Comparison of Levels of BFRs and PBDD/Fs in Consumer Products Made of Recycled Plastic from African, Arab and Latin American Countries

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1 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. 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 endocrine disrupting[6].

Recycling of plastics containing BFRs into new consumer products was discussed in number of previous studies. These products are present everywhere, including Europe or Africa. However some BFRs are accompanied by very toxic polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs)[7], brominated dioxins in short. Their presence in consumer products was studied less than BFRs.

Brominated dioxins exhibit similar health effects as chlorinated dioxins (PCDD/Fs)[8-12]. They can, for example, affect brain development, damage the immune system and fetus, or induce carcinogenesis[11]. "Both groups of compounds show similar effects, such as induction of aryl hydrocarbon hydroxylase (AHH)/EROD activity, and toxicity, such as induction of wasting syndrome, thymic atrophy, and liver toxicity"[9].

The tolerable daily intake (TDI) for PCDD/Fs was lowered by the European Food Safety Authority (EFSA) recently[13]. 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"*[14].

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[15-17]. The current study is aimed at determining whether children's toys, hair accessories, office supplies, and kitchen utensils contain also PBDD/Fs and what is the relation between content of BFRs in these products and levels of brominated dioxins.

2 Materials and methods

Fourteen samples out of 95 Rubik's like cubes included in the study from 2017 and 47 consumer products from recent analysis in eleven African and Arab countries were selected for the analysis for brominated dioxins. Selection of the samples for BFRs analyses was based on measured levels of total bromine and antimony. Selected products were analyzed for PBDEs, HBCD, novel BFRs (nBFRs) and TBBPA by special chemical analysis. Their selection by screening with a handheld NITON XL3t 800 XRF and following chemical analyses for mentioned groups of BFRs were described in previous studies[18,19]. Products analyzed for brominated dioxins come from eleven countries: Argentina, Brazil, Cameroon, Gabon, Jordan, Kenya, Mexico, Morocco, Nigeria, Tanzania and Tunisia.

Sample pre-treatment and chemical analysis for PBDD/Fs: All plastic materials were extracted using ultra sonication with solvent mixture n-hexane-dichloromethane. After pre-concentration, the primary extract was redissolved in methanol. For chemical PBDD/F analysis, the extract portions were taken up with fresh hexane and adjusted to a defined volume. Aliquots of these solutions were fortified with eleven $^{13}C_{12}$-labeled PBDD/F internal standards and further purified by several liquid chromatographic clean-up steps. Prior to the HRGC/HRMS analysis, additional $^{13}C_{12}$-labeled PBDD/F standards were added to the PBDD/F fractions as recovery standards (all standards from CIL, Round Rock, TX 78665, U.S.A.).

A capillary gas chromatograph (Thermo Scientific GC-Ultra), coupled with a high-resolution mass spectrometer (Thermo Scientific MAT 95XP HRMS), was used for instrumental PBDD/F analysis. The GC was equipped with a PTV injection port (Programmable Temperature Vaporizer) and a 30 m DB-5MS capillary column (Agilent J&W GC column, 0,25 mm inner diameter and 0,1 µm film thickness). The HRMS was operated in the SIM–Mode, monitoring selected masses of the molecular ion cluster. Furthermore, masses of the molecular ions of PBDEs were monitored to check for potential co-elution of PBDEs with PBDFs, which can lead to false positive results. Native PBDD/F congeners were quantified via the internal $^{13}C_{12}$-labeled PBDD/F standards (Isotope dilution and method of the internal standard).

All PBDD/F analyses were performed on the basis of the DIN EN ISO/IEC 17025:2005 accredited MAS test method MAS_PA002:2013-10 for the analysis of PCDD/Fs, PBDD/Fs and PCBs in solid matter.

Toxic Equivalency Factors (TEFs) for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) were used for calculation of WHO-TEQ levels of PBDD/Fs in samples, as suggested by World Health Organization (WHO) experts[12].

3 Results

Fourteen samples included in this report, of consumer products made of recycled black plastic, were analyzed for BFRs first and afterwards also for the contents of polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs), or brominated dioxins in short. The results are summarized in Table 1 below, and compared with previously analyzed levels of BFRs. The content of BFRs in these products was discussed and evaluated in previous reports[19-21].

Table 3. Overview of the analytical results for the analyzed PBDD/F congeners in nine samples from seven countries. The results for the sum of PBDEs and TBBPA in those samples are also given for comparison. The level of PBDD/Fs is expressed in total amounts as well as in toxic equivalents (TEQ).

