Toxic recycling, or How unsorted waste may contaminate consumer products in the Czech Republic

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Introduction

Flame retardants are chemical substances that seemed to be helpful in a number of applications. Brominated flame retardants (BFRs) were widely used in furniture upholstery, car seats, electronics, and building insulation [1-3]. Their purpose was to increase fire safety, because plastic materials showing much higher flammability started to be used. However, changes in scientific knowledge, efforts to protect consumers, as well as public pressure, contributed to gradual ban of the most toxic ones of them in the EU (Regulation on Persistent Organic Pollutants, Directive on Restriction of Hazardous Substances in Electrical and Electronic Equipment, or Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals) and globally (Stockholm Convention on Persistent Organic Pollutants). Polybrominated diphenyl ethers (PBDEs: penta-, octa-, and decaBDE), and hexabromocyclododecane (HBCD) are ranked among the so-called persistent organic pollutants (POPs) that are decomposed very hardly 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 human hormonal, endocrine, immune and reproductive systems, and affect nervous system development and children intelligence negatively [5].

One of the most important consumers of brominated flame retardants (BFRs) is electrical and electronic engineering industry that uses them for producing plastic housings of consumer and office electronics, and electronics working with heat sources, in order to meet the safety standards. Because BFRs are added into the material as additives that are not chemically bound to the plastic polymer in question, they are released during the whole lifecycle of the product [6], including the time when it becomes waste [7-10].

In spite of the existing international and European legislation, a number of studies proved presence of polybrominated diphenyl ethers (PBDEs) in new products and household equipment [11], including children's toys [12-14], thermo cups and kitchen utensils [14-16], and carpet padding [17]. The found concentrations of PBDEs showed that the products were not intentionally treated with the banned chemicals, but they contained PBDEs as a consequence of recycling materials containing the toxic substances.

Our study is a continuation of investigations of IPEN an Arnika that found octa- and decaBDE and HBCD in Rubik's cubes [18]. We conducted additional sampling to further examine whether toxic substances are being recycled into different consumer products on the Czech market.

Materials and methods

The black parts of 47 consumer products (toys and hair accessories) bought in the Czech Republic were tested because manufacturers often blacken the colour of recycled plastics for aesthetic reasons. Products were screened for bromine using a handheld XRF analyser to identify samples with significant bromine levels (hundreds of ppm). Fifteen positive samples were analysed for PBDEs and HBCD. Targeted BFRs were isolated by extraction with the solvent mixture n-hexane:dichloromethane (4:1, v/v). Identification and quantification of PBDEs was performed using gas chromatography coupled with mass spectrometry in negative ion chemical ionization mode (GC-MS-NICI). Identification and quantification of 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 of PBDEs ranged between 0.5–5 ppb and was 10 ppb for HBCD.

Results and discussion

Laboratory analyses of 7 samples of toys and 8 samples of hair accessories made of black plastic, bought in the Czech Republic, showed that all the samples were contaminated by octa- and decaBDE in concentrations of 1 - 513 ppm, and 6 – 2234 ppm, respectively. Eleven samples contained HBCD (0.02 – 91 ppm). Concentrations of BFRs in the individual samples are summarized in Table 1 and 2.

Table 1: Concentrations of BFRs (ppm) in toys

Sample	Trans-former	Trans-former	Car	Shoe toy	Cube (mole)	Rubik's cube	Rubik's cube
OctaBDE	1.11	7.80	3.94	30.60	380.15	43.24	120.03
DecaBDE	7.03	42.33	52.34	269.98	2234.12	300.88	1074.64
ΣPBDEs	8.14	50.15	56.30	300.58	2614.34	344.24	1194.71
HBCD	< 0.01	< 0.01	0.40	91.07	0.76	0.30	0.98

Table 2: Concentrations of BFRs (ppm) in hair accessories

Sample	Hair clip	Hair clip	Head-dress	Head-dress	Hair clip	Hair brush	Hair comb	Hair comb
OctaBDE	35.44	220.71	1.51	30.69	31.58	55.86	513.65	31.33
DecaBDE	147.61	1 402.59	6.43	204.14	67.34	132.15	147.55	200.16
ΣPBDEs	183.11	1 623.44	7.94	234.88	99.09	188.42	662.42	231.57
HBCD	<0.01	7.71	<0.01	5.20	0.02	0.04	0.09	0.10

The levels of BFRs found in some of these products exceed regulatory limits. For example, if the products were made of virgin material, 11 of them would break the POPs regulation concerning octaBDE concentrations (>10 ppm). If the products were electronics, 3 of them would exceed the regulatory limit because of high decaBDE concentration (>1000 ppm). The same products would also exceed the limit set by the European legislation, REACH. When these goods become waste, they would be regarded as hazardous waste if the protective limit of 1000 ppm were used. If the stricter protective limit for POPs waste, 50 ppm, were used, 13 of 15 analysed samples would exceed it, in particular because of the high decaBDE content.

The above-mentioned data prove that toxic chemicals, used as flame retardants, present in electronic waste are recycled into plastic toys and hair accessories found on the Czech market. The composition and concentrations of

BFRs in the samples shows the fact that the products were manufactured from recycled plastics obtained from electronic waste. In order to ensure non-flammability of the material, higher concentrations of the chemicals would have to be used [19]. The hair care products and hair accessories themselves are not treated with flame retardants, because it is not required by the safety standards.

In accordance with the previous studies, our research shows the alarming consequence of PBDEs recycling - contamination of products intended for the most sensitive part of the population, namely children and women in productive age. Results of our study are in accordance with the conclusions of the Stockholm Convention expert committee [20] that warned that recycling exemptions for PBDEs would result in contamination of articles where it would be difficult to identify and remove them for technical and economic reasons. In contrast with products intentionally treated with PBDEs in the period before their ban, in the case of recycled products, information is lost on what concentrations of PBDEs enter the new products, and what kind of goods may be contaminated by them.

Returning POPs back into the manufacturing chain raise concerns about the performance of the Stockholm Convention, credibility of recycling, and EU Circular Economy Strategy. If we do not want to allow all the current stock of penta- and octaBDE to circulate in waste, new products, and the environment in an uncontrolled way, it is necessary to ensure immediate end of the recycling exemptions, to set a sufficiently strict protective limit for waste, and to prevent both an entry and recycling of toxic substance into new products and in wastes. It will disable not only free use of electronic waste with PBDEs contents for recycling, but also its export into developing countries. The EU Circular Economy Strategy needs to make sure consumers are protected from toxic substances when the waste is recycled and confront chemical, product and waste legislation.

Technically, PBDEs may be separated from waste materials by means of X-ray (XRF, XRT) and laser methods, or of spark and infrared spectrometry [21-22]. The separated toxic materials may be disposed of by one of the non-combustion technologies [23], i.e. supercritical water oxidation [24] or process Creasolv® [25]. Solutions exist also for reducing flammability of products – both in the field of chemical alternatives to toxic flame retardants and in the field of material design [26].

Our study shows that the banned brominated flame retardants get, because of the recycling exemptions and too high thresholds for toxic waste, into new products where they were not present historically, and, moreover, that are intended for the sensitive part of the population.

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