THE ONGOING HAZARDS OF TOXIC BFRs IN TOYS, KITCHEN UTENSILS AND OTHER CONSUMER PRODUCTS FROM PLASTIC IN CZECHIA AND SERBIA

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Introduction

The original objective of using brominated flame retardants (BFRs) was to increase the fire safety of highly flammable plastic materials used for many different applications including for example, car seats, plastics, electronics, and building insulation[1-3]. Progress in scientific knowledge, efforts to protect consumers, as well as public pressure, have contributed to a gradual ban on 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. 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[4]. Tetrabromobisphenol A (TBBPA), an alternative to PBDEs and HBCD, and the largest-volume flame retardant used worldwide[5], is known to be an endocrine disrupting substance[6].

The electrical and electronic engineering and automotive industries are among the largest consumers of BFRs. Flame retardants are used to produce plastic housings for consumer and office electronics, and for electronics with 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[7], including disposal[8-9].

In spite of the existing international and national legislation to prevent it, a number of studies have proved the presence of PBDEs and HBCD in new products[10], including children's toys[11-12], thermo cups and kitchen utensils[13], and carpet padding[15]. The studies concluded that these products were not intentionally treated with BFRs, but the contamination originated from recycled materials used to make the product.

This 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[14-16]. The current study is aimed at determining whether children's toys, hair accessories, office supplies, and kitchen utensils found on the Czech and Serbian markets are still affected by the same unfortunate practice. There were similar studies conducted in both countries in the years 2015 – 2018, so this new research is also opportunity to look at potential trends in levels of BFRs in consumer products made of recycled black plastic. It is also an opportunity to generate the first data about levels of TBBPA in the studied products.

Materials and methods

Sixty (60) and twenty-five (25) samples of consumer products made of black plastic were obtained in two European countries, Czechia and Serbia respectively in 2020. In the Czech Republic, samples were purchased at small stores while in Serbia, both in small stores and markets. The samples were expected to be made from recycled plastic. Children toys, hair accessories, kitchenware and office supplies were of primary interest.

As X-ray florescence is a useful technique for determining the presence of PBDEs in plastics[17-18], 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[18], samples with bromine and antimony levels over 1000 ppm (mg/kg) 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) were not identified among the collected samples, consumer goods down to 140 ppm (mg/kg) bromine and 100 ppm (mg/kg) antimony were selected and sent for lab analysis. In one case (the lid holder), a sample without any detection of antimony was used.

Together, twenty-one samples (including 6 toys, 2 hair accessories, 5 kitchen utensils, 5 office supplies and 3 other products) out of the total 85 collected items were analyzed for 16 PBDE congeners. For purposes of calculation, the components of the commercial PentaBDE mixtures include congeners BDE 28, 47, 49, 66, 85, 99, 100, and for OctaBDE mixtures include the following congeners: BDE 153, 154, 183, 196, 197, 203, 206, 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-indane (OBIND), 2,3,4,5,6-pentabromoethylbenzene (PBEB), and pentabromotoluene (PBT) were also analyzed in the samples.. Targeted BFRs were isolated by the triple extraction using n-hexane: dichloromethane (4:1, v/v).

Identification and quantification of PBDEs and nBFRs were performed using gas chromatography coupled with mass spectrometry in negative ion chemical ionization mode (GC-MS-NICI). Identification and quantification of HBCD isomers were performed by liquid chromatography interfaced with tandem mass spectrometry with electrospray ionization in negative mode (UHPLC-MS/MS-ESI-). The limit of quantification was 1 ng/g for BDE 206, 207 and 209 and 0.5 ng/g for 13 other analyzed PBDE congeners, ranged between 0.5-5 ng/g for nBFRs, and was 0.5 ng/g for HBCD and 5 ng/g for TBBPA.
The same analytical method was used for samples from 2020 as for the analyses of TBBPA in samples from 2018 which are published in this study for first time. They were conducted on samples described in the Toxic Loophole report[15] which were omitted due to publication time constrains.

Results and discussion
Laboratory analysis of 6 toys, 2 hair accessories, 5 kitchen utensils, 5 office supplies and 3 other products from 2 countries found 16 samples (76%) contained OctaBDE and 19 samples (90%) contained DecaBDE at concentrations ranging from 7 to 157 mg/kg and from 2 to 401 mg/kg respectively. TBBPA was found also in 16 samples (76%) ranging from 4 to 206 ppm. Concentrations under 1 ppm, are understood as an unintentional trace contamination (UTC). The highest measured concentrations of PBDEs were found in office supplies, followed by other consumer products, hair accessories, children's toys and kitchen utensils. Summary of the results is presented in Table 1. Ranges of HBCD, PBDEs, nBFRs, TBBPA and the total of analyzed BFRs concentrations, per country, are summarized in Table 2.

