TOXIC SOUP FLOODING THROUGH CONSUMER PRODUCTS

Brominated dioxins recycled together with flame retardants into toys and other consumer products -now a widespread problem

Decabromodiphenyl ether (DecaBDE) is the last of the polybrominated diphenyl ethers (PBDEs) added to the list of brominated flame retardants (BFRs) that are banned and/or regulated by the Stockholm Convention on Persistent Organic Pollutants (POPs). As such it should also have an international limit for its content in wastes. That limit is the Low POP Content Level (LPCL) which defines whether the waste containing this chemical can be considered as POPs waste or not. Strict provisions for the management and destruction of POPs waste are required under Article 6 of the Stockholm Convention.

DecaBDE was used broadly as an alternative to previously banned or restricted PBDEs (Penta- and OctaBDE), so it is now very common in plastics used in electronics which are becoming waste. Studies have demonstrated that DecaBDE is the most abundant PBDE congener in plastic products from recycled plastic originated mostly from e-waste [1-3].

DecaBDE is not the only problematic chemical found in consumer products made of recycled black plastic. Sampling and analysis has also found unintentionally produced POPs, specifically brominated dioxins (PBDD/Fs), in plastics treated with a variety of BFRs [4, 5]. It is well documented that PBDD/Fs are formed as unintentionally produced POPs during production of different flame retardants [6, 7], and DecaBDE in particular [6]. This is a pattern of contamination that is similar and parallel to the contamination of polychlorinated biphenyls (PCBs) with chlorinated dioxins (PCDD/Fs) as an inevitable by-product during PCB production.

Brominated dioxins

Brominated dioxins (PBDD/Fs) have been found to exhibit similar toxicity and health effects as their chlorinated analogues (PCDD/Fs) [8-12]. They can for example affect brain development, damage the immune system and fetus or induce carcinogenesis [12].

"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." [10].

In general, brominated dioxins are subject to significantly less regulation than chlorinated dioxins. For example, PBDD/Fs are not currently listed under the Stockholm Convention [13], although there is clear evidence that they contain very similar properties to PCDD/Fs, which have been listed in Annex C of the Convention since its origin in 2001. In 2010, the Stockholm Convention POPs Review Committee recommended further assessment of PBDD/Fs including, *"releases from smelters and other thermal recovery technologies, including secondary metal industries, cement kilns and feedstock recycling technologies,"*[14].

Because brominated dioxins tend to be less regulated, there is less data about their presence in the environment. There is also very little information about their presence in consumer products and food, where they can have direct impacts on human health, including in vulnerable groups such as children and women of childbearing age.

Analyses of toys and other products for brominated POPs

IPEN in cooperation with Arnika and University of Technology and Chemistry Prague have previously collected and analyzed for PBDEs, hexabromocyclododecane (HBCD) and other brominated flame retardants (BFRs) in a number of samples of consumer products, particularly children's toys and products for women [1-3, 15-20]. In 2018, we also looked at levels of PBDD/Fs in some products previously analyzed for PBDEs and we found significant levels of these very toxic POPs. The results were published in the report released in November 2018 [21].

Results of analyses for brominated dioxins

IPEN & Arnika also analyzed additional samples of consumer products made of recycled plastics for BFRs and four of samples

Table 1. **Results of analyses for PBDD/Fs, DR CALUX, PBDEs, HBCD and TBBPA**

Country / Sample	Type	PBDD/Fs (pg TEQ/g)[1]	DR CALUX (pg TEQ/g)	PBDEs (ug/g)[2]	HBCD (ug/g)	TBBPA (ug/g)
Argentina ARG_04	Rubik's-like cube	727	1,200	708	1	na[3]
Brazil BRZ-T-7A	Toy, car	750	590	169	0.2	8
Cambodia KAM-H-1	Hair diadem	1,950	1,500	358	0.3	10
Canada CA-H-1C	Hair rack	1,500	1,300	718	< 0.01	1
Czechia JI_11	Cube	2,159	17,000	2,614	91	na[3]
Czechia SIX_02	Hairclip	60	210	1,623	8	na[3]
France FR-T-3	Toy revolver	2,058	520	1,077	1	314
Germany D-TO7	Key fob	3,821	820	511	2	307
India IND_11	Rubik's-like cube	690	1,300	593	2	na[3]
Japan JP-O-1	Smart phone holder	1,200	560	693	0.5	37
Nigeria NIG_06	Rubik's-like cube	860	4,800	1,780	9	na[3]
Nigeria NIG_11	Rubik's-like cube	56	370	1,218	8	na[3]
Portugal PT-T-10a	Toy small guitar	1,137	270	3,318	2	37

1 Zero was used for PBDD/F congeners, declared in the analytical protocol by MAS as not detected above the limits of quantification.

