



# **Brominated Flame Retardants**

11

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## **Executive Summary**

The widespread use of plastics and other synthetic materials has increased the flammability of many products and led to the use of flame retardant chemicals that inhibit ignition and slow the spread of fire. Brominated flame retardants (BFRs) are the most commonly used chemical flame retardants because they are an effective and relatively inexpensive solution for meeting flammability standards.

The class of BFRs known as polybrominated diphenyl ethers, or PBDEs has captured the immediate attention of scientists and policymakers because levels in the environment and humans have increased exponentially since these chemicals came into use in the 1970s. During the last 30 years, PBDE levels in humans have doubled about every 3 to 5 years and continue to increase. Levels in the U.S. are by far the highest in the world.

PBDEs have been found in wildlife species all over the world, including the Arctic. They are present in high concentrations in sewage sludge, and have been found in dust in homes, cars and offices. PBDEs are present in food consumed by humans, with higher concentrations in animal products compared to fruits and vegetables.

Breast-feeding infants receive more PBDEs than any other group because of the presence of these chemicals in mother's milk. Exposure of infants to PBDEs is of particular concern because these chemicals have produced developmental neurotoxicity in laboratory animals, impairing memory, learning and behavior. PBDEs also are endocrine disruptors, interfering with the transmission and regulation of thyroid and reproductive hormones. It therefore is important to eliminate the use of PBDEs and substitute other, safer means of meeting flammability standards.

The sale of products containing the "penta" and "octa" mixtures of PBDE already is banned in Maine and several other U.S. states effective January 1, 2006. The "deca" mixture (herein "decaBDE") is the only PDBE mixture that remains in production in the U.S. The Maine Legislature has said that, beginning January 1, 2008, it intends to implement measures to reduce the health risk posed by decaBDE, including a possible ban on the sale of products containing decaBDE if safer alternatives are identified.

Safer alternatives are available for TV cabinets and textiles, the applications that consume most decaBDE. In the case of textiles, alternatives that do not require the use of chemical flame retardants already are widely employed in the marketplace. In the case of TVs, the use of safer alternatives to decaBDE will require manufacturers to shift from using cabinets made of high impact polystyrene (HIPS) to other types of plastic that can be treated to meet flammability standards using phosphorus compounds such as resorcinol bis diphenyl phosphate (RDP). RDP presents a significantly lower threat to the environment and human health than decaBDE.

<u>Recommendation</u>: To reduce the presence of decaBDE in the immediate surroundings of humans, the Legislature should ban the sale of televisions and other consumer electronics that have plastic casings containing decaBDE effective January 1, 2012.

<u>Recommendation</u>: To prevent decaBDE from being used to meet new national flammability standards for mattresses and pending national standards for residential upholstered furniture, the Legislature should ban the sale of these products if they contain decaBDE effective January 1, 2008.

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## I. Introduction

Maine law at 38 MRSA §1609 directs the Department of Environmental Protection (DEP), in consultation with the Center for Disease Control and Prevention (Maine CDC)<sup>1</sup>, to review relevant information about brominated flame retardants (BFRs) and report annually to the Legislature's Natural Resources Committee.

The term "brominated flame retardant" as defined in section 1609 means "any chemical containing the element bromine that may be added to a plastic, foam or textile to inhibit flame formation."<sup>2</sup> There are numerous commercial BFR formulations on the market. This report, as did our first two reports, focuses on information about a particular formulation called decabrominated diphenyl ether (decaBDE). The Legislature has expressed its intent to place restrictions on the sale of deca-laden products beginning in 2008 "if a safer, nationally available alternative is identified."<sup>3</sup>

This report recaps key information from the first two reports and incorporates new information that has become available in 2006. The report is drawn from research studies, risk assessments and other information that has come to our attention and that, in the judgment of the DEP and Maine CDC, may be useful in the Legislature's deliberations. We do not purport to survey all available data on decaBDE.

Flame retardants are added to plastics and foams and applied to some textiles to reduce the likelihood that products made of these materials will catch fire and to slow the rate at which they burn. Many chemicals are used as flame retardants. Brominated flame retardants predominate in the marketplace due to low cost and high efficiency.

The class of BFRs known as polybrominated diphenyl ethers, or PBDEs, has captured the immediate attention of scientists and policymakers because levels in the environment and humans have increased rapidly since these chemicals came into use. In light of this concern, two of three commercially available PBDE mixtures were voluntarily withdrawn from the market and now have been banned in several U.S. states including Maine. DecaBDE is the only commercial PDBE mixture that remains in production.

DecaBDE is a fine, white to off-white crystalline powder used mainly in plastics but also applied in a backcoating to textiles. It is an "additive" flame retardant, meaning it is mixed into but not chemically bound to the host material, i.e. the resin to which its is added. DecaBDE is used at loadings ranging from 10 to 15% by weight of the host material (Lassen, et al., 1999). Because it is not chemically bound, decaBDE tends to migrate from the product into the environment (Lowell, 2005).

The vast majority of the decaBDE currently produced is thought to be used in the outer casing of TVs. Worldwide, market demand for decaBDE was 56,100 tons in 2001; 65,677 tons in 2002; and 56,419 tons in 2003 (BSEF, 2004; BSEF, 2006). Total worldwide demand for all

<sup>&</sup>lt;sup>1</sup> Formerly the Bureau of Health.

<sup>&</sup>lt;sup>2</sup> 38 MRSA §1609(2).

<sup>&</sup>lt;sup>3</sup> See An Act to Reduce Contamination of Breast Milk and the Environment from the Release of Brominated Chemicals in Consumer Products, PL 2003, c. 629, §2, eff. July 30, 2004.

BFRs was 223,482 tons in 2003 (BSEF, 2006). The four companies known to produce decaBDE are listed below.

Company	Product name	Headquarters
Albemarle Corporation	SAYTEX 102E	Richmond, Virginia, USA
Dead Sea Bromine Group (DSBG)*	FR 1210	Beer Sheem, Israel
Chemtura Corporation (formerly Great Lakes Chemical)	DE-83R, DE-83	West Lafayette, Indiana, USA
Tosoh Corporation	Flamecut 110R	Tokyo, Japan

Table 1. Companies that produce decaBDE

\*Ameribrom, Inc of Fort Lee, New Jersey is responsible for marketing DSBG products in the U.S.

Product	Polymer	Alternative Available?	Comments
TV casings	High Impact Polystyrene(HIPS)	Yes	HIPS must be blended with polyphenylene oxide (PPO) in order to substitute a non- brominated FR. DecaBDE also can be substituted by using other plastics, wood or metal for TV casings.
Coated wire & telecom cable	Polypropylene	Yes	Other BFRs are used in wire & cable. Non- brominated options include magnesium hydroxide and ammonium polyphosphate but use appears limited and may significantly increase costs.
Electrical parts	Plastics polybutylene terephthalate (PBT); polyamide (PA)	Yes	Other flame retardants are used in 90% of electrical parts made of PBT and 94% of electrical parts made of PA. In most cases, these are other BFRs. Non-brominated FRs (magnesium hydroxide, melamine cyanurate, melamine polyphosphate) are used in PA but not PBT; use of phosphinic acid in PBT is a recent development
Mattresses, upholstery & draperies	Acrylic resin; styrene butadiene copolymer; ethylene-vinyl acetate copolymer	Yes	Numerous alternatives are available including barrier technologies; inherently flame resistant fibers; and other chemicals. FR chemicals are not needed to meet flammability standards in most cases.

 Table 2. DecaBDE applications

## **II. DecaBDE: Health Effects and Environmental Contamination**

Our first report on BFRs, submitted to the legislature in February 2005, included an extensive review of the levels of PBDEs in the environment and human tissue, and the toxicity of various PBDE congeners.<sup>4</sup> That initial review was updated in our March 2006 report.

This report incorporates information that has become available since the literature review was completed for the 2006 report. Included are peer-review articles published through November of 2006, as well as some published studies from 2005. Also included are papers presented at three international meetings. Presentations from a meeting on brominated flame retardants held in Toronto in 2006 were available on the Web as PowerPoint slides. Extended (four-page) abstracts were also available on the Web from the 2005 International Symposium on Halogenated Environmental Pollutants and Persistent Organic Pollutants (POPs) held in Toronto. These became available after the last report and are referenced as being published in Organohalogen Compounds, volume 67, 2005. The abstracts for the 2006 International Symposium on Halogenated Environmental Pollutants and POPs held in August in Oslo, Norway, are currently available on the Web, and are referenced as 26th International Symposium on Halogenated Persistent Organic Pollutants, 2006.

This report includes research on the levels of PBDEs in environmental media, wildlife, food consumed by humans, and humans. Data are presented on environmental transport, and conversion of decaBDE in the environment and by living organisms. This report also includes studies on the toxicity of decaBDE and its potential degradation products.

Although the focus is on decaBDE, information on other congeners is included as well. The rationale for this is the increasing evidence for conversion of decaBDE to other congeners, including those that are found in the environment and tissues of animals and humans, and are known to be toxic. It is probably the case that the use of decaBDE is contributing to the presence of these other congeners, and the longer decaBDE remains in the environment, the greater will be its contribution.

Potential degradation products of decaBDE include (but are not limited to) the nonaBDEs 206-208, the octaBDE 203, the hexaBDEs 153, 154 and 183, the pentaBDE 99 and the tetraBDE 47. PBDEs 47 and 99 are also constituents of the commercial penta-PBDE mixture, have been routinely included in analyses of PBDEs in various media, and are found in relatively high concentrations. More recently, however, congeners 153, 154, and 183 have been increasing in the environment and human and animal tissues. All of these congeners have proven toxicity. In addition, degradation and metabolism of decaBDE may produce hydroxylated and methoxylated PBDEs. Although data on the toxicity of these metabolites is limited, there is evidence they are more toxic than the parent PBDE in some cases.

<sup>&</sup>lt;sup>4</sup> Congener (CON je ner) refers to a chemical substance related to another chemical substance in structure. There are 209 theoretically possible congeners or variations of PBDEs. Individual congeners are numbered BDE-1, BDE-2, BDE-3 and so on through BDE-209. Only a few congeners are present in the three commercial PBDE mixtures, called "penta", "octa" and "deca" because the molecules in each mixture have on average five, eight or ten bromine atoms. The exact pattern of congeners in the commercial mixtures depends on the manufacturer and specific product. Approximate percentages of the main congeners in these mixtures are shown in Table 3 of our February 2005 report.

## A. Summary of research findings since the 2006 report to the Legislature

- There is further evidence that decaBDE undergoes long-range environmental transport in air, perhaps as a consequence of binding to atmospheric particles. DecaBDE is the dominant congener in air in Ontario, Europe and Japan (U.S. data were not presented this year).
- Sludge from waste water treatment plants contains high levels of PBDEs. This is particularly worrisome since half of this sludge is used as fertilizer for crops in the U.S.
- DecaBDE is the dominant congener in electronics waste (ewaste) and autoshredder waste.
- Burning of PBDEs may produce polybrominated dibenzodioxins and dibenzofurans, which are highly toxic.
- There is further evidence that PBDEs, including decaBDE, concentrate up the food web, with top predatory birds, mammals and fish having higher levels than species lower in the web.
- There is further evidence that many species, including humans, can metabolize decaBDE to other congeners. In addition, other metabolic products may be formed that may be more toxic than the parent compound.
- There is increasing recognition that decaBDE can be degraded in the environment to lower brominated congeners and other products. Many of the potential products cannot be measured at this time.
- Higher levels of PBDEs are found in fish consumed by humans compared to other animal products. Levels in plants are lower than in animals. The major source of PBDEs from food in the U.S. is meat rather than fish, because in general people eat more meat.
- Studies in Maine have documented PBDEs in farmed fish, and high levels in fish from the Penobscot River downstream of a waste water treatment plant.
- Indoor air is a major source of exposure to individuals in the U.S., and decaBDE is the dominant congener in air. DecaBDE can be degraded by sunlight into lower-brominated congeners.
- Levels of PBDEs in human tissue may be higher than those of PCBs in studies in the U.S. and Canada. However, levels may be stabilizing in Europe as a result of decreased use of the lower-brominated mixtures.
- Levels of PBDEs in human breast milk are highly correlated with levels in the mother's blood and fat. Levels of decaBDE in lipids (the fatty substances present in blood and body tissue) may be higher in milk than in the mother's tissue. Breast-feeding infants receive more PBDEs than any other age group.
- Research has further documented adverse effects on reproduction produced by PBDEs, although decaBDE was not studied. DecaBDE is generally inactive in *in vitro* assays, but there was not the possibility of metabolism in the systems used.

- A single dose of decaBDE in the early postnatal period produced changes in locomotor activity in rats, and its proximal metabolites (octa- and nona-BDEs) produced changes in mice. A previous study had documented changes in locomotor activity in mice produced by decaBDE.
- In a study by researchers at the University of Southern Maine and the Maine CDC, decaBDE given from days 2 to 15 after birth produced changes in locomotor activity and cognitive performance in mice, and decreased levels of thyroid hormone.

#### **B.** PBDEs in the environment

As described in our previous reports, the levels of PBDEs have increased exponentially in the environment since their widespread use began in the 1970s. A review by Hale *et al.* (2006) reports that the release of decaBDE to land, surface water and air increased by about a factor of 10 between 1988 and 2000. A study of sediment from multiple locations in the Great Lakes documented an increase of PBDE levels by a factor of several hundred times since the 1970s (Li *et al.*, 2005a). DecaBDE accounted for 70-98% of the total. PBDE-100, -153, -154, and -183 were also found as a substantial percentage of the total, which may represent, at least in part, biotic or abiotic debromination<sup>5</sup> of decaBDE.

