A survey of PBDEs in recycled carpet padding

Joseph DiGangi, PhD and Jitka Strakova
Dioxin, PCBs, and Wastes Working Group
IPEN
April 2011

Abstract

Polyurethane foam containing brominated flame retardants is recycled in some countries to make products such as foam padding for carpets (known as rebond). The Stockholm Convention Persistent Organic Pollutants (POPs) Review Committee raised concerns about the practice since brominated flame retardants listed in the treaty could be carried over and diluted into the recycled products contributing to further human and environmental exposure. Recycled foam carpet padding from Canada, Hungary, Kyrgyzstan, Nepal, Thailand, and USA was screened using handheld XRF for bromine and analyzed in the laboratory for polybromodiphenyl ethers (PBDEs). Bromine was not detected at significant levels in samples from Nepal, Kyrgyzstan, and Thailand. Laboratory analysis of 26 samples from Canada, Hungary, and USA found that twenty-three samples contained at least one PBDE listed in the Stockholm Convention (88%) with levels ranging from 1 – 1130 ppm. The results raise concerns about recycling materials containing flame retardants which results in worker and consumer exposure to substances listed in the Stockholm Convention for global elimination, particularly for children crawling on carpeted floors. To our knowledge, this is the first publically available investigation of PBDEs in carpet foams which may contain recycled materials.

Acknowledgments

The authors would like to thank IPEN participating organizations and NGOs who performed market surveys and/or provided samples: Alaska Community Action on Toxics (USA), Arnika Association (Czech Republic), Canadian Environmental Law Association (Canada), Center for Environmental Solutions (Belarus), Center for Public Health and Environment Development (Nepal), Chemical Sensitivities Manitoba (Canada), Clean Air Action Group (Hungary), Clean New York (USA), Day Hospital (Egypt), Ecology Center (USA), Eco-Accord (Russia), Ecological Alert and Recovery (Thailand), EDEN (Albania), National Toxics Network (Australia), PAN Afrique (Senegal), PAN Ethiopia (Ethiopia), Reach for Unbleached (Canada), Toxics Link (India), UNISON (Kyrgyzstan), and Washington Toxics Coalition (USA).

Introduction

In May 2009, the 4th Conference of the Parties of the Stockholm Convention (COP4) listed certain congeners contained in commercial pentabromodiphenyl ether (PentaBDE) [1] and

[1] The listing includes tetrabromodiphenyl ether and pentabromodiphenyl ether, meaning 2,2',4,4'-tetrabromodiphenyl ether (BDE-47, CAS No: 40088-47-9) and 2,2',4,4',5-pentabromodiphenyl ether (BDE-99, CAS No: 32534-81-9) and other tetrabromodiphenyl and pentabromodiphenyl ethers present in commercial pentabromodiphenyl ether.

octabromodiphenyl ether (OctaBDE)[2] in Annex A for global elimination.[3] The decision included specific exemptions which may last until 2030 allowing the recycling of materials containing these substances such as plastics and foam into new products. COP4 also requested the POPs Review Committee (POPRC) to evaluate this practice. The POPRC prepared terms of reference and commissioned a technical review of the recycling practice[4] and at its 6th meeting developed recommendations for the 5th Conference of the Parties (COP5).[5]

The key POPRC recommendation from the October 2010 meeting was to *"…eliminate brominated diphenyl ethers from the recycling streams as swiftly as possible"*. The Committee noted that, *"Failure to do so will inevitably result in wider human and environmental contamination and the dispersal of brominated diphenyl ethers into matrices from which recovery is not technically or economically feasible and in the loss of the long-term credibility of recycling."*

The POPRC technical review noted that a principal recycling route of polyurethane foam containing brominated flame retardants is through carpet padding (called rebond), mattresses, and furniture and asserted that the issue was concentrated in developed countries, particularly Canada and the United States of America. Since the recycling of products containing POPs has implications for worker and consumer exposure, IPEN asked whether PentaBDE or OctaBDE were present in recycled foam carpet padding in various developing and developed countries.

