A SURVEY OF PBDES IN RECYCLED CARPET PADDING

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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 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]. The consultant's report[5] and associated Annexes[6] were reviewed at the 6th meeting of the PORC in October 2010. Key recommendations for consideration by the 5th Conference of the Parties (COP5)[7] included taking action 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 indicated 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 we investigated whether PentaBDE or OctaBDE were present in recycled foam carpet padding in various developing and developed countries.

Materials and methods

Brief market surveys were conducted in all UN regions to determine the presence of rebond underlay. As predicted by the POPRC technical review, it was extremely difficult to find the product in developing and transition countries. In contrast, developed country colleagues from Canada, Hungary, and the US easily found and purchased rebond carpet padding for analysis. To target padding likely to contain 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%. For purposes of calculation: components of PentaBDE include the following congeners: BDE47, 49, 66, 85, 99, 100; components of OctaBDE include the following congeners: BDE153, 154, 183, 196, 197, 203, 206, and 207; and DecaBDE included BDE209. Note that in most samples (88%), congeners 196, 197, 203, 206, and 207 contributed less than 10% of the total concentration.

Results and discussion

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. 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.[8] 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.[8] DecaBDE was present in 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[9] which updated the EU POPs regulations[10] 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 ether10mg/kg (ppm)

While these levels appear more protective than those set previously for the original Stockholm POPs (50 mg/kg[8]) the levels for PBDEs are actually only marginally lower because the POPs were always supplied in technical mixtures.

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.

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%)

This is, so far as the authors are aware, the first publicly available information of this kind. The results 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-quarter 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.

Stapleton[11] 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*." Our results show that this exposure is likely to be continued by the exemption allowing recycling of POPs into products.

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 1,012 ng/g (ppb).[12] 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. There are implications for exposure to POPs for workers and consumers in developed countries using recycled foam and increasing risks of exports of POPs to developing countries lacking any capacity to treat these POPs in either products containing rebond or in wastes. COP5 of the Stockholm Convention agreed in April 2011 only to "encourage" parties to ensure that waste materials containing POP BDEs are not exported to developing countries and countries with economies in transition and the COP "encourages" parties to take appropriate steps to facilitate this[13].

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References

[1] Stockholm Convention (2009) Decision SC-4/18 on the listing of tetrabromodiphenyl ether and pentabromodiphenyl ether. 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.

[2] Stockholm Convention (2009) Decisions SC-4/14 on the listing of hexabromodiphenyl ether and heptabromodiphenyl ether. 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] Stockholm Convention (2009)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

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

[8] Basel Convention (2007). Updated general technical guidelines for the environmentally sound management of wastes consisting of, containing or contaminated with persistent organic pollutants (POPs). (note the 50 ppm low POPs limits relates to POPs apart from dioxins for which the provisional low POPs limit is 15 ppb)

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[10] 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.

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[12] Chen SJ, Ma YJ, Wang J, Chen D, Luo XJ, Mai BX, (2009) Environ Sci Technol 43(11): 4200-4206

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