Research has continued into the transport of PBDEs in outdoor air. There is increasing evidence that there is a spatial gradient of PBDEs in air and soil associated with urban areas, with decreasing concentrations with increasing distance from cities (Harner *et al.*, 2006; Harrad and Hunter, 2006). Tree bark was used as a passive sampler of PBDEs in air in 29 locations in the U.S. and Canada (Zhu and Hites, 2006; Hites, 2006). The spatial pattern indicated a dominant source in Arkansas, suggesting that two manufacturing plants, Albemarle and Great Lakes Chemical<sup>6</sup>, are a major source of PBDE levels in air in the U.S. and Canada.

Environmental transport of decaBDE has also been studied. Breivik *et al.* (2006) studied the long-range transport of decaBDE in water bodies in Ontario, Quebec and New York state. DecaBDE was found in the Canadian Arctic (Su *et al.*, 2006), but it is unclear to what extent this is the result of long-range transport or local point sources in that study. It is well established, however, that PBDEs, including decaBDE, are present in abiotic and biotic media in the Arctic (review by de Wit, 2006). DecaBDE is the dominant congener in air in southern Ontario, and is bound to atmospheric particles (Hale *et al.*, 2006). The authors postulate that this mechanism is probably responsible for the majority of long-range transport. Studies in Norway analyzed concentrations of PBDE in soil and moss at numerous locations, and found that decaBDE was the dominant congener, with the pattern consistent with specific point sources of exposure (Mariussen *et al.*, 2005; Schlabach and Gjerstad, 2006). Like bark, moss is also a passive sampler of airborne contaminants. A study of PBDEs in a lake in Norway identified both local and long-range transport of PBDEs (Breivik and Schlabach, 2006). The concentration of decaBDE was equal to that of all other congeners combined.

<sup>&</sup>lt;sup>5</sup> Biotic debromination refers to debromination caused by living organisms, as from metabolism by microorganisms (see page 6). Abiotic debromination refers to debromination caused by non-biological mechanisms, as form exposure to sunlight.

<sup>&</sup>lt;sup>6</sup> Great Lakes Chemical merged with the Crompton Corporation in 2005 to form the Chemtura Corporation.

It is now well recognized, and further documented in the last year, that sludge from waste water treatment plants has significant levels of PBDEs compared to background levels (as much as 200-400 times higher), and that levels in the U.S. are much higher than in Europe (Song *et al.*, 2006; Gorgy *et al.*, 2005). This is particularly worrisome since half of the sludge produced in the U.S. is put on farm land as fertilizer, or may be made available to the home gardener. (See also discussion of fish levels in Maine.) A study in Switzerland found elevated levels of PBDEs in compost, with decaBDE comprising 85% of the total (Zennegg *et al.*, 2005). PBDEs may then be taken up by plants. In a study in Canada, the effluent from a waste water treatment facility contained low levels of decaBDE, with PBDEs -47 and -99 being the dominant congeners (Kolic *et al.*, 2005). The authors speculated that the decaBDE may have undergone debromination, but it may have also remained in the solid fraction.

Recent attention has also focused on the environmental consequences of disposal of products containing PBDEs. High levels of PBDEs are found near plants that dispose of or recycle electronic waste (ewaste) (Cai and Jiang, 2005), and the congener pattern reflects the products being handled (Wang *et al.*, 2005). PBDE levels in ewaste, autoshredder waste (the material created by the shredding of vehicles and major appliances such as refrigerators), and other waste in California were analyzed (Petreas *et al.*, 2005; Petreas and Oros, 2006). Autoshredder waste was dominated by decaBDE, with very high total concentrations of PBDEs, in the high ppm to percent of total weight levels. For ewaste, highest concentrations were from VCRs, with CPUs also having high levels. DecaBDEs were the dominant congener in both these products. "Other" waste (furniture, carpet) was dominated by penta- and octa-PBDEs. PBDEs in waste water treatment sludge was one-third decaBDE.

Burning of PBDEs, for example as the result of a landfill fire, may also represent a significant hazard. Burning of a waste mixture of PBDEs and other flame retardants produced a number of degradation products (Hirai *et al.*, 2005), including polybrominated dibenzodioxins (PCDDs) and polybrominated dibenzofurans (PCDFs). Experimental burning of PBDE-47 or PBDE-153 also produced PBDFs, PBDDs, and benzene products (Rupp and Metzger, 2005). These chemicals are all carcinogens, and PBDFs and PBDDs are potent toxicants, affecting the endocrine and immune systems particularly. Hydrothermal degradation of decaBDE, a procedure that may be used during the disposal process, resulted in 99.999% degradation after 120 minutes, with production of mono- to hexa-PBDEs, as well as PBDDs and PBDFs (Nose *et al.*, 2005).

## C. Metabolism of PBDEs by microorganisms in the environment

Microorganisms in soil or sediment can metabolize PBDEs to less highly-brominated congeners. Anaerobic degradation of commercial octaBDE and nonaBDE has been demonstrated in several species of microorganisms (Robrock *et al.*, 2005; He *et al.*, 2006). Products included PBEs-47, -99, -48, and -154. The former two are typically found in high concentrations in environmental media and animal tissue, have demonstrated toxicity, and have been assumed to be the result of release of pentaBDE. The authors conclude that these findings "could have profound implications for public health and the regulation of these compounds" (He *et al.*, 2006, p. 4429).

Similarly, Skoczynska *et al.* (2005) reported rapid degradation of decaBDE by anaerobic sediment microorganisms. These results are consistent with studies described in our previous reports. In contrast, Rheinstein *et al.* (2005) did not observe microbial degradation of decaBDE under the conditions of their study, but they did find that decaBDE can be released from sediment under some conditions, which may make it bioavailable.

PBDEs may also be metabolized to hydroxy (OH-) or methoxy (CH<sub>3</sub>O-) derivatives. These compounds may be more toxic than the parent compounds (see paragraph G below). Hydroxy-PBDEs are present in rain, snow, and surface water in Ontario (Ueno *et al.*, 2005). They were also found to be elevated in effluent from waste water treatment facilities, which could result from microbial degradation or the use of ozone for disinfection.

Hydroxy- and methoxy-PBDEs, and possibly PBDDs, may also be synthesized by cyanobacteria using a natural metabolic process (Malmvärn *et al.*, 2005 and previous Reports). The contribution of such syntheses to the burden in birds and mammals is unknown.

## **D.** PBDEs in wildlife

As discussed in our previous reports, PBDEs, including decaBDE, are detected in many species all over the world. Research in the past year has continued to document the fact that living organisms absorb decaBDE from the environment (bioaccumulation) and that tissue concentrations may increase moving up the food web, i.e., at higher trophic levels (bioconcentration).

Additional studies have documented the fact that PBDEs bioconcentrate up the food web, including studies in Australia (Hermanussen *et al.*, 2006), Belgium (Voorspoels *et al.*, 2005b), Taiwan (Chen *et al.*, 2006), and the Arctic (Law *et al.*, 2006; Muir *et al.*, 2006), although no biomagnification was found in Hudson Bay (Kelly *et al.*, 2005). BDE 47 was found in Arctic foxes in Greenland and Russia, but at lower levels than PCBs (Lifgren *et al.*, 2006). These studies did not measure decaBDE.

A number of studies did include decaBDE in their analysis, however, and found that it also bioconcentrates up the food web. In a study in Belgium, decaBDE was the dominant congener in the red fox, comprising 80% of the total PBDEs (Voorspoels *et al.*, 2005a). The congener with the second highest concentration was PBDE-153, suggesting metabolism from more highly brominated congeners. Consistent with this are findings of more highly brominated congeners in kittiwakes and fulmars in the North Atlantic (Murvoll *et al.*, 2006; Fängström *et al.*, 2005), as well as cetaceans in Asia (Kajiwara *et al.*, 2006). Savinov *et al.* (2005) analyzed PBDE levels in glaucous gulls in Spitzbergen. DecaBDE was detected in most individuals, albeit at low concentrations. However, high levels of decaBDE were found in a few individuals; in one gull, decaBDE was found at the highest concentration of all PBDEs in the study. These species are all top predators in terrestrial or aquatic food webs.

Jaspers *et al.* (2006) analyzed PBDE levels in seven species of aquatic and terrestrial birds at different trophic levels. BDE-183 and decaBDE were found only in terrestrial birds, whereas lower-brominated congeners were observed in both food webs. Concentrations differed between species depending on feeding habits. Similarly, highly brominated congeners were detected in

peregrine falcons in Spain (Jiménez *et al.*, 2005), including decaBDE, BDE-207, 206, 197, 196 and 183, as well as unidentified nona- and octa- metabolites. The presence of these highly brominated congeners suggests metabolism of decaBDE by organisms in the food web and/or the falcons themselves. The results of this study are consistent with others in peregrine falcons and other predatory species (discussed in previous reports to the legislature). Law *et al.* (2006) analyzed PBDEs in seven fish species at different tropic levels in a freshwater food web in Lake Winnipeg, Manitoba, Canada. They found that PBDEs bioconcentrated from lower to higher trophic levels, and that decaBDE had a greater biomagnification factor than the other six congeners measured.

Studies in Greenland compared levels and patterns of PBDE congeners in polar bears and ringed seals, their main food (Gebbink *et al.*, 2006a, b). DecaBDE was present in the ringed seals, but little or no decaBDE was present in the polar bears. In an experiment using polar bear liver, it was found that polar bears readily metabolize decaBDE to hydroxylated derivatives. (These metabolites can bind to thyroid hormone binding protein, thereby interfering with thyroid function.) If the investigators had not measured decaBDE in both species, and explored the apparent inconsistency of the absence of decaBDE in polar bears, it may have been concluded that polar bears were not exposed to decaBDE. Sørmo *et al.* (2006) also studied the biomagnifications of PBDEs in the food web of polar bears. They found that some PBDEs biomagnified by as much as 200 times from polar cod to ringed seals. Lower PBDE levels were found in bears than in seals, suggesting metabolism by the bears. Consistent with this notion is the observation that BDE 153 did biomagnify from seals to bears.

The presence of hydroxy- and methoxy-PBDEs at different levels of the marine food web was studied in Hudson Bay (Kelly and Ikonomou, 2005). These derivatives were not found in sediment, lichens or macro-algae. Methoxy-PBDEs were found in fish, sea ducks, and marine mammals, with higher concentrations at higher trophic levels. Hydroxy-PBDEs were found only in sea mammals. Methoxy-derivatives were present in higher concentrations than the parent compound in beluga whales. The authors presented an analysis of concentrations of BDE-47 and methoxy-BDE-47 across trophic levels. Levels of the parent compound did not increase across trophic level, whereas the methoxy-BDE-47 increased by a factor of 1000. This presumably reflects significant metabolism of this congener by a number of species. These metabolites have only been analyzed recently, and only in a few studies. Moreover, chemical analytical standards exist only for a few of these metabolites, so most possible hydroxy- and methoxy-derivatives cannot be identified. It is likely, therefore, that the total environmental burden of PBDEs is underestimated, perhaps substantially. Some of these metabolites are more toxic than the parent compounds, and so may represent a significant hazard to wildlife and humans.

In order for PBDEs to enter the food web, living organisms at the bottom of the web must ingest them from environmental media. In a study in Sweden (de Wit *et al.*, 2005), levels of PBDEs were analyzed in worms from farms that used sewage sludge as fertilizer, a flood plain that could become contaminated with PBDEs from the river, and reference sites. Concentrations of PBDEs were higher at contaminated sites compared to reference sites. DecaBDE was the dominant congener in soil and worms, with higher levels in the worms than soil. PBDE levels also were higher at a site that had received no sludge for 20 years compared to the reference

sites, indicating that these chemicals stay in the soil for years. Worms are at the bottom of the terrestrial food chain, and are consumed by many mammals and birds.

Bioaccumulation of PBDEs has also been studied in aquatic environments. PBDEs, including decaBDE, are found in mussels and other bivalves in Asia, Europe, and the U.S. (Ramu *et al.*, 2005; Moon *et al.*, 2005; Gama *et al.*, 2006). In a study of caged mussels in the Niagara River system (Richman *et al.*, 2006), decaBDE was the dominant congener at some sites. In a study in Chesapeake Bay (Klosterhaus *et al.*, 2006), decaBDE comprised 90-99% of the total PBDEs in sediment, and other highly brominated congeners (BBE-206, 207, 208) were also detected. In that study, little or no decaBDE was found in worms or amphipods. In a study in China (Chen *et al.*, 2006), the dominant congener in sediment was decaBDE. Plankton-eating fish bioaccumulated less decaBDE than other PBDE congeners in comparison to sediment levels.

Several studies determined that PBDE levels in animals are higher near urban environments and contaminated sites, including eels (Mariottini *et al.*, 2005), cetaceans (Kajiwara *et al.*, 2006), and harbor seals (Cullen *et al.*, 2005). A study in Japan (Kurunthachalam *et al.*, 2005) measured PBDE congeners at multiple sites in the brown rat, which lives in close contact with humans. Highest levels were observed in the most urban area (Tokyo) and near a landfill. PBE-153 and decaBDE were the dominant congeners, which may represent metabolism and a shared environment with humans (for example, exposure to dust and plastic products).

PBDEs are transported and accumulated in Arctic environment (de Wit and Muir, 2006). In a study in polar bears and ringed seals in the Arctic (Muir *et al.*, 2006), the geographic spatial pattern from various sites was similar for PCBs, PBDEs and another flame retardant, suggesting similar sources of long-range transport, presumably from urban areas.

Past studies documented that levels of PBDEs were increasing exponentially around the world in environmental media and animals. Only a few studies published since the last report were identified on this topic. In a study in British Columbia (Ikonomou and Kelly, 2005), levels of PBDEs in whitefish and Dungeness crab increased as much as 35 times from 1990 to 2000. In ringed seals in the Canadian Arctic, PBDE levels increased until about 2000, and appear to have stabilized subsequently (Ikonomou *et al.*, 2005). Similarly, She *et al.* (2005) found no difference in PBDE levels in shorebirds in San Francisco Bay in the short time span of 2001 to 2003. Shaw *et al.* (2006) measured PBDE levels in harbor seals from the Northwest Atlantic, from Maine to New York, from 1991-2005. They observed no time trend during that period, although there was evidence of a change in the congener pattern over time. However, decaBDE was not measured in these studies.

