Minnesota Pollution Control Agency

Decabromodiphenyl Ether
(Deca-BDE)

A Report to the Minnesota Legislature
January 15, 2008

Azra Kovacevic and Cathy O'Dell of the Minnesota Pollution Control Agency (MPCA) Environmental Analysis and Outcomes Division prepared this report, with advice and assistance from Laura Solem, Summer Streets, Paul Hoff and Marvin Hora. The MPCA would also like to thank Carl Herbrandson, Patricia McCann and Pamela Shubat of the Minnesota Department of Health for their consultation and review assistance during preparation of this report.

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ACRONYMS AND ABBREVIATIONS

ABS	Acrylonitrile-butadiene-styrene
ACS	American Chemical Society
ATO	Antimony oxide
ATSDR	Agency for Toxic Substances and Disease Registry
BAPP, BPADP, BDP	Bisphenol A diphosphate
BFR	Brominated Flame Retardant
BFRIP	Brominated Flame Retardant Industry Panel
BSEF	Bromine Science and Environmental Forum
CA	California
CA BHFTI	State of California Bureau of Home Furnishings and Thermal Insulation
CEPA	Canada Environmental Protection Act
CFR	Chlorinated Flame Retardants
CPCS	Consumer Product Safety Commission
DCP	Diphenyl cresol phosphate
Deca-BDE	Decabromodiphenyl ether
EBTPI	Ethylene bistetrabromo phthalimide
EPA	Environmental Protection Agency
EPDM	Ethylene-propylene terpolymer
EU	European Union
FAA	Federal Aviation Authority
FMVSS	Federal Motor Vehicle Safety Standards
FR	Flame Retardant
HBCD	Hexabromocyclododecane
Hepta-BDE	Heptabromodiphenyl Ether
Hexa-BDE	Hexabromodiphenyl Ether
HI	Hawaii
HIPS	High-impact polystyrene
HIPS/PPO	High impact polystyrene/Polyphenylene ether
IL	Illinois
IRIS	Integrated Risk Information System
IUPAC	International Union for Pure and Applied Chemistry
LCD	Liquid Crystal Desplay
LOAEL	Loves Observed Adverse Effect Level
MD	Maryland
ME	Maine
MI	Michigan
MN	Minnesota
MPCA	Minnesota Pollution Control Agency
NEC	National Electric Code
NFPA	National Fire Protection Association
NHTSA	National Highway Traffic Safety Administration

NOAEL	No Observed Adverse Effect Level
Nona-BDE	Nonabromdiphenyl Ether
NY	New York
Octa-BDE	Octabromodiphenyl ether
OR	Oregon
P,B,T	Persistent, Bioaccumulative, Toxic
PA	Polyamide
PBB	Polybrominated biphenyls
PBDE	Poly-brominated diphenyl ethers
PBT	Polybutylene terephthalate
PC/ABS	Polycarbonate/Acrylonitrile-butadiene-styrene
PC/PS	Polycarbonate/Polystyrene
PCB	Polychlorinated biphenyls
Penta-BDE	Pentabromodiphenyl ether
PP	Polypropylene
PPE	Polypropylene ether
PVC	Polyvinyl chloride
RDP	Resorcinol bis diphenylphosphate
RfD	Reference Dose
RI	Rhode Island
RoHS	Restriction of Hazardous Substances (EU)
SARA	Superfund Amendments and Reauthorization Act
SNUR	Significant New Use Rule
TBBPA	Tetrabromobisphenol A
Tetra-BDE	Tetrabromodiphenyl Ether
TRI	Toxic Release Inventory
TSCA	Toxic Substances Control Act
TTP	Triphenyl phosphate
UL	Underwriter Laboratories
USFA	United States Fire Association
VCCEP	Voluntary Children’s Chemical Evaluation Program
VECAP	Voluntary Emissions Control Action Program
VECAP NAPR	VECAP North American Progress Report
WA	Washington
WEEE	Waste Electrical and Electronic Equipment
WHO	World Health Organization

EXECUTIVE SUMMARY

Flame retardants are chemicals that are added to a variety of consumer and commercial products to improve their resistance to fire. Brominated flame retardants (BFRs) are the highest use flame retardants globally because they are both inexpensive and highly efficient. A class of BFRs known as polybrominated diphenyl ethers (PBDEs) has received increasing attention from scientists and policymakers. This attention is due to the high rate of use of PBDEs and their increasing concentration in the environment, in wildlife, and in people.

Since PBDEs were introduced in the 1960s, PBDE concentrations in human tissue have increased exponentially, with concentrations doubling every three to five years. PBDE concentrations in the general population of the United States are the highest in the world.

PBDEs have been found in wildlife including fish, birds, and seals in the arctic. PBDEs are present in food consumed by people, especially fish, meat and dairy products. In environmental media, PBDEs are found at high concentrations in sediments, in sewage sludge and in house dust. Scientific research indicates the concentrations of PBDEs are increasing in humans and in environmental media.

Because of these increasing PBDE concentrations and results from scientific studies on laboratory animals that indicate negative health impacts from PBDEs at elevated concentrations, the European Union and several U.S. states including Minnesota have banned further use of two of the three primary PBDE formulations.

The third PBDE formulation, Deca-BDE, is still in wide use in the production of television enclosures and in the commercial textile and upholstery industry, as well as in a number of lower volume applications.

The MPCA has prepared this report on Deca-BDE at the request of the Minnesota Legislature. Minnesota Statute 325E.387 directs the MPCA specifically to address the uses of Deca-BDE and fire safety; the availability of technically feasible and safer alternatives to Deca-BDE; evidence of potential harm to human health and the environment from the use of Deca-BDE and its alternatives; and findings and recommendations made by other state and federal agencies that have studied the available information on Deca-BDE.

This report incorporates a great deal of information that has been previously summarized in recent reports on PBDEs prepared by other states and research and/or advocacy organizations. Chief among these are the reports by the states of Washington, Illinois, California, Maine and Michigan; the Lowell Center; and the risk assessment on Deca-BDE prepared by the European Union. The MPCA also conducted its own literature review of recently published scientific studies.

Minn. Stat. 325E.387 also directs the MPCA to consult with the Minnesota Departments of Health and Public Safety and key stakeholders regarding their concerns over the use and potential limitations on the use of Deca-BDE. Insights about stakeholder concerns were obtained through telephone interviews and meetings with a number of parties, including representatives from the bromine industry, the Minnesota State Fire Chiefs Association, the Institute for Agriculture and Trade Policy, Minnesota manufacturers, and ARC of the Greater Twin Cities.

Bromine industry representatives and other stakeholders that rely on Deca-BDE maintain that the flame retardant has been subjected to several in-depth research studies with the result that no significant environmental or human health risks have been identified. These stakeholders have also suggested that those calling for a ban on Deca-BDE are citing study results for Penta- and Octa-BDE, which have already been banned, rather than Deca-BDE.

However, many scientists and environmental advocates disagree with the industry representatives' statements. They point to results of Deca-BDE studies to date and to significant gaps in the understanding of Deca-BDE's behavior and effects, particularly its breakdown to more toxic, lower brominated PBDE congeners. Increasing concentrations of PBDEs in the environment, in the food supply, and in people also provide substantial basis for concern.

Maintaining current standards of fire safety was also a concern voiced by many stakeholders when discussing potential limitations on the use of Deca-BDE. Existing fire safety standards allow different approaches to achieving the standards, whether by using alternative chemical flame retardants, using inherently non-flammable materials, or redesigning the product to achieve the standards. In all cases, for a product to be legally sold in the U.S., applicable fire safety standards must be met.

In the European Union, a ban on sale and use of Deca-BDE was enacted but is delayed until 2010. In the United States, only Maine and Washington have enacted partial bans on Deca-BDE. These bans primarily target the use of Deca-BDE in home furniture (where it is not currently used but could be if pending national flammability standards for home furniture are imposed) and home electronics. During 2007, several states (California, Hawaii, Illinois, Michigan, Minnesota and New York) introduced legislation that would phase out or place restrictions on Deca-BDE.

Review of available data on Deca-BDE produced the following highlights:

- Deca-BDE is widespread in the environment.
- Deca-BDE is present in wildlife, sewage sludge, indoor air, house dust, foods, and people.
- Deca-BDE shows potential to bioaccumulate and concentrate up the food chain.
- PBDE concentrations (including Deca-BDE) in the U.S. are much higher than in Europe.
- Deca-BDE was found to cause developmental neurotoxicity effects in laboratory animals. This result is of great concern to stakeholders due to the potential implications for breast-feeding infants, who have the highest exposure to Deca-BDE. More research is needed to address data gaps in this area, particularly with respect to the metabolism of Deca-BDE and the metabolites that are formed in laboratory animals as well as humans.

- Deca-BDE has been determined to break down into more toxic PBDE congeners including Hexa- , Hepta-, Octa-, Nona-BDEs. Conditions where Deca-BDE breakdown has been confirmed include: in the presence of sunlight; via metabolism in animals; and via metabolism by microbes in sewage sludge. This finding has potentially important implications for the overall evaluation of Deca-BDE toxicity.
- More research is needed to address data gaps related to the extent of Deca-BDE breakdown and the stability of the breakdown products under various conditions. In addition, not all of Deca-BDE breakdown products have been identified or evaluated for potential environmental and health effects.
- More information is needed to understand the environmental fate and possible health effects posed by Deca-BDE.

Effective alternatives for achieving flame retardancy appear to be available for most current Deca-BDE applications. In general, flammability requirements can be met using various strategies that include: using an alternative chemical flame retardant; switching to the use of inherently non-flammable materials; and re-designing the product. According to the State of Maine's 2007 report on PBDEs:

> "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 phosphorous compounds such as resorcinol bis diphenyl phosphate (RDP). RDP presents a significantly lower threat to the environment and human health than decaBDE."

Many electronics manufacturers are phasing-out, or have already stopped the use of Deca-BDE in their products. The cost of making these changes in most cases is considered minor (Illinois, 2007).

However, in the fields of medical devices and transportation, particularly the aircraft and aerospace industries, cost is a concern. This is primarily a result of the highly regulated nature of these industries and the extensive product testing that is required by both regulatory agencies and the manufacturers themselves to qualify their products.

As with other emerging issues and contaminants of concern, policymakers should keep in mind that collective knowledge about brominated flame retardants and alternatives is changing. New research results, governmental actions and marketplace trends all will influence the manufacture and use of flame retardants even as this report is being reviewed and discussed by lawmakers and stakeholders.

INTRODUCTION

Deca-BDE is a manmade chemical that is used as an additive to plastics and textiles to reduce the inherent flammability of these materials. Deca-BDE is one of several brominated flame retardants (BFRs) in use worldwide to reduce the incidence and severity of fires in homes, businesses, and in the transportation industry.

Deca-BDE belongs to a class of BFRs known as polybrominated diphenyl ethers (PBDEs). PBDEs are increasingly being detected in the environment and are accumulating in wildlife and people. Concern about the potential impact of PBDEs on human health and the environment is mounting: several states and the European Union have undertaken extensive studies of the available information on the occurrence, behavior, and effects of various PBDEs on human health and the environment.

Key findings in these reports include the increasing concentrations of PBDEs in breast milk of mothers in the U.S., and the detection of developmental neurotoxicity effects in laboratory animal studies. Moreover, residents of the U.S. and Canada have been found to carry a significantly higher burden of PBDEs in their bodies compared to residents of Europe, where fewer PBDEs are used in consumer products.

Deca-BDE, the subject of this report, is one of three primary commercial formulations of PBDEs. The other two are pentabromodiphenyl ether (Penta-BDE) and octabromodiphenyl ether (Octa-BDE). Based on information suggesting that Penta-BDE and Octa-BDE bioaccumulate and have some risk of toxicity at concentrations approaching those found in the environment, the sole U.S. manufacturer of Penta-BDE and Octa-BDE voluntarily ceased production of these BFRs at the end of 2004. Several U.S. states including Minnesota and the European Union have implemented bans on the use of Penta-BDE and Octa-BDE.

Deca-BDE, however, remains in wide use. Until recently, studies of PBDEs and their potential effect on human health and the environment often excluded Deca-BDE. This was due to the assumption by researchers that Deca-BDE presents a lower risk to human health and the environment because of its molecular size and mass. This assumption has gradually changed as more research has been conducted and interest has grown in the behavior and potential impacts of Deca-BDE on wildlife, human health, and the environment.

Based on the growing information about Deca-BDE, the States of Washington and Maine have enacted limited bans on the use of Deca-BDE. Bans on Deca-BDE have been proposed but not enacted in several other states, including Minnesota. In Europe, the European Union has been studying the issue of Deca-BDE for several years and as of 2007 has delayed implementation of a proposed ban on Deca-BDE, while gathering more information.

The Minnesota Legislature directed the MPCA to prepare this report to summarize existing information concerning the health and environmental risks posed by use of Deca-BDE. Minn. Stat. 325E.387 specifically directs the MPCA to review the following:

- Uses of Deca-BDE and fire safety;
- Availability of technically feasible and safer alternatives to Deca-BDE;
- Evidence of potential harm to human health and the environment from the use of Deca-BDE and its alternatives; and
- Findings and recommendations made by other state and federal agencies that have studied the available information on Deca-BDE.

Minn. Stat. 325E.387 also directs the MPCA to consult with the Minnesota Departments of Health and Public Safety during preparation of this report and to contact key stakeholders regarding their concerns over the use and potential limitations on the use of Deca-BDE.

This report provides an overview and discussion of the subject areas outlined in Minn. Stat. 325E.387. Several appendices are also attached that contain additional, supplementary information to the report.

ABOUT FLAME RETARDANTS

Flame retardants (FRs) are used in a variety of flammable materials and products to make them difficult to burn. FRs are commonly added to plastic resins that are used in electronic parts and equipment, wire and cable, textiles, and other products. The use of FRs has grown significantly since the introduction of petroleum-based synthetic polymers into consumer products and the corresponding development of regulations intended to reduce the impact of fires from these materials.

Currently, there are three major classes of FRs in use around the world: brominated flame retardants (BFRs), which include PBDEs; phosphorus-based FRs; and inorganic FRs (usually magnesium or aluminum hydroxides).

Older categories of FRs that are no longer used include polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs). PCBs are persistent, bioaccumulative and toxic (PBT) chemicals that were banned in the U.S. in 1977. An accidental exposure of humans to PBBs in Michigan in the 1970s caused lasting health effects in those exposed and led to a ban on PBBs in the U.S. and later in Europe and elsewhere (Wolf and Aubrey, 1978).

BFRs including PBDEs were introduced commercially in the 1960s. The use of BFRs increased substantially during the late 1970s with the surging demand for personal computers and other types of consumer electronics, and also the introduction of stricter fire regulations.

BFRs are widely used because they are highly efficient, meaning that less of the chemical must be added to a polymer to achieve the desired effect. For example, the amount of BFR typically added to plastic polymers to achieve flame retardant standards is 10% to 20% (Betts, 2007). By comparison, 30% to 60% of an inorganic FR might be needed to achieve the same standard (Betts, 2007). According to Albemarle Corporation, BFRs provide the best balance between performance, mechanical properties, process ability, and cost in use (Dawson, 2007 and Betts, 2007).

The BFRs with the highest use based on currently available information are:

- Tetrabromobisphenol A (TBBPA);
- Hexabromocyclododecane (HBCD); and
- Polybrominated diphenyl ethers (PBDEs).

PBDEs include Penta-BDE, Octa-BDE and Deca-BDE. Production of Penta- and Octa-BDE was voluntarily phased out by Great Lakes Chemical of West Lafayette, Indiana, in December 2004. Now known as Chemtura Corporation, Great Lakes Chemical was the sole U.S. manufacturer of Penta- and Octa-BDE commercial products. The use of Penta- and Octa-BDE in the U.S. is now assumed to be practically non-existent.

Global use of BFRs for 2001 and 2003 are tabulated in Table 1. These figures were obtained from the Bromine Science and Environmental Forum (BSEF), an industry forum established in 1997 to further scientific and regulatory understanding of bromine and brominated products (BSEF, 2007). Note that Deca-BDE was the highest use BFR in the Americas in 2001, whereas in Europe and Asia TBBPA was the highest use BFR.

Table 1: BFR Volume Estimates in 2001 and 2003 in Metric Tons (MT)

Flame Retardant	*Americas 2001*	*Europe 2001*	*Asia 2001*	*Rest of World 2001*	*Total 2001*	*Total 2003*
TBBPA	18000	11600	89400	600	119700	145113
HBCD	2800	9500	3900	500	16700	21951
Deca-BDE	24500	7600	23000	1050	56100	56481
Octa-BDE	1500	610	1500	180	3790	------
Penta-BDE	7100	150	150	100	7500	------

Source: BSEF, 2007.

USES OF DECA-BDE

In the U.S., as much as 80% of Deca-BDE is used in electronic and electrical equipment in combination with high-impact polystyrene (HIPS) polymers (Lowell, 2005). The vast majority of Deca-BDE is used in television sets, specifically the front and back enclosure panels.

A large part of the remaining Deca-BDE in the U.S. is used in textile applications. The Lowell Center estimates between 10 and 20% of Deca-BDE use is in textiles (Lowell, 2005), with office furniture and drapery being the main areas of use. Deca-BDE is not currently used in clothing such as children's sleepwear or in residential upholstered furniture, according to the Lowell Center for Sustainable Production (Lowell Center). The Lowell Center is a university-affiliated research center that develops, studies, and promotes environmentally sound and economically viable systems of production.

Deca-BDE is also used in many other products. Deca-BDE is combined with polypropylene (PP) or polypropylene ether (PPE) resins which are used as coatings on wire and cable. Deca-BDE is also used in polybutylene terephthalate (PBT) and polyamide (PA) resins, which 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 in a wide range of applications (Maine, 2007). The total amount of Deca-BDE consumed in these applications is proportionately small relative to its consumption in television enclosures and textiles, however the importance of the flame retarded products to these industries is high. Applications in this category where Deca-BDE is known to be used include wiring in automobiles, communication cable for telephone and internet service, and wiring in heating and air conditioning and security system controls.

The high rate of use of Deca-BDE in television enclosure panels results from the suitability of the Deca-BDE-HIPS resin for this application and its low cost. According to the American Plastics Council, 98% of TV enclosures and about 3% of computer monitors are made from Deca-BDE-HIPS (Lowell, 2005). Other BFRs could be substituted for Deca-BDE in HIPS but would cost more (Maine, 2007).

The use of Deca-BDE/HIPS in enclosures of other electronic equipment is rare. Table 2 shows the types of polymer resins that are most often used for electronic enclosures. Note that the enclosures of printers, copiers, scanners, and fax machines are generally not made with flame retarded plastics. These products may be designed to meet fire standards without the use of chemical fire retardants, such as by enclosing the power source in metal housing or by removing the power supply from the product.

Table 2: Resin Systems for Electronic Enclosures (source: Lowell, 2005)

Resin System	*Primary Flame Retardants*	*Printers*	*Copiers*	*TVs*	*Scanners*	*Fax*	*Monitors*
FR HIPS	Deca-BDE			98%			3%
FR ABS	TBBPA, BEO			2%			34%
FRPC/PS	-						<1%
FR PPO/HIPS	Resorcinol bis diphenylphosphate (RDP)						<1%
FR PC	-						<1%
FR PC/ABS	Resorcinol bis diphenylphosphate (RDP)	6%	5%				61%
Non-FR Plastics	-	94%	95%		100%	100%	

FR = flame retarded
HIPS = high-impact polystyrene
ABS= acrylonitrile-butadiene-styrene
BEO= brominated epoxy oligomer
PC = polycarbonate
PPO/HIPS = polyphenylene oxide/HIPS
PC/PS = PC/Polystyrene

In commercial textile applications, the effectiveness of Deca-BDE is usually enhanced with the addition of antimony oxide (ATO). The Deca-BDE/ATO flame retardant mix can be applied to textiles in various ways depending on the material and its end use. The Deca-BDE/ATO flame retardant mix can account for anywhere from 18 to 27% of total weight of the product (Washington, 2006). Lighter fabrics usually require higher flame retardant loadings compared to heavier fabrics.

Current uses of Deca-BDE in consumer products are changing as an increasing number of manufacturers are voluntarily seeking alternative means of complying with fire safety standards. This is discussed in more detail in the section on alternatives to Deca-BDE.

A compilation of materials and products containing Deca-BDE, as well as Penta-BDE and Octa-BDE, is provided in Appendix C.

FIRE SAFETY AND FLAME RETARDANTS

Fire is a major cause of death, injury and property loss in the United States and around the world. During 2006 in the United States, more than 3,000 fire deaths occurred, including the deaths of numerous firefighters (USFA, 2007a). During the same period 46 individuals in Minnesota lost their lives because of fires (Rosendahl, 2007).

The use of flame retardants and fire protection measures has reduced number of injuries and deaths over time (Simpson et al., 2006; Kucewitz, 2006; De Poortere et al., 2000; and USFA, 2007b). Many studies have shown that flame retardants are effective in:

- Releasing only one-fourth of heat compared to a similar product that is not flame-retarded;
- Providing up to 15 times more escape time in case of fire;
- Reducing fire destruction by 50%; and
- Releasing fewer toxic gases during combustion (Stevens and Mann, 1999).

Fire safety regulations have been developed to protect the public from fires that start in consumer products or are made worse by the presence of flammable materials. In order for a product to be legally sold in the U.S., applicable fire safety standards must be met.

The fire safety standards that are most often applicable to products containing Deca-BDE, such as the Underwriters Laboratory and National Electric Code (NEC) flammability standards, do not specify the type of flame retardant that must be used. The choice of flame retardant is left to the product manufacturer (Maine, 2007). In addition, flammability standards can typically be met by means other than using chemical flame retardants. Examples of this are the use of inherently non-flammable materials, and re-designing products to meet the required flammability standards.

