Hexabromocyclododecane (HBCD) found in e-waste is widely present in children's toys

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Introduction

Brominated flame retardants have been widely added to plastics, foams, textiles, and construction materials. Hexabromocyclododecane (HBCD or HBCDD) was mainly applied in extruded and expanded polystyrene foam for building insulation, but also in car upholstery and textiles. HBCD has also been used in high impact polystyrene (HIPS) in casings of electrical and electronic equipment (UNEP 2010).

HBCD is a substance of very high concern requiring REACH Authorisation before it is used in the EU[1]. It is persistent, bioaccumulative and toxic, damaging human fertility and the unborn child and may also cause harm to breast-fed children[2]. In 2013, HBCD was listed in Annex A of the Stockholm Convention for global elimination, with specific exemptions for expanded and extruded polystyrene in buildings[3]. The exempted polystyrene treated with HBCD must be labelled for its easy identification and separation from the waste stream (part VII, Annex A of the Convention). Article 6 of the Convention also obliges parties to take measures to reduce or eliminate releases from stockpiles and wastes for chemicals listed in the Convention Annexes to avoid POPs wastes being *"subjected to disposal operations that may lead to recovery, recycling, reclamation, direct reuse or alternative uses of persistent organic pollutants"* and to ensure that *"wastes are disposed of in such a way that persistent organic pollutant content is destroyed or irreversibly transformed, so that the wastes do not exhibit the characteristics of persistent organic pollutants or are otherwise disposed of in an environmentally sound manner"*. On the other hand, articles containing HBCD that are reaching obsolescence could be subject to the treaty's waste provisions only if they exceed hazardous waste limits known as "low POPs content levels" (LPCL). These levels define the value at which wastes are considered to be POPs wastes. Only wastes containing POPs above the LPCL must be avoided in the recycling stream and be addressed according to strict treaty obligations.

The POPs Review Committee expressed concern about recycling materials containing HBCD noting that, *"HBCD will likely be spread into articles that will be difficult to identify, as previously determined by the POPRC for recycling products containing pentaBDE and octaBDE."* Increasing the waste burden of POPs in developing countries is another consequence of toxic recycling and exemptions for use. The Committee expressed concern about *"articles and products in use containing hexabromocyclododecane being exported, especially to developing countries and countries with economies in transition"* (POPRC 2013).

[1] REACH Authorisation list https://echa.europa.eu/addressing-chemicals-of-concern/authorisation/recommendation-for-inclusion-in-the-authorisation-list/authorisation-list/-/dislist/details/0b0236e1807e0deb
[2] ECHA profile of HBCD https://echa.europa.eu/brief-profile/-/briefprofile/100.042.848
[3] Stockholm Convention decision http://chm.pops.int/Portals/0/download.aspx?d=UNEP-POPS-COP.6-SC-6-13.English.pdf

Our survey asked the question if the recycling of e-waste plastics may lead to contamination of new products with HBCD. To answer the question, we examined HBCD in Rubik's cubes, a children's product usually made of recycled plastic, along with several other types of plastic toys.

Materials and methods

Rubik's cubes and several other consumer goods were screened for bromine using a handheld XRF analyzer to identify samples with significant bromine levels (hundreds of ppm). Positive samples were analyzed for HBCD in an accredited laboratory at the University of Chemistry and Technology, Prague, Czech Republic.

A sample of plastic material from the product was placed into a glass tube and a mixture of n-hexane:dichloromethane (4:1, v:v) was added. The target analytes were leached from the sample for 24h, after that the glass tube was extracted for three hours using ultra-sonication. The pre-concentrated extract was purified using gel permeation chromatography, on the Bio-Beads S-X3 column and cyclohexane ethylacetate as a mobile phase. Finally the eluate was evaporated to dryness and subsequently dissolved in methanol for the final instrumental analysis.

Analysis of HBCD isomers was performed using ultra-high performance liquid chromatography interfaced with tandem mass spectrometry with electrospray ionization in negative mode (UHPLC-MS/MS-ESI-) 6495 Triple Quadrupole (Agilent Technologies): triple quadrupole LC/MS system, 1290 Infinity II UHPLC (Agilent Technologies). Acquity UPLC BEH C18 (100 mm × 2.1 mm ×1.7 μm) column was used for separation of target substances. Mobile phase consisted of 5mM ammonium acetate in deionized water (A) and methanol (B).

Results and discussion

Laboratory analysis of eighty-eight Rubik's cubes and sixteen additional samples from twenty-four countries identified forty-five samples (43%) contained HBCD at concentrations ranging from 1 to 1586 ppm. Seven samples (7%) contained HBCD at concentrations higher than 100 ppm – one of the LPCL for HBCD. Two samples exceeded the higher LPCL of 1000 ppm. Results are demonstrated in Tables 1 and 2 below.

