IT'S ALL ABOUT PENTA: INFORMING DECISION-MAKERS ABOUT THE PROPERTIES OF PENTA-BDE AND ITS REPLACEMENTS

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Introduction

An extensive body of scientific research over the last decades has documented the accumulation of halogenated flame retardants in humans, animals, and all media studied; adverse animal and human health effects; as well as the persistence, bioaccumulation, and toxicity of many chemicals in this class. There is not data to show whether these chemicals increase or decrease fire safety in various applications. While halogenated flame retardants slow ignition and reduce maximum heat release, they also increase carbon monoxide, soot, and other toxic effluents that are the most frequent cause of fire deaths. In spite of well-documented adverse health effects and unproven fire safety benefits, the use of halogenated flame retardants continues to grow, with brominated fire retardant (BFR) sales increasing 50% between 2005 and 2008[1].

Decision-makers need access to comprehensible research results so they can make better decisions about the flammability standards that lead to the use of these chemicals. For example, many exposure and health research papers on pentabrominated diphenyl ethers (PBDEs) begin by saying that they save lives and that there are 209 congeners with a multitude of uses. Such statements leave the public and decision-makers uncertain how to proceed to reduce exposure. However, our review of exposure and health studies shows that most scientific research about PBDEs is actually about one commercial mixture, penta-BDE. Penta-BDE was primarily used in North American to treat polyurethane foam to comply with a California flammability regulation called Technical Bulletin 117 (TB117). As a consequence of TB117 compliance, penta-BDE was used for many years at levels of three to six percent by weight in furniture, baby products and carpet padding foam, all products with high levels of human contact. This high exposure has led to high human body burdens of penta-BDE and an association of exposure with adverse human health effects. However, when reporting results most studies refer to the penta-BDE congeners as "PBDEs" rather than specifying the penta-BDE mixture. If researchers were to explicitly relate their results to penta-BDE, a specific chemical mixture primarily used to meet a specific flammability standard, decision-makers might better understand the problem and try to solve it by modifying the standard to attain fire safety without such chemicals.

Background on PBDEs

The well studied class of brominated flame retardants called PBDEs consist of ten different homologue groups mono- to deca-, that contain 209 congeners, defined by the number and position of bromine atoms on the diphenyl ether backbone. Different compounds have different chemical, accumulation, and toxicological properties [2]. Three commercial mixtures of PBDEs have been used most extensively: (1) decabromodiphenyl ether (deca-BDE), (2) octabromodiphenyl ether (octa-BDE), and (3) pentabromodiphenyl ether (penta-BDE). The major constituents of penta-BDE are BDE-47, -99, and -100, with lesser contributions from BDE-153, -154, and -85. The major congener found in octa-BDE is BDE-183 with minor contributions from BDE-203 and several octa- and nona-BDEs. Deca-BDE contains mostly BDE-209 as well as low levels of nona-BDEs. Penta-BDE was added to Penta-BDE was used at levels of three to six percent of the weight of foam. Octa-BDE was used primarily in plastics in circuit boards and small appliances, while deca-BDE is used in television and computer casings, as well as in textiles [3]. In 1999 and 2001, 98% and 95% respectively, of the usage of penta-BDE, was in North America, in large part to meet TB117 [4, 5]. Penta-BDE was banned in California in 2003 due to its persistence and toxicity; eight other states and the European Union (EU) followed suit. In 2004, Chemtura (previously Great Lakes Chemical), the

sole U.S. manufacturer, voluntarily ceased production and in 2009 penta-BDE was listed as a persistent organic pollutant under the Stockholm Convention. However penta-BDE continues to be a global pollutant, moving from reservoirs in consumer products in homes into the biota. Its replacements are from the same family, used at similar concentrations, and appear to share penta-BDE's adverse characteristics.

Methods

The scientific literature was reviewed to determine which congeners were found to be present at significant levels in exposure studies and which were associated with adverse human health effects. We noted whether authors explicitly called congeners that were from the penta-BDE mixture "penta-BDE" or referred to them only as part of the larger grouping of PBDEs.