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

	Children's toys	Hair accessories	Kitchen utensils	Office supplies	Other products
Number of samples	6	2	5	5	3
OctaBDE	13-46	44-50	0.05-10	6-157	0.02-101
DecaBDE	50-127	52-134	0.03-46	66-401	0.19-232
ΣPBDEs	62-147	96-184	0.04-55	80-419	0.22-259
HBCD	<LOQ-3.8	<LOQ-5	<LOQ	<LOQ-0.95	0.23-0.87
ΣnBFRs	44-123	141-148	0.001-28	40-1311	0.007-302
TBBPA	58-174	76-166	0.05-6	4-206	0.5-122
ΣBFRs	242-334	400-415	0.09-89	130-1910	0.95-677
Total Br	7911- 1349	4580- 5866	140-928	444-15750	773-8647

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

Measured ranges of concentrations (mg/kg; ppm)	Country	Number of samples	HBCD	ΣPBDEs	ΣnBFRs	TBBPA	ΣBFRs
	Czech Republic	13	<LOQ-2	0.037-259	0.001-302	0.051-174	0.09-677
	Serbia	8	<LOQ-4.9	55-419	28-1311	6-206	89-1910

The composition of BFRs differs among individual samples without any specific concentration pattern suggesting heterogeneous plastics were recycled and used as inputs to the products. Moreover, novel BFRs occur in significant concentrations in sampled items except the kitchen utensils group. Among analyzed groups, kitchen utensils contained significantly lower concentrations of all tested substances. HBCD is minor in black plastic products analyzed in this study as this flame retardant was primarily used in polystyrene insulation that is not recycled into studied types of products. In comparison to samples from the Czech Republic, higher concentration of HBCD, PBDEs, nBFR and TBBPA were found in Serbian samples. The pan turner from Serbia is the only exception of TBBPA higher than 1 ppm among analyzed kitchen utensils. The lid holder that contained no antimony but more than 900 ppm of total bromine measured by XRF, had only trace contamination with PBDEs and TBBPA at level of 0.037 and 0.051 mg/kg respectively. It confirms that antimony level is crucial for potential selection of suspected items for following BFRs in both products and wastes[10,18].
Table 3 shows comparison of BFRs measured in samples of consumer products from black plastic obtained in both countries in previous years. Data for TBBPA in products sampled in 2018 have never been previously published. HBCD, DecaBDE and TBBPA levels are decreasing in both countries while the trend in novel BFRs levels moves in the opposite direction, and are slightly increasing in comparison with previous years. HBCD was used in polystyrene products in larger volumes rather than in plastic casings for electronics, so it can also be preferentially found in recycled polystyrene[19]. DecaBDE levels decreased most significantly among measured BFRs. It can be a result of global ban and previous national restrictions of this chemical but it is too early to evaluate this trend as we also see levels of OctaBDE in samples fluctuating up and down over time. We have to bear in mind that the number of samples in all years was very limited. There is missing data for TBBPA and

nBFRs levels from years 2015 – 2017 but comparison between 2018 and 2020 shows a rapid decrease in its content in sampled black plastic products.

Table 3. Comparison of measured levels of BFRs in black plastic products obtained in different years in the Czech Republic and Serbia. Data for 2015 – 2018 come from previous studies by IPEN and Arnika[15,20].

Year(s)	Country	Number of samples	HBCD (mg/kg)	Octa BDE (mg/kg)	Deca BDE (mg/kg)	nBFRs (mg/kg)	TBBPA** (mg/kg)
2015 - 2017	Czechia	33	0-375	0-513	2-2234	-	-
	Serbia*	3	NA	13-57	36-47	-	-
2018	Czechia	13	0-29	0-62	<LOQ-652	0-208	<LOQ-451
	Serbia	5	0-14	7-119	89-1494	20-1211	87-1229
2020	Czechia	13	<LOQ-2	0.005-101	33-232	0.001-302	0.051-174
	Serbia	8	<LOQ-4.9	10-157	45-401	28-1311	6-206

*2017 only; **analytical results for TBBPA from 2018 which are published here for the first time.