Because it is a legal requirement that fire safety standards be met, the removal of a certain FR from the marketplace is unlikely to compromise fire safety. Manufacturers who want to legally sell their products and avoid the worry of product liability suits will replace them with other FRs or will meet the required fire safety standards by other means.

Fire safety regulations that typically apply to electronics and textiles in the U.S. are reviewed below.

<u>Fire Safety Standards for Electronics</u>

The National Fire Protection Association (NFPA) sets safety standards for electronics. In association with NFPA, the Underwriters Laboratories (UL) tests the fire safety of electronic products and components, and sets performance standards manufacturers must meet in order to sell their products in the United States. The most important of the UL fire standards for electronics are the UL94 standards. There are several individual tests included in these standards, including the horizontal burn test (UL 94), and more difficult to meet vertical burn tests (UL94 V-2, V-1, V-0 and 5V).

Fire Safety Standards for Textiles

There are a number of federal and state regulations dictating the fire safety and flame resistance of textiles used in residential and commercial settings.

The U.S. Consumer Product Safety Commission (CPCS) sets federal safety standards for upholstered furniture, mattresses and draperies. In 2006, a federal regulation (mandatory rule 16 CFR part 1633) requiring strict mattress fire safety for all mattresses sold in the U.S. was adopted effective July 2007. The CPCS estimates that 240 to 270 lives will be saved and 1150 to 1330 injuries will be avoided annually by adoption of this standard (CPCS, 2007).

The CPCS has been considering a national flammability standard for upholstered furniture in residential settings that is expected to be finalized soon (Maine, 2007). In the absence of a national standard, the State of California Bureau of Home Furnishings and Thermal Insulation (CA BHFTI)'s fire safety standards for textiles in residential home furnishings has been adopted voluntarily by many manufacturers, for products sold in California as well as other U.S. states. California's standard is the strictest among states that have adopted fire safety standards for residential applications. The majority of products manufactured for sale in California are also sold in other states.

The CA BHFTI standards, which also apply to textiles used in commercial settings, are referenced in building codes throughout the country for public places, commercial offices and high-risk settings (Lowell, 2005).

Fire Safety Standards in Transportation

Safety standards for motor vehicles are issued by The National Highway Traffic Safety Administration (NHTSA). Manufacturers of motor vehicles and equipment must meet and comply with NHTSA-issued Federal Motor Vehicle Safety Standards (FMVSS) and Regulations.

The aircraft and aerospace industry must comply with regulatory requirements set by the Federal Aviation Administration (FAA). These standards are very stringent, and there is a lengthy process required to obtain product certification from the FAA.

PBDEs, THE ENVIRONMENT AND HUMAN HEALTH (EMPHASIS ON DECA-BDE)

This section provides an overview of important and recent findings relating to PBDEs, the environment and human health. Findings specific to Deca-BDE are emphasized when available. A more detailed summary of current research in these areas is provided in Appendices D and E.

Background on the chemistry of PBDEs is provided first.

Chemistry of PBDEs

PBDE molecules consist of two, six-carbon rings (phenyl rings) that are joined by the same oxygen atom, which is bonded to a carbon atom in each phenyl ring (Figure 1). This basic molecular configuration leaves ten carbon bonding sites on the two phenyl rings that can be bonded to other elements; in the case of PBDEs, the element is bromine.

Figure 1: General Structure of PBDEs

The names Penta-BDE, Octa-BDE and Deca-BDE correlate with the number of bromine atoms that are bonded to the phenyl rings (i.e. five bromines, eight bromines, ten bromines). The degree of bromination of the phenyl rings, (i.e. the number of bromine atoms attached to each ring), and the position of the bromine atoms on the carbon rings define a congener. There are 209 potential forms or “congeners” of PBDEs.

Figure 2 illustrates two possible congeners of Penta-BDE. Each PBDE molecule has five bromine atoms, making it Penta-BDE, but the locations of the bromine atoms on each molecule are different. The different locations of the five bromine atoms on the molecules make them different PBDE congeners, and also different Penta-BDE congeners (a.k.a. homologues).

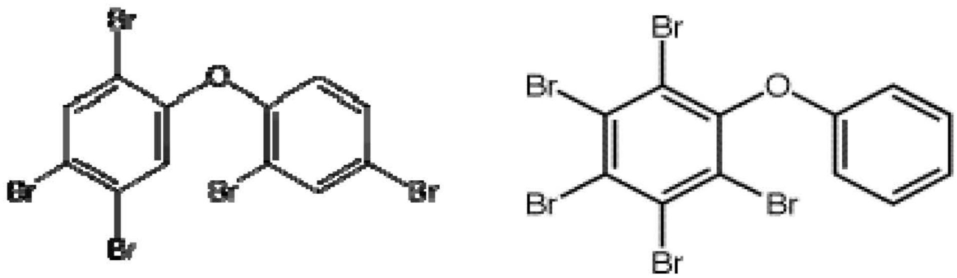


Figure 2. Two Congeners of Penta-BDE.

Individual congeners are identified using a number, such as BDE-47 or BDE-100, according to standards set by the International Union for Pure and Applied Chemistry (IUPAC). Deca-BDE, with all ten carbon atoms bonded to a bromine atom, has only one possible molecular structure. Identified using the IUPAC system, Deca-BDE is BDE-209 (Figure 3).

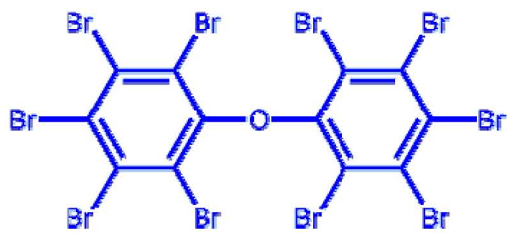


Figure 3. Deca-BDE (a.k.a. BDE-209)

It is important to understand that PBDEs do not occur in nature. PBDEs are manmade chemicals that are synthesized by chemical manufacturers under very specific conditions. The commercial PBDE formulations of Penta-BDE, Octa-BDE and Deca-BDE are actually not pure products but are mixtures of different PBDEs that are created during the synthesis process (WHO, 1994). The general compositions of the commercial PBDE formulations are presented in Table 3. Note that the commercial formulation of Deca-BDE is relatively pure (97-98% Deca-BDE) compared to the commercial formulations of Penta- and Octa-BDE.

Table 3. General Composition of PBDE Commercial Products (by percentage)

Commercial Product	*Tri-BDE*	*Tetra-BDE*	*Penta-BDE*	*Hexa-BDE*	*Hepta-BDE*	*Octa-BDE*	*Nona-BDE*	*Deca-BDE*
Penta-BDE	<1	24-38	50-60	4-8				
Octa-BDE				10-12	43-44	31-35	10-11	<1
Deca-BDE							<3	97-98

Source: WHO, 1994

The scientific literature typically reports identifies PBDEs by congener using the IUPAC numbering convention, or, alternatively, the total concentration of PBDEs detected.

PBDEs and the Environment

PBDEs are ubiquitous environmental contaminants. They have been detected in indoor and outdoor air; in house and office dust; in rivers and lakes and sediments; in sewage sludge; in remote arctic regions (providing evidence of the occurrence of long range environmental transport); in food; and in animals, including fish, birds, terrestrial and marine mammals, and human beings (Kodavanti, 2007).

The concentrations of Deca-BDE in sediments and sewage sludge are of particular concern. Studies show that Deca-BDE has been detected in sediments (i.e. soil deposited in aquatic environments such as lakes, rivers, and wetlands) all over the world (Pan et al., 2007; Marvin et al., 2007; Minh et al., 2007). This is important because chemicals with molecular structures similar to PBDEs have been shown to cycle from sediments through the aquatic food web. The concentrations of Deca-BDE in sediment have been steadily increasing, and Deca-BDE accounts for the largest percentage of total PBDE concentration in sediments.

The presence of Deca-BDE in sewage sludge is of concern in part because more than half of the total sewage sludge generated by wastewater treatment plans in the U.S. is applied to land (Hale et al., 2001). Although sewage sludge is treated for odor and pathogen content and monitored for heavy metals, it is not treated or evaluated for the presence of PBDEs or other persistent pollutants. The reported concentrations of PBDEs in sewage sludge samples collected in the U.S. are about an order of magnitude higher than those measured in some European countries (Germany, Sweden, Netherlands, Switzerland) (Knoh et al., 2007).

Numerous studies indicate that Deca-BDE degrades or breaks down chemically once released into the environment. Lower PBDE congeners including Hexa-, Hepta-, Octa- and Nona-BDE, as well as PBDE congeners not used in any commercial PBDE products, and several unidentified chemicals are formed. The breakdown of Deca-BDE and the formation of more toxic, lower congeners of PBDE is important to the overall evaluation of the risk posed by Deca-BDE's presence in the environment and its effect on wildlife and humans. Little is currently known about the extent of breakdown of the Deca-BDE molecule and the stability of the breakdown products.

Toxicity to Wildlife

Deca-BDE has been detected in fish throughout the U.S., including Minnesota (EPA, 2007a; MPCA, 2006). Deca-BDE has also been measured in eggs of Swedish peregrine falcons (Hale, et al., 2001); eggs of sparrow hawks in the United Kingdom, and eggs of the Glaucous Gull in the Arctic (Leslie et al., 2007).

Few studies on the aquatic toxicity of Deca-BDE to aquatic organisms have been conducted. Those that have indicate that acute toxicity to aquatic organisms is very low, as the toxicity limit for fish and algae is well in excess of Deca-BDE's solubility in water (Stuer-Lauridsen et al., 2007).

One study is known to have evaluated the chronic toxicity of Deca-BDE to fish (Stuer-Lauridsen et al., 2007). The exposure to Deca-BDE caused increased liver weights and lactate levels in fish blood after 120 days of exposure. However the commercial product used in the test had a higher fraction of lower brominated PBDEs than is found in current Deca-BDE formulations, which raises the concern that the study results may be related to the build up of lower, more toxic PBDE congeners in the fish rather than Deca-BDE (Stuer-Lauridsen et al., 2007).

It is clear that PBDEs are ubiquitous in the environment and that their concentrations are increasing in various environmental settings. However, understanding of the mechanisms by which the chemicals are entering the environment is incomplete. Scientists suggest that better quality and more information is needed on the behavior and degradation of Deca-BDE in sediments and sewage sludge and on its concentrations in biota. In addition, the fate and transport of Deca-BDE in the environment is still not well understood.

Appendix D provides additional information about PBDEs and Deca-BDE in the environment. Appendix F provides an overview of mechanisms by which PBDEs are released to the environment, and also summarizes industry and regulatory agency driven efforts to reduce environmental releases of Deca-BDE.

PBDEs and Human Health

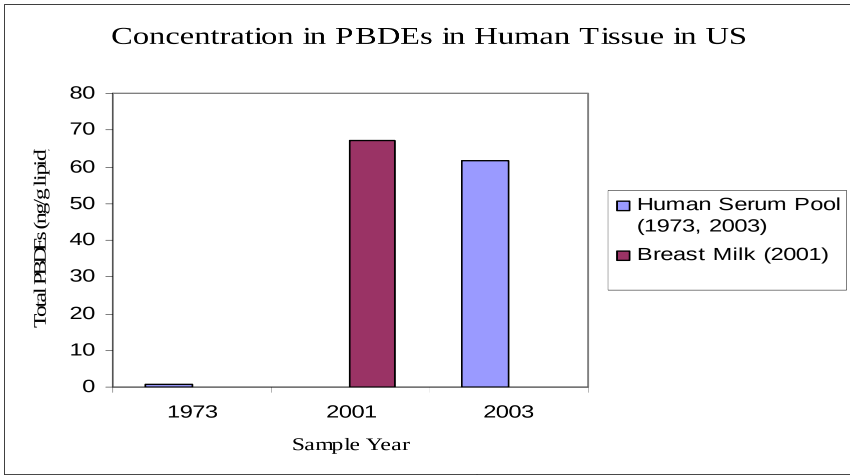
PBDEs in Human Tissue

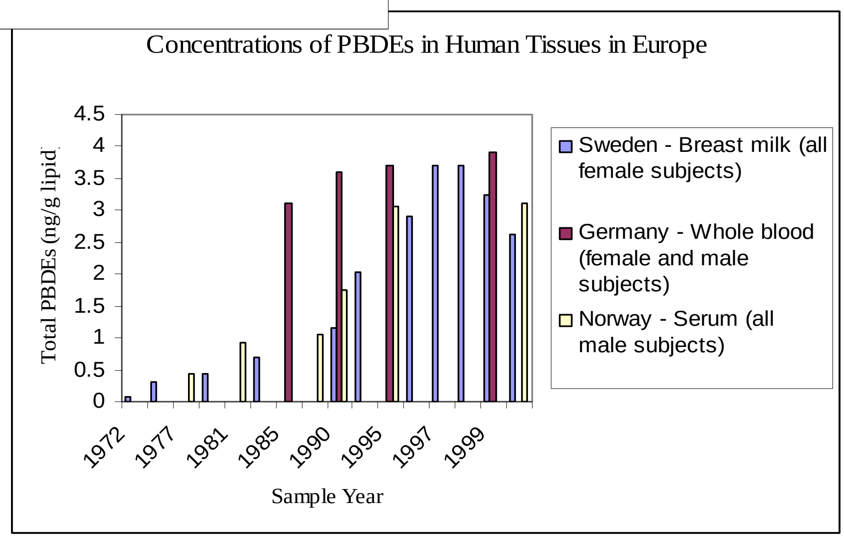
Until recently, studies of the presence of PBDEs in human beings have analyzed only the lower brominated congeners of PBDEs (Penta-, Octa- etc.). Deca-BDE was not included in the studies because it was not thought to bioaccumulate in humans, in part because of the very large size of the molecule.

In 1999, a Swedish study sparked intense interest in the issue of PBDEs worldwide. The study showed that between 1972 and 1999, the concentration of PBDEs in the breast milk of mothers in Sweden increased exponentially, with concentrations of PBDEs doubling every five years (Noren and Merionyte, 2000).

A number of studies subsequently looked at PBDE trends in the U.S. population. Similar trends of rapidly increasing PBDE concentrations were observed, however the measured concentrations of PBDEs in U.S. residents were at least an order of magnitude higher (i.e. at least ten times higher) than in Europe (Schecter et. al., 2003). This is shown in Figure 4; note that PBDE concentrations reported for the U.S. population were between about 60-70 ng/g lipid (nanograms per gram lipid) whereas in Europe they were somewhere between 2.5 and 3.5 ng/g lipid.

Figure 4: Temporal Trends of PBDE Concentrations in Human Tissues in the U.S. and Europe





Sources: Sjodin et al, 2003, Schecter et al, 2005

Recent studies that have analyzed for Deca-BDE in the general population reveal that it is present at much lower concentrations than is common for lower PBDE congeners (Schecter et. al., 2007; and Wu et. al., 2007).

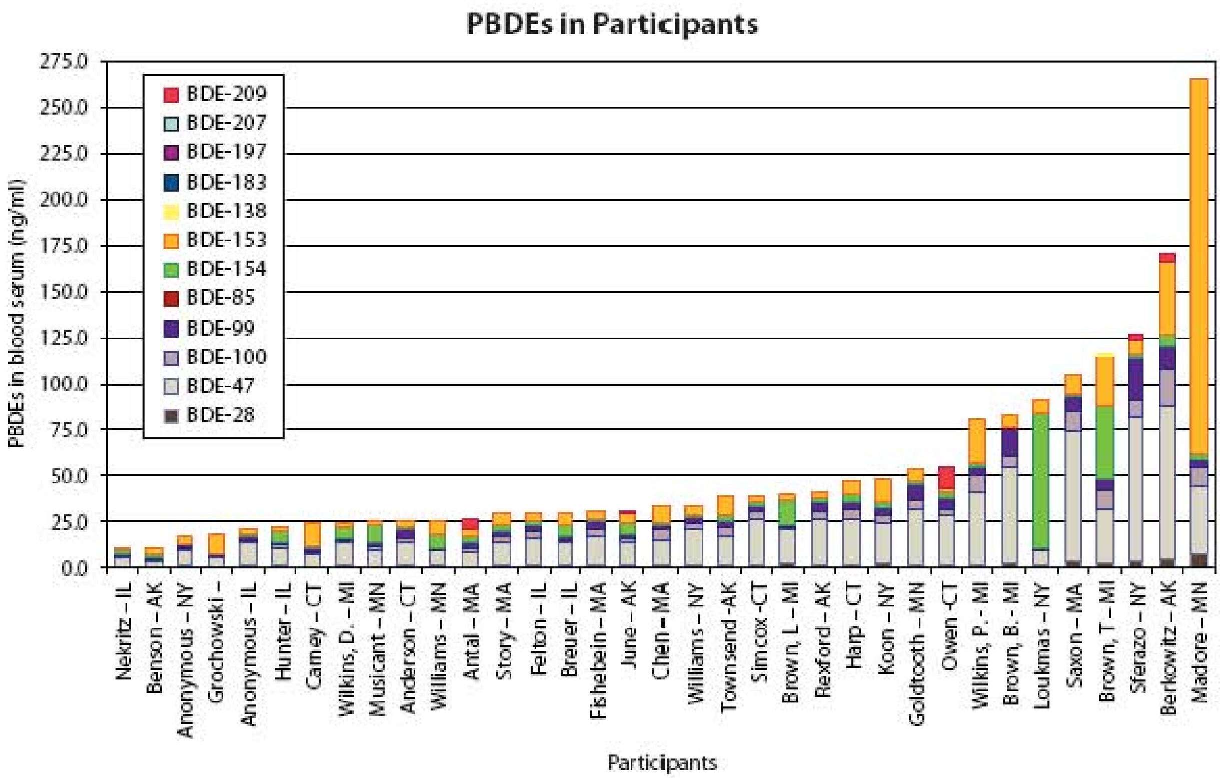
A November 2007 survey conducted by the Body Burden Work Group and Commonweal Bio-monitoring Resource Center Report provides recent information on the concentration of PBDEs in the blood of five Minnesotans. For the survey, 35 people from seven states volunteered to provide samples of blood and urine for testing of three types of industrial chemicals. The chemicals tested were bisphenol A (BPA) (plasticizer); phthalates (plasticizer); and PBDEs. Twelve different PBDE congeners were tested.

The survey results showed that detectable concentrations of PBDEs were present in all volunteers tested. Almost all the volunteers (34 of 35) were reported to have BDE-209 in their blood serum, although the concentrations were too low to quantify in all but five of the volunteers.

The results for the Minnesota volunteers showed that one, State Representative Shelley Madore of Apple Valley, Minnesota, was reported to have an unusually high concentration of BDE-153, a PBDE congener that is associated with Penta-BDE.

The PBDE results from this survey are displayed in Figure 5. Most of the volunteers' PBDE results fall in the range of 25 to 50 ng/ml blood serum (Figure 5), which is similar to the concentration range found in previous studies of PBDE body burden concentrations in the U.S. (Note: in the case of blood serum, ng/g and ng/ml are equivalent units).

Figure 5: PBDE Concentrations Measured in Blood Serum of 35 Volunteers from Alaska, Connecticut, Illinois, Massachusetts, Michigan, Minnesota, and New York



Source: Body Burden Work Group & Commonweal Biomonitoring Resource Center, 2007.

In general, studies show that measured PBDE concentrations in human tissue range over several orders of magnitude; the reasons for the observed variability in concentration are unknown. An estimated 5% to 10% of the population has elevated PBDE levels (Scheter et al., 2005). Researchers have found no correlation between PBDE concentrations in human tissue and age, suggesting that PBDE concentrations in humans may not be caused by bioaccumulation over time.

A more complete summation of information on this subject is included in Appendix E2.

Routes of Exposure

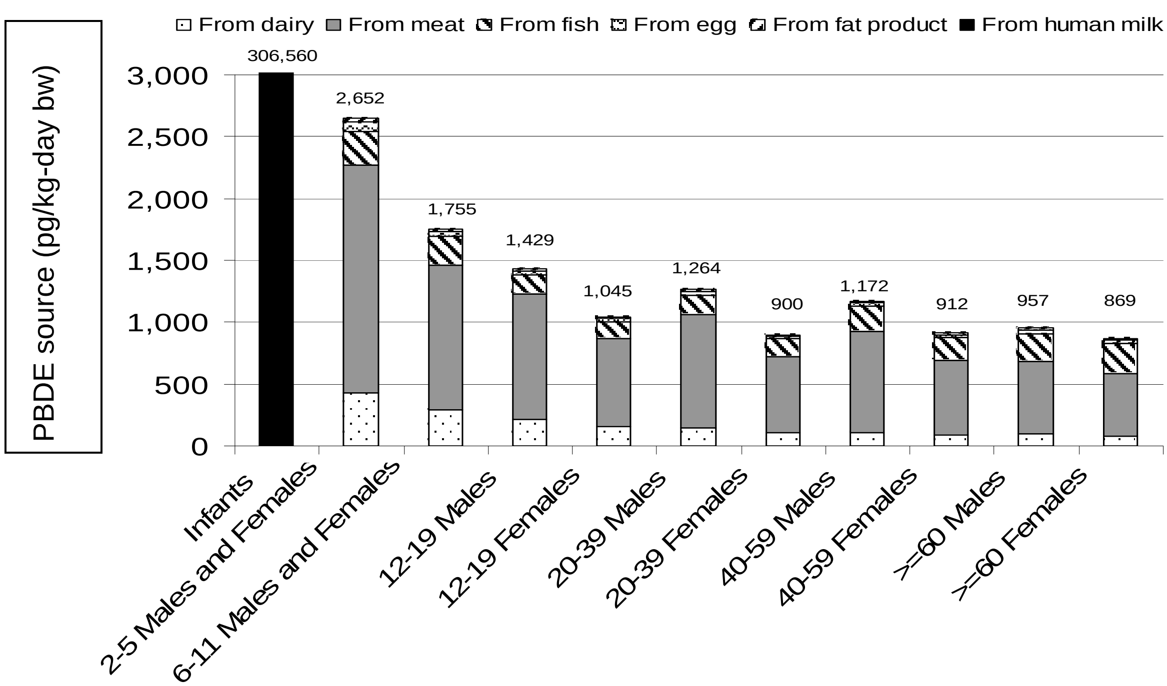
How are we exposed to PBDEs? Researchers have identified a number of potential routes of exposure. Those that have been most investigated are:

- Dietary exposure (especially from fats, meats, fish, and dairy products);
- Ingestion and inhalation of PBDE-containing house dust; and
- Direct contact with PBDE-treated products.