## E. Sources of human exposure

#### **PBDEs** in Food

As described in our 2005 and 2006 reports, PBDEs are present in food consumed by humans, with much higher concentrations in animal products compared to fruits and vegetables. Fish may be particularly high in PBDEs, as a result of bioaccumulation and bioconcentration in aquatic environments. A number of studies available since the 2006 report further documented the presence of PBDEs in food. Not all of these studied measured deca BDE or other highly brominated congeners.

Investigators from around the world documented the occurrence of PBDEs in seafood and other foods, including in the Baltic Sea, Indonesia, China, Korea, France, Germany, Ireland, Japan, Spain, Norway, Canada and the U.S. (Cha *et al.*, 2006; Sudaryanto *et al.*, 2005; Vuorinen *et al.*, 2005; Peng *et al.*, 2005; Liu *et al.*, 2005; Johansson *et al.*, 2006; Nakagawa *et al.*, 2005; Ashizuka *et al.*, 2005; Domingo *e al.*, 2006; Tlustos *et al.*, 2005a, b; Knutson *et al.*, 2006; Hermann *et al.*, 2006; Schecter *et al.*, 2006; Nielson *et al.*, 2005; Hamilton and Fisher, 2006; Cullen *et al.*, 2005; Bethune *et al.*, 2006; Shaw *et al.*, 2005; Anderson and MacRae, 2006). Thus, PBDEs are global pollutants.

Fish contain higher levels of PBDEs than do other animal products in both North America and Europe (Hamilton and Fisher, 2006; Knutsen *et al.*, 2006; Tlustos *et al.*, 2005a, b). Animal products contain significantly higher concentrations than fruits, vegetables and cereals, although PBDEs can be incorporated into plants, especially if grown on contaminated soil (e.g., sludge fertilizer) (Mueller *et al.*, 2006). Not unexpectedly, fatty fish have the highest levels of PBDEs, with highest levels in salmon, followed by mackerel and herring (Domingo *et al.*, 2006; Nielson *et al.*, 2005; Tlustos *et al.*, 2005a). Shellfish generally had lower levels than other seafood. Farmed fish generally had higher PBDE levels than wild fish (Nielson *et al.*, 2005; Tlustos *et al.*, 2005a; Hamilton and Fisher, 2006), and concentrations in farmed salmon could be decreased by substituting vegetables for fish oil in the feed (Bethune *et al.*, 2006).

A study in Germany analyzed PBDE congeners in fish, fish oil, and fish meal, including deca BDE (Hermann *et al.*, 2006). Levels in fish oil were two times higher than in fish tissue on a lipid basis. It was reported that decaBDE was usually a minor component in fish tissue (data not presented), but in one it was the dominant congener with a level of 4800 ng/g lipid. (The 95<sup>th</sup> percentile for total PBDEs was 35 ng/g lipid.)

Schecter *et al.* (2006) analyzed PBDE levels, including decaBDE, in 62 samples of fish, meat, and dairy products purchased in U.S. grocery stores. Highest levels were found in fish. As in other studies, fatty fish had high total PBDE levels, including salmon, herring and sardines. It was unclear whether farmed fish had more PBDEs than wild fish in this study. PBDE-47 was the dominant congener, followed by 99, 100 and decaBDE. Meat had more PBDEs than dairy products. DecaBDE was also a major contaminant of these products. Human milk contained more PBDEs than any other sample. Schecter and colleagues also estimated the average PBDE intake for various age groups, and the contribution of the food groups to total PBDE intake. The greatest intake was by nursing infants, and children consumed more PBDEs per body weight per day than adults. The main contribution is from meat (except for nursing infants) because the U.S. population consumes a lot more meat than fish, on average. The authors concluded that PBDEs -47, -99, -100, -153, -154, and in some cases decaBDE were the major constituents in food and therefore contributed most to PBDE intake.

A similar analysis was performed for the contribution of 14 marine fish species to PBDE intake in Spain (Domingo *et al.*, 2006). Tuna was estimated to be the greatest contributor from fish to the human body burden, even though other species had higher PBDE levels, because of the greater overall consumption of tuna. In a study in the U.K. (Silva *et al.*, 2006), it was estimated that decaBDE was the greatest contributor to total PBDE levels in humans from food.

#### PBDE Levels in Maine Fish

Two studies measured PBDE levels in fish from Maine waters, although neither measured decaBDE. Shaw *et al.* (2005) analyzed a total of 70 farmed and wild salmon. The farmed salmon were from two fish farms in eastern Maine, three in eastern Canada, and one in Norway. Wild Chinook salmon from Alaska were also purchased. Nine congeners were analyzed. Levels in farmed salmon from the seven farms were roughly comparable. These levels are lower than those reported in other studies, including in samples from Maine. Levels in farmed fish were somewhat higher than those in wild salmon.

Anderson and MacRae (2006) measured nine congeners in small mouth bass, white sucker, and eels from various sites in the Penobscot River, as well as wastewater and biosolids from wastewater treatment plants (WWTPs) on the Penobscot River. Concentrations of total PBDEs increased from upstream to downstream locations. Levels were high compared to other studies in the U.S., and 100-1000X higher than levels in Europe. Concentrations in small mouth bass were 2800 ng/g lipid upstream and 17,000 ng/g lipid downstream. PBDEs were also detected in wastewater and biosolids, the latter of which is spread onto land by communities in Maine or made available to homeowners for compost.

#### Contribution of Non-Dietary Sources

Schecter *et al.* (2006), in their analysis of PBDE intake from food discussed in the previous section, concluded that food cannot account for the high body burdens of PBDEs in the U.S. Intake from food was estimated to be comparable to that in Spain and the UK, and yet U.S. body burdens are many times higher than those in Europe. This suggests an additional pathway of exposure to people in the U.S., most probably house dust. As outlined in the previous Reports to the Legislature, levels of PBDEs, including decaBDE, are 20 or more times higher in the U.S. compared to Europe. Additional studies from Europe documented this finding (Harrad *et al.*, 2006; Fabrellas *et al.*, 2005).

There was a very high correlation between total PBDEs in house dust and PBDE concentrations in breast milk of nursing mothers (Allen *et al.*, 2006; Wu *et al.*, 2005). There was also an association between PBDE levels in human breast milk and consumption of dairy products (Wu *et al.*, 2005).

Consistent with previous studies in the US, the dominant congeners found in dust in homes in Massachusetts was decaBDE (Allen *et al.*, 2006). Similarly, decaBDE was the dominant congener in lint in U.S. homes (Pless-Mulloli *et al.*, 2006). Even so, the contribution of deca BDE to the total PBDEs in the home environment may be underestimated. Stapleton and Dodder (2006) studied the photodegradation by sunlight of decaBDE in house dust, and calculated a half-life of 400 hours for natural dust. Hepta- octa-, and nona- products were identified, which increased in concentration over the 200 hours of exposure to sunlight. In general, there is little correlation between characteristics of the home (electronics, foam-containing furniture) and total PBDE levels (Wu *et al.*, 2006; Hazrati and Harrad, 2006a).

PBDE levels in cars are higher than in homes, and are higher in newer cars than in older ones (Hazrati and Harrad, 2006a). Cars were found to have the highest levels of PBDEs, followed by office air, public indoor air, and homes in the UK (Hazrati and Harrad, 2006b). Little decaBDE was found on windshield films, even though decaBDE comprised 87% of dust in vehicles

(Gearhart and Posselt, 2006). This is in contrast to findings from homes and offices, in which high concentrations of decaBDE are found in window films. The low levels of decaBDE in window film in vehicles are presumably the result of photodegradation at the high temperatures that may occur in vehicles. The authors conclude that the use of deca BDE should be phased out.

In homes, PBDE levels are higher in personal air (adjacent to the body) than in the surrounding room air (Allen *et al.*, 2006). The reason for this is unknown, but suggests a "personal dust cloud".

#### F. PBDEs in human tissue

As described in the previous reports to the legislature, PBDE levels in the U.S. are by far the highest in the world, and overall levels in humans have increased exponentially over the last 30 years. Moreover, the relative concentrations of the various congeners have changed over time, reflecting environmental degradation and metabolism of commercial mixtures as PBDEs move up the food chain. Studies published in 2005-2006 further document these findings.

There is further evidence since the last report that PBDE levels in human tissue are increasing, and that concentrations in individuals in the U.S. are higher than those in Europe or Japan. In a comparison of levels of PBDEs in milk in 17 industrialized and non-industrialized countries (Kotz *et al.*, 2005), the range was 0.7 to 10.3 ng/g lipid for 16 countries, and 373 ng/g lipid in the U.S. Levels in Singapore are approximately the same as those in Europe (Li *et al.*, 2005). In Japan, decaBDE is found in the highest concentrations in human tissue compared to other congeners (Fukata *et al.*, 2005; Inoue *et al.*, 2006), which is presumably a reflection of the fact that pentaBDE is not used in Japan. DecaBDE is also the highest concentration in powdered milk fed to infants in Japan, but not Germany (Ohta *et al.*, 2005). Similarly, in a study in Norway (Thomsen *et al.*, 2005), serum levels of decaBDE were about seven times higher than levels of BDE-47. Several studies reported that levels of PBDEs in human tissues are now higher than PCBs, including the U.S. (Sjödin *et al.*, 2006; She *et al.*, 2005) and Canada (Ryan *et al.*, 2006). In a study in New York, levels of PBDEs were higher than those of PCBs in 24 of 52 fat samples, including in two individuals with very high levels in which PBDE levels were 100x greater than PCBs (9630 and 4060 ng/g lipid) (Kannan *et al.*, 2005).

There is evidence, however, that body burdens of PBDEs may be decreasing in some circumstances, at least for the lower-brominated congeners. Consistent with previous studies in Sweden, Fängström *et al.* (2006) reported that levels of PBDEs -47, -99, and -100 in Swedish breast milk increased between 1980 and 1995, were stable until about 2000, and decreased thereafter. This may reflect the phase-out of commercial products containing those congeners in Sweden. Total PBDE levels in blood have also recently decreased in Norway (Thomsen *et al.*, 2005). In contrast, PBDE-153 is still increasing, possibly as a result of biotic or abiotic transformation of highly-brominated PBDEs such as decaBDE. Data from Canada also suggest that levels of PBDEs in breast milk increased by a factor of 10 between 1992 and 2003, but now may be decreasing or stable (Ryan *et al.*, 2006).

The pattern of the body burden of PBDEs in the population differs from that of PCBs. Unlike PCBs, levels of PBDEs in blood are not age-dependent (Sjödin *et al.*, 2006), and body burdens of PCBs and PBDEs are not correlated with each other (She *et al.*, 2005). In a study of 2150 people representative of the U.S. population, PBDE levels were not associated with age, sex or ethnicity, unlike levels of PCBs and pesticides (Jones, 2006). This suggests that exposure to PCBs and PBDEs is at least in part via different pathways. The degree to which fish consumption may have contributed to PBDE body burdens in humans is somewhat unclear. Thomsen *et al.* (2006) measured PBDE levels in consumers of high amounts of fish from a PBDE-contaminated lake in Norway. They found that PBDE levels in blood were associated with fish intake from the lake. In contrast, Jakobsson *et al.* (2005) found no relationship between PBDE levels and fish consumption in Swedish men. In that study, blood concentrations of PBDE-47 and decaBDE were approximately equal, with levels of PBDE-153 being the highest. This latter finding further documents previous conclusions that the congener pattern in humans (and other animals) is different from that of commercial mixtures as a result of metabolism. As reported in our 2006 report, Morland *et al.* (2005) found a relationship between fish consumption and PBDE levels in U.S. anglers, but the authors did not consider it to be a major pathway.

Exposure of the fetus and infant to PBDEs is of particular concern, because of the ability of these chemicals to produce developmental neurotoxicity and disruption of endocrine function. Schecter *et al.* (2005) reported the presence of PBDEs in fetal liver in humans, documenting passage across the placenta. In addition, concentrations of PBDEs in maternal blood are approximately equal to those in milk (review by Schecter *et al.*, 2006). The ratio of levels between blood and milk is less than 1.0 for the lower brominated congeners, and greater than 1.0 for the more highly brominated congeners (which includes decaBDE and its proximal metabolites). There is also a high correlation between maternal adipose tissue and breast milk for individual congeners (Antignac *et al.*, 2006).

## Metabolism of decaBDE in experimental and human studies

As discussed in our 2005 and 2006 reports, decaBDE can be metabolized by animals, including humans, into congeners with fewer bromine atoms, as well as hydroxylated and methoxylated metabolites. Some of these latter metabolites may be more toxic than the PBDEs themselves. Recent studies have continued to document metabolism of decaBDE in fish and mammals, particularly with respect to identification of specific congeners. Studies also further documented the fact that decaBDE is absorbed from food by fish and mammals.

In a study in rats, purified decaBDE was administered orally for 21 days (Huwe, 2005). Levels of decaBDE in liver were increased 25 times over control concentrations. A number of nona- and octa-PBDE metabolites were identified, including PBDEs -183, -203 and -206.

A 30-week feeding study was performed in Atlantic salmon to determine tissue accumulation (Isosaari *et al.*, 2005). Adult fish were fed fish pellets with fish oil containing different concentrations of PBDEs. Fish accumulated 95% of the total dose of PBDEs, with different congeners having different degrees of accumulation. DecaBDE was not measured. Accumulation was as great or greater than for PCB congeners. There was also evidence of metabolism of congeners to lower-brominated congeners.