Survey design

NGOs conducted brief market surveys in all UN regions to determine the presence of rebond underlay. As predicted by the POPRC technical review, colleagues in developing and transition countries had extreme difficulty finding the product. In contrast, developed country colleagues from Canada, Hungary, and the US easily found and purchased rebond carpet padding for analysis. To target likely samples containing PBDEs, most samples were screened for bromine using an Olympus InnovX Delta XRF device and positive samples were analyzed for PBDEs at the Institute of Chemical Technology, an accredited laboratory in the Czech Republic. Polybrominated diphenyl ethers (PBDEs) were extracted from the foam samples in a Soxhlet apparatus (7hrs, dichloromethane), the solvent evaporated, and samples re-dissolved in a mixture of hexane:dichloromethane (1:1, v/v). Clean-up of crude extract was employed on florisil mini-column for GC/MS analysis with a quadrupole analyzer operated in negative chemical ionization (NCI). The samples were injected onto the GC system using a pulsed split-less injection technique and a DB-XLB capillary column (15m x 0.18 mm x 0.07 um) was used for the chromatographic separation of target analytes. Uncertainty in measurements varied 15 – 20%.

[2] The listing includes hexabromodiphenyl ether and heptabromodiphenyl ether, meaning 2,2',4,4',5,5'-hexabromodiphenyl ether (BDE-153, CAS No: 68631-49-2), 2,2',4,4',5,6'-hexabromodiphenyl ether (BDE-154, CAS No: 207122-15-4), 2,2',3,3',4,5',6 heptabromodiphenyl ether (BDE-175, CAS No: 446255-22-7), 2,2',3,4,4',5',6-heptabromodiphenyl ether (BDE-183, CAS No: 207122-16-5) and other hexabromodiphenyl and heptabromodiphenyl ethers present in commercial octabromodiphenyl ether.

[3] Decisions SC-4/14 on the listing of hexabromodiphenyl ether and heptabromodiphenyl ether and SC-4/18 on the listing of tetrabromodiphenyl ether and pentabromodiphenyl ether.

[4] UNEP/POPS/POPRC.5/10, annex I, decision POPRC-5/1

[5] UNEP/POPS/POPRC.6/2/Rev.1 also reported as the Annex to UNEP/POPS/COP.5/15

Results

Foam samples were collected from six countries: Canada, Hungary, Nepal, Kyrgyzstan, Thailand, and USA (Table 1). Screening results with the XRF device showed that some foam samples from Canada and Hungary contained bromine above 50 ppm indicating the possibility of brominated flame retardant contamination. In contrast, bromine was not detected at significant levels in samples from Nepal, Kyrgyzstan, and Thailand. Samples from the USA were not screened with the XRF device due to scheduling difficulties. Samples containing bromine by XRF screening were sent for laboratory testing for PBDEs along with samples purchased from five cities in the USA. All together, 26 samples from Canada, Hungary, and USA were analyzed in the laboratory using GC/MS for congeners corresponding to PentaBDE, OctaBDE, and DecaBDE.

Table 1. Origin of the samples

Country	City
Canada	Ottawa, Toronto, Victoria, Winnipeg
Hungary	Budapest
Kyrgyzstan	Bishkek
Nepal	Kathmandu
Thailand	Bangkok
USA	Ithaca (NY), Schenectady (NY), Anchorage (AK), Ann Arbor (MI), and Seattle (WA)

Twenty-three samples contained at least one PBDE listed in the Stockholm Convention (88%). Three samples contained no PBDEs: Stainmaster from Toronto, Canada; Healthier Choice from Anchorage, USA; and Right Step 28/Mohawk in Ithaca USA. Data in Annex 1 shows that different samples from the same manufacturer could contain widely varying amounts and types of PBDEs. For example Vitafoam produced recycled foam for sale in Canada with levels of PentaBDE that varied from 0 to 1052 ppm. In the USA, Legett and Carpenter produced recycled foam with levels of PentaBDE ranging from 1 to 1033 ppm.

The highest levels measured in the samples were for PentaBDE followed by OctaBDE and DecaBDE respectively. The highest PentaBDE levels were measured in Black Gold from Ottawa, Canada (1130 ppm), Vitafoam from Victoria, Canada (1052 ppm), and Leggett and Platt from Anchorage, Alaska (1033 ppm). The OctaBDE levels were measured in Eco Foam from Toronto, Canada (263 ppm), Eco Foam from Winnipeg, Canada (145 ppm), and Black Gold from Ottawa, Canada (86 ppm).