2 Reflects the sum of congeners contained in commercial PentaBDE, OctaBDE and DecaBDE (BDE 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, 196, 197, 203, 206, 207, 209).

3 Not analyzed

with positive results for PBDEs were also analyzed for PBDD/Fs by both the bioassay DR CALUX method as well as GC-MS instrumental analysis in BDS (Netherlands) and MAS (Germany) laboratories. Their analytical methods are described in Annex to this brief paper. Results for all samples analyzed for previous papers as well as this one, are summarized in Table 1.

Nine toys, three hair accessories and one smart phone holder made from black recycled plastic were selected for analysis. These samples had already been analyzed for PBDEs from previously researched sets of samples.

Dioxin-like activity and PBDD/Fs were found in all thirteen consumer products (Table 2). Levels of DR CALUX dioxin-like activity ranged between 210 to 17,000 pg TEQ/g. Note that 1,000 pg TEQ/g can be considered as equivalent to the proposed hazardous waste limit[1] for chlorinated dioxins in the Stockholm Convention [22, 23]. Consumer products exceeding this proposed chlorinated dioxin hazardous waste limit included a hair diadem (ornament) from Cambodia, hair rack from Canada, a toy cube from Czechia and Rubik's-like cubes from Argentina, India, and Nigeria. In addition, the dioxin-like activity found in many of these consumer products is similar to levels found in waste incineration bag filter ash, which can contain 370 – 25,000 pg TEQ/g as measured by DR CALUX [24]. Toy samples with levels of dioxin-like activity similar to waste incineration bag filter ash included a toy car from Brazil, a cube toy from Czechia, a toy revolver from France, a key fob from Germany and Rubik's-like cubes from Argentina, India, and Nigeria. In addition, samples of consumer products from Canada, Cambodia and Japan were found with levels of dioxin-like activity similar to waste incineration bag filter ash.

Levels of 17 toxic PBDD/F congeners ranged from 5,600 – 386,000 pg/g and 56 – 3,800 pg WHO-TEQ/g. These levels are similar to and in some cases higher than PBDD/F levels measured in waste incineration bottom ash from Taiwan (1,600 – 31,000 pg/g and 28 – 61 pg TEQ/g) [25]. In addition, levels observed in some toys, as well as in consumer products from Cambodia, Canada and Japan exceeded those found in residues of pyrolyzed printed circuit boards (231–490 pg I-TEQ/g) [26] and in waste incineration ash (after de novo synthesis) (7,200 pg/g PBDD/Fs) [27].

Taken together, the data showed that the sampled children's products and consumer products obtained in Canada, Cambodia and Japan contained significant levels of PBDD/Fs. The measured PBDD/F levels were on the scale 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. More than half of the products exceeded the proposed chlorinated dioxin hazardous waste limit.

1 The Low POPs Content Level defines whether waste is considered as POPs waste or not. POPs waste, according to Article 6 of the Stockholm Convention should be: „Disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed so that they do not exhibit the characteristics of persistent organic pollutants or otherwise disposed of in an environmentally sound manner when destruction or irreversible transformation does not represent the environmentally preferable option or the persistent organic pollutant content is low," and at the same time it is *„(iii) Not permitted to be subjected to disposal operations that may lead to recovery, recycling, reclamation, direct reuse or alternative uses of persistent organic pollutants; and (iv) Not transported across international boundaries without taking into account relevant international rules, standards and guidelines;"* 13. Stockholm Convention, *Stockholm Convention on Persistent Organic Pollutants (POPs) as amended in 2009. Text and Annexes*. 2010: Geneva. p. 64.