Sample ID	Sample description	Country	TBBPA (ppm)	ΣPBDEs (ppm)	nBFRs (ppm)	17 PBDD/F congeners (pg TEQ/g)	17 PBDD/F congeners (pg/g)
ARG_04	Rubik's-like cube	Argentina	na	708	463	727	170,753
BRZ-T-7A	toy car	Brazil	8	169	55	750	153,827
CMR-0009-HA	Headdress	Cameroon	52	210	116	774	261,923
Ga-29-01	Lipstick	Gabon	85	194	81	378	88,197
Ga-08-01	Knife	Gabon	2	182	32	1,430	243,422
Jo-T-1N	toy car	Jordan	99	390	689	3,580	741,123
Jo-T-1C	Rubik's-like cube	Jordan	185	254	441	8,180	1,120,526
KEN-T-6	toy car	Kenya	0.5	270	48	6,590	1,590,463
GUAD-RECPL	semi-finished prod.	Mexico	<10	32	379	14,100	2,622,294
MOR-HA-3A	Headdress	Morocco	29	315	263	885	173,957
NIG_06	Rubik's-like cube	Nigeria	na	1,780	1,390	860	203,362
NIG_11	Rubik's-like cube	Nigeria	na	1,218	537	56	6,694
TZ-K-33A	Spoon	Tanzania	33	52	57	210	28,751

TUN-T-18A	toy chess	Tunisia	36	195	116	513	176,370

Levels in the range of 56 – 14,100 pg TEQ/g were measured in the fourteen consumer products from African, Arab and Latin American countries. The highest levels were found in toys from Jordan and Kenya among consumer products, while the lowest level of 56 pg TEQ/g of PBDD/Fs was measured in a Rubik's like cube from Nigeria. Level of 14,100 pg TEQ/g in semi-finished product used for shoe heels exceeded highest levels in toys from Jordan or Kenya by two folds.

4 Discussion

The level of PBDD/Fs, 8,180 pg TEQ/g, which was measured in a Rubik's-like cube from Jordan in this report, is twice as much as the highest level of PBDD/Fs of 3,821 pg TEQ/g measured in black plastic consumer products so far, which was observed in a key fob obtained in Germany[7]. Even much higher level was measured in semi-finished product for shoe heels obtained from the workshop in Mexico.

The minimum levels of PBDD/Fs in the collection of samples investigated in this report are also several times higher than those measured in previous samples. 1,305 pg TEQ/g was the average level of PBDD/Fs measured in 13 samples from 11 various countries previously[22], and that equals approximately half the average level of 2,780 pg TEQ/g of PBDD/Fs in the samples from the current report. High levels of PBDD/Fs were measured in samples from African, Arab and Latin American countries despite the levels of the sum of PBDEs being below 500 ppm, which is the current UTC level set for recycled products in EU legislation.

PBDD/Fs have previously been found in plastics treated with a variety of BFRs[23,24]. It is well documented that PBDD/Fs are formed as unintentionally produced POPs during the production of different kinds of flame retardants[25,26]. They can be also formed during further reprocessing when plastics containing brominated flame retardants experience thermal stress[27].

Brominated dioxins have been observed in the environment in various levels. They are not always expressed in TEQs, and thus hard to compare with the levels measured in TEQs in this study. For example, levels around 40 pg TEQ/g have been observed in dust in elementary schools in Taiwan[28].

In total values, the levels of PBDD/Fs in consumer products in this study ranged from 6,694 – 2,622,294 pg/g. These levels are in most of cases higher than the PBDD/F levels measured in waste incineration bottom ash from Taiwan in a previous study (1,600 – 31,000 pg/g)[29]. The levels observed in most of the toys and other consumer products in this study also exceeded those previously found in residues of pyrolyzed printed circuit boards (231–490 pg I-TEQ/g)[30] and in waste incineration ash after de novo synthesis expressed in total levels (7,200 pg/g PBDD/Fs)[31].

Taken together, the data demonstrates that the sampled children's products and consumer products included in this study, obtained in African, Arab and Latin American countries, contained significant levels of PBDD/Fs. The measured PBDD/F levels in this study were on a scale previously found in a variety of hazardous wastes, including waste incineration bag filter ash, waste incineration bottom ash, residues of burned printed circuit boards, and in waste incineration ash after de novo synthesis.

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 (mg/kg) as proposed by the African region, and accompanied with setting an unintentional trace contamination level at 10 ppm (mg/kg), the same level as is applied in the EU for virgin plastics[37].

5 Conclusions

The present study has shown that children's toys, hair accessories, office supplies, and kitchen utensils found on markets in African, Arab and Latin American countries are affected by unregulated recycling of e-waste plastics which carry also brominated dioxins into new consumer products at levels higher or equal to those observed in hazardous waste such as waste incineration ashes for example. PBDD/Fs accompany BFRs as unintentionally produced by-products already during their production. To stop this toxic cycle, strict Low POPs content levels for PBDEs need to be set. Also nBFRs recycling in plastics has to be stopped in order to address contamination with brominated dioxins.

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