PBDEs are present in foods consumed by humans. Several studies have measured PBDE concentrations in foods. A recent study by Schecter et. al. (2006) analyzed PBDE concentrations including Deca-BDE in 62 samples of meat, fish and dairy products that were bought in U.S. grocery stores. The highest concentrations of PBDEs were found in fish, followed by meat and dairy products. Deca-BDE was found in high concentrations in catfish, salmon fillet, ground turkey, and cream cheese.

Although PBDEs appear to be present in fruits and vegetables (Bocio et al. 2003; and Ohta et al., 2002), the concentrations are significantly lower than the concentrations found in meats, fish and dairy products. Therefore, it is concluded that PBDE exposure from fruits and vegetables poses a significantly lower concern than exposure from fish, meats, and dairy products.

Figure 6. PBDE Dietary Intake of U.S. Population by Age and Food Group (Schecter et al., 2006) (Taken from: Kodavanti, 2007)



Based on these studies, Schecter et al. (2006) estimated the average daily PBDE intake from food for the U.S. population by age group. The greatest daily intake of PBDEs per unit of body weight was in nursing infants, followed by young children and then adults (Figure 6). Note that the intake of infants is off the scale at 306,560 pg/kg-day body weight – two orders of magnitude (100 times) higher that the next highest intake of PBDEs per unit of body weight for ages 2 to 5 years old.

Food alone, however, cannot account for the high body burden of PBDEs in the general U.S. population (Schecter et al., 2006). The intake of PBDEs from food in the U.S. is comparable to that in Spain and in the United Kingdom (Washington, 2006), yet U.S. body concentrations of PBDEs are much higher (one to two orders of magnitude) than in Europe. This result suggests the existence of other exposure pathways for the U.S. population.

One such exposure pathway is house dust, which has been shown by numerous studies to be contaminated with PBDEs. The most abundant PBDEs detected in house dust studies are the congeners BDE-47, BDE-99 and BDE-209 (Deca-BDE).

A study by Tan et al. (2007), measured the PBDE concentrations in samples of household dust collected in Singapore, and compared the concentrations and congener profiles to the results from similar studies conducted in the U.S. (the Cities of Dallas, Texas and Washington DC) and Canada (the City of Ottawa). The authors observed that similar PBDE profiles (i.e. the types and concentrations of detected congeners) were reported in all studies. In addition, Deca-BDE (BDE-209) was the main congener detected in the majority of dust samples. The samples of house dust collected in the U.S. and Canada had double the concentration of PBDEs when compared to dust samples collected in Singapore.

A similar study conducted on house dust samples collected in the United Kingdom and Canada by Harrard et al. (2006) showed that PBDE concentrations in Canadian house dust were 20 times higher than those from the United Kingdom, and comparisons of estimates of total exposure to PBDEs from all sources in theses countries indicate that dust accounts for a much larger percentage of exposure in Canada. The causes of higher PBDE concentrations in house dust in the U.S. and Canada compared to Europe and Asia are not well understood.

Another exposure pathway that is regularly mentioned in reports and literature on PBDEs is direct contact with the PBDE-treated or containing consumer products. However, scientific evaluation of this potential exposure pathway is difficult. Studies looking at PBDE dust concentrations and residential characteristics (i.e. the number of TVs, computers, etc. in the household) found no significant correlations (Tan et al., 2007). Similarly, a study by Wu et al. (2007) found no significant correlation between PBDE concentrations in breast milk and the usage of electronic equipment.

A more complete summation of this information is included in Appendix E3.

PBDE Toxicity

Knowledge of the potential human health effects from exposure to PBDEs is extrapolated from the results of laboratory animal toxicity studies. Generally, the studies show that the lower brominated PBDE congeners, such as those found in the commercial Penta- and Octa-BDE formulations, are more toxic than Deca-BDE. However, given that Deca-BDE has been found to breakdown into lower brominated congeners, the toxicity of Penta- and Octa-BDE is relevant to the discussion of Deca-BDE.

Early PBDE researchers thought the large size of the Deca-BDE molecule as well as some of its other physical-chemical properties would prevent it from being absorbed into the body (Washington, 2006). However, laboratory animal toxicity studies show that Deca-BDE can be absorbed by the oral route and does not accumulate in tissues. Deca-BDE undergoes metabolism primarily in the liver and is excreted in the bile.

The results from a recent study of workers exposed through their workplace to PBDEs (Thuresson et al., 2006) were used to estimate a half-life for Deca-BDE (BDE-209) of 15 days in humans. Biological half-life is a measure of how long it takes the body to excrete half of an accumulated amount of a chemical from the body (Washington, 2006). Half life is an important measure for evaluating the biological pathways of chemicals in the body. Because the half-life of Deca-BDE is not exceedingly long and because Deca-BDE is detectable in the general population, the results of the study suggest that humans are continually exposed to Deca-BDE.

Laboratory animal toxicity studies provide evidence of toxic effects associated with exposure to Deca-BDE at concentrations above those that occur in the environment. These effects include thrombosis of the liver, liver degeneration, fibrosis in the spleen, lymphoid hyperplasia, centrilobular hypertrophy of liver, follicular cell hyperplasia of thyroid and neurobehavioral changes (EPA, 2006b). The last effect – neurobehavioral changes – has raised the most concern among stakeholders because of its potential implications for breast feeding infants, who have the highest exposure to PBDEs, including Deca-BDE.

An overview of health effects associated with the commercial Deca-BDE formulation is presented in Table 4. This information was obtained from the draft EPA Integrated Risk Information System (IRIS) for Deca-BDE (EPA, 2006b). The draft IRIS is a summary of several important studies that demonstrate slight to severe health effects associated with Deca-BDE exposure.

Table 4: Lowest Observed Adverse Effect Levels (LOAELs) in Deca-BDE Animal Toxicity Studies (EPA, 2006b)

Associated PBDE product	*PBDE congener or product*	*Endpoint*	*Duration of exposure*	*Lowest Observed Adverse Effect Level (mg/kg/day)*	*Reference*
Deca-BDE	BDE-209	Developmental neurotoxicity	1 day/post-natal day 3 (mouse)	20.1	Viberg et al 2003
Deca-BDE	Deca-BDE	Thyroid changes, liver and kidney effects and fetal death	30 days (rat)	80	Darnerud et al 2001
Deca-BDE	Deca-BDE	Cancer	103 weeks (rat and mouse)	1120-3200	Darnerud et al 2001

Note that the lowest dose of Deca-BDE resulted in the observation of developmental neurotoxicity effects in mice (Viberg et al., 2003) (Table 4). The results from this study were used by EPA to calculate the non-cancer oral reference dose (RfD) for Deca-BDE of 0.007 mg/kg/day. EPA defines the Non-Cancer Oral Reference Dose as a numerical estimate of a daily oral exposure to the human population, including sensitive subgroups such as children, that is not likely to cause harmful effects during a lifetime. RfDs are generally used for health effects that are thought to have a threshold or low dose limit for producing effects.

EPA notes that, "overall confidence in the RfD assessment of BDE-209 is low (EPA, 2006b)." Consequently, the non-cancer oral reference dose value is considered uncertain. However, this is the most up-to-date value available.

More research is needed to address data gaps in toxicokinetics, specifically the metabolism of Deca-BDE and the metabolites that are formed in laboratory animals as well as humans. Results from these studies as well as additional PBDE toxicity studies could be used to determine whether humans are more sensitive or less sensitive to Deca-BDE than laboratory animals.

Table 5: Non-Cancer Oral Reference Dose (RfD) for Deca-BDE
(Source: EPA, 2006b)

Non-cancer/Oral RfD (0.007 mg/kg/day)
based on NOAEL of 2.2 mg/kg (observed neurobehavioral changes in mice)
Uncertainty factor of 300
Overall confidence in RfD assessment is low

Table 6: Cancer/Oral Risk for Deca-BDE
(Source: EPA, 2006b)

Excess Cancer Risk	Doses Associated w/ Excess Cancer Risk
10^{-4} (1 in 10,000)	0.1 mg/kg/day
10^{-5} (1 in 100,000)	0.01 mg/kg/day
10^{-6} (1 in 1,000,000)	0.001 mg/kg/day

More complete summaries of existing information on human toxicity are included in Appendices E1, E4 and E5, respectively.

Summary of Concerns about PBDEs and Deca-BDE

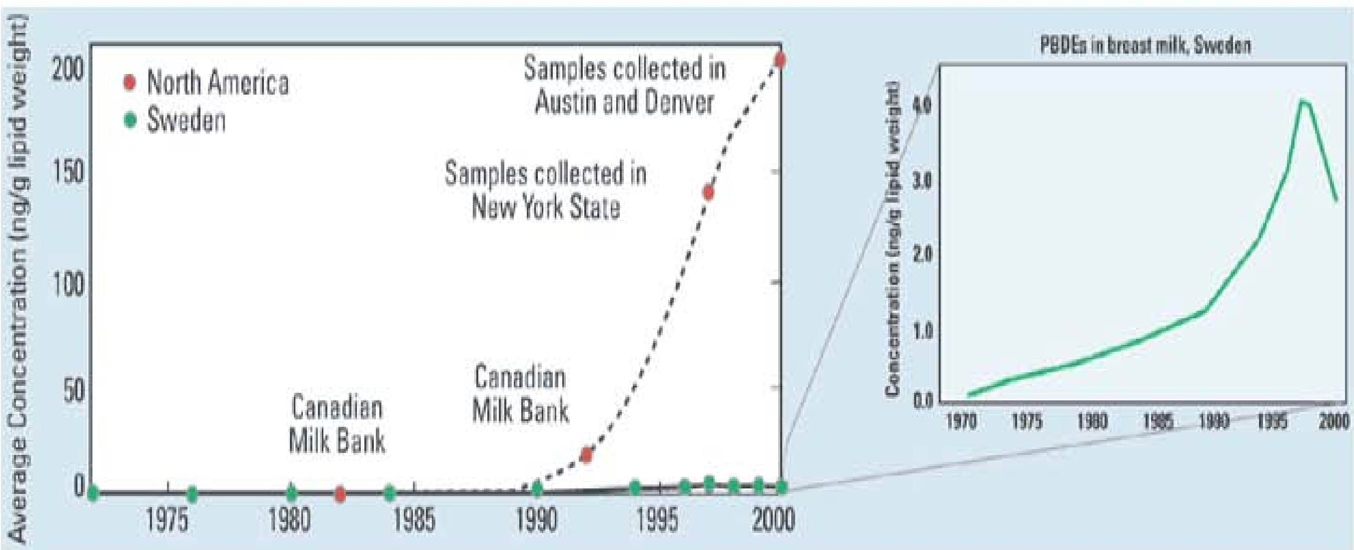
The preceding sections provide the most important and relevant findings about PBDEs and Deca-BDE with respect to the environment and human health. The following two illustrations pull much of that information together.

Figure 7 is borrowed from a presentation made by Mr. Prasada Rao S. Kodavanti of the USEPA, Neurotoxicology Division, NHEERL/ORD, Research Triangle Park, North Carolina at the

Federal-State Toxicology Risk Analysis Committee (FSTRAC) conference in Durham, North Carolina on October 19, 2007.

It compares trends in PBDE concentrations in human milk over time in North America and in Sweden. Note the significantly higher concentrations of PBDEs in breast milk collected from North American mothers (graph on left side of figure) compared to mothers in Sweden (graph on right side of figure). The green dots on the left graph show where the data from Swedish mothers plots relative to North American mothers. Note also how the concentrations of PBDEs in breast milk from Swedish mothers began to decrease beginning in the late 1990s after PBDEs were banned in that country (right side of figure).

Figure 7. Trends of PBDEs in Human Milk (Betts, 2002)
(from: Kodavanti, 2007)



Note that Penta-BDE was voluntarily phased out in Sweden in the mid-1990s and this appears to be reflected in declining PBDE concentrations in breast milk of Swedish mothers.

Table 7 is from the State of Illinois' 2006 report on Deca-BDE. It summarizes the results of studies that have estimated the daily human intake of PBDEs from food and other sources. Review of the estimated PBDE intakes shows they are at least an order of magnitude less than the EPA RfD for Deca-BDE of 0.007 mg/kg/day. The RfD is considered a safe level of daily exposure to Deca-BDE, however EPA considers this value uncertain, as discussed previously.

Table 7: Estimated Daily Human PBDE Intake from Food (mg/kg/day)
(Source: Illinois, 2006)

Daily Intake	Source	BDE Congeners Included	Country	Group Exposed	Data From
0.00000019-0.000003	Food	47, 99, 100, 153, 154	Netherlands	Adults	Washington, 2005
0.0002-0.0026	Air, Water, Food, Dust, Breast Milk	Multiple, Tetra-Through Deca	Canada	Children	Washington, 2005
0.000355	Breast milk	Multiple	US	Infants	Washington, 2005
0.000004(max)	Food	Multiple	US	Children	Washington, 2005
0.000003(max)	Food	Multiple	US	Adults	Washington, 2005
0.00004-0.0009	Multiple	Penta-BDE	US	Children	Washington, 2005
0.000014-0.000054	Multiple[(a)]	47, 99, 100, 153, 154	US	Adult Women	Washington, 2005
0.000016 (median)	Multiple	47, 99, 100, 153, 154	US	Adult Women	McDonald, 2005
0.000015(average)-0.000082(max)	Multiple[(a)]	47, 99, 100, 153, 154	US	Adult Women	Gill et al, 2004
0.000016-0.0028	Breast milk	Not Specified	US	Infants	Maine, 2005
0.000008-0.00008, 0.0000032-0.000032	Dust	Multiple, DecaBDE	US	Children	Stapleton et al, 2005

(a) Values back-calculated from BDE concentrations in tissues

Note: The yellow circles indicate Deca-BDE was included in the estimate of daily intake of total PBDEs.

Some stakeholders assert that the concentrations of PBDEs observed in the general population of North America are now reaching the level at which adverse effects were seen in laboratory animal studies. Two studies referenced in the State of Washington report (2006) appear to be the source of this statement (McDonald 2004, and McDonald 2005). These studies focused on PBDE congeners associated with Penta-BDE, not Deca-BDE, and the finding applies only to the 5% of the population that carries a significantly higher concentration of PBDEs in their bodies relative to average concentrations. (The finding that 5-10% of the general population has elevated concentrations of PBDEs in their blood has been documented in studies by Sjodin et al., 2003; Hites, 2004; and Schecter et al., 2005.) The MPCA was unable to obtain copies of the cited references.

While Deca-BDE concentrations in humans are low relative to the PBDE congeners associated with Penta-BDE, and while the PBDE congeners associated with Penta-BDE are generally considered more toxic than Deca-BDE, the finding that some individuals appear to carry PBDE body burdens that approach the concentrations at which adverse effects were seen in laboratory animals is of concern. It is even more so given the documented breakdown of Deca-BDE to lower PBDE congeners and the current limited understanding of this process.

FINDINGS AND RECOMMENDATIONS ON PBDES AND DECA-BDE BY U.S. STATES AND THE EUROPEAN UNION, AND ADOPTED REGULATIONS

Several U.S. states and the European Union (EU) have undertaken significant study of the risks posed to human health and the environment by PBDEs and/or Deca-BDE. Several states have consequently implemented or proposed regulations that phase out the use of PBDEs and/or Deca-BDE. A summary of this information is provided in the sections below. Executive summaries from the state reports as well as the EU risk assessment are in Appendix H.

Findings and Recommendations on PBDEs and Deca-BDE by U.S. States, the European Union and Canada

U.S. States

States that have issued reports on PBDEs or Deca-BDE are as follows: Washington (2006); Illinois (2006); California (2006); Maine (2007); and Michigan (draft 2007). Of these, the State of Washington's January 2006 report is one of the most comprehensive and most cited. The report totals more than 300 pages. Its findings with regard to PBDEs and Deca-BDE encapsulate many of the findings in subsequent reports prepared by other states.

The State of Washington's findings on PBDEs in general:

- PBDEs have been found in the environment, people and food. The highest PBDE concentrations measured in the world have been in the U.S. and Canadian populations.
- PBDE concentrations in human beings are not yet at levels shown to be toxic to laboratory animals and are not an immediate health concern; however, increasing PBDE concentrations in the environment may cause some serious environmental and health consequences (i.e. neurotoxicity, reproductive impacts and/or liver disorders).

The State of Washington's findings specific to Deca-BDE:

- Deca-BDE is predominantly found in sediments and house dust, with lower concentrations detected in human beings and food relative to Penta- and Octa-BDE.
- Deca-BDE is less toxic than other PBDE formulations, but may break down in the environment to more toxic and bioaccumulative forms of PBDEs.

The State of Michigan's May 2007 (draft) report states its findings more definitively than the State of Washington, but also carefully outlines the uncertainties:

- Deca-BDE animal toxicity studies show it causes neurodevelopmental effects and reductions in thyroid hormone levels.

- Deca-BDE can degrade in the environment, but the extent and importance of degradation is not well understood, neither is its significance as a source of lower congener PBDEs.
- Deca-BDE concentrations in human tissue are not of significant concern [*based on existing information*], however there are many uncertainties associated with its assessment.

The reports of Washington, Maine and Michigan all include the recommendation that a ban on Deca-BDE be implemented. The California report stopped short of recommending a ban, but recommended that the use of PBDE-free products should be encouraged and the need for more regulation should be considered.

European Union

The EU's risk assessment of Deca-BDE is regularly referenced by many stakeholders. The original, draft final risk assessment on Deca-BDE was published by the EU in 2002, but was updated in 2004 and 2005 and is undergoing another update at present. The basic conclusions of the 2002 EU risk assessment of Deca-BDE and its 2004 and 2005 updates are that: 1) there is no present need for measures to reduce the risks for consumers, and 2) more information is needed to confirm or evaluate the potential effects of Deca-BDE on human health and the environment.

A draft version of the 2007 update, which is not yet publicly available but was obtained courtesy of Mr. Ray Dawson of Albemarle Corporation, states that consumers may be exposed to Deca-BDE from products, but, "…this exposure has not yet been quantified and considered in the risk assessment based on the current hazard profile."

Not all members of the EU or the European Parliament have been satisfied with the conclusions of the Deca-BDE risk assessment. This is discussed in more detail in the next section on regulations on Deca-BDE.

Canada

The Canadian Ministers of Environment and Health released a report titled, "Ecological Screening Assessment on Polybrominated Diphenyl Ethers," in July 2006. The report concludes that PBDEs including Deca-BDE meet the criteria to be listed as toxic under Section 64 of Canadian Environmental Protection Act of 1999. This determination enables the government to address and take action against the presence of PBDEs in the environment.

<u>Regulations on PBDEs</u>

U.S. States

Several U.S. states (CA, HI, IL, MD, ME, MI, MN, NY, OR, RI, WA) have banned the use and manufacture of Penta- and Octa-BDE. To date, only the states of Maine and Washington have enacted laws that place partial restrictions on the use of Deca-BDE, although legislation that would phase out or place restrictions on Deca-BDE was introduced in several other states in

2007 (CA, HI, IL, MI, MN, and NY). The restrictions on Deca-BDE adopted by Maine and Washington are targeted at home furniture and home electronics.

A summary of the enacted legislation by state is presented in Table 8. An overview of proposed legislation during 2007 is included in Table 9.

Table 8: States with Regulations that Place Limitations on PBDEs

State	*Effective Date*	*Limit on PBDE type and content*	*Exceptions*
California	2006	0.1% penta or octa	Recycling, research
Hawaii	2006	0.1% penta or octa	Recycling
Illinois	2006	0.1% penta or octa	Recycling
Maine	2006	1.0% penta or octa	
	2008	1.0% deca in mattresses and indoor furniture	
	2010	1.0% deca in electronics (if exteriors contain Deca-BDE)	
Maryland	2007	Penta or octa	
Michigan	2006	0.1% penta or octa	Recycling, replacement parts
Minnesota	2008	0.1% penta or octa	
New York	2006	0.1% penta or octa	
Oregon	2006	Penta or octa	
Washington	2007	0.1% penta, octa,	
	2008	0.1% deca	Vehicle parts; equipment for military or space programs

Table 9: States with Proposed Legislation on PBDEs in 2007

State	*Bills*	*Major Features*	*Last Action*
California	AB 706	Ban of all BFRs and CFRs in furniture and bedding by 2010 (Exemption for aerospace)	Passed in California State Assembly
	AB 513	Ban use of deca-BDE in electronics	Eligible for 2008 legislative session
Hawaii	SB 1045	Ban use of deca-BDE in TV, computer, residential upholstered furniture effective January 1, 2009	Eligible for 2008 legislative session

Illinois	HB 1421	Ban use of deca-BDE in mattresses, mattress pads, articles of furniture effective January 1, 2011, ban deca-BDE in electronics (if exteriors contain deca-BDE) effective January 1, 2011. (exemptions for used products, the processing and recycling material, vehicles used for transportation, products used in such vehicles, medical devices)	In May of 2007 it was re-referred to House Rules Committee. No further action taken
Michigan	HB 4465	Ban use of deca-BDE in mattresses and upholstered furniture by 2008 and in TVs and computers by 2012	Referred to the House Committee on Great Lakes and Environment
Minnesota	SF 651	Partial ban on use of deca-BDE	Passed with amendment to exclude ban and review Deca-BDE as SF 2096.
New York	A 79777	Ban use of deca-BDE in textiles and electronics effective January of 2008	Passed in New York Assembly

BFR = Brominated Flame Retardants
CFR = Chlorinated Flame Retardants

European Union

The EU's 2002 risk assessment of Deca-BDE concluded that: 1) there is no present need for measures to reduce the risks for consumers, and 2) more information is needed to confirm or evaluate the potential effects of Deca-BDE on human health and the environment. However, in January 2003 the EU Parliament and EU Council included Penta-, Octa- and Deca-BDE on a list of substances to be phased out of electrical and electronic equipment in Directive 2002/95/EC, better known as RoHS or the "Restriction of Hazardous Substances."