Lebeuf *et al.* (2006) studied the metabolic effects and metabolism of decaBDE in Atlantic tomcod. They documented increased tissue concentrations of nona- and octa-BDEs, as well as activated liver enzymes, which affected the metabolism of other PBDE congeners. Stapleton *et al.* (2005, 2006) studied the metabolism of decaBDE in juvenile rainbow trout and carp in a five-

month feeding study. DecaBDE was absorbed by the fish, and bioaccumulated over the fivemonth feeding period. Sixteen hepta-, octa-, and nona-BDE metabolites were identified, including PBDE-153 and PBDE-183, which are increasing in animal and human tissues, as well as PBDE-203 and PBDE-206. It is important to remember that some of these congeners can be further metabolized to PBDE-47 and PBDE-99, congeners at high concentrations in biota. All of these congeners are neurotoxic (see next section).

The disposition and excretion of PBDEs were compared in ten-day-old and adult mice after a single dose of PBDE-47 (Staskal *et al.*, 2005). Over the course of five days, the pups excreted almost no PBDE, and concentration increased in blood, brain and kidney. In contrast, tissue levels decreased in adults, and PBDE-47 or its metabolites were excreted in urine. This study suggests that young organisms may be at increased risk for toxicity from PBDEs because of an inability to metabolize and eliminate the compounds.

The half-lives of the more highly brominated congeners were estimated in Swedish workers and non-exposed individuals (Thuresson *et al.*, 2006). A half-life is the time it takes for one-half of the initial concentration to be eliminated (from blood, whole body, etc.). Complete elimination would require 4-5 half-lives, assuming no additional exposure. The half-life of decaBDE was estimated to be about 15 days, with rapid uptake after a one-day exposure. This relatively short half-life is consistent with results from animals, including fish, rats, and seals. Half-lives of nonaBDEs were 18-39 days, and octaBDEs had half-lives of 37-91 days. Consistent with previous reports from these authors, congeners 183, 206-208, and 203 were found at higher concentrations in workers previously exposed to decaBDE compared to non-exposed individuals. These congeners may be further metabolized to lower brominated congeners, including PBDE-47 and PBDE-99. These results provide further evidence that the body burden of decaBDE in humans underestimates the contribution of decaBDE to total body burden as a result of metabolism. The authors also concluded that the fact that decaBDE is commonly present in humans suggests more or less continuous exposure.

#### G. Toxicity of PBDEs

As outlined in the previous reports to the legislature, PBDEs interfere with regulation of endocrine function, including thyroid and reproductive function; nervous system function, including neurochemistry and behavior; immune function; liver function; and various metabolic pathways. A number of research articles were published in the last year or so further documenting these effects, including effects of decaBDE or its metabolites.

## Endocrine disruption

Specific PBDE congeners interfere with thyroid hormone, and research is ongoing to elucidate the mechanisms responsible for this effect (Hamers *et al.*, 2006a,b; Richardson *et al.*, 2006). A study in two species of arctic gulls determined the effects of BDE-47 and its hydroxylated derivatives on binding to  $T_4$  binding protein in liver and brain (Ucán-Marín *et al.*, 2006). The derivatives were more active than the parent compound. This suggests that birds may be similar to mammals in this respect. In a study in American kestrels, eggs were injected with a mixture of PBDEs-47, -99, -100 and -153 at an environmentally relevant concentration (Fernie *et al.*, 2005). Chicks had lower thyroid hormone levels and liver vitamin A levels, as well as an increase in measures of oxidative stress and decreased metabolic capacity. Injection

of PBDE-99 into eggs reduced liver vitamin content in duck hatchlings (Murvoll *et al.*, 2005), indicative of oxidative stress. Increased oxidative stress may lead to cancer and other pathological changes in multiple organ systems in the body, by producing reactive oxygen species that react with lipids, proteins, and DNA. PBDEs-47 and -99, and DE-71 (a penta mixture) all delayed metamorphosis of tadpoles into frogs (Balch *et al.*, 2006), an event which is thyroid-hormone dependent. Van der Ven *et al.* (2006) studied the effects of a number of PBDE congeners on thyroid hormones, blood biochemistry, and organ weights in adult rats. DecaBDE decreased  $T_3$  levels, thymus weight, and brain weight. DecaBDE was less active than other congeners.

PBDEs also interfere with regulation of reproductive hormones, and may produce reproductive failure. In a study in mink, a commercial mixture of pentaBDE produced reproductive failures and increased liver weight (indicative of toxicity) at intakes that are within the range of those of wild mink (Bull et al., 2006). A study in rats assessed the effects of a single dose of BDE-99 on day 6 of gestation on reproduction endpoints in the female offspring (Talsness et al., 2005). Changes were observed in the ovaries of the offspring when they reached adulthood. When female offspring were mated, there was no difference in pregnancy rate, but more resorptions compared to controls. (Rodents may resorb developing pups for a number of reasons, including abnormality in the pups or toxicity in the dam.) The offspring of these females, which had been exposed to a single dose in utero, produced pups with an increased frequency of skeletal malformations. A subsequent study (Talsness et al., 2006) found that a single dose of PBDE-47 during gestation decreased ovarian weight and the number of ovarian follicles in the female offspring, as well as decreased circulating levels of the reproductive hormone estradiol. The decreased number of follicles could potentially result in early reproductive senescence. PBDE-99 administered over nine days during gestation affected sex hormones in males and time to puberty onset in both sexes (Lilienthal et al., 2006). In addition, treated males behaved more like females in a sexually-dimorphic behavior (preference for a sweet substance, in which females usually prefer a sweet taste to a greater degree than males).

Several investigators studied the effects of a number of congeners on reproductive and other hormones using in vitro systems, which allows direct determination of the effects of PBDEs on the mechanisms of endocrine disruption. Several studies provided further documentation that PBDEs bind to the aryl hydrocarbon receptor (AhR) (Hamers et al., 2006; Peters et al., 2005, 2006; Stoker et al., 2005), although not as strongly as do PCBs (Wang et al., 2005). The AhR is critically important to the actions of sex hormones and reproduction. Olsman et al. (2006) determined the AhR activity of decaBDE after exposure to ultraviolet light, which produces debromination to other congeners and related chemicals. They found that high levels of Ah activation were produced as a result of photodegradation. Hamers et al. (2006) assessed the ability of a number of congeners to interfere with sex steroids, thyroid hormone and liver metabolism. In their in vitro assays, decaBDE was relatively inert; however, exposure to ultraviolet light rendered decaBDE active in disrupting thyroid hormone regulation and changing the activity of liver enzymes (which are involved in regulation of steroid hormones). The commercial mixture DE-71 and PBDEs -47, -99, and -153 also affect enzymes (CYP2B and 3A) that are biomarkers for activation of sex hormone receptors (Sanders et al., 2005). In contrast, it appears that CYP1A1, a biomarker of Ah receptor activation, was only upregulated at very high concentrations, and was probably the result of dioxin-like contaminants.

PBDEs also interfere with reproductive hormones in other ways, including specific effects on the estrogen, androgen, and progesterone systems (Nakari and Pessala, 2005; Hamers *et al.*, 2006). For some endpoints, PBDE congeners were more potent than the natural hormone. In most studies, decaBDE was not assessed. Hamers *et al.* (2006) found decaBDE to be inactive in their assays of endocrine effects; however, there was no ability to metabolize decaBDE in these *in vitro* systems to potentially active congeners. Congener 205, a metabolite of decaBDE, produced estrogenic effects in trout liver cells (Nakari and Pessala, 2005).

A commercial pentaBDE mixture was found to increase activity of liver enzymes in intact rats (Germer *et al.*, 2006), which would affect hormone regulation. Methoxy- and hydroxy-PBDEs also interfere with steroidogenic metabolism (Canton *et al.*, 2005).

There is some evidence that PBDEs also interfere with reproductive function and fetal development in humans. PBDE levels in breast milk, collected two weeks after delivery, were associated with several outcomes in the infants and mothers in Taiwan (Chao *et al.*, 2006). Birth weight, birth length, and head and chest circumference were measured in the infants, and the relationship of these outcomes with breast milk levels of 12 congeners were determined. DecaBDE levels predicted lower birth weight and length, and smaller chest circumference. Five of the other 11 congeners were also associated with some of these endpoints. The correlations between the levels of these congeners was not presented, and it is unclear which congener or congener combinations may be contributing to the observed effects. In the mothers, decaBDE was associated with decreased menstrual cycle length and duration of menstrual bleeding. Congeners 100 and 153 were also associated with decreased cycle length. These associations were no longer present for effects on the menstrual cycle after covariate adjustment in this small group of women (n = 20).

## Nervous system effects

Since the literature review for the 2006 report, several studies documented behavioral toxicity and effects on neurochemical systems resulting from developmental exposure to PBDEs, including deca BDE or its metabolites.

Several studies found effects on neurochemical systems in the brain in *in vitro* studies: in particular, intracellular signaling mechanisms (Kodavanti and Ward, 2005; Kodavanti *et al.*, 2005; Reistad and Mariussen, 2005). A commercial mixture of PBDEs was about as potent as a mixture of PCBs for some endpoints. PBDEs -47, -99 and -153 were all active. DecaBDE was not active in the system in which it was tested, nor was the octaBDE commercial mixture (Reistad and Mariussen, 2005). However, there was not the possibility for active metabolism of decaBDE in this study. The commercial penta0BDE mixture DE-71 was as potent as the commercial PCB mixture Aroclor 1254 in producing cell death in rat cerebellar granule cells *in vitro* (Mariussen *et al.*, 2006).

Several studies further documented the behavioral effects of early postnatal exposure to PBDEs. The early postnatal period in the rat or mouse corresponds to the last trimester of pregnancy in the human, such that the dosing regimens in these studies represent exposure to the human fetus or newborn rather than the older infant. The effects of the commercial pentamixture DE-71 on learning and neurochemistry were studied in rats exposed from postnatal days 6-12 (Dufault *et al.*, 2005) and tested beginning on postnatal day 30. Treated rats exhibited

impairment on a visual discrimination task, performing less accurately and exhibiting an attentional deficit. They were less affected by a drug that interfered with the cholinergic neurochemical system than were controls, indicating that the PBDE mixture produced a lasting effect on brain chemistry. Effects of PBDEs on cholinergic function have been reported in other studies.

As was discussed in our 2006 report, Swedish investigators documented changes in motor activity in male mice exposed to a single dose of a number of PBDE congeners administered separately during early postnatal development, including PBDE-47, PBDE-99, PBDE-153 or deca BDE. For all congeners, treated mice were less active than controls at the beginning of the one-hour observation period, but did not decrease their activity over time as did controls. This is referred to as failure of habituation, and may result from cognitive or attentional deficits or changes in arousal level.

The Swedish investigators have replicated the effects of decaBDE on activity using rats (Viberg *et al.*, 2006a). Male rats were given a single dose of decaBDE on postnatal day (PND) 3 and tested during early adulthood. The high dose group exhibited lower activity at the beginning of the observation period, and failed to habituate over the one-hour session. The low dose rats, on the other hand, were more active than controls at the beginning of the session, and habituated normally. Such a bi-phasic dose-effect curve (e.g., increase at lower doses and decrease at higher) is commonly observed for motor activity, for drugs as well as environmental chemicals. (Amphetamine is a classic example.) The cholinergic drug nicotine decreased activity in the high-dose group.

This same investigative team assessed the effects of PBDE-206, PBDE-203 or PBDE-183 on locomotor activity and learning in male mice (Viberg *et al.*, 2006b). PBDEs -203 and -206 are impurities of the commercial decaBDE compound, and all three congeners are potential metabolic or degradation products of decaBDE. Mice pups were given a single dose on either PND 3 or 10, and were tested beginning at 2 months of age (early adulthood). For PBDE-206, exposure on PND 3 was ineffective, whereas exposure on PND 10 produced an initial lower activity compared to controls as well as failure to habituate. A similar pattern of effects was observed with PBDE-203 after exposure at either age. For PBDE-183, effects were observed after exposure on PND 3 but not PND 10. Pups exposed to PBDE-203 or -206 were subsequently tested for their ability to learn and remember the location of a hidden submerged platform in a water maze. Both PBDE-206 and PBDE-203 produced learning impairment when administered on PND 10.

The Swedish team also investigated the potential for PBDEs to interact with other environmental neurotoxic agents. They documented neurotoxicity as a result of exposure to a higher but not lower dose of PCB-52 or BDE-99, and an additive effect of a lower dose of PCB-52 plus PBDE-99 (Eriksson *et al.*, 2006). The administration of PCB and BDE together also produced persistent effects. These data provide evidence that PCBs and PBDEs can produce behavioral impairment at a dose that is ineffective if administered alone. This is consistent with *in vitro* studies suggesting that PCBs and PBDEs act via the same neurochemical mechanisms, and that some congeners of PCBs and PBDEs are approximately equipotent. Additionally, however, PBDEs may interact with environmental toxicants that may act by different mechanisms. Fischer *et al.* (2006) found that PBC-153, PCB-126 or PBDE-99 all interacted synergistically (in a greater than additive manner) with methylmercury to produce effects on locomotor activity. Similarly, decaBDE interacted with perfluorinated chemicals (PFOA) on the locomotor behavior of mice pups (Eriksson *et al.*, 2006).

Study of endocrine and behavioral effects of deca BDE by USM and the Maine CDC

As described in last year's presentation to the legislature, a study is ongoing at the University of Southern Maine by Dr. Vincent Markowski in collaboration with Dr. Deborah Rice at the Maine CDC, under contract to Maine CDC. Mice were dosed on PND 2-15 with 6 or 20 mg/kg/day of decaBDE, and locomotor activity and cognitive function were tested during adulthood. As young adults, males in the higher dose group were more active than controls over a two-hour period, but habituated (decreased their activity) over the observation period in the same manner as controls (Rice *et al.*, submitted). There was no effect in the treated females. Treated mice made more errors on a visual discrimination task compared to controls, indicative of cognitive impairment. Blood concentrations of the thyroid hormone  $T_4$  were decreased in males at 21 days of age in a dose-dependent manner.