Table 2 shows that twenty samples contained PentaBDE (77%) with levels ranging from 1 – 1130 ppm. Thirteen samples (50%) contained PentaBDE levels above 50 ppm, the provisional low POPs content limit for PCBs and other original POPs listed in the Stockholm Convention.[6] Seventeen samples contained OctaBDE (65%) with levels ranging from 1 – 263 ppm. Seven samples (27%) contained OctaBDE levels above 50 ppm, the provisional low POPs content limit for PCBs and other original POPs listed in the Stockholm Convention.[6] DecaBDE was present in

[6] apart from dioxins for which the provisional low POPs limit is 15 ppb

more samples, but at lower levels than PentaBDE and OctaBDE which ranged from 1 – 163 ppm.

Table 2. Summary of PBDE levels in recycled carpet padding foam samples

BDE	No. samples containing specific BDE	Range (ppm)	No. samples >50 ppm
Penta	20 (77%)	1 – 1130	13 (50%)
Octa	17 (65%)	1 – 263	7 (27%)
Deca	23 (89%)	1 – 166	6 (23%)

In August 2010 the European Union (EU) adopted Commission regulation 757/2010[7] which updated the EU POPs regulations[8] with low POPs content limits for the POP PBDEs. The values included are:

Tetrabromodiphenyl ether 10mg/kg (ppm)
Pentabromodiphenyl ether 10mg/kg (ppm)
Hexabromodiphenyl ether 10mg/kg (ppm)
Heptabromodiphenyl ether 10mg/kg (ppm)

While these levels appear more protective than those set previously for the original Stockholm POPs (50 mg/kg apart from dioxins and furans) the levels for PBDEs are actually only marginally lower because the POPs were always supplied in technical mixtures. IPEN considers that all the current provisional low POPs content limits are unreasonably high and are not consistent with the aims of the Convention. A more appropriate and protective standard for the low POPs content limit would be 10mg/kg (ppm) total POP concentration and 1 ug/kg (ppb) for dioxins and furans. [9]

Table 3 shows that 13 samples (50%) exceeded EU low POPs limits for both TetraBDE and PentaBDE, both components of the PentaBDE commercial mixture. Twelve samples (46%) exceeded EU low POPs limits for HexaBDE, a major component of the OctaBDE commercial mixture.

[7] European Commission, (2010). Commission Regulation (EU) No 757/2010 of 24 August 2010 amending Regulation (EC) No 850/2004 of the European Parliament and of the Council on persistent organic pollutants as regards Annexes I and III Text with EEA relevance. Official Journal of the European Union OJ L 223: 29–36
[8] European Commission (2004). Commission Regulation (EC) No 850/2004 of the European Parliament and of the Council of 29 April 2004 on persistent organic pollutants and amending Directive 79/117/EEC NOTE: Whilst this was published in the Official Journal of the European Union L158 of 30th April 2004. A Corrigendum to the Regulation was subsequently published in the Official Journal L229/5 of 29th June 2004, Official Journal of the European Union L 229/5.
[9] IPEN Dioxin, PCB and Waste Working Group (2009) POPs Waste COP4 Brief: Low POPs Position Paper http://www.ipen.org/ipenweb/documents/ipen%20documents/low%20pops%20cop4.pdf

Table 3. Summary of PBDE levels in recycled carpet padding foam samples compared to EU low POPs content levels (10 ppm)

BDE	No. samples containing specific BDE	Range (ppm)	No. samples >10 ppm
TetraBDE	19 (73%)	1 – 398	13 (50%)
PentaBDE	19 (73%)	1 – 732	13 (50%)
HexaBDE	14 (54%)	1 - 81	12 (46%)
HeptaBDE	10 (38%)	1 - 5	0 (0%)

Discussion

The results of this brief survey indicate that recycled foam containing PentaBDE, OctaBDE, and DecaBDE was readily available on the market in three developed countries. Most of the recycled foam samples contained at least one PBDE listed in the Stockholm Convention (88%) with levels ranging from 1 – 1130 ppm. A significant portion of the samples exceeded the provisional low POPs content limit for PCBs and other original POPs listed in the Stockholm Convention (50 ppm). Half the samples contained PentaBDE at levels that exceeded this limit. Approximately one-fourth of the samples contained OctaBDE at levels that exceeded this limit. Recently, the European Union updated low POPs content limits for congeners present in the PentaBDE and OctaBDE commercial mixtures. The data shows that half the samples exceeded the EU low POPs content limits for congeners in the commercial PentaBDE mixture. For congeners in the OctaBDE mixture, 46% of the samples exceeded the EU low POPs content limits.