Discussion

1. A review of studies of PBDE exposure shows that the penta-BDE congeners are most frequently detected.

PBDEs have been measured in human serum, breast milk, and adipose tissue [6]. The congeners found in the greatest concentration in human serum in the U.S. general population are BDE-47, -99, -100, and,-153, which are the primary components of the penta mixture [7]. Deca-BDE is produced at much higher levels globally compared with penta-BDE. However the penta-BDE congeners are more persistent and bioaccumulative than those of the octa- or deca-BDEs [8]. A review 35 human breast milk biomonitoring studies from North America, Europe, Asia, and Australia found penta-BDE congeners at the highest levels in every study [3]. In human adipose tissue, BDE-47 and -153 are the most abundant congeners [9, 10, 11, 12]. Moreover, BDE-47 and BDE-99 are global pollutants and have been detected in populations in remote areas such as the Inuit and residents of the Faroe Islands [13, 14]. The half-lives of the penta congers in humans have been estimated to be 2 to 3 years except for BDE-153 which has an estimated half-life of 4 to 6 years [15]. Congeners of the octa-BDE and deca-BDE commercial mixtures appear to have shorter half-lives in humans, on the scale of days [16].

2. A review of studies of PBDE levels and health effects shows that penta-BDE congeners are the congeners most often associated with adverse health effects.

Associations between PBDE body burdens and measures of health effects (predominantly reproductive, endocrine, and neurodevelopmental effects) have been investigated in both human and animal studies. In 13 human epidemiology studies, most adverse health effects are associated with penta-BDE congeners (Table 1). Although, all of the studies reviewed show associations with one or more penta-BDE congeners and 11 studies found significant associations with only penta-BDE congeners, **12 of the 13 human health studies reviewed referred to the congeners as the larger category of PBDEs rather than penta-BDE.** Similarly, laboratory animal studies of PBDE toxicity also show most associations with penta-BDE congeners. In a 2007 review of the neurobehavioral effects of developmental PBDE exposures, 15 of 19 studies found neurotoxic effects with penta-BDE congeners [3]. In the same review, 10 of 11 studies finding adverse developmental thyroid effects were examining penta-BDE congeners.

Outside the U.S, deca-BDE is often the major PBE exposure, especially in e-waste disposal regions in Asia. Nonetheless most current human health associations are primarily with penta-BDE congeners.

3. Since a large portion of the penta-BDE ever produced is still found in furniture in use in North American, knowledge of its effects can encourage consumers to take precautions to reduce exposure.

Despite restrictions on its use, large amounts of upholstered furniture, carpet padding, and automobiles containing penta-BDE are still in use in the United States and Canada and will need to be disposed of after their lifetimes, creating outdoor reservoirs. Penta-BDE has been shown to leach from landfills and contaminate the environment [17, 18, 19, 20]. Because of its persistence, penta-BDE will remain in landfills and leach into the environment for decades. Over these extended time frames, landfill engineering systems, including basal and capping liners, gas and leachate collection systems, will inevitably degrade and lose their ability to contain the contaminants [21, 22]. Moreover, large volumes of materials containing penta-BDE are in the global recycling flow and will continue to be used in consumer products for a considerable time. The identification and responsible disposal of penta-BDE-

treated products is essential to prevent its future dispersal into the environment and the food supply. Consumers who are alerted to the problem of penta-BDE in their furniture can take measures to reduce dust exposure such as hand-washing, wet-mopping, and vacuuming with a HEPA filter.

A further problem is that the Stockholm Convention, while banning the production and use of penta-BDE and octa-BDE, is allowing the recycling of PBDE containing products. Polyurethane foam containing penta-BDE is being reused in rebonded carpet cushion and could be used other recycled products. Due to this exemption for recycled materials, carpet cushion that is contaminated with penta-BDE continues to be produced; recycling and carpet cushion installation workers are highly exposed [23]; and the exposure of the general public will continue for many more decades.

