the Stockholm Convention on Persistent Organic Pollutants for global elimination. PBDEs and HBCD belong among the persistent organic pollutants (POPs) that are not easily degraded in the environment, and are able to travel far from the place of their origin in water and air currents[4]. They are known to disrupt the human hormonal, endocrine, immune and reproductive systems, and negatively affect the development of the nervous system and the intelligence in children[1-3,5]. Some of their regrettable substitutes, including decabromodiphenyl ethane (DBDPE) or 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) have also been shown to be persistent, bioaccumulative, and able to travel long distances[6]. Tetrabromobisphenol A (TBBPA), an alternative to PBDEs and HBCD, and the largest-volume flame retardant used worldwide[7], is known to be endocrine disrupting[8].

The electrical and electronic engineering industry is one of the largest consumers of BFRs. Flame retardants are used to produce plastic housings for consumer and office electronics, and for electronics in heat sources, in order to decrease their flammability. Because BFRs are added into the material as additives that are not chemically bound to the plastic polymer in question, they are released from the material during the whole lifecycle of the product[9], including the disposal[10-13].

In spite of the existing international and national legislation, a number of studies have proved the presence of polybrominated diphenyl ethers (PBDEs) and HBCD in new products and household equipment[14], including children's toys[15-17], thermo cups and kitchen utensils[17-19], and carpet padding[20]. Novel brominated flame retardants (nBFRs) have also been found to be present in products made of recycled plastics in significant concentrations[21]. The studies concluded that these products were not intentionally treated with BFRs, but they originated from the recycled materials.

Our current study is a continuation of previous investigations by IPEN and Arnika that have warned against unregulated recycling of e-waste plastics, which carry brominated flame retardants into new products[20-22]. The current study is aimed at determining whether children's toys, hair accessories, office supplies, and kitchen utensils found on the African market are affected by the same unfortunate practice. The data collected for this study is a contribution to the discussion on setting appropriate standards to improve the control over the circulation of harmful BFRs in consumer products and waste.

Materials and methods

Two hundred and forty-four (244) samples of consumer products made of black plastic were obtained from markets and stores in seven African countries: Cameroon, Ethiopia, Gabon, Kenya, Morocco, Tanzania, and Tunisia. The samples were expected to be made from recycled plastic. Children's toys, hair accessories, kitchen utensils, and office supplies were of primary interest.

As X-ray fluorescence is a useful technique for determining the presence of PBDEs in plastics[23-24], all samples were screened using a handheld NITON XL3t 800 XRF analyzer in order to select samples for further laboratory analysis. As bromine is a key component of BFRs and antimony trioxide is a common BFR synergist[25], samples with bromine and antimony levels over 1,000 ppm were selected for lab analysis. When a minimum of three samples representing different product categories (i.e., children's toys, hair accessories, kitchen utensils, and office supplies) could not be identified among the collected samples, consumer goods down to 150 ppm of bromine and 40 ppm of antimony were selected instead and sent for lab analysis. One-fifth of all 244 samples were sent for special chemical analysis to the University of Chemistry and Technology, Prague.

Forty-seven samples (including 11 toys, 18 hair accessories, 10 kitchen utensils, 4 office supplies, and 4 other products) out of the 244 collected items were analyzed for 16 PBDE congeners. For the purpose of calculation, the components of the commercial PentaBDE mixtures include congeners BDE 28, 47, 49, 66, 85, 99, and 100, and for the OctaBDE mixtures include the following congeners: BDE 153, 154, 183, 196, 197, 203, 206, and 207. The component of the commercial DecaBDE mixture is BDE 209.

Three isomers of HBCD (α-, β-, γ-HBCD), TBBPA, and six nBFRs, i.e., 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), decabromodiphenyl ethane (DBDPE), hexabromobenzene (HBB), octabromo-1,3,3-trimethylpheny-1-indan (OBIND), 2,3,4,5,6-pentabromoethylbenzene (PBEB), and pentabromotoluene (PBT) were analyzed in the laboratory at the University of Chemistry and Technology, Prague, the Czech Republic. The targeted BFRs were isolated by extraction with n-hexane: dichloromethane (4:1, v/v). Identification and quantification of the PBDEs and nBFRs was performed using gas chromatography coupled with mass spectrometry in negative ion chemical ionization mode (GC-MS-NICI). Identification and quantification of the HBCD isomers was performed by liquid chromatography interfaced with tandem mass spectrometry with electrospray ionization in negative mode (UHPLC-MS/MS-ESI-). The limit of quantification was 5 ppb for BDE 209 and 0.5 ppb for 15 other analysed PBDE congeners, ranging between 0.5-5 ppb for the nBFRs, and was 0.5 ppb for HBCD and 5 ppb for TBBPA.