The levels of PBDEs found in this study were substantially higher than those found by Chen et. al. in a sample of foam toys in China which had a median value of 1012 ng/g (ppb).[10] Another difference between this survey and the data from Chen et. al. is that in the toy study the concentrations decreased in order of DecaBDE, OctaBDE, and PentaBDE. This led the authors to suspect debromination of DecaBDE. In contrast, in this survey of recycled foam carpet backing, PentaBDE was found at the highest levels followed by OctaBDE and DecaBDE respectively. This indicates predominant contamination of PentaBDE as a result of recycling.

The results raise concerns about human exposure to persistent organic pollutants listed in the Stockholm Convention. The POPRC technical review notes that, *"The incorporation of PentaBDE in carpet cushion which generates the highest levels of dust in the zones where children are playing is therefore of particular concern. It is notable that dust release increases as carpet ages thus exposing the children of poorer families more heavily – an exposure reflected in the published literature"*.[11] Resuspension of dust from carpet has been reported in research commissioned by US EPA which found that up to 40% of the particulate matter between 1 – 10 um could be re-suspended with older carpets having significantly higher

[10] Chen SJ, Ma YJ, Wang J, Chen D, Luo XJ, Mai BX, (2009). Brominated flame retardants in children's toys: concentration, composition, and children's exposure and risk assessment. Environ Sci Technol 43(11): 4200-4206
[11] UNEP/POPS/POPRC.6/INF6

emission factors.[12] The POPRC technical review indicates that *"The consequences of increased exposure of toddlers and children playing close to the floor together with the higher dust intake is consistent with the much higher levels of PBDE reported in children compared with adults."* [13] Johnson-Restepo[14] estimated that 77% of body burdens in one- to five- year-olds and 58% in those aged six to 11 could be attributable to dust and because these compounds are semi-volatile and are not chemically bound to substrates, they can migrate into the indoor environment - particularly into house dust. [15] Worker exposure to PBDEs is another concern about recycling materials containing them since it can occur during the recycling process as well as during carpet removal and installation.

Stapleton[16] reported that foam recyclers and carpet layers in the United States have body burdens that are an order of magnitude higher than those in the national health and nutrition examination survey (NHANES) of the general population. She concluded that "…*these data suggest individuals recycling foam-containing products, and/or using products manufactured from recycled foam (i.e.,carpet padding), have higher body burdens of PBDEs, and thus may be at higher risk from adverse health effects associated with brominated flame retardant exposure*."

The POPRC evaluated both PentaBDE and OctaBDE before recommending them for listing in the Stockholm Convention. The Risk Profile for PentaBDE notes POPs properties such as long-range transport, persistence, and bioaccumulation along with adverse effects such as *"…reproductive toxicity, neurodevelopmental toxicity and effects on thyroid hormones in aquatic organisms and in mammals.*"[17] The PentaBDE Risk Profile also notes that PentaBDE can be transferred from the mother to the embryo and to the infant during breast feeding. A recent study by Herbstman et. al. examined associations between PBDE levels in cord blood and at different ages and various indices of neurodevelopment and found significant associations between pre-natal levels of PentaBDE congeners and decreased IQ in children. [18] More recently Gascon[19] found that postnatal exposure to PBDE 47 (a component of PentaBDE) was statistically significantly related to an increased risk of symptoms of attention deficit and to higher risk of poor social competence. Exposure to PentaBDE congeners is thus potentially significant to childhood development both pre- and post-natally. Furthermore, exposures in some