4. Emerging studies suggest that replacements for penta-BDE in North America may be similarly toxic and persistent.

Penta-BDE replacements currently in use in the United States and Canada include Chemtura's Firemaster 550® and tris (1,3-dichloro-2-propyl) phosphate, also called chlorinated Tris or TDCPP. Firemaster 550® contains: (1) triphenyl phosphate (TPP); (2) triaryl phosphate isopropylated; (3) 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB); and (4) Bis (2-ethylhexyl) tetrabromophthalate (TBPH) . These brominated compounds appear to be persistent and bioaccumlative and lack adequate health information. Two Firemaster 550® components, TBB and TBPH, have been detected in blubber of dolphins and porpoises near flame retardant production facilities in south China [24] as well as in seven arctic species [25]. Chlorinated Tris was removed from children's pajamas in the 1970s because it caused genetic mutations [26]. According to the Consumer Product Safety Commission, chlorinated Tris is a probable human carcinogen [27]. Recent studies show chlorinated Tris and Firemaster 550® components can migrate from foam products into indoor house dust [28].

5. There is no proven fire safety benefit from penta-BDE's primary use which was to meet California TB117, an ineffective flammability standard for furniture and baby product foam.

California's flammability standard TB117 has led to the use of flame retardants in California furniture for more than thirty years. Accordingly, the average penta-BDE levels in serum and house dust of Californians are the highest in the country [29]. Despite this, an analysis of fire data from 1980 to 2005 by the National Fire Protection Association (NFPA) does not show a greater reduction in the rate of fire deaths in California compared to that of other states without such a standard [30]. While flame retardants may reduce the time for a material to ignite and the peak heat release, they increase the carbon monoxide, toxic gases, and soot produced once the fire begins. Most fire deaths and most fire injuries result from inhalation of these gases and soot [31]. Table 2 shows the addition of penta-BDE to foam provided a three second delay in ignition and somewhat reduced heat release, but generates seven times the carbon monoxide and 70 times the soot [32]. Chlorinated tris shows a similar modest benefit while significantly increasing CO and soot. Moreover, when the flame retardants themselves eventually burn, they can produce highly toxic dioxins and furans [33]. Firefighters have high levels of several cancers which may be related to their high inhalation exposure to brominated dioxins and furans during fire events [34, 35].

Reducing the sources of ignition can prevent fires without adding potentially hazardous chemicals to consumer products. A 60% decrease in fire deaths in the United States since 1980 parallels the decrease in per capita cigarette consumption [36, 37]. Increased enforcement of improved building, fire, and electrical codes and the increased use of smoke detectors and sprinkler systems in new construction have also contributed to an increase in fire safety. An estimated 65% of reported home fire deaths in 2000-2004 resulted from fires in homes without working smoke alarms [36].

Conclusions

Although penta-BDE is no longer being manufactured, a substantial fraction of the penta-BDE commercial mixtures ever produced is still present in furniture, carpet padding, and seating for transportation. Already, penta-BDE is a widespread contaminant in remote places such as polar regions and the deep oceans, effectively acting as environmental "time bomb" as the compounds continue to migrate from indoor reservoirs to the environment [38].

In conclusion, it is actually about more than penta-BDE. While the primary exposure studied in the U.S. and more developed world is indeed to penta-BDE, new research is suggesting adverse health effects linked with deca-BDE in e-waste workers and residents in e-waste recycling regions in China and other developing nations [39].

Action is warranted to reduce exposure to penta-BDE, deca-BDE and their replacements. Banning chemicals has not proven effective in protecting health as related chemicals with similar properties are often substituted for the banned chemicals. Instead, the fire safety benefit as well as the health and environmental costs of flammability standards should be evaluated. Clear, focused scientific papers are needed to guide policy-makers as they consider new flammabity standards as well as possible modifications to current standards. If researchers clearly express in their studies that exposure risks and adverse health associations are being found specifically with penta-BDE or with deca-BDE, decision-makers can better investigate how to modify flammability standards to maintain fire safety without such harmful chemicals.