## III. DecaBDE: Current Usage and Alternatives

## A. DecaBDE in HIPS

The predominant use of decaBDE is in plastics, and in a particular type of plastic known as high impact polystyrene or HIPS. HIPS may consume as much as 80% of the worldwide decaBDE production (Lowell, 2005).

HIPS is a hard, dense plastic used in numerous products because of its ease of processing and low cost. HIPS is manufactured in many different grades, only some of which contain flame retardants. Unmodified HIPS (i.e., HIPS without flame retardants) finds application in some office equipment, toys, drinking cups, toilet seats and instrument control knobs among other things (AZoM, 2006a; British Plastics Federation, 2006; Kingsbury, 2002). Flame retarded grades of HIPS are produced mainly for TV cabinetry but also are used for distribution boxes and the casings of cassette tapes (AZoM, 2006b).



Up to 80% of decaBDE is used in the manufacture of TV cabinets

Flame-retarded HIPS is used in TVs because of the fire risk inherent in the TV power supply. Unmodified HIPS is highly flammable, ignites easily and burns violently. The addition of a flame retardant reduces the risk that the HIPS casing will ignite in the event of a fire caused by electrical arcing, overheating of current-carrying parts, or other problems with the power supply.<sup>7</sup>

DecaBDE is the most cost efficient and widely used compound for imparting flame retardancy to HIPS (Albemarle, 1995). Other brominated flame retardants could be substituted but cost more (Albemarle, 1995). The Albemarle Corporation makes a brominated flame retardant—SAYTEX 8010® based on ethane-1,2-bis(pentabromophenyl)—that it markets as a cost effective substitute for decaBDE in HIPS (Albemarle, 2006a). An Albemarle spokesperson reports that this product currently is used to some degree in TV casings but could not identify specific models (Landry, 2006).

The use of flame-retarded HIPS in the casings of electronic equipment other than TVs is rare. HIPS with decaBDE once was used in office machines such as printers, copiers and fax machines, but these products now are made from other types of plastics that use other types of flame retardants (Lassen *et al.*, 1999). It has been suggested that flame-retarded HIPS may be used to make the outer casings of some small home appliances such as VCRs, hair dryers, toasters and coffee machines, but this usage could not be confirmed. Some home appliances may, however, have internal parts made of other types of plastic that contain decaBDE as discussed in paragraph B below.

HIPS appears to have emerged as the resin of choice for TV cabinets because of the ease with which it can be used in the injection-molding process<sup>8</sup> and because it can be combined with inexpensive decaBDE to meet fire safety standards while maintaining good physical properties. HIPS has limited impact strength, however, and is susceptible to cracking. This limitation may be less critical in TVs, which are rarely moved and therefore less apt to be dropped, than in smaller devices that are moved more frequently (Lowell, 2005). It is perhaps for this reason that a plastic called acrylonitrile butadiene styrene (ABS) was favored over HIPS in the exterior casings of early computers.

Computer casings continue to be made of flame-retarded ABS plastic today, although that market increasingly is turning to PC/ABS blends, plastics made by blending ABS with a resin called polycarbonate (PC). This trend presumably is driven by the desire to avoid the use of brominated flame retardants. Whereas ABS requires a brominated flame retardant, PC/ABS blends can be flame-retarded using phosphorus-based chemicals. PC/ABS blends are now used in 60 to 80% of new computer casings (Leisewitz *et al.*, 2001; Lowell, 2005).

Although a 2004 study by McPherson *et al.* found that some computer manufacturers have increased their use of HIPS, the use of HIPS in the outer casings of computer components

<sup>&</sup>lt;sup>7</sup> Flame retardants presumably are not used in plastic products that are not electrically powered or otherwise lack an internal ignition source.

<sup>&</sup>lt;sup>8</sup> Injection molding is defined in Merriam Webster's Collegiate Dictionary (11<sup>th</sup> edition, 2003) as a method of forming articles (as of plastic) by heating the molding material until it can flow and injecting it into a mold.

remains relatively rare. According to the Lowell Center for Sustainable Production, 98% of TVs but only 3% of computer monitors have casings made from HIPS (Lowell, 2005).

A number of computer manufacturers, including Compaq, Dell, IBM and HP, have adopted policies that specifically prohibit their materials suppliers from using decaBDE. In 2006, when testing by the group Greenpeace revealed decaBDE in an HP laptop, HP was quick to investigate and reaffirm its policy against the use of decaBDE (Greenpeace, 2006). According to HP, the use of decaBDE in the laptop was due to misinterpretation of HP's material specifications by a supplier, and the laptop found to contain decaBDE no longer is in production (HP, 2006).

Although TV casings on the U.S. market continue to be made predominantly of HIPs, decaBDE no longer is used to any significant extent, if at all, in TVs sold in Europe. In fact, the trend in Europe until recently has been to completely dispense with the use of flame retardants in TV casings (Leisewitz *et al.*, 2001). Manufacturers instead addressed the fire risk by redesigning the TV to maintain safe distances between the plastic and current carrying parts, or by putting a barrier between the plastic and the current carrying parts. This technique meets European fire safety standards because the objective of those standards is protection from fires that might start *within* the TV.<sup>9</sup> However, it leaves the TV unprotected from external ignition sources like candles.

A study sponsored by the Brominated Flame Retardants Industry Panel (EBFRIP) attributes one third of all TV fires to candles and other external ignition sources (De Poortere *et al.*). The same study documented an upsurge in the number TV fires in Europe in the late 1990s, a trend attributed to the decreased use of flame retardants. According to the study authors, there is "plenty of anecdotal evidence that consumers do not recognize the danger of placing a naked flame near a TV set."

The concern about external ignition sources as a cause of TV fires has led manufacturers to reintroduce flame retarded TV casings in Europe. Sony, for example, began doing so in the year 2000 (Leisewitz and Schwarz, 2001). By June 2004, Panasonic and Phillips had announced their intent to follow suit (EFRA, 2004) and later joined Sony in signing a commitment to achieve at least a UL V-1 rating for the housings of all CRT-based TVs sold in Europe (ACFSE, 2006).

This voluntary action by TV manufacturers doing business in the European market followed an aggressive campaign by the flame retardant industry to characterize TVs without flame retardants as unsafe. Although those allegations do "not stand up to scientific scrutiny" and are "inconclusive" according to some (Leisewitz and Schwarz, 2001), TV manufacturers presumably found it prudent to resume using flame retardants to avoid any suggestion that their products are unsafe. They also may have been motivated by the desire to make a uniform product that can be sold both in Europe and in the US where a different fire safety standard prevails (Leisewitz and Schwarz, 2001).

Fire safety in TV sets sold in the U.S. is governed by standards developed by Underwriters Laboratories (UL). UL has established ignition-resistance classifications for plastics ranging

<sup>&</sup>lt;sup>9</sup> The relevant European standard is EN 60065, *Safety Requirements for Mains Operated Electronic and Related Apparatus for Household and Similar General Use.* See also note 10.

from HB (the least resistant) to V-0 (the most resistant).<sup>10</sup> The UL standard for TV enclosures requires a V-0 rating for any plastic within 50 mm (2 inches) of a potential ignition source. Manufacturers could use a lower rated plastic by increasing the distance between the casing and current-carrying parts but the UL standard, unlike the European standard, does not allow manufacturers to altogether eliminate the use of flame retardants.

Most TVs sold in the U.S. have casings made with V-0 rated plastic even though manufacturers, by careful design, could meet UL standards using a lesser-rated material (Lowell, 2005). The trend in Europe appears to be in a similar direction, i.e., toward the use of plastic meeting the stringent V-0 standard. Sony for one already is doing so, as evidenced by this label on Sony TVs sold in Sweden:

## "SONY TVs HAVE THE HIGHEST CLASSIFICATION V-0 FOR FIRE SAFETY

In Europe one generally follows IEC 60065 when deciding the level of fire protection. All Sony Vega TVs pass the tougher UL94 standard (used in the USA), whose highest level V-0 is obtained without extra cost in these Sony TVs"

(NASFM, 2002).

#### **B.** Alternatives to decaBDE in HIPS

#### Bromine-free HIPS/PPO

Perhaps most notable about the European experience is that manufacturers have been able to reintroduce V-0 rated TV casings to the European market **without using decaBDE or other brominated flame retardants**. They have accomplished this in the same way it has been accomplished by manufacturers of office equipment and home computers, i.e., by making the casing from plastics other than HIPS or by blending HIPS with polyphenylene oxide (PPO).<sup>11</sup> It is not practical to use a non-brominated flame retardant in HIPS without adding PPO because the required loading level is too high; the HIPS would not retain its cost and processing advantages over other plastics (Chemtura, 2006). The addition of about 20% of PPO improves flame retardancy and makes it possible to meet the UL V-0 flammability standard using a phosphorus-based flame retardant such as resorcinol bis diphenyl phosphate (RDP) (Lowell, 2005).

UL V-0 rated HIPS/PPO plastic with bromine-free flame retardants is available to U.S. TV manufacturers. To date, however, large quantity sales of this resin appear to be confined to manufacturers doing business in the European Union (Lowell 2005). Nevertheless, a U.S. electronics recycler estimates that roughly 5% of TVs they process have panels made of HIPS/PPO (Lowell, 2005). HIPS/PPO blends cost more pound—roughly \$1.90/lb compared to \$0.90 lb for unblended HIPS—but fewer pounds are needed per TV set because HIPS/PPO blends have higher mechanical strength, which allows for thinner walls (Lowell, 2005).

<sup>&</sup>lt;sup>10</sup> The relevant UL standards are *UL 94 Tests for Flammability of Plastic Materials for Parts in Devices and Appliances* and *UL 1410 Television Receivers and High Voltage Video Products*. The European standard EN 60065 is based on UL 94 but differs from UL 1410, which has more stringent flammability standards for TV casings.

<sup>&</sup>lt;sup>11</sup> Polyphenylene oxide (PPO) is the same polymer called polyphenylene ether (PPE).

#### Bromine-free PC/ABS

TV manufacturers also can avoid the need for decaBDE by using PC/ABS plastic, the resin blend currently used for most computer cabinetry. Unblended ABS could be used as well but requires a brominated flame retardant such as bis(tribromophenoxy) ethane or tetrabromobisphenyl-A (TBBPA). As with HIPS, the blending of ABS with another polymer—in this case polycarbonate—makes it possible to substitute non-brominated, phosphorus-based compounds.

All major resin manufacturers, including Bayer AG, Dow Chemical and GE Plastics, offer UL V-0 rated grades of PC/ABS that are bromine free (Lowell, 2005). Dow markets its Emerge PC/ABS 7560 resin as an ideal option for molding TV enclosures (Dow, 2003). Dow PC/ABS resins are used by Sharp Electronics in its Aquos line of LCD TVs, and by Philips Electronics in a flat panel TV it sells in Europe (Lowell, 2005). Dow reportedly uses bisphenol A diphosphate (BAPP) as a flame retardant in these resins (Lowell, 2005); Bayer and AG and GE Plastics use RDP (McPherson *et al.*, 2004).<sup>12</sup>

## Bromine-free PC

Polycarbonate (PC) resin unblended with ABS is a third bromine-free alternative to HIPS. The use of unblended PC for electronics casings currently is relatively rare (Lowell, 2005) but increasing (NEC, 2006). PC can be compounded with phosphate esters to meet the UL V-0 standard (Lowell, 2005). Apple Computer used PC to make one version of its IMac computer monitor and Philips Electronics uses PC in the rear housing of a flat screen TV (Lowell, 2005). The Phillips TV is made of a flame-retardant grade of polycarbonate manufactured by Bayer specifically for electronics enclosures (Bayer, 2006). Japanese electronics manufacturer NEC also has developed a bromine-free, flame retardant PC resin that it aims to begin marketing for commercial application in electronic equipment in 2007 (NEC, 2006). NEC claims to have found a way to reduce the energy required to produce PC, a development that is expected to lower costs and lead to wider use of this plastic in the casings of electronic equipment (NEC 2006).

#### Wood and metal

From an environmental and health perspective, it would be preferable to avoid using materials that require the addition of chemical flame retardants. In that regard, we note that, when TVs first came into use in the 1940s and 50s, the cabinets typically were made of wood. Wood does not ignite quite as easily or burn as violently as most plastics. TV fire safety only became a matter of urgency with the widespread introduction of plastic cabinetry in the 1970s. Although TVs with wood cabinets are not now widely available, the possibility of a wider return to wood cannot be dismissed. The web encyclopedia Wikipedia states that wood grain TV cabinets already are making a comeback, a trend that could accelerate if the cost of petroleum remains high.

TV casings made of metal are possible and could gain a wider market share along with wood, especially if concern about chemical flame retardants like decaBDE persists. The exterior

<sup>&</sup>lt;sup>12</sup> Our literature review suggests that RDP and BAPP are the phosphorus-based flame retardants most likely to be used in TV casings made of PC/ABS and HIPS/PPO plastic (Lassen *et al.*, 1999; Lowell; 2005; Washington, 2006). Other phosphorus-based compounds may be used as well but this could not be confirmed. Manufacturers typically do not disclose the specific flame retardants used in TV grades of these plastics.

casings of amplifiers, CD players, tuners and other hifi system components often have exterior casings made in whole or part of metal. Apple Computer replaced the plastic exterior casings on its laptops with metal to negate the need for flame retardants (McPherson *et al.*, 2004)

## **Bioplastics**

Several electronics manufactures reportedly are attempting to develop a grade of polylactide (PLA) suitable for use in electronics enclosures (Lowell, 2005). PLA is a bioplastic derived from lactic acid. It is attractive as an alternative to petrochemical-derived products since the lactic acid from which it is produced can be obtained from fermentation of corn or other starchrich agricultural products including potatoes (Wikipedia, 2006).