Results and discussion

The laboratory analysis of the 11 toys, 18 hair accessories, 10 kitchen utensils, 4 office supplies, and 4 other products from 7 countries found that 46 samples[a] contained OctaBDE and DecaBDE at concentrations ranging from 3 to 151, and from 4 to 296 ppm respectively. The highest measured concentrations of PBDEs were found in office supplies, followed by hair accessories, children's toys, other consumer products, and kitchen utensils. A summary of the results is presented in Table 1. The ranges of HBCD, PBDEs, nBFRs, and TBBPA, and total of the analyzed BFR concentrations per country are summarized in Table 2.

Table 1. Overview of the analytical results for the analyzed BFRs according the groups of consumer products, in ppm (mg/kg).

	Children's toys	Hair accessories	Kitchen utensils	Office supplies	Other products
Number of samples	11	18	10	4	4
OctaBDE	6-60	13-151	3-15	9-83	0.16-33
DecaBDE	56-243	46-273	4-167	81-296	0.38-161
ΣPBDEs	82-269	75-315	11-182	87-332	0.54-194
HBCD	<LOQ-11	<LOQ-1.8	<LOQ-49	<LOQ-1.3	<LOQ-0.4
ΣnBFRs	6-251	21-434	12-68	10-125	0.03-81
TBBPA	0.48-243	24-196	1.2-44	12-89	0.4-85
ΣBFRs	98-646	182-897	30-216	112-439	1-359
Total Br	456-13550	1045-16200	174-2298	626-8523	205-1309

Table 2. Overview of the analytical results for the analyzed BFRs, per country where the samples were obtained.

	Country	Number of samples	HBCD	ΣPBDEs	ΣnBFRs	TBBPA	ΣBFRs
Measured ranges of concentrations (ppm)	Cameroon	5	<LOQ-1.5	49.5-210	19-225	19-113	112-495
	Ethiopia	4	<LOQ-2.5	35-149	25-187	1.2-243	72-646
	Gabon	7	<LOQ-4.7	0.54-209	0.03-125	0.4-89	1-424
	Kenya	5	<LOQ-1.1	90-269	10-154	0.5-50	111-318
	Morocco	7	<LOQ-3.1	37-315	6-434	10-196	98-897
	Tanzania	10	<LOQ-1.8	50-332	21-107	30-91	138-439
	Tunisia	9	<LOQ-49	11-308	12-325	3.5-151	30-608

The composition of BFRs differs among the individual samples and has no specific concentration patterns, suggesting that heterogeneous recycled materials were used. DecaBDE, followed by TBBA, dominated the samples. Moreover, new BFRs occur in significant concentrations in our sampled items. HBCD is not very prominent in the black plastic products analyzed in this study, as this flame retardant has primarily been used in polystyrene insulation, which is not recycled into any of the types of products included in this study. The kitchen

[a] It is 98% of 47 analyzed and 19% of 244 collected samples.

utensil from Tunisia is the only exception among the analyzed samples, demonstrating a substantial HBCD level. In comparison with the former studies conducted by IPEN and Arnika until 2017[21,22], the concentrations of HBCD in the recycled products seem to be decreasing. This trend can be a result of the global ban of HBCD in 2013[26], and decreasing amounts of HBCD-treated products therefore entering the waste streams. HBCD has also been used in large volumes in polystyrene products, rather than in plastic casings for electronics, so it would also more probably be found in recycled polystyrene[27, 28].

The average concentrations of PBDEs in the samples of children's toys from Kenya remain at the same levels as in 2017[22]. However, previously detected levels of PBDE in products from Nigeria (up to 1,174 and 672 ppm of OctaBDE and DecaBDE respectively)[22] are significantly higher than the levels measured in the other African countries today.