Although the difference between the sum of BFRs measured in this study and total content of bromine (Table 1) show potentially more BFRs present in the products, trends over time seems to be optimistic for most of the measured BFRs in this study except for nBFRs. However, the measured levels are still alarming.

Only five samples from Czechia had levels of PBDEs below 50 ppm (mg/kg) which is the optional provisional level for definition of hazardous POPs waste[a]. Those samples are four kitchen utensils and a shoehorn (other product). None of the Serbian samples had PBDEs below this threshold. EU applies less strict rules, not only for definition of POPs waste, but also for recycled products which are allowed to contain PBDEs in sum up to 500 ppm (mg/kg; UTC limit) while new virgin plastic products must meet a threshold of 10 ppm for each individual mixture of PBDEs (penta-, octa- and decaBDE)[23]. All products in this study meet the weak UTC limit set by the EU. Levels of PBDEs in Serbian samples were also higher than those observed recently in samples from African countries[24].

Health aspects: The brominated flame retardants found in the analyzed samples 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[1,25]. It is well documented that brominated flame retardants migrate from consumer products made of plastic including those analyzed in this study to household dust[26], and therefore are available for human absorption. Dermal exposure to PBDEs has, in a recent study, been shown to also be a significant exposure route[27].

The appearance of kitchen utensils with BFR-content adds to the concern and scale of PBDE intake by the human body through food ingestion. Cooking experiments with kitchen utensils containing PBDEs demonstrated considerable transfer of the POP-chemicals into the cooking oil[28]. When kitchen utensils containing PBDE are used, the transfer of PBDEs from the products is significantly intensified in comparison to the dermal contact.

Contamination of children's toys adds to the existing exposure paths, as children spend a significant amount of time on the ground in indoor having hand-to-mouth contact and playing with toys[29]. According to a Belgian survey[30], PBDE exposure from mouthing toys was found to be higher than the exposure through diet or dust.

Our findings of children's toys contaminated with PBDEs are alarming, because exposure occurs at the time of children's development. Developmental neurotoxicity and endocrine disruption[31] are part of PBDEs' properties that adversely affect children.

Potential health effects from the content of unintentional contaminants: 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[32-33]. These substances exhibit similar health effects as chlorinated dioxins (PCDD/Fs), for which the tolerable daily intake (TDI) recently was lowered by the EFSA[34]. Their influence on toddlers has been studied from several examples of toys made out of recycled black plastic. The conclusion of a recent study was 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"*[35].

Risks from the content of TBBPA: TBBPA is a cytotoxicant, immunotoxicant, and thyroid hormone agonist with the potential to disrupt estrogen signaling[6,36]. Recent studies identified this chemical as "probably carcinogenic to humans"[37]. Human exposure studies revealed dust ingestion and diet as the major pathways of TBBPA exposure in the general population. Dust ingestion constitutes for toddlers 90% (TBBP-A) of overall exposure[38]. Furthermore, exposure to TBBPA may occur prenatally and via breast milk. It is therefore important that women of childbearing age avoid exposure to TBBPA, including usage of consumer products containing this chemical. As it is shown in this study many consumer products contain TBBPA in significant levels.

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[a] For definition of POPs waste so called Low POPs Content level (LPCL) is used. See Article 6 of the Stockholm Convention which defines what is POPs waste[21]. LPCL for each of the POPs listed under the Stockholm Convention is set in General Technical Guidelines for POPs Waste, updated by the Basel Convention[22].

Conclusion and recommendations

The present study has shown that children's toys, kitchen utensils and other consumer products found on the Czech and Serbian markets are affected by unregulated recycling of e-waste plastics which carry BFRs into new products. Levels of PBDEs, HBCD and TBBPA decreased in studied products in comparison with previous years while the concentration of novel BFRs increased. Observed levels of toxic BFRs are still too high and evidence of their influence on human health shows the need for stricter regulation, not only of already banned BFRs (PBDEs and HBCD), but also of their regrettable substitutes (TBBPA and novel BFRs).

To stop the practice of using electronic and automotive waste plastic for production of recycled plastic and making consumer products out of it, strict Low POPs Content Levels need to be set. Without further regulation of BFRs as a class it is likely that toxic new BFRs that are currently used without any regulation will continue to circulate in the waste streams, just as their persistent counterparts. It is a challenge for the rising circular economy.

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