PLA is a promising option for electronics enclosures because it can be compounded with metal hydroxide to meet flammability standards (Lowell, 2005). JVC introduced a DVD player made from PLA in 2004 (Lowell, 2005). A web search uncovered examples of PLA usage in cell phone casings made by BASF, NEC and Unitika and in a laptop made by Fujitsu, but no evidence that PLA currently is used in TV casings.

## C. DecaBDE in other plastics

About 2 to 3% of global decaBDE production is consumed in the plastics polybutylene terephthalate (PBT) and polyamide (PA). Flame retarded grades of these plastics are used to make circuit breakers, sockets, plugs, electrical connectors and other small inner parts in contact with the current carrying parts of electrical and electronic equipment, including computers, appliances, automobiles and aircraft.

A wide variety of brominated flame retardants other than decaBDE are used in PBT and PA (Akzo Noble, 2004; Munro *et al.*, 2004). DecaBDE accounts for only about 10% of the total flame retardant used in electrical parts made from PBT and 6% of the flame retardant usage in parts made with PA (Munro *et al.*, 2004). The trend since the early 1990s suggests the gradual replacement of decaBDE with other BFRs in these plastics. Other BFRs generally provide superior performance but decaBDE appears to have retained a small market share primarily due to its low cost (Munro *et al.*, 2004).

Non-brominated flame retardants suitable for use in PBT were unavailable until 2005 when Swiss-based Clariant began commercial production of a product (Exolit® OP) based on alkyl phosphinic acid (De Boysère, J. and Dietz; Akzo Nobel, 2004). In the case of PA, the type of flame retardant used depends on the type of PA. There are several different versions of polyamide sold for electrical parts (Akzo Nobel, 2004). PA 6 and PA 6.6, which are similar to PBT in many respects (AZoM, 2006c), constitute the majority of commercially produced PA and therefore perhaps are most apt to be used in electrical applications that require flame resistance.

Several non-brominated alternatives are marketed as suitable for use in PA, including a product made by Albemarle based on magnesium hydroxide, products made by Clariant based on red phosphorus, and products made by Ciba Specialty Chemicals based on melamine cyanurate and melamine polyphosphate. Non-brominated flame retardants are estimated to account for 15% of total volume of flame retardants used in PA (Munro *et. al.*, 2004). Dell has eliminated decaBDE from all plastic parts in its server chassis, laptops and desktop computers (Dell, 2007).

Unlike with HIPS, where the use of BFRs can avoided by replacing HIPS with the copolymers HIPS/PPO and PC/ABS, the properties of PBT and PA cannot be readily obtained by using other types of plastic (Lassen *et al.*, 1999). PBT and PA each have characteristics that are difficult to substitute (Lassen *et al.*, 1999).

#### **D.** DecaBDE in wire and cable

DecaBDE is used to impart flame retardancy to polypropylene (PP) or polypropylene ether (PPE) for coated wire and cable (Harriman *et al.*, 2003; BSEF, 2006b). Numerous other brominated and non-brominated flame retardants also are used with these polymers. Non-brominated alternatives include ammonium polyphosphate, magnesium hydroxide; and melamine phosphate (Munro and Farner, 2001; Clariant, 2007). Flame retardants are used in wire and cable insulation to prevent ignition of the coating and the spread of fire along the wire.

The total amount of decaBDE used in wire and cable applications is not known, nor were we able to ascertain the extent to which decaBDE is used in wire and cable compared to other flame retardants. Information from flame retardant manufacturers suggests that many of the available alternatives are superior in performance to decaBDE, and that the main advantage of decaBDE is its relatively low cost (Albemarle, 2006f). In 2001, the Great Lakes Chemical Company (now Chemtura) predicted that the superior performance of its Reogard-1000<sup>®</sup> flame retardant (then known as CN-2616) would lead to its increased use in polypropylene (Munro and Farner, 2001). Reogard-1000 is a non-brominated flame retardant based on melamine phosphate.

Our literature review suggests that the specific applications using wire or cable impregnated with decaBDE are numerous and diverse. The Central Maine Power Company (CMP), for example, currently uses cable containing decaBDE in its electrical substations and to connect transformers to meters for medium to large commercial and industrial customers. CMP's practice is to give preference to the procurement of materials that are environmentally friendly, and the company would consider phasing out its use of cable containing decaBDE on this premise pending evaluation of the performance and cost of the available alternatives. CMP already has identified several possible non-brominated alternatives; but has not fully evaluated their performance (Mirabile, 2006).

Wiring also is the automobile component most likely to contain decaBDE. A typical vehicle has dozens of electrical and electronic components that contain decaBDE according to an industry trade association (Dana, 2006). Although the exact number and identity of each such component is difficult to determine because vehicles have thousands of components from hundreds of suppliers, one automaker estimates that over 80% of the decaBDE in its vehicles is in electrical wiring (Aho, 2006). That decaBDE migrates from these components is suggested by two studies. Dust samples from the interior of 22 privately owned vehicles were found to contain an average decaBDE concentration of 9.5 ppm, about five times higher than concentrations found in studies of dust from homes and offices (Gearhart and Posselt, 2006b). Levels of PBDEs in car interiors were higher than in office air, public indoor air, and homes in the UK (Hazrati and Harrad, 2006b).

As for possible residential applications of wire and cable containing decaBDE, the U.S. National Electrical Code requires that communication cable—including, for example, cable for telephone and internet service, HVAC control and security systems—meet applicable UL flame

retardancy standards if the cable will be installed in a plenum space, i.e., in an air space within the walls and floors of a structure (Harriman, 2003). The UL standard does not specify the use of a particular flame retardant but decaBDE is used in at least some of these products to meet the UL standard according to one supplier (Mirabile, 2006).

The U.S. Environmental Protection Agency and the Massachusetts Toxics Use Reduction Institute have formed a partnership with representatives of the wire and cable industry to evaluate the environmental impacts of current wire formulations and alternative formulations (U.S. EPA, 2006c). The partnership will examine the impacts of heat stabilizers, flame retardants and polymers used in insulation and jacketing for wire and cable products, and help companies make environmentally sound product and material choices. The results of a life cycle analysis of plenum-rated communications cable is scheduled for release in 2007.

## E. Use of decaBDE in textiles

Flame retardant coatings on textiles consume the second largest amount of decaBDE, with estimates ranging from 10 to 20% of the U.S. total (Lowell, 2005). The main textile applications reported in the literature are office furniture and drapes. DecaBDE is one of numerous chemical flame retardants that can be used to meet flammability standards in building codes governing office buildings, schools, hotels, theatres and other commercial buildings. DecaBDE also may be used in automotive fabrics (Lowell, 2005). DecaBDE is not currently used in clothing or residential upholstered furniture (Lowell, 2005).

In its 1999 report, the Danish EPA observed that BFRs were becoming less popular in textiles than other flame retardants, and that there was a general tendency to use bromine-free alternatives (Lassen *et al.*, 1999). Alternatives include direct substitution of other chemical flame retardants, the use of inherently flame-resistant fibers that make the use of a flame retardant backcoating unnecessary, and the use of flame-resistant barrier layers between fabric and padding of upholstered furniture and mattresses. Some manufacturers also have redesigned their products to reduce the fuel load by, for example eliminating or reducing the use of polyurethane foam (Lowell, 2005).

Textiles present a possible growth market for chemical flame retardants as manufacturers undertake to comply with new and pending fire safety regulations for mattresses and upholstered furniture. The U.S. Consumer Product Safety Commission (CPSC) recently promulgated regulations that, for the first time, establish a national flammability standard for mattresses.<sup>13</sup> The new regulations go into effect on July 1, 2007. A national flammability standard for upholstered furniture has not yet been promulgated but has been under consideration by the CPSC for over a decade and is expected to be finalized soon.

The concern that the promulgation of these standards could lead to an increase in the use of chemical flame retardants arises from an April 2000 report by the National Research Council (NRC, 2000). The NRC assessed 16 chemicals likely to be used in upholstery fabric to meet the flammability standards under consideration by CPSC. Eight of the chemicals, including decaBDE, were determined to pose no appreciable health risk to people who may be exposed to them in the home. Subsequent assessments by CPSC staff generally have concurred with the

<sup>&</sup>lt;sup>13</sup> The regulations are codified at 16 CFR Part 1632.

NRC in finding that decaBDE is safe for use in upholstery fabrics and mattresses (Babich and Thomas, 2001; Thomas and Brundage, 2006).

Since the NRC report was released, however, information has emerged that calls into the question the premise that manufacturers are likely to use a chemical flame retardant, and in particular decaBDE, to meet the standards. We now know, for example, that there are many ways to modify fibers and fabrics to meet flammability standards without using chemical flame retardants (Lowell, 2005). There also is the potential to use inherently flame resistant fibers and fabrics (Lowell, 2005).

Some mattress manufacturers historically used decaBDE (Lowell, 2005) but this no longer appears to be the case. Mattress manufacturers increasingly are choosing to meet flammability standards by placing a barrier layer of inherently flame resistant material between the exterior cover fabric and the inner cushioning material (Lowell, 2005). The International Sleep Products Association (ISPA), a trade association representing mattress manufacturers, reports that all its members use fire-resistant barriers that minimize the need for flame retardant chemicals. Serta and other mattress manufacturers who do not belong to ISPA also employ barrier technology (Lowell, 2005). Serta, the second largest U.S. mattress manufacturer, uses a barrier layer called FireBlocker® that consists of a proprietary blend of natural and synthetic fibers treated with boric acid (Serta, 2005; Skrzycki, 2005). Fire barriers consisting of blends of natural and synthetic fibers also are commonly used in bus and airplane seating (U.S. EPA, 2004).

Furniture manufacturers, in anticipation of adoption of national flammability standards for upholstered furniture, also can be expected to eschew chemical flame retardants and employ barrier technologies or other non-chemical alternatives whenever feasible. To assist them in this endeavor, the U.S. EPA has convened the Furniture Flame Retardancy Partnership "to better understand fire safety options for the furniture industry."<sup>14</sup> Participants include furniture makers, chemical manufacturers, environmental groups, the American Fire Safety Council and CSPC. The goal of the partnership is to identify and move toward environmentally friendly approaches to meeting fire safety standards for foam and fabric.

According to furniture industry sources, 80% of upholstered furniture already meets a voluntary industry standard designed to protect against ignition from cigarettes and, in 99% of the cases, chemical flame retardants are not needed to meet this standard (Lowell, 2005). To the extent furniture manufacturers nevertheless opt to use chemical flame retardants, there are numerous commercially available alternatives to decaBDE. The Lowell Center for Sustainable Production, in Appendix D of its 2005 report on substitutes for decaBDE in textiles, lists over 30 separate non-brominated chemical mixtures that are marketed as suitable for use in textiles (Lowell, 2006). Given the ongoing and highly visible debate about the health effects of PBDEs, it seems unlikely that a manufacturer would choose decaBDE over the available alternatives and thereby risk characterization of their product as unsafe.

The situation is similar in the case of flammability standards for drapes and curtains in buildings frequented by the public. Some manufacturers have used decaBDE to meet these standards because it is relatively inexpensive and stands up to repeated washing (Lowell, 2005).

<sup>&</sup>lt;sup>14</sup> U.S. EPA, Furniture Flame Retardancy Partnership, www.epa.gov/oppt/dfe/projects/flameret.

Many other manufacturers, however, offer draperies that are flame retarded with chemicals other than deca-BDE or that are made of inherently flame resistant fibers (Lowell, 2005).

## F. Cost of alternatives

## TV casings

HIPS with decaBDE tends to be used in lower priced TVs because it is the least expensive option (Leisewitz and Schwartz, 2001). Phosphorus-based flame protection, which requires a shift to another plastic, generally is more expensive. The cost increase depends mainly on the type of plastic chosen, which in turn determines which flame retardants can be used (Leisewitz and Schwarz, 2001). Polycarbonate is expensive relative to HIPS, PC/ABS less so (Leisewitz and Schwarz, 2001).

In PC/ABS, the decisive cost variable is the proportion of PC to ABS (Leisewitz and Schwarz, 2001). The Lowell Center for Sustainable Production estimates that replacing HIPS with PC/ABS in a 27-inch TV that sells for \$300 would increase the purchase price by \$7.50 at most or about 2.5%. The State of Washington, in its 2006 PBDE Action Plan, estimates that a shift from HIPS to other plastics would increase the price of the TV by 5 to 15% (Washington, 2006).

Swiss chemical manufacturer Clariant writes that, while phosphorus based flame retardants are not suitable for HIPS, plastics other than HIPS "can be used for the same applications albeit at slightly higher prices" (Clariant, 2004). Clariant observes, however, that:

"...offering a more environmentally friendly product is often not sufficient for market success, even if the price and technical properties are comparable to established flame retardants. Therefore, legally binding requirements together with market pull— manufacturers and consumers of end use products demanding more environmentally friendly solutions—will encourage the development of alternative non-halogen flame retardants. Once they gain a considerable share of the market, economies of scale can materialise and lower the cost of alternatives."

The fact that TV's without decaBDE already appear in the marketplace is further evidence that cost is not a significant barrier to substitution of decaBDE in that application. The State of Washington estimates that 57% of TVs already are deca-free (Washington, 2006). TV manufacturers that have ended the use of decaBDE or offer at least some deca-free models include Panasonic/Matsushita, Samsung, Sharp and Sony (Lowell, 2005; McPherson *et al.*).

## Electrical parts

Flame retardant manufacturer Clariant writes:

"Flame retarding [PA or PBT] with Exolit® phosphinates will result in compounds which are (at current prices) comparable or only slightly more expensive than compounds with brominated flame retardants like PBDEs...Phosphinates are more expensive on a per kg flame retardant basis, however, realistically the price per volume of flame retarded polymer compound should be compared. The necessary dosage of phosphinates is lower compared to brominated flame retardant systems which usually consist of the brominated flame retardant plus antimony trioxide as a synergist, i.e. phosphinates are more effective..."