Table 1: Studies of human health associations with PBDE congener exposures

Study	Associated Health Effect	Congeners
[40] **Prenatal Exposure to PBDEs and Neurodevelopment** Herbstman et al. 2010	Lowered levels of mental and physical development in children	47, 99, 100
[41] **PBDE Concentrations in Women's Serum and Fecundability** Harley et al. 2010	Reduced fecundability	47, 99, 100, 153
[42] **Levels of polybrominated diphenyl ethers (PBDEs) in breast milk from central Taiwan and their relation to infant birth outcome and maternal menstruation effects** Chao et al. 2006	Adverse birth outcome	47, 99, 100, 209
[43] **Prenatal exposure to organohalogens, including brominated flame retardants, influences motor, cognitive, and behavioral performance at school age** Roze et al. 2009	Attention problems Decreased fine manipulative abilities	47 154
[44] **Polybrominated Diphenyl Ethers in Human Serum and Sperm Quality** Akutsu et al. 2008	Decreased sperm concentration Decreased testis size	153
[45] **Association of Brominated Flame Retardants With Diabetes and Metabolic Syndrome in the U.S. Population, 2003–2004** Lim et al. 2008	Diabetes Metabolic Syndrome	153
[46] **Flame retardants in placenta and breast milk and Cryptorchidism in newborn boys** Main et al. 2007	Cryptorchidism Increased serum LH	47, 100, 28, 66, 154
[47] **Polybrominated diphenyl ethers induce developmental neurotoxicity in a human in vitro model: evidence for endocrine disruption** Schreiber et al. 2010	Reduced hNPC migration Inhibition of hNPCs into neurons and oligodendrocytes Interference with THR signal transduction	47, 99
[48] **Hormone disruption by PBDEs in adult male sport fish consumers** Turyk et al. 2008	Increased T4 and Reverse T3 Decreased T3 and TSH Increased %of T4 bnd to albumin Decreased % of T4 bound to TBG Increased Testosterone	47, 99, 100, 153 47
[39] **Polybrominated diphenyl ethers in umbilical cord blood and relevant factors in neonates from Guiyu, China** Wu et al. 2009	Adverse birth outcomes (stillbirth, low birth weight, premature delivery)	28, 47, 99, 153, 183
[49] **Polybrominated diphenyl ether (PBDE) concentrations in house dust are related to hormone levels in men** Meeker et al. 2009	Decreased FAI, FSH, and LH Increased inhibin B, SHBG, free T4	47, 99, 100
[50] **Influence of prenatal exposure to selected organohalogens on infant sexual and neurological development** Meijer et al. 2008	Increased SHBG, inhibin B, and estradiol	154
[51] **Case-control study on concentrations of organohalogen compounds and titers of antibodies to Epstein-Barr virus antigens in the etiology of Non-Hodgkin lymphoma** Hardell et al. 2001	Non-Hodgkin Lymphoma Epstein Barr IgG	47
[52] **Polybrominated diphenylether (PBDE) flame retardants and Thyroid Hormone during pregnancy** Chevrier et al. 2010	Decreased TSH and subclinical hyperthyroidism in pregnant women	28, 47, 99, 100, 153

Table 2: Foam put through cone calorimeter burn test with no fire retardants, with penta-BDE, and with chlorinated tris

	No FR	Treated with Penta-BDE	Treated with TDCPP (chlorinated tris)
Time to Sustained Ignition (seconds)	**16**	**19**	**18**
Peak Heat Release Rate (kW/m^2)	**412**	**259**	**326**
Total Heat Release (MJ/kg)	**57**	**40**	**48**
Smoke generation (m^2/kg)	**413**	**833**	**745**
Ave. CO (kg/kg)	**0.018**	**0.13**	**0.082**
Ave. Soot (kg/kg)	**0.013**	**0.88**	**0.11**

*This abstract does not necessarily reflect the position of the National Institutes of Health.

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