Conclusions and recommendations

The data showed that the sampled children's toys and hair clip contained significant levels of PBDD/Fs ranging from 5,600 – 386,000 pg/g and 56 – 3,800 pg WHO-TEQ/g. The measured PBDD/F levels were on the scale 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. Half of the products exceeded the proposed chlorinated dioxin hazardous waste limit.

The use of contaminated plastic for toys and personal care products is a direct route of consumer exposure in children and adults, not only to PBDEs, but also to brominated dioxins.

More than half of analyzed products made of recycled plastic with levels of PBDEs that meet current regulatory proposals of 1,000 ppm PBDEs, contained 730 - 3,800 pg WHO-TEQ/g of brominated dioxins. This signals that weak regulation of PBDEs can pose potential harms not only from PBDEs, but also from PBDD/Fs. To provide more protective regulations the following policies are needed:

1. **Not to allow the proposed 1,000 ppm limit for DecaBDE in recycled plastics, but rather establish a 10 ppm limit.**
2. **A more stringent limit for definition of POPs waste (Low POPs Content Level),[2] ideally to establish it as 50 ppm for the sum of all regulated PBDEs.**
3. **To withdraw the recycling exemptions for commercial Penta- and OctaBDE as they are currently established in Brazil, Cambodia, Canada, EU, Japan, South Korea and Turkey.**
4. **Add PBDD/Fs to the Stockholm Convention for global reduction and elimination.[3]**
5. **Improve the definition of electronic waste within the framework of the Basel Convention.**

The problem of PBDD/Fs as contaminants in plastic and their potential route into recycled plastics appears to be significant. The total amount of PBDD/Fs as an impurity in the produced volume of PBDEs is estimated to be 1,000 t [4]. This amount represents a significant burden for human health and environment, considering that PBDD/Fs exhibit toxicity similar to PCDD/Fs [28].

There is also a need to stop the uncontrolled movement of electronic waste and BFR-contaminated plastics from the automotive industry into developing and transition countries. Up to 80% of electronic waste produced globally was likely *"dumped, traded or recycled under inferior conditions"* [29]. Large volumes of PBDD/Fs have been found in electronic waste disposed in Nigeria [4, 30, 31]. Plastics from these types of waste flows were the likely origin of recycled plastics for the production of toys analyzed in this study. New analyses confirm that it is worldwide problem and exposure to PBDEs from recycled plastic is widespread problem.

Annex: Analytical methods
DR CALUX® analyses

Briefly, H4IIE cells (70–95 % confluence) stably transfected with an aryl hydrocarbon receptor (AhR)-controlled luciferase reporter gene construct were cultured in α-minimum essential medium (MEM) supplemented with 10 % (v/v) fetal calf serum (FCS) under standard conditions (37 °C, 5 % carbon dioxide (CO2), 100 % humidity). Cells were exposed in triplicate on 96-well microtiter plates containing the standard 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) calibration range, a DMSO blank (99.9 %) and samples. Following a 24-h incubation period, cells were lysed. Finally, 100 µL of luciferin-containing solution was added, and the luminescence was measured using a luminometer (Centro XS3, Berthold Technologies, Germany). The 2,3,7,8-TCDD calibration curve, generated from DR CALUX® readings, resulted from a serial dilution of 2,3,7,8-TCDD standards (0.3, 0.6, 1.0, 2.0 and 3.0 pM per well). The amount of 2,3,7,8-TCDD bioanalytical equivalents (TEQs) was quantified by comparison of the response in the test sample with the calibration curve for 2,3,7,8-TCDD [32].

GC-HRMS analysis for PBDD/Fs

For chemical PBDD/F analysis, the extract portions provided by BDS 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 [28, 33].

2 This limit is called "Low POPs Content" level according to the definition in the Stockholm Convention, and its definition is established by the technical experts group under the Basel Convention in General Technical Guidelines for ESM of POPs waste. This level is defined in Annex IV to POPs Regulation No 850/2004 (POPs Regulation) in EU.

3 Analysis guidelines for screening and chemical analysis of all toxic relevant PBDD/Fs, PBBs and PCDD/Fs in recycled plastic and products thereof could also help.

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