[12] RTI International (2007) Resuspension and tracking of particulate matter from carpet due to human activity, EPA/600/R-07/131, US EPA
[13] UNEP/POPS/POPRC.6/INF6
[14] Johnson-Restrepo B, Kannan K, (2009) An assessment of sources and pathways of human exposure to polybrominated diphenyl ethers in the United States. Chemosphere 76(4): 542-548
[15] Eskenazi B, Fenster L, Castorina R, Marks A R, Sjödin A, Rosas LG, et al. (2011) A comparison of PBDE serum concentrations in Mexican and Mexican-American children living in California. Environ Health Perspect. in Press
[16] Stapleton HM, Sjődin A, Jones RS, Niehuser S, Zhang Y, Patterson DG (2008) Serum levels of polybrominated diphenyl ethers (PBDEs) in foam recyclers and carpet installers working in the United States. Environ Sci Technol 42(9): 3453-3458
[17] Stockholm Convention POP Review Committee (2006) Risk Profile for Pentabromodiphenyl ether, UNEP/POPS/POPRC.2/17/Add.1
[18] Herbstman JB, Sjödin A, Kurzon M, Lederman SA, Jones RS, Rauh V, Needham LL, Tang D, Niedzwiecki M, Wang RY, Perera F (2010a). Prenatal exposure to PBDE and neurodevelopment. Environ Health Perspect 118(5): 712-719
[19] Gascon M,Vrijheid M, Martínez D, Forns J, Grimalt J, Torrent M, Sunyer J. (2011). Effects of pre and postnatal exposure to low levels of polybromodiphenyl ethers on neurodevelopment and thyroid hormone levels at 4years of age, Environ International 37(3): 605-611

vulnerable groups are already too high. Eskenazi[20], reporting high levels of PBDEs in the serum of Mexican children living in California concluded "*Given the growing evidence documenting potential health effects of PBDE exposure…the levels in young children noted in this study present a major public health challenge*." The Risk Profile for OctaBDE notes POPs properties and hazards such as, *"….delayed neurotoxicity and immunotoxicity which may be particularly relevant in the assessment of both human health and ecosystem risks."* [21]

The foam recycling industry has defended the practice of recycling foams and plastics containing PentaBDE and OctaBDE despite the global agreement to eliminate them under the Stockholm Convention. The industry recognized potential regulatory pressures as early as 2003 when the International Sleep Products Association recommended working with the polyurethane foam industry to, *"…remove and prevent further legal restrictions on the recycling of foam. Specifically several [USA] states have or are considering bans on the use of certain PBDE fire retardants in foam. These laws may have the effect of limiting the use of post-consumer foam in foam carpet underlay, the primary market for used mattress foam."* [22] One of the arguments made by proponents of recycling foam containing PBDEs is the economic benefit of recycling. However, this also needs to take into account the harm from human and environmental PBDE exposure. The POPRC technical review addressed this argument using the example of the USA recycling market and concluded that, *"An indicative assessment of the health costs associated with PUF[polyurethane foam] recycling shows that total damages can be estimated at close to $USD 6 billion/year. The commercial value of the North American rebond market, by contrast, is estimated to be less than $USD 15 million/year."*[23]

The data presented in this study shows significant levels of PBDEs listed in the Stockholm Convention that are present in a developed country consumer product that occupies large areas of homes and public spaces. The Stockholm Convention expert committee recognized this problem along with the companion problem of recycling plastics containing PBDEs. In 2010, the POPRC recommended eliminating PBDEs from recycling streams such as foam and plastics as soon possible. The POPRC Technical Review notes that, "*The PBDE in the current stocks and recycling flow is contributing to further contamination at levels which the evidence presented in this report indicates are causing harm to human health and the environment. The reduction of further damage requires strict control of these flows and the cessation of recycling."* [24]

Recommendations

COP5 should welcome the recommendations of the PORPC on the elimination of brominated diphenyl ethers from the waste stream; request special consideration by developed country Parties to implement the POPRC recommendations; and request the Secretariat to update COP6 on efforts to eliminate brominated diphenyl ethers from the recycling streams as swiftly as possible.