Subsequently, a decision to exempt Deca-BDE from the RoHS directive was adopted and published by the European Commission (EC) on October 13, 2005. (The EC is the EU's executive body.) The exemption decision was based on the conclusions of the EU's risk assessment of Deca-BDE and the authority granted to the EC in RoHS that enables the 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 (Maine, 2007). The exemption for Deca-BDE remains valid until 2010.

However, not all members of the EU were in favor of the EC's decision to exempt Deca-BDE from RoHS (Maine, 2007). Denmark and the European Parliament (part of the governing structure of the EU) brought separate actions asking the European Court of Justice (ECJ) to annul the EC's decision to exempt Deca-BDE from RoHS, alleging that the EC did not comply with the conditions in RoHS for granting exemptions.

In support of Denmark's case, the Danish Environmental Protection Agency commissioned a study of the use of Deca-BDE and its alternatives in electrical and electronic equipment; this report has been submitted to the ECJ and is publicly available. It was expected that the United Kingdom would be submitting testimony with regard to this report in support of the EC; and that Sweden, Norway, Finland and Portugal would be doing the same in support of the European Parliament and Denmark (Maine, 2007).

In the meantime, EU member Sweden acted on its own to ban Deca-BDE in textile, upholstery and electrical wiring effective January 1, 2007. And German plastics and textile manufacturers voluntarily stopped producing and using Deca-BDE in 1989 (Maine, 2007).

Canada

The Canada Gazette published a Polybrominated Diphenyl Ethers Regulation to be made under the subsection 93(1) of the Canadian Environmental Protection Act of 1999 in December 2006. The purpose of the proposed legislation is to protect the environment from risks posed by use and emissions of PBDEs. The proposed regulation would ban manufacture of PBDEs (Tetra-BDE, Penta-BDE, Hexa-BDE, Hepta-BDE, Octa-BDE, Nona-BDE and Deca-BDE), and ban use, sale or offer for sale and import of Tetra-BDE, Penta-BDE and Hexa-BDE (Canada Environmental Protection Agency (CEPA) Environmental Registry, 2007). The MPCA was not able to ascertain the current status of this proposed regulation.

ALTERNATIVES TO DECA-BDE

Much of the concern surrounding a potential phase out of Deca-BDE centers on concern about the health risks posed by potential alternatives. Would a phase-out of Deca-BDE push manufacturers to use other types of chemical FRs that may be as harmful – or even more harmful- than Deca-BDE?

This is a realistic concern. There are a large number of potential alternatives for Deca-BDE, including other BFRs such as the high volume chemicals TBBPA and HBCD. Generally speaking, the brominated and chlorinated FRs have been found to be environmentally persistent, bioaccumulative and toxic to varying degrees. TBBPA and HBCD are currently being evaluated by the EU using the same risk assessment process applied to Deca-BDE.

The state reports on PBDEs have generally included risk evaluations of potential chemical FRs that could be used in place of Deca-BDE. In 2007, the State of Illinois prepared a report that focuses exclusively on the evaluation of potential alternatives to Deca-BDE.

Most of the state reports find that less is known about the environmental behavior and toxicology of alternative FRs than is known about Deca-BDE. Because of this, it is difficult to conclude that a potential alternative FR for Deca-BDE poses little or no risk and therefore is more safe for human health and the environment than Deca-BDE. However, Illinois' 2007 report concludes that some of the chemical alternatives do appear to be safer than Deca-BDE.

In this section, commonly mentioned alternatives to Deca-BDE are reviewed and discussed. However, other means are available than an alternative chemical flame retardant to meet flammability requirements. Reports indicate that many manufacturers are voluntarily looking for alternatives to Deca-BDE or are finding ways to redesign their products so that the use of chemical flame retardants is not necessary. These market and consumer driven changes will be discussed following the review of alternative chemical flame retardants.

Alternative Chemical Flame Retardants

The two types of alternative chemical FRs that may be substituted for Deca-BDE are discussed separately below: non-halogenated FRs and halogenated (i.e. brominated or chlorine-based) FRs.

Non-halogenated Alternatives

According to the Lowell (2005) report, non-halogenated alternatives cannot be used as direct substitutes for Deca-BDE in high impact polystyrene (HIPS) – the polymer where Deca-BDE has its primary use (80% of total volume). This is because HIPS that is flame-retarded with non-halogenated FRs cannot meet the required flammability standards.

However, other types of plastic, including high impact polystyrene/polyphenylene ether (HIPS/PPO) and polycarbonate/acrylonitrile-butadiene-styrene (PC/ABS) are compatible with non-halogenated FRs and can meet the required flammability standards. Most often, phosphorus-based FRs such as resourcinol bis diphenylphosphate (RDP) are used for this purpose (Lowell, 2005).

In Europe, HIPS/PPO with RDP is commonly used to construct enclosures for televisions, and the trend is to manufacture TV enclosures that meet European and the stricter U.S. flammability requirements so that the products can be sold in both markets (Maine 2007). Some manufacturers of LCD (Liquid Crystal Display) TVs are known to use PC/ABS resin with phosphorus based FRs to construct the enclosures. The cost of these flame-retarded plastic resin systems is about 1.5 to 2.5 times more expensive than Deca-BDE flame retarded HIPS (Lowell, 2005).

The most commonly mentioned phosphorus-based FRs used in combination with HIPS/PPO and PC/ABS are listed in Table 10. Of these, the first five are most frequently mentioned (numbers 1 through 5). Table 10 provides a summary of toxicity, persistence and bioaccumulation potential information for the listed alternatives, based on information provided in the various state PBDE reports (Washington, 2006; Maine, 2007; Illinois, 2007; Syracuse Research Corporation, 2006; Pakalin et al., 2007).

The state reports on PBDEs differ somewhat on the suitability of the non-halogenated alternatives. Only RDP, red phosphorus, and magnesium hydroxide were considered potential alternatives by at least one state and not also considered unsuitable by another state.

BAPP, one of the top five phosphorus-based FRs, breaks down to form bisphenol A (BPA). BPA is considered a potent endocrine disruptor and is accumulating in people; this chemical is receiving a great deal of scrutiny by organizations concerned about public health (e.g. Body Burden Work Group and Commonweal Bio-monitoring Resource Center, 2007).

However, the primary human exposure route for BPA is thought to be direct contact with consumer products that contain BPA, especially polycarbonate plastic products such as water bottles, baby bottles, and food storage and heating containers. The level of concern that may arise from BPA as a breakdown product of BAPP in the environment is less clear.

The Illinois 2006 Deca-BDE report suggests there is a potential for formation of toxic phosphine gas during combustion of products containing phosphorus-based flame retardants. This includes all of the non-halogenated alternatives in Table 10 except melamine cyanurate, magnesium hydroxide, and zinc borate. No data are available to evaluate this concern. However, there remains a possibility that if this is a significant issue, the toxicity of combustion-related gases from resin systems incorporating phosphorus-based FRs could be higher than is currently assumed.

Table 10. List of Commonly Cited Non-Halogenated Alternatives to Deca-BDE

	Chemical Name (Abbreviation) and CAS Number(s)	*Comments*	*Potential Alternative*	*Not Suitable as Alternative*
1	Resorcinol bis diphenylphosphate (RDP) 57583-54-7 and 125997-21-9	Low persistency; more toxicity info needed	WA, IL, ME, Syracuse 2006	
2	Bisphenol A diphosphate (BAPP, BPADP, BDP) 181028-79-5 and 5945-33-5	High persistency; more toxicity info needed; degrades to Bisphenol A.	IL, WA	ME
3	Diphenyl cresol phosphate (DCP) 26444-49-5	Persistent; moderate human and aquatic toxicity	WA	IL
4	Triphenyl phosphate (TTP) 115-86-6	Not persistent; more human toxicity info needed; high aquatic toxicity	WA	IL
5	Red phosphorus 7723-14-0	Inorganic (i.e. does not break down); low screening toxicity	ME	
6	Melamine cyanurate 37640-57-6	Biodegrades; little toxicity data		IL (insufficient data to make recommendation)
7	Magnesium hydroxide 1309-42-8	No known env. concerns; considered non-toxic.	IL, WA	
8	Zinc borate 1332-07-6	High human and aquatic toxicity	WA	IL
9	Ammonium polyphosphate 14728-39-9 and 68333-79-9	Biodegrades; little toxicity data	ME	IL (insufficient data to make recommendation)

CAS = Chemical Abstract Service

Halogenated Alternatives

Table 11 lists potential halogenated alternatives to Deca-BDE.   Note that both HBCD and TBBPA are included on this list. These BFRs are both undergoing risk assessments by the EU. The descriptions of toxicity, persistence and bioaccumulation potential of the halogenated alternatives are based on review of other published evaluations (Washington 2006; Pakalin et al., 2007) and peer-reviewed studies of the alternatives (Birnbaum and Staska, 2004).

Note that the State of Illinois, in its 2007 report evaluating the availability of safer and affordable alternatives to Deca-BDE, decided not to evaluate bromine- and chlorine-based alternatives. This decision was based on concern about the generation of toxic byproducts such as dioxins and furans upon the burning or incineration of the resin systems containing these FRs. The State of Maine categorically ruled out consideration of other brominated FRs as potentially safer alternatives to Deca-BDE, since other brominated chemicals share the characteristics that make Deca-BDE problematic.

Table 11: Lists of Commonly Cited Halogenated Alternatives to Deca-BDE

	Chemical Name (Abbreviation) and CAS Number(s)	*Comments*	*Potential Alternative*	*Not Suitable as Alternative*
1	Bis(pentabromophenyl) ethane 84852-53-9	Limited toxicity & other information (indications of low toxicity, and bioaccumulation, expected to be very persistent)	WA	
2	1,2-bis (tetrabromophthalimido) ethane 32588-76-4	Limited toxicity & other information (indications of low toxicity, and bioaccumulation, expected to be very persistent)	WA	
3	Tetrabromobisphenol A epichlorohydrin polymer 40039-93-8	Limited toxicity & other information	WA	
4	Bis(tribromophenoxy) ethane 37853-59-1	Fairly limited toxicity & other information (indications of low toxicity, show tendency to persist and bioaccumulate)	WA	
5	Hexabromocyclo-dodecane (HBCD) 3194-55-6 and 25637-99-4	Concentrations in biota and environment are increasing; toxic (meets persistence, toxic and bioaccumulation criteria by EU, and WA		EU is conducting a risk assessment of HBCD, WA

6	Tetrabromobisphenol A (TBBPA) 79-94-7	Very persistent; bisphenol A is a likely breakdown product (meets persistence, toxic and bioaccumulation criteria by WA)		EU is conducting a risk assessment of TBBPA, WA
7	Tetrabromobisphenol A bis (2,3-dibromopropyl ether) 21850-44-2	Fairly limited toxicity & other information		

CAS = Chemical Abstract Service

Voluntary Market Changes

Many manufacturers have already eliminated the use of Deca-BDE in their products. One of the first companies to do so was Ikea, the Swedish furniture manufacturer. Its products have been free of PBDEs since 2002 (Betts, 2007).

Computer and television manufacturers are also voluntarily moving away from the use of Deca-BDE. Clean Production Action, a nonprofit that helps organizations design greener products and manufacturing processes, documents manufacturer's progress in a fact sheet dated November 15, 2006. It states that manufacturers of personal computers have largely eliminated their use of Deca-BDE, and by 2010 four of the eight largest TV manufacturers selling in the U.S. will have eliminated Deca-BDE use, if they follow through on their plans to do so.

The list of manufacturers that are phasing out the use of Deca-BDE from some or all of their products include:

Apple	Cannon
Dell	Ericsson
HP Monitors	IBM
Intel	Toshiba
LG Electronics	Nokia
Panasonic	Samsung
Sony-Ericsson	Motorola

Source: Environmental Working Group (EWG), 2006

A news article in the journal *Environmental Science and Technology* reported on September 27, 2007 that FR formulators are acknowledging that many of their customers are steering them towards offering of non-halogenated products. Computer manufacturers such as Dell are also clearly stating that they are competing to be viewed as "green," and halogen-based flame retardants do not have a green image (Betts, 2007).

Product redesign, including the use of metal components to protect the power supply, removal of the power supply from inside electronic product enclosures, and use of inherently flame resistant fibers, are ways that the need for chemical FRs can be reduced or eliminated.

According to Maine's 2007 report, the textile industry has many choices in chemical flame retardants beside Deca-BDE. There are also many ways to modify fibers and fabrics to meet flammability standards without using chemical flame retardants. There is also the choice of using inherently flame resistant fibers and fabrics.

Mattress manufacturers needing to comply with the new national CPSC standard that went into effect in July 2007 have shunned the use of Deca-BDE, according to the Maine report (2007). The Maine report (2007) also reports that furniture industry sources suggest that in most cases, chemical flame retardants will not be needed to meet pending national standards for residential upholstered furniture.

Quoting directly from Maine's 2007 report:

> "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 phosphorous compounds such as resorcinol bis diphenylphosphate (RDP). RDP presents a significantly lower threat to the environment and human health than decaBDE."

The cost of making these changes in most cases is considered minor (Illinois, 2007). However, in the fields of medical devices and transportation, particularly the aircraft and aerospace industries, cost is a concern. This is primarily a result of the highly regulated nature of these industries and the extensive product testing that is required by both regulatory agencies and the manufacturers themselves to qualify their products.

In its 2007 report, the State of Maine recommended that a ban of televisions and other consumer electronics that are encased in plastic containing more than 0.1% Deca-BDE be delayed until 2012 to ensure that manufacturers have sufficient lead time to retool their production processes. The Maine report also underlines the fact that manufacturers of products that have many small electrical parts or extensive wiring, such as in automobiles, airplanes, and ships, may not be able to easily ascertain which components contain Deca-BDE. Several years may be needed to complete the process of identifying all instances of Deca-BDE usage in these products.

SUMMARY OF KEY FINDINGS

This report has been prepared for the Minnesota Legislature as required by Minnesota Statue 325E.387 to provide information on the health and environmental risks posed by the use of Deca-BDE. The MPCA has conducted a review of current scientific literature and recent studies on PBDEs and Deca-BDE prepared by other states and the European Union. Key findings are summarized below.

Deca-BDE Bioaccumulation

Numerous studies have documented the presence of PBDEs in the environment, including in Minnesota. Deca-BDE has been detected at relatively higher concentrations relative to other media in house dust, sediments, and sewage sludge. Deca-BDE has been detected in fish and birds and in human fat, blood, and breast milk. The concentrations of Deca-BDE detected in human tissue are much lower than the detected concentrations of other PBDEs. The concentrations of Deca-BDE in environmental media are increasing.

Routes of Human Exposure

The primary ways that people are exposed to Deca-BDE are through diet and through inhalation of Deca-BDE-containing house dust. Other routes of exposure have not been extensively studied. Nursing infants and young children have the highest intake of PBDEs including Deca-BDE.

Although it is thought that the general population may be exposed to PBDEs including Deca-BDE through contact with PBDE-containing consumer products, such as TVs, the few existing studies of this pathway have not yielded evidence supporting it.

Human Health Effects and Current Levels of Exposure

Laboratory animal toxicity studies indicate that toxic effects are associated with exposure to Deca-BDE at concentrations above those that occur in the environment. These include liver, thyroid, reproductive, developmental and neurological effects. More research is needed to address data gaps in toxicokinetics, specifically with respect to the metabolism of Deca-BDE and the metabolites that are formed in laboratory animals as well as humans. Results from such studies and additional studies of PBDE toxicity could be used to determine whether humans are more sensitive or less sensitive to Deca-BDE than laboratory animals.

Studies estimating human exposure to Deca-BDE conclude that current exposure levels are not of concern; however these estimations include many uncertainties and need to be treated with caution.

Breakdown of Deca-BDE in the Environment

Numerous studies have shown that Deca-BDE breaks down to more toxic, lower brominated PBDEs in the presence of sunlight, and that it can be broken down by metabolic processes in animals and by microorganisms in sewage sludge. The extent of Deca-BDE breakdown and the identity and stability of the breakdown products in the environment and in people is not well understood. This is an important issue in the overall evaluation of the toxicity of Deca-BDE.

Deca-BDE Alternatives

A phase-out of Deca-BDE can be accomplished without affecting fire safety. Effective alternatives for achieving flame retardancy appear to be available for most Deca-BDE applications. In general, flammability requirements can be met using strategies that include: using alternative chemical flame retardants; switching to the use of inherently non-flammable materials; and re-designing the product.

The majority of Deca-BDE is used in the production of TV enclosures and in the textiles industry (commercial applications). In the case of TVs, switching to alternative FRs will require manufacturers to shift from the use of HIPS to other types of plastic that can be treated to meet flammability standards. The phosphorus-based FRs such as resorcinol bis diphenylphosphate (RDP) are already in use in this application. RDP is generally thought to present a lower threat to the environment and human health than Deca-BDE.

In the case of textiles, alternatives that do not require the use of other flame retardants are already widely used. Many manufacturers are reportedly modifying mattresses and furniture to meet fire safety standards without the use of chemical flame retardants.

The cost to accomplish a phase out of Deca-BDE is concluded to be minor for the consumer electronics and textile industries. However, in the fields of medical devices and transportation, particularly the aircraft and aerospace industries, cost is a concern. This is primarily a result of the highly regulated nature of these industries and the extensive product testing that is required by both regulatory agencies and the manufacturers themselves to qualify their products.

Toxicity data for Deca-BDE alternatives is very limited, including that for the phosphorus-based FRs such as RDP. Most studies conclude that phosphorus-based FRs pose fewer health and environmental concerns than PBDEs. This is because the phosphorus-based FRs generally appear not to bioaccumulate or break down into more toxic chemicals. At least two of the state studies conclude that halogenated FRs are not appropriate alternatives to Deca-BDE because: 1) they are expected to behave similarly to Deca-BDE in the environment or 2) because they create toxic dioxins and furans upon burning.

Regulatory Overview

Several U.S. states (CA, HI, IL, MD, ME, MI, MN, NY, OR, RI, WA) have banned the use and manufacture of Penta- and Octa-BDE. So far only the states of Maine and Washington have enacted laws that place partial restrictions on the use of Deca-BDE, although legislation that would phase out or place restrictions on Deca-BDE use was introduced in several other states in 2007 (CA, HI, IL, MI, MN and NY). The restrictions on Deca-BDE adopted by Maine and Washington are targeted at home furniture (where it is not currently used but could be if pending national flammability standards for home furniture are imposed) and home electronics.

In Canada, PBDEs including Deca-BDE are listed as “toxic” under section 64 of Canadian Environmental Protection Act of 1999. Further regulatory action has been proposed but the status of the proposed regulation is unknown.

The European Union has exempted Deca-BDE from a ban under its Restrictions on Hazardous Substances (RoHS) directive that resulted in Penta- and Octa-BDE being withdrawn from the marketplace. This action was taken after the EU’s risk assessment of Deca-BDE concluded that: 1) there is no present need for measures to reduce the risks for consumers, and 2) more information is needed to confirm or evaluate the potential effects of Deca-BDE on human health and the environment. The draft 2007 update to the risk assessment includes an additional statement that consumers *may* be exposed to Deca-BDE from consumer products. Not all EU members are in agreement with the EU’s decision to exempt Deca-BDE from the RoHS provisions.

In its 2007 report on PBDEs, the State of Maine report recommended that a ban on Deca-BDE in televisions and other consumer electronics be delayed until 2012, to give manufacturers sufficient time to retool their production processes. The Maine report also highlighted the difficulties that manufacturers of products containing small electrical parts or extensive wiring, such as automobiles, airplanes, and ships, may have in determining which components contain Deca-BDE. Because the process of identifying all instances of Deca-BDE usage in these products and finding substitutes could take several years, any phase out of Deca-BDE needs to consider a fair way to address this issue.

As with other emerging issues and contaminants of concern, policymakers should keep in mind that collective knowledge about brominated flame retardants and alternatives is changing. New research results, governmental actions and marketplace trends all will influence the manufacture and use of flame retardants even as this report is being reviewed and discussed by lawmakers and stakeholders.

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Decabromodiphenyl Ether (Deca-BDE): A Report to the Minnesota Legislature

APPENDICES

Appendix A

Stakeholder Consultations

Albemarle Corporation (Ray Dawson)
ARC Greater Twin Cities (Beth Fondell)
Bromine Science and Environmental Forum (Lloyd Grooms, Winthrop and Weinstein)
Goodrich Corporation (Randy Morris, McGrann Shea and Maria Kortan-Sampson, Goodrich)
Institute for Agriculture and Trade Policy (Kathleen Schuler)
Minnesota Center for Environmental Advocacy (Samuel Yamin)
Minnesota Chamber of Commerce (Tony Kwiles)
Minnesota Department of Health (Pam Shubat and Larry Gust)
Minnesota Department of Public Safety (Jerry Rosendahl, State Fire Marshall and Bob Dahm, Chief Deputy)
Minnesota State Fire Chiefs Association (Nyle Zikmund)
Minnesota Retailer's Association (Buzz Anderson)
RTP Corporation (Steve Maki, Vice-President)

Appendix B

2005 MPCA Background Paper on PBDEs

In 2005, at the request of Minnesota Legislature, the MPCA produced a report titled “Retardants: Polybrominated Diphenyl Ethers (PBDEs) Background Paper.” The link to the document is provided below.