The fact that decaBDE is used in only about 10% of all electrical parts flame retarded with PBT and only about 6% of parts flame retarded with PA is further suggests that the cost of alternatives is not a significant barrier to their use. Alternatives already are used in the vast majority of these parts.

On the other hand, a phase-out of decaBDE in electrical and electronic equipment cannot be accomplished overnight. Manufacturers may need several years to ascertain which flame retardants were used in the electrical parts of their products, and, where decaBDE is found, to re-engineer, test and procure a replacement that meets the product specifications.

The automobile industry, which has already begun making a voluntary shift to bromine-free retardants, says it will need 5 more years to fully eliminate decaBDE from automobiles (Dana, 2006). The transition could be even longer in airplanes, which are estimated to have nearly 400 separate components that contain decaBDE. Many or most of those components cannot be substituted without extensive testing and regulatory approval.

## Wire and cable

The extent to which decaBDE is used in electrical wire and communications cable could not be ascertained. A few specific applications were identified—automobile wiring, plenum-rated communication cable, and control cable in electrical substations. However, wire and cable is a diverse product group with a multitude of possible applications. In the absence of a more comprehensive inventory of the specific types of wire and cable in which decaBDE is used, there is little useful that can be said about the feasibility and cost of substituting alternatives. Here is what we can say:

- There is nothing in the literature to suggest that decaBDE provides exceptional properties that make it uniquely suitable for a particular wire or cable application. In fact, decaBDE's propensity to bloom<sup>15</sup> may be a disadvantage (Albemarle, 2006f). DecaBDE's main advantage in wire and cable applications appears to be its low cost.
- Preliminary investigation by Central Maine Power Company suggests that bromine-free instrumentation and control cable for electrical substations costs 30 to 45% more than cable flame retarded with decaBDE (Mirabile, 2006).

#### **Textiles**

In its review of substitutes for decaBDE in textiles, the Lowell Center for Sustainable Production observed that, while decaBDE is a low-cost method for treating textiles, there are a multitude of non-brominated replacements on the market, including other chemical flame retardants, inherently flame resistant fibers and fiber blends, barrier layers and other approaches. "These substitutes have their own individual cost, performance and aesthetic tradeoffs. While there is no single replacement for decaBDE, the multitude of options on the market make it clear that viable market-ready approaches exist" (Lowell, 2005)

<sup>&</sup>lt;sup>15</sup> Bloom is a phenomenon in which the flame retarding agent migrates from the polymer, forming a powdery or greasy film on the polymer surface. The film attracts dirt and moisture which can detrimentally affect electrical properties when the polymer is used as insulation for wire and cable. Bloom also can result in the eventual loss of the flame retarding agent to the extent that the wire insulation is no longer adequately flame retardant. See Breza, J.M. Bloom Inhibited Flame Retardant Compositions. U.S. Patent No. 3,730,929, May 1, 1973.

The CPSC conducted separate qualitative and quantitative risk assessments of five chemicals—antimony trioxide, boric acid, melamine, vinylidene chloride and decaBDE—that might be used by mattress manufacturers as a low-cost option to meet the new national flammability standards. These assessments demonstrate that, in the event mattresses manufacturers opt to use flame retardant chemicals, there are safer, low-cost alternatives to decaBDE.

In its qualitative risk assessment, the CPSC concluded that melamine and vinylidene chloride present only a negligible risk of health effects to consumers. DecaBDE, on the other hand, was considered to be toxic by CPSC, although it lacked sufficient exposure data to make a definitive conclusion about the potential health risk to consumers who sleep on mattresses that contain decaBDE (Thomas and Brundage, 2004).

In its quantitative risk assessment, the CPSC found that none of the five chemicals, including decaBDE, pose any appreciable risk to consumers (Thomas and Brundage, 2006) The CPSC also found that, in contrast to decaBDE, two of the low-cost alternatives—melamine and ammonium polyphosphate—are not toxic. A third—vinylidene chloride—could not be detected in rigorous extraction tests of treated mattresses, leading CPSC to conclude that risk of health effects is minimal because there is no significant exposure to consumers.

## IV. Safety of chemical alternatives

As previously stated, the Maine Legislature has declared its intent to restrict or prohibit the sale of products containing decaBDE **if a safer, nationally available alternative is identified**. By "safer", we understand the Legislature to mean an alternative that, compared to decaBDE, has not been shown to pose the same or greater risks to human health or the environment. It is further understood that alternatives must meet flame retardancy regulatory requirements including all applicable standards of the National Electrical Code, the National Fire Protection Association and Underwriters Laboratories Inc.

## A. Evaluation criteria

In evaluating the safety of alternatives to decaBDE, we bring the following observations and criteria to bear:

- The evaluation does not call for a ranking of <u>fire</u> safety. Flame retardants can vary widely in efficiency, but it is not accurate to characterize one flame retardant as more fire safe than another (De Boysère, J., 2006). UL and NEC flammability standards do not specify the type of flame retardant that must be used. The choice of retardant is left to the product manufacturer. The manufacturer adds just enough of the selected retardant to meet the applicable standard. The efficiency of the retardant dictates the loading rate—the amount of retardant that must be added. Loading rates can vary widely depending on the type of flame retardant selected, and the loading rate can, in turn, influence the choice of retardant, but a flame retardant is not less fire safe simply because more of it must be used.
- Alternatives that allow flammability standards to be met without using a chemical flame retardant are presumed to be safer.

- Alternatives that replace decaBDE with other brominated chemicals cannot be fairly characterized as safer because they share the characteristics that make decaBDE problematic. BFRs have been subjected to far more scientific study than other flame retardants, a focus that can be attributed to the ubiquity and persistence of BFRs in the environment and their propensity to bioaccumulate. Replacing decaBDE with another BFR is not a demonstrably safer alternative.
- Alternatives that have been classified as a "PBT"—a chemical that is persistent, bioaccumulative <u>and</u> toxic—are not safer than decaBDE.
- The use of persistent or bioaccumulating flame retardant chemicals should be avoided independent of their toxicity.
- Chemical flame retardants likely to be released from the host material to the indoor environment during product use should be avoided.
- The use of chemicals with carcinogenic, mutagenic or reproductive toxic effects should be avoided.

## **B.** Evaluation of decaBDE

As outlined in Section II of this report, as well as in our two previous reports on BFRs, decaBDE undergoes global transport, is found in animals around the world, and bioconcentrates in food webs. It is degraded in the environment and metabolized in animals and humans to toxic congeners. Administration of decaBDE to intact animals results in toxic effects. It therefore meets the definition of a persistent bioaccumulative toxic, or PBT. It is classified as such in a recent report by the Washington State Department of Ecology (2006). Therefore it is important that the use of decaBDE be eliminated, and other, safer means of flame retardation substituted.

## C. Evaluation of chemical alternatives to decaBDE

Below is a summary of what is known about the characteristics of the <u>non-brominated</u> chemicals that, based on our review of the literature as discussed in section III, are most likely to be used as alternatives to decaBDE. The amount of information available on most of these chemicals is limited.

#### Bisphenol A diphosphate (BAPP)

BAPP is not a suitable alternative to decaBDE. There is evidence that it is persistent in the environment, although its potential for bioconcentration in the environment is presumed to be low (Syracuse, 2006). Information on the toxicity of BAPP to mammals is limited. Of significant concern, however, is the fact that one of the degradation products is bisphenol A, a potent endocrine disruptor. Bisphenol A affects multiple reproductive endpoints at low levels of exposure, as well as affecting immune function and brain development. Humans have detectible levels of bisphenol A in their bodies as a consequence of the presence of bisphenol A in plastics.

## Resorcinol bis diphenylphosphate (RDP)

RDP is similar in structure to BAPP in that it contains two diphenylphosphate moieties; however, it does not contain bisphenol A. As with BAPP, there is relatively little information on

the fate and toxicity of RDP. Syracuse (2006) considers that it would not be persistent in the environment or bioconcentrate, based on experimental studies (that is, rather that actual performance in the environment). Toxicity to mammals was considered to be moderate based on limited data, but laboratory studies documented high toxicity to aquatic organisms. The German Federal Environmental Agency (GFEA), in its evaluation of flame retardants, could not make a recommendation concerning the suitability of RDP due to lack of data (Leisewitz *et al.*, 2001). (For comparison, the use of decaBDE was rejected by this agency). Nonetheless, based on available evidence, it seems that RDP presents a significantly lower threat to the environment and human health than does decaBDE or other brominated chemicals (not reviewed here).

## Alkyl phosphinic acid

Little data could be found on alkyl phosphinic acids. Only two toxicity studies were identified; little or no toxicity was observed in rats in a 30-day study, and it appears not to be mutagenic. No reports were identified that included a discussion of environmental fate and toxicity of these compounds.

### Red phosphorus

Red phosphorus is readily degraded in the environment, and aquatic toxicity is considered to be unlikely (Leisewitz *et al.*, 2001). Little toxicity information is available, but it is unlikely to be toxic based on its chemistry. The GFEA considers its use as a flame retardant to be "unproblematic."

### Ammonium polyphosphate

Ammonium polyphosphate is readily degraded or metabolized to ammonia and phosphate (Leisewitz *et al.*, 2001). No specific studies on toxicity were identified. The concentration that would be expected to be achieved would present no environmental or human health hazard. Ammonium polyphosphate is classified as "unproblematic" by the GFEA.

#### Magnesium hydroxide

The Danish Environmental Protection Agency (Lassen *et al.*, 1999) reports that no information was identified on environmental fate or toxicity. More recent studies were not identified. Magnesium hydroxide is used as an antacid in over-the-counter medicine.

#### Melamine cyanurate

There are little toxicity data available for melamine cyanurate (Leisewitz *et al.*, 2001). Although melamine cyanurate would not be expected to be persistent in the environment, no data are available. The GFEA considers that there are insufficient data to make a determination of whether melamine cyanurate is suitable for use as a flame retardant. More recent studies were not identified on either melamine cyanurate or melamine polyphosphate. Melamine produced cancer of the urinary tract at high doses in several studies in rats following chronic administration although the mechanism may not be relevant to humans. The toxicity potential of melamine itself is considered low by the Consumer Product Safety Commission (Thomas and Brundage, 2004).

## V. DecaBDE: Existing Regulatory Initiatives

#### A. European Union

On January 27, 2003, the European Parliament and the Council of the European Union jointly issued a legislative directive (Directive 2002/95/EC) that, among other things, requires the member states<sup>16</sup> of the European Union (EU) to ensure that new electronic and electrical equipment put on the market after July 1, 2006, does not contain any PBDE. This directive is commonly referred to as the "Restriction on Hazardous Substances" or the "RoHS". The RoHS subsequently was amended by the European Commission, the EU's executive body, to establish 0.1% by weight as the maximum concentration of PBDEs tolerated in electrical and electronic equipment.<sup>17</sup>

Article 5(1)(b) of the RoHS authorizes the European Commission to exempt materials from the ban if their elimination or substitution is technically or scientifically impracticable, or if the negative environmental, health or consumer safety impacts caused by substitution are likely to outweigh the benefits. On October 13, 2005, the Commission issued a decision exempting "polymeric applications" of decaBDE from the RoHS (EC, 2005a). The Commission based its exemption decision on the EC's risk assessment of decaBDE (EC, 2004a; EC, 2004b; EC, 2005b) and, in particular, on the conclusion from that assessment that there is "at present no need for measures to reduce the risks for consumers." The Commission, however, also noted that the risk assessment concludes that further study of decaBDE is needed, and so reserved the right to re-examine the exemption at any time based on new evidence (EC 2005a). Under the terms of the ROHS, the Commission must re-examine the exemption by July 1, 2010 at the latest.

On June 21, 2006, the Commission issued an opinion letter clarifying that the exemption does not apply to products containing more than 0.1% by weight of any PBDE other than decaBDE (EC, 2006). Because commercial decaBDE mixtures typically contain about 3% nonaBDE, the Commission's interpretation means that products incorporating decaBDE at loading levels required to meet flame retardancy standards likely would contain nonaBDE in amounts exceeding the 0.1% regulatory threshold and therefore would remain subject to the RoHS ban. The Commission's opinion in this matter is not legally binding as a legally binding ruling only can be made by the European Court of Justice (ECJ).

In January 2006, EU member Denmark and the European Parliament brought separate actions asking the ECJ to annul the Commission's decision to exempt decaBDE from the RoHS.<sup>18</sup> The actions, which subsequently were joined by the court, allege that the Commission failed to comply with the conditions laid down in the ROHS for granting exemptions by, among other things, failing to find that there are no practicable alternatives to decaBDE and by extending the exemption to all polymeric applications of decaBDE without exception.

<sup>&</sup>lt;sup>16</sup> The member countries are Austria, Belgium, Bulgaria, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden and United Kingdom.

<sup>&</sup>lt;sup>17</sup> See Commission Decision 2005/618/EC of August 18, 2005.

<sup>&</sup>lt;sup>18</sup> Official Journal of the European Union, Nos. C 074, 3/25/06, pp 28, 29 and C 086, 8/4/06, p 11.

In support of Denmark's case, the Danish Environmental Protection Agency commissioned two reports: a study of the use of decaBDE and its alternatives in electrical and electronic equipment; and an environmental and health assessment of selected alternatives. Both reports have been submitted to the court and are expected to be made public in January 2007. Submissions from third-party intervenors—the United Kingdom on the side of the commission; Sweden, Norway, Finland and Portugal on the side of Parliament and Denmark—are expected within the next month. The parties then will have the opportunity to submit written responses, with oral argument to follow later this year. An ECJ Advocate General is expected to issue an initial opinion on the case by the end of year, but the ECJ itself is not expected to deliver its final judgment until well into 2008 (Maxson, 2007).

In the meantime, EU member Sweden has acted on its own to ban the sale of decaBDE in textiles, upholstery and electrical wiring effective January 1, 2007.<sup>19</sup> German plastics and textile manufacturers voluntarily stopped producing and using decaBDE in 1989, suggesting that suitable alternatives have long been available (Lassen *et al.*, 1999; Leisewitz *et al.*, 2001).