---

[20] Eskenazi, B., Fenster, L., Castorina, R., Marks, A. R., Sjödin, A., Rosas, L. G., et al. (2011). A comparison of PBDE serum concentrations in mexican and mexican-american children living in california. Environ Health Perspect. in Press

[21] Stockholm Convention POP Review Committee (2007) Risk Profile for Octabromodiphenyl ether, UNEP/POPS/POPRC.3/20/Add.6

[22] UNEP/POPS/POPRC.6/INF6

[23] UNEP/POPS/POPRC.6/2/Rev.1

[24] UNEP/POPS/POPRC.6/2/Rev.1

COP5 should request developed country Parties and other Parties practicing recycling of materials containing brominated diphenyl ethers to:

- Notify the Secretariat of their intent to use this exemption in accordance with Decision SC-4/14
- Immediately stop the export of these materials except for the purpose of environmentally sound disposal
- Rapidly implement effective screening and separation techniques to separate materials containing the substances before recycling proceeds
- Minimize occupational exposure and assess occupational exposures of staff working in facilities where articles and wastes potentially containing brominated diphenyl ethers are stored, sorted, treated, recycled, recovered or disposed
- Promote and facilitate public awareness-raising on the potential harm of materials containing polybrominated diphenyl ethers currently in use
- Generate and collect information on releases of brominated diphenyl ethers and unintentionally produced brominated organic compounds such as polybrominated dibenzodioxins and polybrominated dibenzofurans (PBDD/PBDF) in emissions to air and in the solid residues from thermal processes used in treating materials contaminated with brominated diphenyl ethers
- Report on their efforts to eliminate brominated diphenyl ethers from the recycling streams as swiftly as possible during the interim period between COP5 and COP6

Annex 1. PBDEs in recycled carpet backing foam samples (ppm)

Note that it is not possible to be precise about the distribution of the commercial mixtures because of the temporal changes in the components of these mixtures (see, for example, the Appendices to the POPRC technical review[25] for a detailed review.)

No.	Location	Producer	PentaBDE[1]	OctaBDE[2]	DecaBDE[3]	Total
1	Ottawa, Canada	Black Gold	1130	86	100	1316
2	Toronto, Canada 2	Vitafoam Pizazz Blue	0	0	2	2
3	Toronto, Canada 3	Vitafoam Chormex Grey	1	0	7	8
4	Toronto, Canada 5	Vitafoam	3	1	2	6
5	Toronto, Canada 6	Stainmaster Yellow/White	0	0	0	0
6	Toronto, Canada 7	Vitafoam Gold Back	531	49	68	648
7	Toronto, Canada 8	Eco Foam	1	263	16	280

[25] UNEP/POPS/POPRC.6/INF/6

8	Victoria, Canada 2	Vitafoam	1052	76	76	1204
9	Winnipeg, Canada 1	Ultra-Bond	436	34	42	512
10	Winnipeg, Canada 2	Vita-Guard	532	40	37	609
11	Winnipeg, Canada 3	Eco Foam	1	145	20	166
12	Budapest, Hungary	Diego Padiszonyeg Alatet	12	1	5	18
13	Ithaca, New York USA 1	Mohawk Vitality Green	3	0	26	29
14	Ithaca, New York USA 2	Mohawk Right Step 28	0	0	0	0
15	Ithaca, New York USA 3	Mohawk Absolute	64	12	166	242
16	Schenectady, New York USA 1	Leggett and Platt Plush Step Deluxe	280	27	15	322
17	Schenectady, New York USA 2	Leggett and Platt Berber Bond Deluxe	222	29	51	302
18	Anchorage, Alaska USA 1	Leggett and Platt Super Magic	575	45	10	630
19	Anchorage, Alaska USA 2	Leggett and Platt Ultra Magic	1033	65	30	1128
20	Anchorage, USA 3	Healthier Choice Light Green	0	0	0	0
21	Anchorage, Alaska USA 4	Leggett and Platt Syntex III	1	0	0	1
22	Ann Arbor, Michigan USA 1	Carpenter 9b-386lb Pad	707	60	36	803
23	Ann Arbor, Michigan USA 2	Carpenter 18b-7 16th Memory Foam	2	0	0	2
24	Ann Arbor, Michigan USA 3	Carpenter 45 – 7 16th 8 lb pad	992	65	13	1070

25	Ann Arbor, Michigan USA 4	Healthier Choice sov based 7 16th	0	0	1	1
26	Seattle, Washington USA	Legett and Platt Rebond 6 pound	67	41	99	207

[1] Components of PentaBDE include the following congeners: BDE47, 49, 66, 85, 99, 100

[2] Components of OctaBDE include the following congeners: BDE153, 154, 183, 196, 197, 203, 206, and 207. Note that in most samples (88%), congeners 196, 197, 203, 206, and 207 contributed less than 10% of the total concentration.

[3] DecaBDE includes BDE209