MPCA (2005). Flame Retardants: Polybrominated Diphenyl Ethers (PBDEs) Background Paper, Minnesota Pollution Control Agency: 32.
http://www.pca.state.mn.us/publications/reports/tdr-g1-02.pdf

Appendix C

Materials and Products Containing PBDEs

BDE	*Material used in*	*End products containing BDE*
Penta	Polyurethane foams, epoxies, laminates, adhesives, coatings	Mattresses, seat cushions, other upholstered furniture and rigid insulations
Octa	Acrylonitrile butadiene styrene (ABS), nylon, thermoplastic elastomers and polyolefins	Housings for fax machines, and computers, telephone headsets, automobile trim, and kitchen appliances casings
Deca	High-impact polysturene (HIPS), nylon, polypropylene, polyethylene (PE), styrene butadiene rubber (SBR), unsaturated polyester, epoxy, polyvinyl chloride (PVC), polyester resins (PET/PBT), acrylonitrile butadiene styrene (ABS), polycarbonate (PC), ethylene-propylene-diene rubber and ethylene-propylene terpolymer (EPDM)	*Electric and electronic equipment* (housing and internal components of TVs, mobile phones, fax machines, audio/video equipment, remote controls, communication cables, capacitor films, building cables, wire and cables, connectors in E&E equipment, circuit breakers, coils of bobbins, printing and photocopy machine components – toner, cartridge, connectors, scanner components) *Ships, boats, airplanes* (electrical wiring and cables, electric and electronic equipment – navigation and telecommunication equipment, air ducts for ventilation systems, electrical ducts and fittings, switches and connectors, components of fans, heating fans and hair dryers) *textiles and furniture* (household/furniture appliances – upholstered textiles, PU flexible foam, army tents) *automobiles/mass transportation* (fabric (backcoating of article) –rear deck, upholstery, headliner, sun visor, head rest, trim panel; reinforced plastics – instrumental panel interior trim; under the hood – terminal/fuse block, higher amerage wire and cable jacketing; electrical and electronic equipment – battery case and tray, engine control, electrical connectors, components of radio disk, GPS, and computer system) *household* (lamp sockets, kitchen hoods, electrical kitchen appliances, curtains and hanging drapes,

		components of water heating devices, components of electrical appliance such as transformer and switches, components of fans, heating fans and hair dryers) *public, private, and industrial buildings/construction applications* (pipes, lamp holders, stadium seats, reinforced plastics, switches and connectors, facing laminates for insulation panel, film for use under the roof and to protect building areas, electrical ducts and fittings, components in analytical equipment in industrial and medical laboratories, air ducts for ventilation systems, pillars for telephone and communication

Sources: (Washington, 2006) www.bsef.com, (Lowell, 2005)

Appendix D

Available Information on PBDEs in the Environment (Emphasizing Deca-BDE)

Brominated Flame Retardants (BFRs) including Deca-BDE are of concern because of their widespread usage, environmental persistence and bioaccumulation. Increased concentrations of deca-BDE have been detected in North American environments including Minnesota.

Deca-BDE in Abiotic Samples

Air Samples

PBDE concentrations in indoor air are generally higher than in outdoor air because more PBDE sources are found indoors. House dust is a major source of PBDEs. A study by (Tan *et al.* 2007) measured PBDE concentrations in house dust in Singapore and compared them to house dust concentrations reported in similar studies conducted around the world. In all cases Deca-BDE was the dominant congener and accounted for 20 to 70% of the total PBDE concentration. House dust is thought to be one of the primary routes of exposure for humans.

A study by (Strandberg *et al.* 2001) reported PBDE concentrations in air samples collected around the Great Lakes region of North America. Total PBDE concentrations ranged from 5 pg/m^3 (picograms per meter cubed) (Lake Superior) to 52 pg/m^3 (Chicago). Deca-BDE was detected at only trace levels with concentration ranging from less then 0.1 pg/m^3 (Lake Superior) to 0.3 pg/m^3 in Chicago. A similar study was conducted in England and air concentrations there ranged from 3 to 23 pg/m^3 (Harrad and Hunter 2006). In both studies the total PBDE concentrations were higher in urban areas and decreased with increasing distance from urban centers.

Sediment

Deca-BDE has been detected in sediments (i.e. soil deposited in aquatic environments such as lakes, rivers, and wetlands) all over the world ((Pan *et al.* 2007); (Marvin *et al.* 2007); (Minh *et al.* 2007)). Studies show that concentrations of Deca-BDE in sediment have been steadily increasing, and that deca-BDE accounts for the largest percentage of total PBDE concentration.

A recent study by (Li *et al.* 2006) reported PBDE concentrations in sediment samples collected around the Great Lakes. A total of 199 samples were collected from 16 locations. Excluding Deca-BDE (BDE-209), total PBDE concentrations ranged from 0.5 to 6.7 ng/g (nanograms per gram) dry weight. The concentrations of Deca-BDE were up to two orders of magnitude higher then sum of other PBDE congeners, ranging from 4 to 240 ng/g dry weight. On average, Deca-BDE accounted for 94% of total PBDE concentrations. Sediment concentrations of PBDEs increased near populated, urban areas.

Sewage Sludge

More than half of total sewage sludge generated by wastewater treatment plans in the U.S. is applied to land (Hale *et al.* 2001). Although sewage sludge is treated for odor and pathogen content and monitored for heavy metals, it is not treated or evaluated for the presence of PBDEs or other persistent pollutants.

(Hale *et al.* 2001) examined eleven bio-solid samples collected in the U.S. and all contained elevated PBDE concentrations. The concentrations of Deca-BDE ranged from 85 to 4890 μg/g (micrograms per gram) dry weight. A similar study was conducted by (North 2004) on bio-solids samples from a waste water treatment plant in California. In this study Deca-BDE concentrations ranged from 1010-1440 μg/g dry weight.

In general, the reported concentrations of PBDEs in sewage sludge samples collected in the U.S. are about an order of magnitude higher than those measured in some European countries (i.e. Germany, Sweden, Netherlands, Switzerland) (Knoth *et al.* 2007).

<u>Deca-BDE in Biotic Samples</u>

Fish

Deca-BDE has been detected in fish throughout the United States. In 2005 and 2006 the Washington Department of Ecology analyzed PBDEs in freshwater fish. Data was obtained for thirteen PBDE congeners (including Deca-BDE) in 120 fish fillet samples and 23 whole fish samples collected from 32 water bodies. Total PBDE concentrations were less then 10 μg/kg wet weight in fish fillets. Deca-BDE was detected in six percent of the samples (EPAa, 2007)**.**

In 2006, the Minnesota Pollution Control Agency analyzed PBDE concentrations in fish collected from Lake Superior. Lake trout, lake herring and white sucker were collected at two locations (Two Harbors and Grand Portage MN) and data was obtained for nine PBDE congeners (including Deca-BDE). Deca-BDE contributed 0.1% to 4% of total PBDE concentration (Polybrominated Diphenyl Ethers: The Emerging Contaminants in the Lake Superior Watershed, (MPCA 2006)).

Birds

Swedish scientists reported high Deca-BDE concentrations in Swedish peregrine falcon eggs (Hale *et al.* 2001). This was the first report that showed that Deca-BDE bioaccumulates in birds.

In 2005 and 2006, following implementation of a mandated environmental monitoring program that was set up by European Commission, Deca-BDE concentrations were analyzed in eggs of the Sparrow Hawk in the United Kingdom, and in eggs of the Glaucous Gull in an Arctic region of Norway. Concentrations of Deca-BDE in Sparrow Hawk eggs ranged from 2.4 to 36 ng/g lipid, and in glaucous gull eggs <.45 to 4.3 ng/g lipid (Leslie *et al.* 2007).

Gaps in Understanding

As the number of scientific reports on environmental presence of PBDEs increases, it is clear that these chemicals are ubiquitous in the environment and that their concentrations are increasing in various environmental compartments. However there is still an incomplete understanding on the mechanism by which the chemicals are entering the environment. Some scientists suggest that better quality and more information is needed on behavior and degradation of Deca-BDE in sediments and on its concentrations in biota. In addition, the fate and transport of Deca-BDE in the environment is still not well understood.

Appendix E
Available Information on PBDEs and Human Health (emphasizing Deca-BDE)

Appendix E1

Chemical Degradation (Breakdown)

Numerous studies have shown that Deca-BDE degrades or breaks down chemically once released into the environment. The studies indicate that lower PBDE congeners including Hexa-, Hepta-, Octa- and Nona-BDE are formed as well as PBDE congeners not used in any commercial PBDE products. A number of unidentified chemicals are also formed. Results concerning the extent of breakdown of the Deca-BDE molecule and the stability of the breakdown products are inconclusive. However, the existence of unidentified chemical breakdown products raises concern about the potential for additional, unexamined environmental and human health effects from these compounds.

<u>Photolytic Breakdown of Deca-BDE (i.e. via exposure to sunlight)</u>

It has been know for some time that Deca-BDE is degraded by sunlight to lower brominated-congeners in the presence of organic solvents under laboratory conditions (Watanabe and Tatsukawa, 1987). However, researchers thought Deca-BDE would not degrade under ambient environmental conditions because of the molecule's large size, chemical stability and other physical-chemical properties. Numerous recent studies have been conducted to test this assumption.

(Soderstrom *et al.* 2004) examined the degradation of Deca-BDE under natural conditions when placed on sand, soil, and sediment in natural sunlight. The half-lives of Deca-BDE were 53 hours (h) in sediment and 150 to 200 h in the soil. In this study half-life is defined as the amount of time it takes for half of a substance (Deca-BDE) to degrade in various environmental media. The half-life of Deca-BDE in organic solvents is relatively short: 0.25 h in toluene and 0.5 h in methanol/water solvent. It was observed that although the Deca-BDE half-lives were different for various media, the pattern of debromination was the same in all matrices. Breakdown products formed included four Octa-BDE congeners, three Nona-BDE congeners, one Hepta-BDE, several Hexa-BDE congeners, and a number of unidentified breakdown products. The unidentified breakdown products may be a cause for concern because they are not being evaluated for potential environmental and health effects and in addition we do not really know the extent to which Deca-BDE breakdown products are present in the environment.

(Stapleton and Dodder 2007) exposed both natural, PBDE-containing house dust and Deca-BDE (BDE-209)-spiked house dust to sunlight. The study measured approximate half-lives of 408 h for natural house dust and 301 h for BDE-209 spiked dust. The degradation of Deca-BDE was observed in both matrices, but accumulation of the lower brominated PBDE congeners was most distinctive in the spiked dust, since it was originally spiked with only Deca-BDE and the natural house dust contains other PBDEs. The degradation products included Octa- and Nona-BDE congeners. At the end of exposure period about 25% of the original spiked Deca-BDE mass was unaccounted for and lost to unknown pathway/products.

Microbial Breakdown of Deca-BDE

One recent study has investigated degradation of Deca-BDE under anaerobic (i.e. unoxygenated) conditions. (Gerecke *et al.* 2005) used microflora from sewage sludge to examine the bacterially-mediated degradation of Deca-BDE. The study results showed that debromination of Deca-BDE occurred to Nona- and Octa-BDE congeners. The observed half-live of Deca-BDE was 3.8 years. The conclusion reached by the authors was that anaerobic bacteria can initiate the debromination of Deca-BDE, although at much slower rates than seen by photolytic degradation. This may, however, be significant due to the large volumes of sewage sludge generated in this county and the potential that Deca-BDE may act as a source of lower brominated and more toxic PBDEs to the environment.

Metabolic Breakdown of Deca-BDE

Several studies have also evaluated metabolic processes and shown through animal-based, laboratory studies that Deca-BDE can breakdown via metabolism.

A recent study by (Stapleton *et al.* 2006) examined the debromination of Deca-BDE in juvenile rainbow trout and common carp. The fish were exposed to Deca-BDE in their food (i.e. diet) over a period of five months. Analysis of the fish revealed the presence of several Hepta-, Octa-, and Nona-BDE congeners that accumulated as a result of debromination.

Another study by (Huwe and Smith 2007) examined the debromination of Deca-BDE in rats. The rats were exposed to Deca-BDE via diet for 21 days and then the concentration of PBDEs in their tissue was measured during a 21 day withdrawal period. Deca-BDE, three Nona-BDE congeners and four Octa-BDE congeners accumulated in the rats, in tissue located throughout their bodies.

(Van den Steen *et al.* 2007) examined Deca-BDE debromination in birds (European starlings) and observed the accumulation of Octa- and Nona-BDE congeners in muscle and liver.

A study by (La Guardia *et al.* 2007) looked for evidence of Deca-BDE debromination in biota collected near a waste water treatment plant. Fish (sunfish, creek chub, and crayfish) collected near the outfall of the plant contained Octa- and Nona-BDE congeners that are not present at detectable concentrations in commercial deca-BDE formulations. This finding suggests that metabolic debromination of Deca-BDE is the source of these Octa- and Nona-BDE congeners.

Appendix E2

Presence in Human Tissue

Until recently, studies of the presence of PBDEs in human beings have analyzed only the lower brominated congeners of PBDEs (i.e. Penta-, Octa- etc.). Deca-BDE was not included in these studies because it was thought not to bioaccumulate in humans, and because it is difficult to measure. Review of the early studies is important in illustrating how concern developed about PBDEs in general and in illustrating some of the differences in our knowledge and understanding of Deca-BDE in comparison to the lower congener PBDEs.

Occurrence of PBDEs in Humans

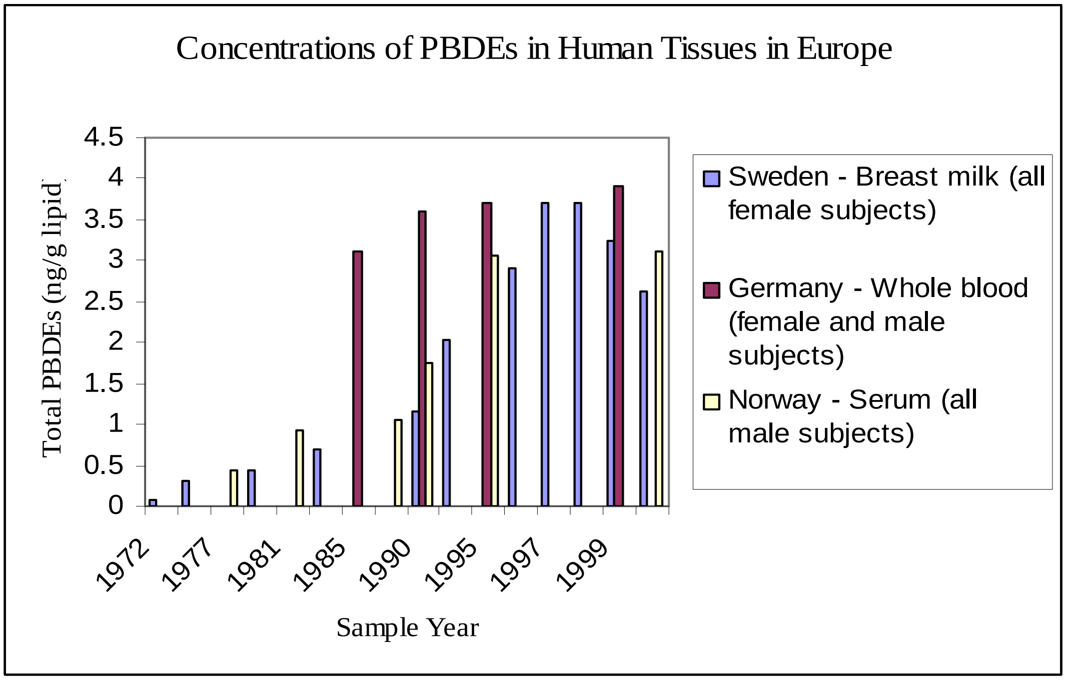
The publication in 1999 of a Swedish study on the presence of PBDEs in human breast milk sparked intense interest in the issue of PBDEs worldwide. The study showed that between 1972 and 1999, the concentration of PBDEs in the breast milk of Swedish mothers increased exponentially, with concentrations of PBDEs doubling every five years (Noren and Merionyte 2000).

Subsequently, a number of studies were published that looked at the trend of PBDE concentrations in the general population of the U.S. Similar trends of increasing PBDE concentrations were observed, but with the additional finding that the measured concentrations of PBDEs were at least an order of magnitude higher in the U.S. than in Europe (Schecter *et al.* 2003). It is thought that this result may be due to the fact that an estimated 95% of consumer products that contain PBDEs as flame retardants are used in the U.S. and Canada.

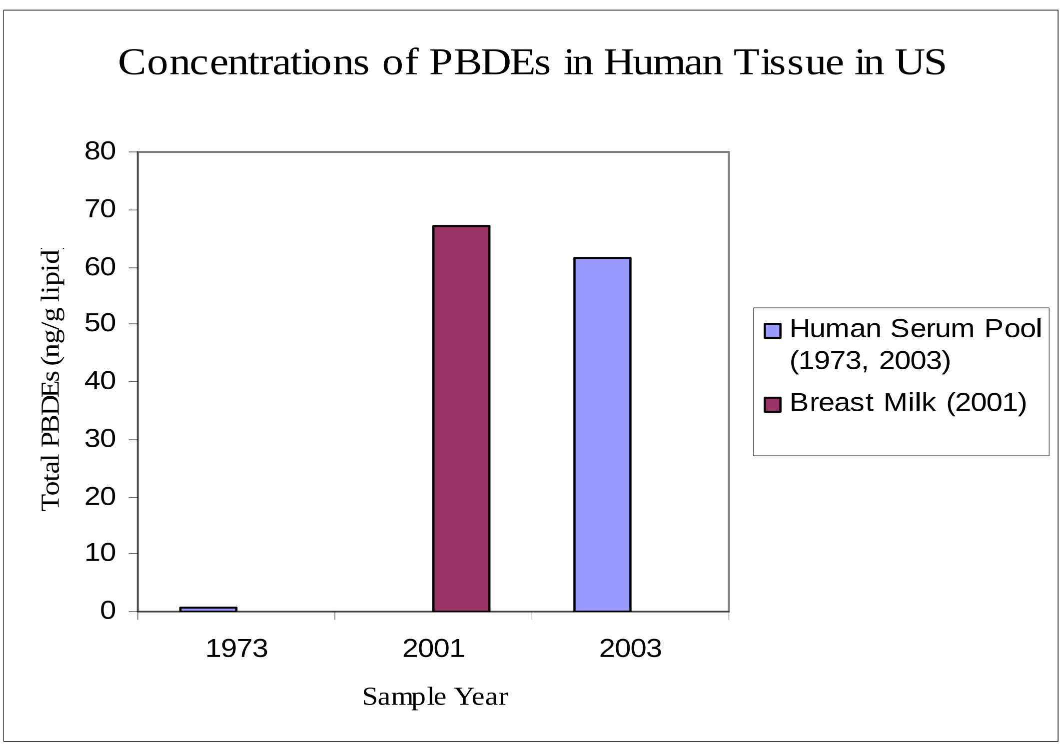
PBDE concentrations have been measured and reported in various human tissues including breast milk, fat, serum blood, and liver. PBDE tissue concentrations range over several orders of magnitude and the reasons for the observed variability are unknown. Researchers have found no correlation between PBDE concentrations and age.

It is estimated that about 5 to 10% of the U.S. population has unusually high concentrations of PBDEs in their bodies (Scheter *et al*. 2005, Sjodin *et al*. 2003, Hites 2004). Because there is a lack of correlation between PBDE concentration and age, it is suggested that these cases may be due to recent PBDE exposure and not bioaccumulation over time, as is the case with other persistent organic pollutants (e.g. PCBs, dioxins).

Figure 1: Temporal Trends of PBDE Concentrations in Human Tissues in U.S. and Europe



(Sjodin *et al.* 2003)



(Schecter *et al.* 2005)

Current studies that have analyzed Deca-BDE in the general population reveal that it is present at much lower concentrations than the lower brominated congeners ((Schecter *et al.* 2007); (Wu *et al.* 2007); (Curtis and Wilding 2007)).

A study by Body Burden Work Group and Commonweal Bio-monitoring Resource Center (2007) measured concentrations of three toxic chemicals (bisphenol A (BPA), phthalates, and PBDEs) in 35 participants from seven U.S. states including Minnesota. Researchers measured PBDE concentrations in blood serum for twelve different congeners including Deca-BDE (BDE-209). Thirty four out of thirty five participants had "detectable levels" of Deca-BDE, however only five participants (none from Minnesota) had Deca-BDE concentrations high enough to be quantifiable. Similar to other studies, the majority of PBDE congeners found in high concentrations in participants are those commonly found in the Penta-BDE commercial formulation.

Occurrence of PBDEs and Deca-BDE in Humans as a Result of Occupational Exposure

Two recent studies looked at the bioaccumulation of PBDEs in workers in industries where Deca-BDE is used. Deca-BDE is used in the textile industry, manufacture of plastic castings for computers and TVs, and rubber for electric applications. These workers are exposed to higher amounts of deca-BDE than the general public.

A study by (Thuresson *et al.* 2005) examined the occupational exposure of workers manufacturing or handling Deca-BDE, flame retarded rubber. They measured the concentration of several PBDE congeners in samples of the rubber workers' blood serum. Deca-BDE concentrations were 50 to 100 times higher in the rubber workers than in blood serum samples considered to be representative of the general population (they were collected from slaughterhouse workers). Additionally, the concentrations of Nona-BDE and Octa-BDE congeners were higher in the blood serum of the rubber workers compared to the reference samples.