Overall, the results indicate that HBCD found in e-waste is widely present in children's toys made of recycled plastic. The key provision to address the HBCD recycling issue in the Stockholm Convention is the value set for "low POPs content level" (LPCL). LPCL defines the value at which wastes are considered to be POPs wastes and therefore must be *"Disposed of in such a way that the persistent organic pollutant content is destroyed or irreversibly transformed"* (Stockholm Convention Article 6.1 d ii). Thus, LPCL is a crucial tool to control potential releases of POPs due to improper handling of POPs wastes. In the absence of national regulations, strict LPCLs may be the only mechanism to prevent widespread transboundary movements of POPs-contaminated products and wastes, accelerating the rate and scope of human exposure to POPs.

There are two LPCL proposals for HBCD. These numbers come from a comprehensive report elaborated by EU consultants (ESWI and BiPRO 2011). The authors preferred to set LPCLs at the level of 100 ppm, which covers all pure waste fractions but also relatively strong diluted waste mixtures. The higher value of 1000 ppm was restricted to separated waste types *„for a restricted time frame in order to facilitate the enforcement of the LPCLs once the LPCLs will be put into force"* (ESWI and BiPRO 2011).

Table 1: Range of concentration (ppm) of HBCD in Rubik's cubes per country

Purchased in	Number of samples	HBCD
Argentina	3	0 - 1586
Bangladesh	2	1 - 5
Brazil	2	0
Canada	4	1 - 20
China	5	0
Czech Republic	6	0 - 42
Germany	2	0
Hungary	1	0
India	6	0 - 78
Indonesia	5	0 - 541
Japan	4	0
Kenya	3	0 - 1280
Mexico	5	0 - 2
Nepal	3	0 - 1
Nigeria	14	0 - 9
Philippines	4	0 - 13
Poland	4	0
Russia	3	2 - 691
Slovakia	1	0
South Africa	3	1 - 60
Sri Lanka	2	0 - 1
Sweden	1	0
Thailand	2	0 - 5
United Kingdom	3	0 - 5

Table 2: Concentration (ppm) of HBCD in children's products from the Czech Republic, Slovakia, and the Netherlands

Item	Purchased in	HBCD
Toy - robot	Czech Republic	0
Toy - finger skateboard	Czech Republic	0
Toy - gun	Czech Republic	375
Toy – car 1	Netherlands	21
Toy – car 2	Netherlands	0
Children painting brush	Czech Republic	2
Children hockey stick	Czech Republic	0
Thermo cup	Czech Republic	0
Hair clip 1	Czech Republic	1
Hair clip 2	Czech Republic	5
Headdress 1	Czech Republic	0
Headdress 2	Czech Republic	19
Headdress 3	Czech Republic	24
Headdress 4	Slovakia	0
Comb 1	Czech Republic	0
Comb 2	Slovakia	0

The finding of this study demonstrates that unfavourable management of waste containing HBCD may result in dispersal of HBCD into children's articles and in the loss of the long-term credibility of recycling. If weak LPCLs are adopted, then more POPs can flow into consumer products and transboundary movement of POPs in contaminated materials such as e-waste, incineration residues, polystyrene, or polyurethane foam will expand and accelerate. The weaker value of 1000 ppm could encourage toxic recycling and waste dumping in the absence of national regulations prohibiting the practices. The recycling issue is especially relevant to HBCD due to widespread informal sector recycling of e-waste in developing countries. The flow of this contaminated material is likely to be from developed countries to developing countries where management costs are lower and regulations weaker. If this is allowed to happen then the objectives of the Stockholm and Basel Conventions will be permanently undermined at the expense of human health and the environment. This effect has already been demonstrated by Breivik et al (2011) due to POPs waste export from developed countries to Africa and Asia. A secretariat noted that, *"It is estimated that at least 50 % of WEEE [waste electrical and electronic equipment] is collected outside of the official take-back systems in the EU, part of which is then exported to developing countries as used equipment or illegally. Illegal shipments originate mainly from Europe, North America, Japan, Australia and the USA with common destinations in Asia (including China, Hong Kong, India, Pakistan and Vietnam) and Africa (including Ghana, Nigeria, and Benin). In addition to WEEE, plastics from WEEE are also reported to be exported to developing countries in Asia."* (UNEP 2016). A weak LPCL will enshrine this arrangement and unnecessarily expose new populations to POPs when contaminated materials are shipped as recycled materials or other products without restriction.

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