## **B. U.S. Environmental Protection Agency**

The U.S. Environmental Protection Agency (EPA) has promulgated a regulation—called a significant new use rule (SNUR)—that complements the decision by Chemtura, the only U.S. manufacturer of octaBDE and pentaBDE, to voluntarily discontinue their production (U.S. EPA, 2006b). The rule took effect on August 14, 2006.

The SNUR designates any new production or importation of octa or pentaBDE as "significant new uses", thereby ensuring that these two chemicals cannot be reintroduced to the U.S. market without first being subject to evaluation by EPA under section 5 of the Toxic Substances Control Act (TSCA).<sup>20</sup> Section 5 of TSCA requires manufacturers and importers to notify EPA at least 90 days before commencing a significant new use of chemicals. This gives EPA the opportunity to evaluate the intended use, and to prohibit or limit that use if necessary to protect human health.

The SNUR applies only to the importation of the chemicals themselves. Imported products that contain pentaBDE or octaBDE are exempt because the EPA lacks authority to issue a SNUR covering an ongoing activity. EPA considers importation to be an ongoing activity in that there is evidence that products containing polyurethane foam, some of which is impregnated with pentaBDE, continue to be imported (U.S. EPA, 2006a).

EPA is developing a SNUR that would require prior notification to EPA before decaBDE could be used in residential furniture, an application in which decaBDE is not currently used. As mentioned in Section 111(E), decaBDE is one of 16 chemical substances evaluated by the National Research Council as candidates for use in meeting flammability standards for residential upholstered furniture under consideration by the CPSC. The proposed SNUR would apply to all 16 (U.S. EPA, 2006a).

<sup>&</sup>lt;sup>19</sup> Swedish Code of Statutes 1998:944 as amended by 2006:1075 eff. January 1, 2007.

<sup>&</sup>lt;sup>20</sup> 15 USC §§ 2601, et seq.

## C. U.S. States

No U.S. state has yet restricted the sale of products containing decaBDE, although bans have been proposed in Connecticut, Hawaii, Illinois, Michigan, Rhode Island and Washington (NCEL, 2006).

In January 2006, the State of Washington Department of Ecology (DOE) and Department of Health (DOH) issued a PBDE Chemical Action Plan that calls for a ban on the sale of products containing decaBDE provided safer alternatives are identified (Washington, 2006). In December 2006, a bill banning the use of decaBDE in certain applications was introduced to the Washington State Legislature at DOE's request.<sup>21</sup> The bill, which was approved by the House Committee on Environmental Health on January 11, 2007, would apply to mattresses effective January 1, 2008 and to residential upholstered furniture, TV enclosures and computer enclosures effective January 1, 2011. The ban on decaBDE in mattresses would take effect without further analysis because, based on studies by the CPSC and others,<sup>22</sup> the DOE and DOH are satisfied safer alternatives are available for meeting the new national flammability standard for mattresses (LaFlamme, 2007). The ban on decaBDE in residential furniture, TVs and computers would go into effect only if the DOE, DOH and fire safety experts find that "a safer and technically feasible alternative that meets applicable fire safety standards is available." The bill would require DOE and DOH to report their findings to the Legislature by December 15, 2008.

On December 18, 2006, the Maryland Department of the Environment issued a report in which it recommends postponing any decaBDE legislation. The agency found that decaBDE "should not be banned unless safer alternatives are identified or new toxicological data shows that there is an unacceptable risk to public health or the environment" (Maryland, 2006).

Eight U.S. states including Maine have banned the sale of products containing pentaBDE or octaBDE.<sup>23</sup> In each of these states except Maine, the sales prohibition applies to products containing more than one-tenth of 1% by mass of these chemicals. This regulatory threshold is derived from European Union legislation, and was set to coincide with detection level for PBDEs using standard analytical techniques such as gas chromatography and mass spectrometry.<sup>24</sup>

Maine's law, on the other hand, sets a regulatory threshold of 1%, 10 times higher than any other jurisdiction. As a consequence, it arguably remains legal in Maine to sell products with several components containing more than 1% octaBDE or pentaBDE where the total mass of those PBDEs is less than 1% of the mass of the product. This interpretation could have the anomalous result of allowing the sale of the larger product while prohibiting the sale of replacement parts for that product.

This issue is mainly of academic interest in the case of octaBDE and pentaBDE given that they no longer are produced in the U.S. and presumably are no longer widely used. If the Legislature decides to add decaBDE to the sales ban, however, thought should be given to amending the regulatory threshold to ensure the law reaches the targeted products. For example,

<sup>&</sup>lt;sup>21</sup> HB 1024, 2007 Regular Session, Washington State Legislature.

<sup>&</sup>lt;sup>22</sup> See section III(E) of this report, page 25.

<sup>&</sup>lt;sup>23</sup> The others are California, Hawaii, Illinois, Maryland, Michigan, New York and Oregon.

<sup>&</sup>lt;sup>24</sup> See Directive 2003/11/EC of the European Parliament and the Council of the European Union, February 6, 2003.

automakers point that, although a typical vehicle has dozen of components containing decaBDE, the overall vehicle is likely to contain significantly less than 1% of decaBDE by weight (Dana, 2006).

The Legislature also should consider amending Maine's PBDE law to include exemptions for the sale of replacement parts manufactured before the effective date of the sales ban and products made from recycled material. Most states with bans on octaBDE and pentaBDE already have such exemptions. Automakers, for example, point out that their service departments generally stock parts made years ago at the same time as the original components in the vehicle. They often do not know which of the thousands of replacement parts in stock have PBDEs. And where PBDEs were used, there may not be a drop-in PBDE-free substitute, meaning that the replacement part would have to be re-engineered.

## VI. Conclusions

DecaBDE is a persistent, bioaccumulative and potentially toxic chemical used as a flame retardant in consumer products. The slow release of decaBDE from these products has led to widespread environmental contamination. Levels in human tissue, human breast milk and the food we eat are cause for concern. These levels are higher in the U.S. and Canada than in Europe where the use of decaBDE is restricted.

The products most likely to contain decaBDE are TVs, office furniture and draperies but decaBDE also finds application in electrical wire, communications cable and numerous small, plastic parts for electrical and electronic equipment. TV housings and textiles account for up to 90% or more of the current decaBDE consumption.

Safer alternatives are available. In the case of textiles, alternatives that do not require the use of chemical flame retardants already are widely employed in the marketplace. There are many ways to modify mattresses, upholstered furniture and drapes to meet flammability standards without using decaBDE or other BFRs. Mattress manufacturers uniformly have eschewed the use of decaBDE to meet a national flammability that takes effect on July 1, 2007. And furniture industry sources suggest that, in 99% of cases, chemical flame retardants will not be needed to meet pending national standards for residential upholstered furniture,

In the case of TV cabinetry, the use of safer alternatives to decaBDE will require manufacturers to shift from using the plastic HIPS to other plastics that can be flame-retarded with phosphorus-based compounds. The use of wood or metal cabinets, a presumptively safer alternative to flame-retarded plastics, is possible but rare.

There are no significant technological barriers preventing TV manufacturers from discontinuing their use of decaBDE by shifting to another plastic. The choice of plastic does not affect the serviceability of the TV or entail a reduction in fire safety. The choice is mainly a cost issue. HIPS plastic flame retarded with decaBDE is available at relatively low cost compared to plastics flame retarded with other chemicals. A shift to other plastics likely will lead to a small increase in the price of low-end TVs.

The plastics used as alternatives to HIPS include HIPS/PPO and PC/ABS. These two resin blends already are widely used in TV cabinets. This appears to be the case for most, if not all,

TVs sold in Europe where a ban on the sale of electronics containing decaBDE has been pending for several years. HIPS/PPO and PC/ABS typically are flame-retarded with phosphorus compounds. The exact compound used generally is closely guarded proprietary information, but the most frequently mentioned of the phosphorus-based flame retardant marketed for this purpose is resorcinol bis diphenyl phosphate (RDP). RDP, in our judgment, presents a significantly lower threat to the environment and human health than does decaBDE.

In the case of electrical parts, coated wire and communication cable, decaBDE is not the principal flame retardant used. Where it is used, substitution is feasible and has been accomplished by some users. However, manufacturers of products that have many small electrical parts or extensive wiring (e.g., automobiles, airplanes, and ships) may not be able to easily ascertain which components contain decaBDE. The process of identifying all instances of decaBDE usage in such products and replacing them a deca-free substitute could take several years especially if extensive testing or regulatory approval is required.

For all applications in which decaBDE currently is used, alternatives without decaBDE are available. The fact that a number of manufacturers who historically used decaBDE in electronics and electrical applications have substituted alternatives shows that the alternatives are technically feasible and affordable. No applications were identified in which decaBDE is the only flame retardant used or in which decaBDE offers unique or exceptional properties. No application was identified in which the use of alternatives requires a compromise in fire safety.

## VII. Recommendations

- 1. To ensure Maine's PBDE law is consistent with corresponding laws in other U.S. states and the European Union, the Legislature should amend the existing ban on the sale of products containing octaBDE and pentaBDE so that it applies to any product that has a component containing more than one-tenth of 1% of octaBDE of pentaBDE. Products that contain either of these PBDE mixtures solely due to the use of recycled material should be exempted from the ban. Replacement parts containing octaBDE or pentaBDE also should be exempted provided the part is sold for use in a product manufactured before January 1, 2006.
- 2. To reduce the presence of decaBDE in the immediate surroundings of humans, the Legislature should ban the sale of televisions and other consumer electronics encased in plastic containing more than one-tenth of 1% of decaBDE. The ban should be made effective January 1, 2012 to ensure that manufacturers have sufficient lead time to retool their production process.
- 3. To forestall the use of decaBDE to meet new federal flammability standards for mattresses and pending standards for residential upholstered furniture, the Legislature should ban the sale of these products effective January 1, 2008 if they contain more than one-tenth of 1% of decaBDE.
- 4. Primary responsibility for compliance with Maine's PBDE law should rest with the product manufacturer.

Appendix A sets forth proposed legislation to implement these recommendations.

**Appendix A: Proposed Legislation** 

## An Act to Reduce Contamination in the Home from the Release of Brominated Flame Retardants

## Be it enacted by the People of the State of Maine as follows:

Sec. 1. 38 MRSA § 1609, as enacted by PL 2003, c. 629, §1, is amended to read:

**1. "Penta" mixture and "octa" mixture of polybrominated diphenyl ethers.** Effective January 1, 2006, a person may not sell or offer to sell, or distribute for promotional purposes, a product containing more than <u>one-tenth of</u> 1% <u>by mass</u> of the "penta" or "octa" mixtures of polybrominated diphenyl ethers.

## 1-A. "Deca" mixture of polybrominated diphenyl ethers.

A. Effective January 1, 2008, a person may not sell or offer to sell, or distribute for promotional purposes, a mattress, an article of furniture or any other product intended for household use if the product has a textile component containing more than one-tenth of 1% by mass of the "deca" mixture of polybrominated diphenyl ethers.

**B.** Effective January 1, 2012, a person may not sell or offer to sell, or distribute for promotional purposes, a television, computer or other electronic device if the exterior casing of the device contains more than one-tenth of 1% by mass of the "deca" mixture of polybrominated diphenyl ethers.

2. Review; report. The department, with the Department of <u>Health and</u> Human Services, <u>Center for Disease Control and Prevention</u> <del>Bureau of Health</del>, shall review relevant risk assessments <u>and other information</u> in connection with brominated flame retardants <u>and their</u> <u>alternatives, including and</u> relevant findings and rulings by the United States Environmental Protection Agency and the European Union. <u>By January 31, 2009 and every two years</u> <u>thereafter, the</u> The department shall <del>annually, no later than January 5, submit</del> a report <u>summarizing the results of it review</u> regarding the regulation of brominated flame retardants to the joint standing committee of the Legislature having jurisdiction over natural resources matters. For purposes of this subsection, "brominated flame retardant" means any chemical containing the element bromine that may be added to a plastic, foam or textile to inhibit flame formation.

**3. Application.** This section does not apply to the sale of used products. <u>This section</u> does not apply to the sale of products if the presence of polybrominated diphenyl ether is due solely to the use of recycled material. This section does not apply to the sale of replacement parts that contain the octa or penta mixtures of polybrominated diphenyl ether provided the parts are for use in a product manufactured before January 1, 2006.

4. Enforcement. If there are grounds to suspect that a product is being offered for sale in violation of this section, the commissioner may request the manufacturer of the product to provide a certificate of compliance. Within 10 days of receipt of a request, the manufacturer shall: A. <u>Provide the commissioner with a certificate attesting that the product complies with</u> the requirements of this section: or

**B.** <u>Notify persons who sell the manufacturer's products in this state that the sale of the product is prohibited and provide the commissioner with a list of the names and addresses of each person that was notified.</u>

Whenever it appears that a product has been sold, offered for sale or distributed in this state in violation of this section, the commissioner may take enforcement action in accordance with section 347-A against the product manufacturer. For the purpose of this section, the "manufacturer" is the company, corporation or other person who manufactured or assembled the final product or whose brand name is affixed to the product. In the case of a product that was imported into the United States, the importer or domestic distributor of the product is the "manufacturer" if the person who manufactured or assembled the product or whose brand name is affixed to the product or whose brand name is affixed to the product or whose brand name is affixed to the product does not have a presence in the United States.

## **Statement of Fact**

This bill further restricts the sale of products containing a class of chemical flame retardants known as polybrominated diphenyl ethers. The bill exempts products made from recycled material and certain replacement parts from the restrictions. The bill relieves the Departments of Environmental Protection and Health and Human Services from the responsibility to report annually on brominated flame retardants; from now on, the report will be due to the Legislature every two years. **Appendix B: References** 

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