(Bi *et al.* 2007) measured PBDE concentrations among residents of Guiyu, China. Guiyu is the largest electronic waste recycling center in China; 80% of families in the city are engaged in recycling work. The researchers compared Deca-BDE concentrations in residents of Guiyu to those in residents of Shantou City, a city where residents are mainly occupied by fishing industry. The researchers found that the median PBDE concentrations were three times higher in Guiyu then in Shantou City. Additionally Octa-and Deca-BDE accounted for more then 80% of total PBDE concentrations measured.

Appendix E3

Routes of Exposure

Many questions remain as to how we are exposed to PBDEs, however, researchers have identified a number of potential routes:

- Dietary exposure (especially fats, meats, fish, and dairy products);
- Ingestion and inhalation of PBDE-containing house dust; and
- Direct contact with PBDE-treated products.

<u>Exposure to PBDEs and Deca-BDE through Diet</u>

PBDEs are present in foods consumed by humans. Several studies have measured PBDE concentrations in foods. A recent study by (Schecter *et al.* 2006) analyzed PBDE concentrations including Deca-BDE in 62 samples of meat, fish and dairy products that were bought in U.S. grocery stores. The highest concentrations of PBDEs were found in fish, followed by meat and dairy products. Deca-BDE was found in high concentrations in catfish, salmon fillet, ground turkey, and cream cheese.

Researchers have also estimated the average PBDE intake from food for various age groups. The greatest intake (per unit of body weight per day) was by nursing infants, followed by young children and then adults. Although fish contains the highest PBDE concentrations, for the U.S. population the main contribution is from meat, because on average, the U.S. population consumes much more meat than fish.

Studies examining dietary exposure also looked at correlation between PBDE (including deca-BDE/BDE-209) concentrations in breast milk and consumption of dairy products and meat. (Wu *et al.* 2007) observed a positive, statistically significant relationship between the concentrations of PBDEs in breast milk and the daily intake of meat and dairy products. In this study, the strongest association was between PBDEs in breast milk and dairy products.

Two studies by (Bocio *et al.* 2003) and (Ohta *et al.* 2002) have examined PBDE concentrations in fruits and vegetables. (Bocio *et al.* 2003) measured PBDE concentrations in vegetables (lettuce, tomato, potato, green beans and cauliflower) and in fruits (apple, orange and pear) in Belgium. The researchers did not detect PBDEs in their samples. In contrast, a study by (Ohta *et al.* 2002) done in Japan, has detected PBDEs in vegetables (spinach, potato and carrot). Leafy vegetables (e.g. spinach) had higher PBDE concentrations and different congener pattern compared to root vegetables (e.g. potatoes and carrots). This suggests that atmospheric contamination may play an important role in vegetable contamination. Although PBDEs appear to be present in fruits and vegetables, the concentrations are significantly lower than the concentrations found in meats, fish and dairy products. The researchers conclude that PBDE exposure from fruits/vegetables posses a significantly lower concern then exposure from fish/meats/dairy products.

Exposure to PBDEs and Deca-BDE from Non-Dietary Sources

House Dust

According to (Schecter *et al.* 2006), the estimated daily intake of PBDEs from food cannot account for the high body burdens of PBDEs in the general U.S. population. The intake of PBDEs from food in the U.S. is comparable to that in Spain and in the United Kingdom (Washington, 2006), yet U.S. body concentrations of PBDEs are much higher (one to two orders of magnitude) than in Europe. This result suggests the existence of other exposure pathways for the U.S. population, which probably include house dust.

House dust is contaminated with PBDEs. The most abundant PBDEs in house dust are the congeners BDE-47, BDE-99 and BDE-209 (i.e. Deca-BDE). A study by (Tan *et al.* 2007), measured the PBDE concentrations in samples of household dust collected in Singapore, and compared the concentrations and congener profiles to the results from similar studies conducted in the U.S. (the Cities of Dallas, Texas and Washington DC) and Canada (the City of Ottawa). The authors observed that similar PBDE profiles (i.e. the types and concentrations of detected congeners) were reported in all studies. In addition, Deca-BDE/BDE-209 was the main congener detected in the majority of dust samples. The samples of house dust collected in the U.S. and Canada had double the concentration of PBDEs when compared to dust samples collected in Singapore.

Similar results with regard to house dust and PBDEs were obtained by (Harrad *et al.* 2006). In this study, the authors measured PBDE concentrations in house dust samples collected in the United Kingdom and compared them to PBDE concentrations in house dust samples collected in Canada. The PBDE concentrations measured in the Canadian dust samples were 20 times higher than in the samples collected in the United Kingdom. Comparisons of the estimates of total exposure to PBDEs (i.e. from all sources) for the United Kingdom and Canada revealed that in Canada, dust accounts for a much larger percentage of the total PBDE exposure. This suggests that differences in dust contamination are the likely cause of higher PBDE body burdens in North America compared to Europe.

Studies have also found a statistically significant relationship between house dust and PBDE concentrations in breast milk (Wu *et al.*, 2007; and Washington, 2006). The study by (Wu *et al.* 2007) attempted to correlate concentrations of Deca-BDE (BDE-209) in breast milk, with Deca-BDE (BDE-209) concentrations in dust, but due to low detection rates of Deca-BDE (BDE-209) in the breast milk the researchers were unable draw conclusions about the association.

Finally, a study by (Allen *et al.* 2007)examined the PBDE concentrations in personal air (i.e. the air in the breathing zone around a person) and compared it to PBDE concentrations measured in samples of surrounding room air for 20 residents residing in Boston, Massachusetts area. The results showed that PBDE concentrations in personal air were significantly higher than in the surrounding room air (760 picograms per meter cubed or pg/m^3, compared to 460 pg/m^3). The reasons for this are unknown but the results suggest a “personal dust cloud”.

Direct Contact

Estimating human exposure from direct contact with PBDE treated/containing consumer products is difficult. Studies looking at PBDE dust concentrations and residential characteristics (e.g. the number of TVs, computers, etc. in the household) found no significant correlations (Tan et. al., 2007). Similarly, a study by (Wu *et al.* 2007) found no significant correlation between PBDE concentrations in breast milk and the usage of electronic equipment.

Appendix E4

Toxicity

Knowledge of the potential human health effects from exposure to PBDEs comes primarily from laboratory animal toxicity studies. Generally, the studies show that the lower brominated PBDE congeners such as those found in the commercial Penta- and Octa-BDE formulations are more toxic than Deca-BDE. Most of the concern about Deca-BDE (BDE 209) toxicity comes from its potential to degrade and be metabolized to the more toxic, lower brominated forms of PBDEs (see previous section on Degradation of DecaBDE). This Appendix however, focuses on the information available about the toxicity of Deca-BDE itself.

Deca-BDE is a large molecule. Researchers thought that Deca-BDE's size, as well as some of its other physical-chemical properties, would prevent it from being absorbed into the body (Washington, 2006). Recent studies, however, have detected Deca-BDE (BDE-209) in samples of human tissue ((Wu *et al.* 2007); (Schecter *et al.* 2007); (Curtis and Wilding 2007)).

Laboratory animal toxicity studies show that Deca-BDE can be absorbed by the oral route, does not accumulate in the tissues and undergoes rapid clearance largely as a result of metabolism in the liver and excretion in the bile. However, these studies provide evidence of toxic effects associated with exposure to Deca-BDE including thrombosis of the liver, liver degeneration, fibrosis in the spleen, lymphoid hyperplasia, centrilobular hypertrophy of liver, follicular cell hyperplasia of thyroid and neurobehavioral changes (EPAb, 2006).

An overview of health effects associated with the commercial Deca-BDE formulation is presented in Table 1. This information comes from the draft EPA Integrated Risk Information System (IRIS) for Deca-BDE (EPAb, 2006). The draft IRIS is a summary of several important studies that demonstrate slight to severe health effects associated with Deca-BDE exposure.

Developmental neurotoxicity effects were observed at the lowest dose of Deca-BDE (Viberg *et al.* 2003) (Table 1), and were used by EPA to determine the non-cancer oral reference dose (RfD) for Deca-BDE of 0.007 mg/kg/day. EPA notes that, "overall confidence in the RfD assessment of BDE-209 is low (EPAb, 2006)." Consequently, this value is considered very uncertain.

Although a number of toxic endpoints in animal test studies of Deca-BDE have been observed, sometimes the results are questioned because of statistical design, high dose levels used in the study and relevance of animal test results for predicting human hazard (Washington, 2006).

Table 1: Lowest observed adverse effect levels in Deca-BDE animal toxicity studies (EPAb, 2006)

PBDE congener or product used in Study	*Endpoint*	*Duration of exposure*	*Lowest Observed Adverse Effects Level (mg/kg/day)*	*Reference*
BDE-209	Developmental neurotoxicity	1 day/post-natal day 3 (mouse)	20.1	(Viberg *et al.* 2003)
Deca-BDE	Thyroid changes, liver and kidney effects and fetal death	30 days (rat)	80	(Darnerud *et al.* 2001)
Deca-BDE	Cancer	103 weeks (rat and mouse)	1120-3200	(Darnerud *et al.* 2001)

Appendix E5

Bioaccumulation and Half-Life in Humans

PBDEs can build up in the body and remain there for long periods of time. Biological half-life is a measure of how long it takes the body to excrete half of an accumulated amount of a chemical from the body (Washington 2006). Studies indicate that different PBDEs have different half-lives. Half life is an important measure in evaluating biological pathways of chemicals in the body.

In general, PBDEs with more bromine atoms (the more brominated congeners) have shorter half-lives. A study by (Thuresson *et al.* 2006) estimated the half-lives of Hepta-, Octa-, Nona- and Deca-BDEs in occupationally exposed workers. The estimated half-life for Deca-BDE (BDE-209) was 15 days. The estimated half-lives for Octa- and Nona-BDE congeners were 18 to 39 days, and 37 to 91 days, respectively. The estimated half-lives for Tetra- to Hexa-BDE congeners were even longer, ranging from 19 to 119 days. Because Deca-BDE is detectable in the general population, the results of the study suggest that humans are continually exposed to Deca-BDE.

Appendix E6

Gaps in Understanding

There are large data gaps in the field of toxicokinetics, specifically in understanding the metabolism of Deca-BDE, which metabolites are formed, and what enzymes are involved. Further studies on the mechanisms of thyroid toxicity, possible effects on other hormonal systems and reproduction, and developmental toxicity are needed. Several researchers point out that reproductive and developmental toxicity studies should focus on multi-generation studies and peri- and post-natal toxicity.

Appendix F
Release of PBDEs to the Environment (Emphasizing Deca-BDE)

Appendix F1

Life Cycle Analysis

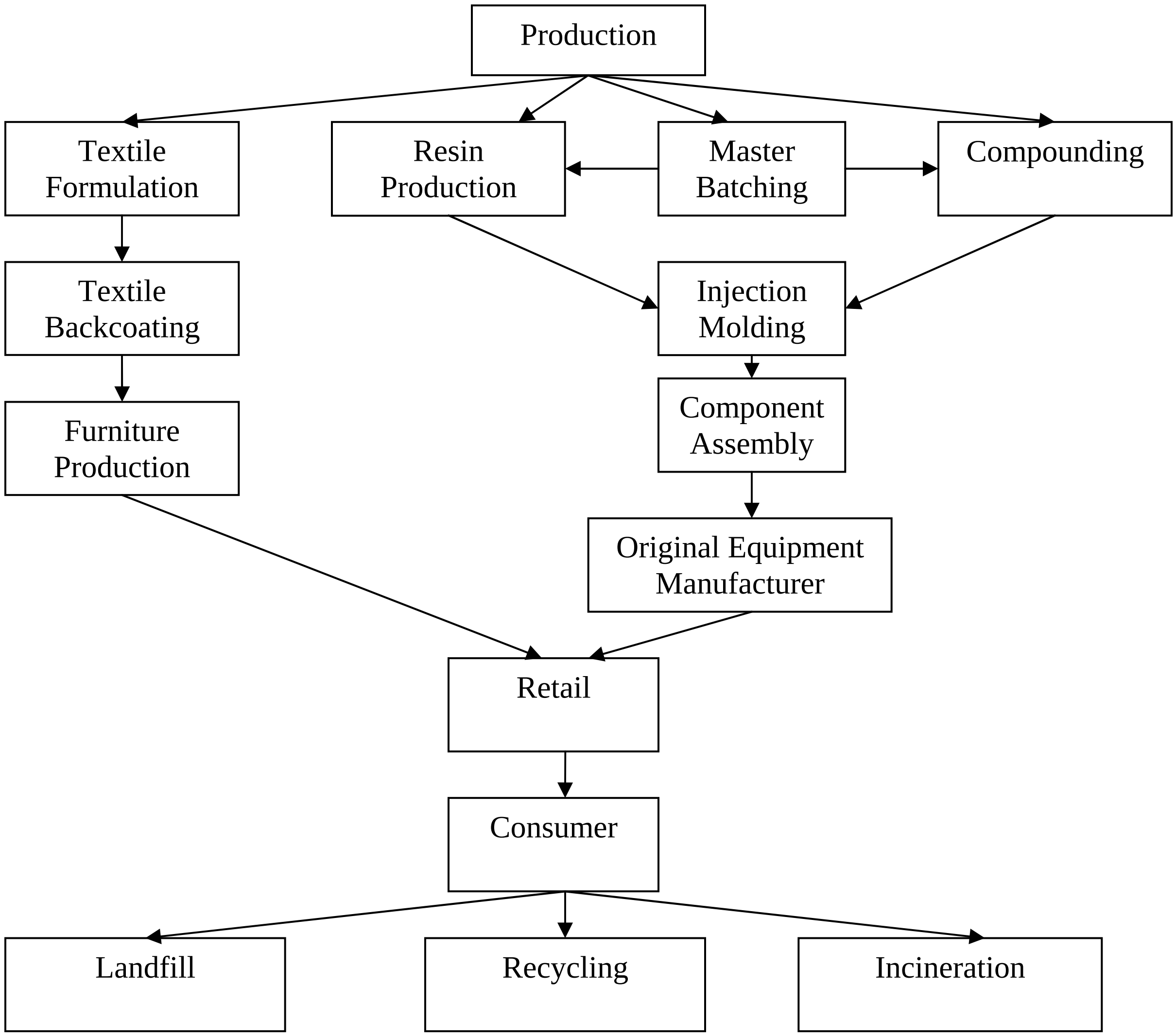
PBDEs are released into the environment when:

- they are manufactured at chemical production facilities;
- when they are blended into thermoplastics to produce flame retarded polymer resins;
- when the flame-retarded resins are manufactured into products;
- at the point of use of the product containing the flame retarded product;
- at the point of disposal or recycling of the flame retarded product.

The highly brominated PBDE congeners like Deca-BDE are commonly found in environmental media near point sources such as manufacturing facilities (ATSDR, 2004).

Wastes containing Deca-BDE may be land-filled, incinerated, discharged to municipal sewage treatment plants or emitted to the atmosphere. The life cycle of Deca-BDE from its synthesis at a chemical production facility to its end-of-life fate is shown in Figure F1. The figure depicts the primary uses of Deca-BDE.

Figure F1: Life-Cycle Analysis of Deca-BDE (Source: European Union, 2002)



Releases of Deca-BDE to Air

It is likely that some Deca-BDE is released during polymer processing. Unlike lower PBDE congeners such as Penta- and Octa-BDE, Deca-BDE has very low volatility (EU, 2002). Because of this, it is assumed that Deca-BDE would be released as small particles or dust from the polymer products and then released to air and transported (EU, 2002).

Manufactured products containing Deca-BDE are likely sources of Deca-BDE dust at their point of use in outdoor and/or indoor air. The dust is released over the lifetime of the products due to use and wear. Deca-BDE-containing dust may also be generated during disposal of Deca-BDE plastics, specifically during disassembly of products containing Deca-BDE.

Ultimately, the products will be disposed of and end up incinerated or disposed of in a landfill. The incineration process will produce little (nearly zero) Deca-BDE emissions (EU, 2002), while land-filling is also unlikely to contribute Deca-BDE to air, due to Deca-BDE's very low vapor pressure volatility (EU, 2002).

Releases of Deca-BDE to Water

According to the Agency for Toxic Substance and Diesease Registry (ATSDR) (2004), industrial and urban effluents are significant sources of PBDEs to surface water and sediments. Several studies have analyzed samples of water collected upstream and downstream from manufacturing plants, with the result that higher concentrations of PBDEs were found in samples collected downstream of the plants. This result indicates that the manufacturing plants are the most likely source of these PBDEs.

Another potential source of PBDEs to water is leachate generated in landfills. Landfill leachate is a common source of contamination to ground water and sometimes surface water. According to ATSDR, there is little data to suggest that Deca-BDE in products disposed of in a landfill will leach out and contaminate groundwater (ATSDR, 2004). Landfills are designed to minimize the generation of leachate.

However, a study conducted by the MPCA in 1999-2001 showed evidence of PBDE accumulation (specifically Deca-BDE/BDE-209) in landfill leachate. For the study, leachate samples were collected from five landfills (3 municipal, 1 industrial and 1 demolition) and analyzed for PBDEs. Deca-BDE (BDE-209) concentrations accounted for the highest percentage (60 to 98%) of total PBDE concentrations measured in the samples (MPCA 2005).

Releases of Deca-BDE to Soil

According to ATSDR, Deca-BDE is released to soil as waste material from manufacturers (both as raw product waste and as waste polymer, after the addition of Deca-BDE); and via disposal of consumer products in municipal waste (ATSDR, 2004).

Deca-BDE is also released to farmland via land spreading of bio-solids (sewage sludge) on agricultural and other land. A number of studies have detected Deca-BDE (BDE-209) in sewage sludge that is destined for land applications.

In the MPCA study, the researcher measured PBDE concentrations in sewage sludge from two domestic wastewater treatment plants. Deca-BDE (BDE-209) was the dominant congener in all samples (MPCA, 2005).

Appendix F2

Industry Reported Releases of Deca-BDE

In the U.S., regulated industries are required to report releases of Deca-BDE from their facilities to the EPA under the Superfund Amendments and Reauthorization Act (SARA) Section 3.13. EPA compiles the reports each year in the Toxic Release Inventory (TRI).

The only PBDE commercial product required to be reported in the TRI is Deca-BDE. Deca-BDE-containing waste may be disposed of in an on-site landfill; released in air emissions; or released in wastewater discharges. Deca-BDE-containing waste may also be transferred off-site for disposal.

In 2005, a total of 160,217 pounds (lbs) of Deca-BDE were released from U.S. facilities. An additional 782,604 lbs of Deca-BDE were transferred off-site for disposal (TRI, 2007). Note that the quantities reported in the TRI are only a partial indication of the amount of Deca-BDE being released to the environment, since there are minimum reportable quantities and not all facilities are required to report their emissions.

The reported totals for 2005 can be broken down further as follows: releases of Deca-BDE to the atmosphere from manufacturing, processing and waste disposal facilities totaled 71,205 pounds (lbs); about 2675 lbs of deca-BDE was released to surface water; about 4,671 lbs of deca-BDE were land-applied; and about 83,429 lbs of Deca-BDE was released to on-site landfills (TRI, 2007).

In Minnesota, only four facilities reported releases of Deca-BDE in 2005 (TRI, 2007). None of the facilities released Deca-BDE waste on-site; rather, the waste was transferred off-site for disposal. Table F2 identifies the Minnesota facilities that generated Deca-BDE waste and the amount of Deca-BDE waste generated (TRI 2007).

Table F2: Amount of TRI-Reportable Deca-BDE Waste Generated by Minnesota Facilities in 2005.

Facility Name	*City*	*State*	*Total Onsite Releases (lbs)*	*Total Waste (lbs)*
Miller Waste Mills (DBA RTP CO)	Winona	MN	0	847
Strongwell-Chatfield Div	Chatfield	MN	0	1124
3M CO New Ulm	New Ulm	MN	0	0
Multek Flexible Circuits Inc	Northfield	MN	0	5887
Totals			*0*	*7858*

Source: TRI, 2007.

Appendix F3

Industry Efforts to Reduce Environmental Releases

To limit industrial releases of Deca-BDE to the environment, chemical manufacturers in the U.S. have started a Voluntary Emissions Control Action Program (VECAP). The VECAP is modeled after the successful VECAP in Europe, where it was established by the brominated flame retardant industry in 2004. The European program has produced significant reductions in emissions from end users (VECAP NAPR, 2007).

VECAP strives to manage, monitor, and minimize Deca-BDE emissions in a “sustainable and measurable manner” from both manufacturers, and end users (VECAP North American Progress Report, 2007). The program is based on development and application of “best practices” in all uses of Deca-BDE. At least one Minnesota company, RTP Corporation of Winona, is employing the best practices outlined in VECAP in its production practices.

Appendix F4

EPA-Sponsored Efforts to Reduce Deca-BDE Risks

After the voluntary phase-out of production of Penta-BDE and Octa-BDE by Great Lakes Chemical in 2004, the EPA Design for the Environment (DfE) program started the Furniture Flame Retardancy Partnership. It is a joint program between the EPA, the furniture industry, chemical manufacturers, and environmental groups that has the objective of evaluating alternatives for achieving flame retardancy in the furniture industry (EPA, 2007a). The EPA hopes that through the program they will be able to identify and develop environmentally safer approaches to meet fire safety standards (EPAa, 2007). More information is available at: http://www.epa.gov/dfe/pubs/projects/index.htm.

In addition, the U.S. EPA proposed a Significant New Use Rule (SNUR) under the Toxic Substances Control Act (TSCA) that requires manufacturers and importers to notify the EPA ninety days prior to use or manufacture of Penta or Octa-BDE, effective January 1, 2005. This rule allows the EPA to evaluate intended practices and, if necessary, limit or prohibit the activities related to new uses of these PBDEs. The SNUR for Penta and Octa-BDE took effect on August 14, 2006 (EPA, 2006a).