There are no official limit values for the content of BFRs in products or waste established in any legislation in the African countries. However, the African region's representatives advocate for stricter limits for PBDEs in waste,[b] to stop both the import of hazardous PBDE-containing e-waste into the region, and the recycling of this waste into new products. Stricter levels are proposed to be set, for the sum of PBDEs at 50 ppm in total and for HBCD at 100 ppm[29].

After the implementation of the levels mentioned above, 39 out of the 47 analyzed products included in this study would be classified as POPs waste. It is 16% out of all 244 samples collected in seven African countries for this study. The wastes exceeding those levels should after implementation not be allowed to be freely imported to Africa, or recycled (see Article 6 of the Stockholm Convention)[30].

Potential health effects

The brominated flame retardants found in the analyzed samples are known to migrate from the products[9,31]. Dermal exposure to PBDEs has in a recent study been shown to be a significant exposure route, comparable to diet and dust ingestion, for adults[32]. They are related to the negative effects on the endocrine, immune and reproductive systems, and also negatively affect the nervous system development and intelligence in children[1,5]. Moreover, we can also expect that there will be other harmful brominated substances such as brominated dioxins (PBDD/Fs) present in the analyzed products, as they accompany the BFRs in the original products[33,34]. These substances exhibit similar health effects as chlorinated dioxins (PCDD/Fs), for which the tolerable daily intake (TDI) recently was lowered by the EFSA[35]. Their influence on toddlers has been studied from several examples of toys made out of recycled black plastic, providing the conclusion that ingestion of pieces of plastic toys by children may represent an intake of 2,3,7,8-TCDD equivalents up to a level that is *"9 times higher than the recommended TDI for dioxins of 0.28 pg TEQ/kg body weight/day"*[36].

The potential human exposures to PBDEs and related harmful chemicals in products, including PBDD/Fs in waste, call for setting strict limit values for POP BFRs in products and a Low POPs content level for waste that defines POPs waste according to Article 6 of the Stockholm Convention. This should be established at a level of 50 ppm as proposed by the African region, and accompanied with setting an unintentional trace contamination level at 10 ppm, the same level as is applied in the EU for products from virgin plastics[37].

Separation techniques

In the informal plastic recycling sector in India, a simple sink-and-float method is used for BFR plastic separation[38]. Identical plastic materials are first shredded and then placed into a bath. This method is based on the different densities of BFR plastic (which is significantly more dense), which sinks, and its non-flame retardant counterpart, which floats on the surface of the bath.

In Europe, X-ray fluorescence (XRF) and X-ray transmission (XRT) for measuring total bromine concentrations are operated on an industrial scale[38]. The typical bromine concentrations in plastics used in electric and electronic appliances are well known (6-10% in high impact polystyrene (HIPS), 4-5% in polycarbonate (PC), and 6.8-9.6% in acrylonitrile butadiene styrene (ABS))[39] and this can be used to indicate what plastics should be separated from the materials destined for recycling. When the total bromine measurement indicates more than 300 ppm and the total antimony level is more than 70 ppm, the material is likely to contain over 50 ppm PBDEs[40].

These methods can also be used for border control of the consumer products and/or waste entering the African countries.

Regulation of BFRs other than PBDEs and HBCD

No limit values are currently set for nBFRs and/or TBBPA in consumer products or wastes. The elevated levels of POP-PBDE and new BFRs in some consumer products reported in this study and the known and unknown

[b] The Stockholm Convention requires that POPs wastes be treated so that POP content is destroyed or irreversibly transformed to that they no longer exhibit POPs characteristics. The Convention sets low POPs content limits (LPCL) above which treatment is required. POPs waste is prohibited to be recycled and cannot be transported across the international borders of the countries – see Article 6 of the Stockholm Convention [30].

adverse effects of these chemicals require a class-based approach to restriction of BFRs. The same approach is currently being discussed for PFASs in the EU[41].

Conclusions

The present study has shown that children's toys, hair accessories, office supplies, and kitchen utensils found on the African market are affected by unregulated recycling of e-waste plastics which carry brominated flame retardants into new products. To stop this practice, strict Low POPs content levels need to be set. Only a class-based approach can address the regrettable substitutes and likely toxic new BFRs that are currently used without any regulation and which will continue to circulate in the waste streams, just as their persistent counterparts.

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