EPA is currently working to conduct risk assessments for Penta, Octa and Deca-BDEs in partnership with industry through the Voluntary Children's Chemical Evaluation Program (VCCEP). VCCEP was established by EPA in December 2000 to fulfill a goal included in EPA's 1998 Chemical Right-to-Know Initiative to ensure that adequate data is made publicly available to assess the special impact that industrial chemicals may have on children (EPA, 2007b).

EPA asked companies that manufacture or import the chemicals of interest to volunteer to provide information on health effects, exposure, risk and data needs. The Brominated Flame Retardant Industry Panel (BFRIP) stepped forward to conduct phase one evaluations of Penta-, Octa-, and Deca-BDEs. In August 2005, EPA requested that the manufacturers further evaluate the environmental fate and transport of Deca-BDE. During 2006, BFRIP and EPA have been working on developing a matrix for phase two evaluations (EPA, 2007b).

Appendix F5

Green Screen for Safer Chemicals

Clean Production Action (CPA) is a non-profit organization that helps design greener products and manufacturing processes. The organization helped create the Green Screen for Safer Chemicals (Green Screen). The Green Screen is a hazard-based chemical screening method designed to identify the risks posed by specific chemicals and promote the use of less hazardous, more environmentally friendly chemicals.

The Green Screen evaluates chemicals on the basis of a number of risks, including the potential for a chemical to be persistent and bio-accumulative, and its potential to cause endocrine disruption. The Green Screen defines four screening benchmarks that define progressively safer chemicals:

- Benchmark 1 -- Avoid -Chemical of high concern
- Benchmark 2 -- Use but search for safer substitutes
- Benchmark 3 -- Use but still opportunity for improvement
- Benchmark 4 -- Prefer-Safer chemical (The Green Screen For Safer Chemicals: Evaluating Flame Retardant for TV Enclosures, CPA 2007)

To test the Green Screen, the CPA evaluated three flame retardant that currently meet the performance criteria for use in front and back enclosure panels of televisions:

- decabromodiphenyl ether (Deca-BDE)
- resorcinol bis diphenylphosphate (RDP)
- bisphenol A diphosphate (BAPP or BPADP)

Of the three flame retardants, RDP was the only one to pass all the criteria of Benchmark 1 and get to Benchmark 2. As such, it is the most preferred of the three alternatives (CPA, 2007).

Further information is available at: Clean Production Action — Green Chemistry.

Appendix G

Available Information about Proposed Alternatives to Deca-BDE

Non Halogenated Alternatives

Below is a brief description of what is known about the characteristics (toxicity, persistence and bioaccumulation potential) of the non-halogenated alternatives. The descriptions are based on our review of other published evaluations ((Washington 2006); (Maine 2007); (Illinois 2007); (Syracuse Research Corporation 2006; (Pakalin *et al.* 2007)).

Resorcionol bis(diphenylphosphate) (RDP)
(CAS Numbers 57583-54-7 and 125997-21-9)

RDP is considered one of the more promising alternatives. Recent environmental and health risk assessment conducted by Syracose Research Corporation in 2006 concluded that the chemical has low persistence potential. It chemical half-life in water was calculated to be 7 to 21 days depending on water pH (Pakalin *et al.* 2007). Results of toxicity studies indicate low toxicity in lab animals and medium/high aquatic toxicity. There are no carcinogenicity studies on this chemical, and no data on potential human exposure. Mutagenicity studies are negative. According to the (Washington 2006) the chemical does not meet the criteria to be listed as persistent, bioaccumulative and toxic, however more toxicity information is needed.

Bisphenol A diphosphate (BAPP, BPADP, BDP)
(CAS Numbers 181028-79-5 and 5945-33-5)

The conclusions on human health/environmental safety of BAPP are mixed. Report on Deca-BDE alternatives by Illinois EPA (2007) concludes the chemical is potentially unproblematic, while the report on Brominated Flame Retardants by Maine Department of Environmental Protection and Center for Disease Control and Prevention (2007) concludes the chemical is not a suitable alternative. Recent environmental and health risk assessment by Syracuse Research Corporation completed in 2006 concluded that the chemical has high persistence potential. Its half-life in water is about a year (Pakalin *et al.* 2007). Results of toxicity studies indicate it has low acute toxicity (>2000 mg/kg rat), and low subchroinc toxicity (NOAEL 2000 mg/kg), and it is not mutagenic (Pakalin *et al.* 2007). There are no carciongenity studies available and there is no information on potential human exposure. A degradation product of BAPP is bisphenol A, a potent endocrine disruptor. Bisphenol A affects multiple reproductive endpoints at low level of exposure; it also affects immune function and brain development (Maine 2007). Humans have detectable levels of bisphenol A in their bodies, because of its use in plastics.

Diphenyl cresyl phosphate (DCP)
(CAS Numbers 26444-49-5)

Toxicity studies on DCP indicate moderate human and aquatic toxicity. Some studies have shown reproductive and developmental toxicity (Pakalin *et al.* 2007). There are no animal cancer studies for DCP. There is little information on human exposure, primarily in the workplace (Washington 2006). The chemical has a tendency to persist in the environment and bioaccumulate in species. Its half-life in water is 4.86 years in water (Pakalin *et al.* 2007). The chemical is considered potentially problematic by Illinois EPA.

Triphenyl phosphate (TTP)
(CAS Numbers 115-86-6)

TTP is not persistent; the chemical biodegrades extensively under both aerobic and anaerobic conditions in various systems (Pakalin *et al.* 2007). It does not show the tendency to bioaccumulate in organisms. TTP toxicity studies show low to moderate concern for human health, and high aquatic toxicity concern (Illinois 2007 and Syracuse 2006). There are no animal cancer studies for this chemical and it is not mutagenic.

Red phosphorus
(CAS Numbers 7723-14-0)

Red phosphorus is an inorganic substance, thus its biodegradation is not relevant. The chemical slowly undergoes abiotic transformation to phosphoric acid. Its reactivity in water is very low, hence it is considered a persistent chemical (Pakalin *et al.* 2007). Toxicity information for red phosphorus is limited, but at screening level it does not appear toxic (Pakalin *et al.* 2007). Little information is available on human health concerns.

Melamine cyanurate
(CAS Numbers 37640-57-6)

There are limited toxicity studies for melamine cyanurate. The chemical might be toxic to aquatic environment. There is some evidence of acute toxicity in fish and daphnia (Pakalin *et al.* 2007). It is inherently biodegradable, thus it’s not expected to be persistent in the environment. Recent melamine studies (not identified on either melamine phosphate or melamine cyanurate) show bladder tumors in male mice and rats at high exposure doses, although these results may not be relevant to humans (Maine, 2007).

Magnesium Hydroxide
(CAS Numbers 1309-42-8)

No environmental issues regarding magnesium hydroxide were identified by (Pakalin *et al.* 2007) report. The chemical is generally considered non-toxic. There is lack of information on cancer, reproductive/developmental, and chronic aquatic toxicity studies. Illinois 2007 report lists the chemical as potentially unproblematic.

Zinc Borate
(CAS Numbers 1332-07-6)

Toxicity studies for zinc borate are limited; there are no studies on reproductive/developmental effects, chronic toxicity studies, or animal cancer studies. The chemical has high acute aquatic toxicity. Based on zinc toxicity studies, the chemical has high human toxicity. Based on its chemical structure it is not considered persistent or bioaccumulative. The Illinois 2007 report does not recommend this substance as an alternative.

Ammonium polyphosphate
(CAS Numbers 14728-39-9 and 68333-79-9)

Ammonium polyphosphate is biodegradable in the environment (>95% within 28 days) (Pakalin *et al.* 2007). Toxicity studies for this chemical are limited. According to Maine 2007 the concentrations expected to be achieved would not present environmental or human health hazard.

<u>Halogenated Alternatives</u>

Below is a brief description of what is known about the characteristics (toxicity, persistence and bioaccumulation potential) of the halogenated alternatives. The descriptions are based on our review of other published evaluations (Washington 2006 and Pakalin *et al.* 2007) and peer-reviewed studies of the alternatives (Birnbaum and Staskai 2004).

Bis(pentabromophenyl)ethane
(CAS Number 84852-53-9)

Toxicity studies for this chemical are limited; animal studies on rats and rabbits indicate low toxicity, while there are no studies on aquatic acute/chronic toxicity (Pakalin *et al.* 2007). The chemical is not susceptible to degradation in aquatic environment. Due to its low water solubility, and because it is a large halogenated compound it is expected to be persistent in the environment. Currently there are not data on its half-live in water or other media. Bis(pentabromophenyl)ethane has low bioaccumulation potential.

1,2-bis(tetrabromophthalimido) ethane
(CAS Number 32588-76-4)

Based on molecular properties of this chemical (molecular weight, molecular dimensions, water solubility) it is not considered bioaccumulative. The toxicity studies are very limited; lab animal studies indicate low toxicity. There is one study on aquatic toxicity and results indicate the chemical is not acutely toxic at concentrations up to the water solubility limit (Pakalin *et al.* 2007). 1,2-bis(tetrabromophthalimido) ethane is expected to be persistent because it's a large halogenated molecule. There are not data on its half-life in the environment. Additionally, there is no information on human exposure to this chemical (Washington 2006).

Tetrabromobisphenol A epichlorohydrin polymer
(CAS Number 40039-93-8)

There is no available information to evaluate the persistence or bioaccumulation of this chemical in the environment. The toxicity studies (based on limited animal toxicity studies) indicate the chemical is not acutely toxic. Additionally, there is no information on human toxicity and no carcinogenicity studies (Pakalin *et al.* 2007).

Bis(tribromophenoxy)ethane
(CAS Number 37853-59-1)

The toxicity studies for this chemical indicate low acute and sub-chronic toxicity. Additionally the chemical is not mutagenic, it has low reproductive potential (Pakalin *et al.* 2007). The chemical shows a tendency to persist in the environment. Its half-life in water is 150-1700 days (Pakalin *et al.* 2007). Also it is bioaccumulative (Washington 2006). There is no information about potential human exposure to the chemical.

Hexabromocyclododecane (HBCD)
(CAS Numbers 3194-55-6 and 25637-99-4)

The chemical is biodegradable in the environment (its half-live in water is 60 days), however because it concentrations in biota and the environment are increasing it is considered persistent (Pakalin *et al.* 2007). HBCD is subject to bioaccumulation/biomagnification; studies show its concentration in aquatic organisms and birds are increasing. The toxicity studies indicate that the chemical is toxic (Pakalin *et al.* 2007).

Tetrabromobisphenol A (TBBPA)
(CAS Numbers 79-94-7)

TBBPA is considered very persistent. Its half-life in water is 180 days, 320 day in soil and 1600 days in sediment (Pakalin *et al.* 2007). The chemical itself does not meet the bioaccumulation criteria, but may breakdown to produce increased levels of bisphenol A an endocrine disruptor. Toxicity studies indicate the chemical is toxic towards aquatic organisms, but more toxicity data is needed (Pakalin *et al.* 2007).

Tetrabromobisphenol A bis(2,3-dibromopropyl ether)
(CAS Numbers 21850-44-2)

Toxicity studies for this chemical are limited; animal studies indicate low acute and subchronic toxicity, however it is mutagenic. Based on it structural properties it has carcinogenic potential (Pakalin *et al.* 2007). There is not sufficient data to evaluate if it is persistent in the environment, however it has low degradability. Tetrabromobisphenol A bis(2,3-dibromopropyl ether) shows bioaccumulation potential (Washington 2006).

Appendix H
Executive Summaries from PBDE Reviews Undertaken by Other States and the European Union

This appendix provides a collection of executive summaries taken from the published reports on PBDEs by different states and the European Union. The original reports can be found at the provided web links.

State of Washington **January 2006**

Citation: Washington State Polybrominated Diphenyl Ether (PBDE) Chemical Plan: Final Plan (2006), pp. 328. Web address: <http://www.ecy.wa.gov/pubs/0507048.pdf>

Executive Summary

This is the final version of the Chemical Action Plan (CAP) for a class of flame retardants called polybrominated diphenyl ethers, or PBDEs. It is the second CAP done as part of the Department of Ecology (Ecology)'s *Proposed Strategy to Continually Reduce Persistent, Bioaccumulative Toxins (PBTs) in Washington State* (issued December, 2000). Ecology is also finalizing a rule (Chapter 173-333 WAC, Persistent Bioaccumulative Toxins Regulation) to guide the development of CAPs. This CAP is consistent with both the *Strategy* and the PBT rule. The first CAP, for mercury, was completed in January 2003.

In January 2004, Governor Locke directed Ecology, in consultation with the Department of Health (DOH), to investigate and recommend options to reduce the threat of PBDEs in the environment. The final result is this PBDE CAP, which has been developed through a multiprogramming, multi-agency effort, with external stakeholders involved at each step. External advisory committees included representatives from such varied interests as business and consumer and environmental protection.

When Governor Locke directed Ecology and DOH to focus on these chemicals, we knew very little about them. What was known was that PBDEs were showing up in people and in the environment in increasing amounts, and those levels were significantly higher in North America than elsewhere. PBDEs are a source of growing interest and concern around the world. New studies and information continue to appear on an almost weekly basis.

This document builds on the *Interim PBDE CAP* which was released in December, 2004. Based on the available information at that time, Ecology and DOH believed that a ban on products containing PBDEs was warranted. However, further study of how a ban could be structured was needed, including research on chemical alternatives for PBDEs and on costs and benefits. This research, and a thorough review of the most current scientific information about the environmental and human health risks of PBDEs, was considered in the development of this plan. In addition, Ecology and DOH kept a close watch on the experiences of other states and Europe where policies to reduce PBDEs have been crafted.

A great deal has been learned, and there is still a great deal more to understand. At each step of the way, Ecology and DOH have struggled with limited data and limited access to data, and the uncertainty that comes with a new field of study (emerging information). We know that:

- There is already a reservoir of PBDEs in humans and in the environment. In 2001 alone, almost 70,000 metric tons of PBDEs were produced globally, almost half of which wasused in products sold in the U. S. and Canada.

- The various commercial grades of PBDEs have been used in a wide variety of products, from carpet pads to TV plastic. The production of two PBDEs, Penta-BDE and Octa-BDE, has been phased out in the U.S. and in most international markets as well. And thee use of Deca-BDE is anticipated to increase.
- Current research indicates that the most likely pathways of exposure for people are through indoor dust and various foods
- PBDEs have been found in fish, polar bears, grizzly bears and Puget Sound orcas.
- PBDEs initially drew attention because they were found in women's breast milk and the levels in breast milk were rising quickly. While levels of PBDEs found in breast milk in the U.S. are not yet at a level of concern, levels in U.S. women are 10 to 100 times that found in women in Europe.
- There are potentially serious health and environmental consequences as the amounts of PBDEs increase, such as neurotoxicity (i.e. effects to neurological development from exposures to unborn and newborn infants), leading to impacts on behavior, learning and memory. Other health effects may include bone malformations, reproductive impacts, and liver disorders.
- Deca-BDE is likely to breakdown in the environment to more toxic and bioaccumulative forms of PBDEs.
- Banning these substances, as long as a safer alternative exists, can avoid negative health effects from PBDEs for people, and to the environment in Washington

Unfortunately, there is a lot we do not know. We lack adequate toxicity information on the alternatives to Deca-BDE. This is likely due to the fact that, under current U.S. chemical policies, toxicity studies on these chemicals are not required or are not published. We don't know the rate of breakdown of PBDEs in the environment, or exactly what congeners are produced as a result of breakdown of PBDEs. (However, in the laboratory, deca-BDE has broken down to penta- and octa-BDE, so there is concern that other breakdown products may be more toxic than the parent compounds.) We don't know exactly how PBDEs move from products into our bodies and the environment, or how much Deca-BDE breakdown products will contribute to levels in our bodies and the environment. We don't know how PBDEs impact other species such as fish, orcas or bears. And we don't know how much more PBDE could be produced and sold as manufacturers try to comply with future fire protection rules from the Consumer Product Safety Commission.

The recommendations in this Chemical Action Plan were developed after a thorough consideration of what is known and what is not known. We believe these recommendations represent prudent policy, and that the suggested actions are commensurate with the risk involved, both to human health and the environment as well as to Washington businesses. What we want to avoid is adopting a policy that allows the continued build-up of PBDEs in our bodies and in the environment as we try to resolve the unknowns.

PBDE basics

PBDEs are members of a broad class of brominated chemicals used as flame retardants. Flame retardants like PBDEs are added to products so that they will not catch on fire or burn so easily if exposed to flame or high heat. In the event of a fire involving these products, PBDEs slow ignition and the rate of fire growth. The result is that people have more time to extinguish or escape the fire. PBDEs have been added to plastics, upholstery fabrics and foams in such common products as computers, TVs, furniture and carpet pads.

There are three main types of PBDEs used in consumer products: Penta-BDE, Octa-BDE and Deca-BDE. Each has different uses and different toxicity. In 2001, the total PBDE volume worldwide was estimated at over 67,000 metric tons, including 56,100 metric tons of Deca-BDE.
Manufacturers of Penta- and Octa-BDE in the U.S. agreed to voluntarily stop producing these two forms of PBDEs at the end of 2004. With the discontinuation of Penta- and Octa-BDE,

Deca-BDE will account for 100 percent of PBDE usage.

The highest levels of PBDEs in people have been found in the U.S. and in Canada, which are the largest producers and consumers of products with PBDE flame retardants. Levels of total measured PBDEs in human tissues in the U.S. are 10 to 100 times higher than reported for Europe and Japan. While these numbers are significant, it is important to understand that the mere presence of chemicals does not necessarily represent a health risk. Although PBDEs are present in people and many foods, these levels have not yet reached those shown to be toxic in lab animals and do not pose an immediate health threat. If PBDE levels continue to rise, however, real health risks can be expected, particularly for our children. This is especially significant given the existing large volume of PBDEs already in the environment and the possibility of the increasing use of them in products.

New work completed since December, 2004

With production of Penta- and Octa-BDE discontinued, Deca-BDE became the focus of Ecology and DOH's PBDE work**.** Since the release of the *Interim PBDE CAP*, DOH and Ecology focused on three key areas related to the need for action on Deca-BDE. As a result, three new chapters have been added to the Plan: 1) a review of studies on the degradation of Deca-BDE (Chapter IV); 2) an alternatives assessment (Chapter V); and 3) a cost-benefit analysis (Chapter VI). The additional information discussed in these chapters provided the framework for assessing whether or not to ban Deca-BDE from commerce in Washington State.

Degradation

Even at the time the *Interim PBDE CAP* was published, Ecology and DOH's research indicated that while Deca-BDE in its original form is considered relatively safe, it is likely to degrade into more toxic forms. A more in-depth review (presented in Chapter IV) continues to reinforce this assumption. The degradation of Deca-BDE is central to Ecology and DOH's concern about the human health and environmental safety of this flame retardant. Laboratory studies indicate that the breakdown of Deca-BDE takes place through exposure to sunlight and through biological activity. Therefore, the Deca-BDE that is already in the environment is likely to be a long-term source of the more toxic forms of PBDEs long into the future.

Deca-BDE Alternatives Assessment

DOH conducted an extensive survey of the available literature to determine if safer, effective alternatives to Deca-BDE exist for use in electronic enclosures. It is important to note that "safer" relates to impacts on human health and the environment, not the ability of the alternative to work as a flame retardant. **The alternatives assessment considered only those chemicals already proven to meet fire protection standards.**

DOH limited its focus to electronic enclosures because the black plastic used to enclose the rear of TVs accounts for somewhere between 45 and 80% of Deca-BDE commercial use. DOH considered only those alternatives previously shown to work in the same plastics and products as Deca-BDE while providing adequate fire protection. As with so much of the PBDE work, the undertaking was hampered by both limited and emerging information. There is a general lack of toxicity and other testing information on many of the alternatives. While companies are often willing to share their data, much of it has never been published. However, there was sufficient data collected to conclude that promising alternatives exist, ones which are already in use and meet fire protection standards, and we want to continue this research.

Cost Benefit Analysis

Ecology conducted a Cost Benefit Analysis (CBA) of a statewide ban on Deca-BDE in electronic enclosures in order to weigh the benefits to human health and the environment against the costs to business.

Information on costs was hindered by difficulties getting information from businesses about their Deca-BDE use. Many businesses were reluctant to share cost data with us, possibly because the state could not provide confidentiality for this information. When it became apparent that critical data would not be available, Ecology developed an alternative model which we believe might be successfully used to compare costs to benefits. However, this model hinges on the identification of at least one safer, effective alternative to Deca-BDE, which has not yet been identified. In addition, there is considerable uncertainty in the data needed to quantify health benefits. Ecology is therefore unable to determine whether benefits exceed costs (or vice versa). Consequently, Ecology has concluded that the cost benefit analysis has limited utility at this time to inform decisions on phasing-out uses of deca-BDE.

Recommendations

Recommendations for reducing PBDEs in the environment and for protecting human health are detailed in the body of this plan. Many of the policy options that were considered are also presented, and the rationale for the policies recommended is provided. Key recommendations are summarized as follows:

- The Washington State Legislature should prohibit the manufacture, distribution (but not transshipment) or sale of new products containing Penta-BDE and Octa-BDE in Washington State. The ban may include an exemption for new products that contain recycled material from products that contained Penta-BDE and Octa-BDE, pending further review.

- The Washington State Legislature should ban Deca-BDE provided that safer, effective, affordable alternatives are found or upon additional evidence of Deca-BDE harm.

- If safer alternatives are not identified, Ecology and DOH should work with stakeholders to explore incentives to encourage manufacturers to develop safer, effective alternatives as well as product redesign changes that eliminate the need for PBDEs.
- Ecology should establish appropriate disposal and recycling practices for products containing PBDE flame retardants.
- Ecology and DOH should work with other states and interested parties in a dialogue toward improving U.S. chemical policy. Current U.S. chemical policy, based upon the Toxic
- Substances Control Act (TSCA), has resulted in only minimal testing of many chemicals currently in use. The lack of adequate testing data on promising alternatives to Deca-BDE already in use exemplifies the need to improve TSCA and/or its implementation.
- The state's purchase of products containing PBDEs should be restricted in appropriate contracts, consistent with Executive Order 04-01.
- DOH should continue to develop methods and materials for educating the public on how to minimize exposure to PBDEs. This will include information on the benefits of breastfeeding and advice about eating fish as part of a healthy diet.
- To ensure that workers in certain industries are not exposed to unacceptable levels of PBDEs, DOH and the state Department of Labor and Industries should continue to investigate the feasibility of implementing a workplace exposure study in collaboration with the federal Center for Disease Control and Prevention.

Note: A number of the recommendations presented in the *Interim CAP* are underway, and some have been completed. For example, the state Department of Labor and Industries has already begun providing information to employees on how to minimize PBDE exposures. And DOH has created brochures and a website to educate the public on reducing exposure to PBDEs.

State of Illinois **January 2006**

Citation: Deca-BDE Study: A review of Available Scientific Research (2006), pp. 59.
Web address: < http://www.epa.state.il.us/reports/decabde-study/available-research-review.pdf>

Executive Summary

This report has been prepared to address the five issues posed by the Illinois Legislature to the Illinois Environmental Protection Agency in HB2572 regarding the use of Decabromodiphenyl ether (DecaBDE). The Agency reviewed numerous data sources, including some very recent information, pertaining to the five issues in order to respond in as thorough a manner as possible.
However, data gaps exist in certain key areas that have hampered our ability to fully address some issues. The five issues and our findings follow.

The first issue asks whether DecaBDE is bio-accumulating in the environment, and if so whether the levels of DecaBDE are increasing, decreasing, or staying the same. We find that DecaBDE is bioaccumulating in the environment, and levels are increasing in some types of samples (sediments, some top predators, and possibly human blood and breast milk).

The second issue asks how humans are exposed to DecaBDE. We find that humans are exposed to decaBDE from many sources including the diet, workplace, and home, with diet the primary source for adults and breast milk and house dust important sources for infants and small children.

The third issue asks what health effects could result from exposure to DecaBDE, and are current levels of exposure at levels that could produce these effects. We find that the most important health effects from exposure to decaBDE and/or lower-brominated congeners appear to be liver, thyroid, reproductive/developmental, and neurological effects, although the relevance of some of the effects reported in animal studies for human health risks has been questioned, and significant data gaps in the decaBDE toxicity database have been identified; estimates of current human exposures to the PBDEs indicate that effects on the liver should not be occurring, but two recent studies suggest that exposures could be occurring that are in the range of doses causing adverse effects in laboratory animals.

The fourth issue asks whether DecaBDE breaks down into more harmful chemicals that could damage public health. We find that DecaBDE can be broken down by ultraviolet light and direct sunlight, and also by metabolic processes in animals and microorganisms, but uncertainty and controversy exists about the extent of breakdown by light under environmentally relevant conditions and the human health implications of the breakdown products; therefore, we believe that the information available at this time regarding DecaBDE's breakdown products is not sufficient to allow us to confidently address this issue.

The fifth issue asks whether effective flame retardants are available for DecaBDE uses, and whether the use of available alternatives reduces health risks while still maintaining an adequate level of flame retardant performance. We find that effective, though more costly, alternatives exist for most of the plastics and textiles/fabrics uses of DecaBDE, and these alternatives will likely reduce risks while maintaining an adequate level of flame retardant performance; however, significant toxicity data gaps exist for many of the main potential alternatives, and further research is needed to better evaluate the health and environmental consequences of these alternatives.

We also reviewed the actions of other jurisdictions regarding the polybrominated diphenyl ethers (PBDEs). USEPA's Voluntary Children's Chemical Evaluation Program has determined that a significant data gap exists regarding the environmental transport and fate of decaBDE, and DecaBDE manufacturers will soon begin studies to fill these gaps. The European Union (EU) has included the PBDEs on a list of chemicals to be phased out of use in electrical and electronic equipment, but DecaBDE manufacturers have successfully petitioned for an exemption for DecaBDE from this ban. This exemption may be challenged in the European Court of Justice. The EU will also conduct studies of the reproductive/developmental and neurological effects of decaBDE to fill important gaps in the toxicity database. Several states have recently legislated bans on the use of the Penta- and OctaBDE flame retardant formulations in products, and Maine will ban DecaBDE in 2008 if effective alternatives to DecaBDE are identified. Some states have also required studies of DecaBDE to help decide what actions, if any, are appropriate for DecaBDE.

The research noted above on the potential for reproductive/developmental and neurological effects of decaBDE and the studies on the environmental transport and fate of decaBDE, plus other on-going or planned studies, should provide valuable information to assist in evaluating the issues raised in HB2572.

State of California **February 2006**

Citation: PBDEs: Recommendations to Reduce Exposure in California (**2006**), pp. 53.
Web address: <http://www.oehha.ca.gov/pdf/PBDEWrkgrpRptFeb06.pdf>

Executive Summary

The manufacture, distribution and processing of products containing pentabrominated diphenyl ether (pentaBDE) and octabrominated diphenyl ether (octaBDE) flame retardants will be prohibited in California as of June 1, 2006 (California Health and Safety Code Sections 108920 *et seq.*); only products manufactured after June 1, 2006, are subject to the prohibition. This prohibition was prompted by findings that exposures to polybrominated diphenyl ethers (PBDEs) are widespread, and may pose health risks. However, the manufacture, distribution and processing of products containing the most commonly used PBDE mixture, decabrominated diphenyl ether (decaBDE), has not been prohibited. PentaBDEs and octaBDEs are ubiquitous and Californians will continue to be exposed to them after June 1, 2006. On May 27, 2005 the California Environmental Protection Agency (Cal/EPA) Secretary directed the formation of a workgroup of representatives from Cal/EPA Boards, Departments and Office (BDO) to consider the nature and extent of the PBDE problem and to recommend actions Cal/EPA could take to mitigate exposures to reduce risks of potential PBDE health effects. The California Department of Health Services (DHS) also contributed expertise and provided representatives to the Cal/EPA PBDE Workgroup. This report was prepared in response to the Cal/EPA Secretary’s directive.

The principal focus of this report is to address continuing exposures of Californians to PBDEs after June 1, 2006. The report provides information on PBDEs and briefly summarizes past and ongoing Cal/EPA BDO and DHS activities related to PBDEs. Based on this preliminary evaluation, the Cal/EPA PBDE Workgroup proposes specific steps to be taken by Cal/EPA BDOs and DHS to reduce PBDE exposures.

PBDEs have been widely used as flame retardants in home and office building materials, motor vehicles, electronics, furnishings, textiles, high-temperature plastics and polyurethane foams. The general public is exposed to PBDEs through the use of consumer products in homes, offices, cars and schools. Exposures to PBDEs in some occupational settings, e.g., in computer recycling facilities, can be much higher than those of the general public. As consumer products are used and after they are discarded, PBDEs are released into the environment where they can bioaccumulate in wildlife and food animals. PBDEs have been measured in house and office dust, indoor air, plant and animal-based foods, terrestrial and marine animals, and in human breast milk, blood and fat. The levels of PBDEs measured in humans in the US and Canada are typically at least 10 times higher than those in Europe, and appear to be doubling every few years. Cal/EPA scientists have reported the highest tissue concentrations of PBDEs measured in the world in California wildlife (shorebird eggs and fish), and rapid accumulation of PBDEs in the tissues of San Francisco Bay harbor seals.

PBDEs have structural similarities to polybrominated and polychlorinated biphenyls (PBBs and PCBs), and to certain other persistent polyhalogenated organic pollutants. In the limited toxicity testing to date, PBDEs have produced some of the toxic effects and physiologic changes typical of many persistent polyhalogenated organic pollutants, in particular the PBBs and PCBs. These effects include developmental and nervous system toxicity, as well as mimicry of estrogen and interference with the activity of thyroid hormone. These effects are observed in experiments with octaBDE and pentaBDE. DecaBDE has been shown in one study in mice to cause similar toxic effects on the developing nervous system as pentaBDE. Although PBBs and PCBs are both carcinogenic, neither pentaBDEs nor octaBDEs have been tested for carcinogenicity.

DecaBDE is not affected by the recent legislation and its use and release into the environment will continue unabated. *Direct* exposure to decaBDE appears to pose lower human health risks than those of the other PBDEs, due to its lower toxicity, absorption, and generally lower environmental concentrations. Still, decaBDE is the predominant PBDE measured in house and office dust, and the risk from such exposures requires further evaluation. Also, levels of decaBDE found in sewage sludge suggest that decaBDE from the indoor environment is released through municipal sewage systems into the environment.

Use of decaBDE may result in human exposure to lower brominated PBDEs of greater toxicological concern, such as the pentaBDEs and octaBDEs. Recent studies indicate that decaBDE breaks down by the actions of sunlight, heat, and bacteria to these and other PBDEs that contain fewer bromine atoms. Such compounds are also formed through metabolism in certain animals consumed by humans (i.e., fish and chicken). These lower brominated PBDE congeners can undergo further debromination. In addition, during combustion of plastics containing decaBDE and other PBDEs (e.g., incineration), brominated dioxins and related compounds may form.

After June 1, 2006, exposures in California to pentaBDEs and octaBDEs that result from new products should decrease. Nevertheless, exposures due to building materials, furnishings, and consumer products produced before June 1, 2006, containing pentaBDE and octaBDE flame retardants will continue for years to come. These releases will result in ongoing exposure to and increased bioaccumulation of the prohibited PBDEs by humans and wildlife. The workgroup has made numerous recommendations to reduce the continuing exposures to PBDEs, including pentaBDEs, octaBDEs, and decaBDEs. The main recommendations are given in the table below.

Main Recommendations to Reduce PBDE Exposures[1]

Outreach and Education
- Educate key governmental officials and the public about the PBDE prohibition and hazards to encourage compliance with the prohibition and exposure reduction behavior. This would include development of educational materials such as fact sheets.

Pollution Prevention
- Encourage the purchase of PBDE-free products.

Measurement and Monitoring[2]
- Conduct human biomonitoring to evaluate the effectiveness of the pentaBDE and octaBDE prohibition and other PBDE reduction efforts.
- Conduct environmental monitoring to identify sources, pathways and trends in PBDE levels, and to characterize the environmental fate of decaBDE.

Regulatory Initiatives
- Develop health guidance levels (e.g., reference exposure levels) for PBDEs to aid in establishing acceptable environmental levels.
- Assess the need for further regulation, such as the development of hazardous waste criteria and management and disposal requirements and practices for PBDE contaminated waste, an Airborne Toxic Control Measure, the addition of PBDEs to the Air Toxics “Hot Spots” list, and the need to limit the use of decaBDE.

[1] Subject to available funding.
[2]DTSC will provide guidance to other Cal/EPA BDOs for the sampling and chemical analyses of PBDEs in environmental matrices.

Recommendations include near-term actions intended to reduce PBDE exposures through outreach and education, and voluntary pollution prevention. Longer-term recommendations include further environmental monitoring of PBDE levels to increase the scientific base for decision-making, and consideration of specific regulatory actions. All of the Workgroup's recommendations for Cal/EPA action are summarized on page 32. For each recommended action the estimated timeframe for implementation and the responsible BDOs are indicated. In recommending these specific steps for Cal/EPA to reduce PBDE exposures and health risks, the Workgroup explicitly did not address the availability of state resources for their implementation. The majority of these recommendations cannot be acted upon without the provision of additional resources. This requirement for additional resources needs to be addressed as Cal/EPA evaluates and chooses recommendations to implement.

State of Maine **January 2007**

Citation: Brominated Flame Retardants (**2007**), pp. 64. Web address: <http://www.maine.gov/dep/rwm/publications/legislativereports/pdf/finalrptjan07.pdf>

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. 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.

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

<u>State of Michigan</u> (draft report) **May 2007**

Citation: Polybrominated Diphenyl Ethers: A Scientific Review with Risk Characterization and Recommendations, *draft* (2007), pp. 119. Web address: <http://www.michigan.gov/documents/deq/deq-keytopics-tsg-pbdereview_187119_7.pdf>

Executive Summary

This document was written in response to a request from the Michigan Department of Environmental Quality (MDEQ) management for information about Polybrominated Diphenyl Ethers (PBDEs). The information was needed to make decisions regarding placement of PBDEs on the Critical Materials Register (CMR) and the Department's response to proposed legislation to ban PBDEs in Michigan.

This document includes the following information about PBDEs:

- Description and Use
- Toxicity and Toxicokinetics
- Environmental Fate and Chemical Characteristics
- Levels in the Environment
- Potential Risks to Humans
- Regulatory and Legislative Actions
- Conclusions and Recommendations

The information presented is not a complete summary of all available data, but focuses on the information that will be most helpful to the decision-making process regarding the CMR and proposed legislation. The data cited includes original research articles, as well as review summaries.

PBDEs are brominated fire retardants (BFRs) used primarily in plastics and textile coatings. In this class of compounds, two-to-ten bromines are attached to the diphenyl ether molecule. PBDEs are of significant environmental concern because they are toxic, bioaccumulative, and persistent. Levels in humans and wildlife are increasing exponentially. The primary commercial products of PBDEs are Penta-, Octa-, and Deca-BDEs. Each is a mixture of specific PBDE chemicals or congeners. For example, commercial Penta-BDE contains 0.1% Tri-BDE, 24-38% Tetra-BDE, 50-62% Penta-BDE, and 4-8% Hexa-BDE. The 209 possible PBDE congeners are identified in the International Union of Pure and Applied Chemistry (IUPAC) numbering system, which arranges them in ascending numerical order of the degree of bromination. For example, BDE-99 is 2,2',4,4',5-Penta-BDE.

Toxicity

Toxicity data for PBDEs are limited. Exposure of laboratory animals to PBDEs has resulted in histopathological changes to the liver, neurodevelopmental effects in developing animals, and/or reductions in thyroid hormone levels. The United States Environmental Protection Agency (EPA) currently uses the induction of liver enzymes or other effects in the liver as the critical effect in the derivation of reference doses (RfDs) for three of the PBDE congeners. Draft EPA RfD documents are currently under review. However, more recent studies suggest that effects on the developing brain may be as, or more, sensitive than effects on the liver. Deca-BDE is the only PBDE congener that has been tested for carcinogenicity. Some evidence of carcinogenicity was found for rats following exposure to very high levels in feed. Overall, the lower brominated congeners and mixtures appear to be more toxic than the higher brominated compounds.

Some PBDE congeners exhibit toxicity similar to dioxins. Dioxins have high affinity for the Ah receptor. The cascade of toxic effects caused by dioxin begins with binding to the Ah receptor. Dioxins also significantly induce ethoxyresorufin-o-deethylase (EROD), which represents an ability to induce CYP1A liver enzymes. Studies have shown that some of the PBDE congeners have a low-to-moderate binding affinity for the Ah receptor and a weak potential to induce EROD, whereas other congeners exhibit no binding affinity for the Ah receptor or have an antagonistic effect. A recent study concluded that the concentrations of PBDEs currently detected in biota contribute negligibly to dioxin-like activity compared with other contaminants found in biota.

Toxicokinetics

Limited toxicokinetic data are available in the scientific literature on PBDEs. There is evidence in animals and humans that PBDEs are bioavailable, although the lower brominated congeners (Tetra- through Hexa-BDEs) appear to be more readily absorbed than the higher brominated congeners (Hepta- through Deca-BDEs). The lower brominated congeners appear to distribute preferentially to lipid rich tissues, especially adipose tissue. The higher brominated congeners once absorbed, appear to be distributed to more highly perfused tissues, with less accumulation in adipose tissue. Metabolism has been directly indicated or strongly suggested, has some species specificity, and occurs more readily for the higher brominated congeners. Oxidative debromination has been observed with some PBDEs resulting in hydroxylated and sometimes methoxylated metabolites. Fecal excretion appears to be the predominant elimination pathway in rats. Metabolites are found in the bile and urine. Metabolism and urinary excretion have been demonstrated to be an equally important elimination mechanism in mice.

The identification of OH-PBDE residues in blood suggests that PBDEs are metabolized in many species. Evidence suggests that some PBDEs may affect hormonal systems or neurodevelopment via formation of active metabolites.

Although previously thought to be biologically unavailable, recent studies indicate some bioavailability for Deca-BDE. A recent study indicates evidence of limited bioavailability of Deca-BDE in Carp. Seven apparent debrominated products of BDE-209 accumulated in whole fish and liver tissues. A study in mice demonstrated uptake in the brain, liver, and heart after oral exposure to ^{14}C-labeled BDE-209. Several recent studies have identified detectable levels of BDE-209 in human tissues.

Environmental Fate and Chemical Characteristics

Based on the chemical characteristics of PBDEs, they are expected to be persistent and bioaccumulative in the environment. The half-life of PBDEs in soil and water was estimated to be 150 days, and 600 days in sediment. Studies show that environmental degradation of PBDEs occurs by both photolytic and bacterial means. The more highly brominated congeners lose bromine atoms more quickly than lower brominated congeners. The rates of degradation are dependent on the solvent, light source, and substrates involved. In particular, BDE-209 does degrade in the environment more quickly than lower brominated compounds, however the rate of degradation and degradation products generated are not well characterized. PBDEs are highly lipophilic indicated by their high log K_{ow} values ranging from 5.9-7.9. The lipophilic nature of these chemicals indicates they would likely bioaccumulate in animals.
Levels in the Environment

<u>Levels in Biota and Food</u>

PBDEs have been detected in aquatic and terrestrial biota from numerous locations around the globe. The most prevalent congeners were BDE-47, BDE-99, and BDE-100. Concentrations in several species of biota have increased dramatically between 1980 and the present. Within some geographic regions, higher concentrations have been observed in relatively warmer climates. Generally, North American biota appears to have higher concentrations than European biota.
PBDE concentrations have been found to be the highest in fish, followed by meat and dairy products. Great Lakes fish have been observed to have relatively high concentrations of PBDEs compared to other foods. However, concentrations in milk and chicken may be considered substantial, given the total quantities of these items consumed by the public.

BDE-209 had been detected in food and wildlife. Studies have shown that terrestrial animals (those feeding on land) may be more likely to bioaccumulate BDE-209 as compared to aquatic feeding organisms. The limited data on BDE-209 is in part caused by the fact that analytical labs have just recently (within the last several years) been able to quantify BDE-209. Furthermore, studies have shown that several species of animals readily metabolize BDE-209 from the parent compound to lesser-brominated congeners. Debromination of BDE-209 reduces or eliminates the presence of BDE-209, but results in higher concentrations of the lower brominated congeners, many of which are more toxic than BDE-209.

Levels in Humans

Data on concentrations of PBDEs in human blood, breast milk, and adipose tissue have consistently shown levels to be significantly higher in North America, compared to Europe or Japan. Levels found in the U.S. are the highest of all countries for which there are data and are about 10-100 times greater than human tissue levels in Europe. Two recent studies of U.S. breast milk levels showed total PBDE concentrations ranged from 6.2-419 ng/g lipid in one study (Schecter et al., 2003) and 9.5-1,078 ng/g in another study (EWG, 2003). Typically, BDE-47 is found at the highest concentration in human tissue and comprises at least half of the total PBDEs. The next most abundant congener often detected is BDE-99. Human samples from Japan, Europe, and North America during the period of 1970-2002, show that BDE-47comprised about 50% of the total PBDEs, followed next by BDE-153 at about 20%, and then BDE-99, BDE-100, and BDE-154 at lower percentages (Hites, 2004). Limited data are available on levels of BDE-209 in humans, as many studies have not included analysis for this congener, although it has been found in human blood, breast milk, and adipose tissue in a few studies. Levels of BDE-209 in human tissues are typically lower than other congeners, with one study reporting a median concentration of 0.4 ng/g lipid in breast milk (Northwest Environment Watch, 2004) and another median concentration of 2.3 ng/g lipid in whole blood (Schecter et al., 2005).

Temporal trends of PBDEs in human tissues show levels in North America are increasing significantly over time. Data on blood levels from 1959-1966 showed no detectable levels of BDE-47 compared to levels of <10-511 ng/g lipid in blood samples from 1997-1999 (Petreas et al., 2003). PBDE levels in breast milk also show similar increases over time and appear to be doubling every two-to-five years in North America (Betts, 2002).

Levels in Environmental Media

PBDEs have been found in ambient air, lakes, rivers, soils, and sediments as well as in the indoor environment. Average concentrations of total PBDEs in ambient air from four sites in the Great Lakes basin, and three sites in Indiana, Arkansas, and Louisiana ranged from 5.5-100 pg/m^3, with the highest concentration found in the urban area of Chicago, Illinois (Strandberg et al., 2001; Hoh and Hites, 2005). At the Chicago site, concentrations increased from 52 pg/m^3 during 1997-1999, to 100 pg/m^3 during 2002–2003. PBDE levels measured in the Lake Michigan water column in 1997-1999 ranged from 31-158 pg/L compared to 6 pg/L in Lake Ontario (Hale et al., 2003). PBDEs have also been found in sediments from freshwater tributaries and lakes, as well as in sewage sludge samples. BDE-209 is the predominant congener found in most sediments, including those of the Great Lakes, where average concentrations ranged from a low of 11 ng/g in Lake Superior to a high of 227 ng/g in Lake Ontario (Song et al, 2004, 2005b; Zhu and Hites, 2005). PBDE concentrations in sewage sludge samples from North America are significantly higher than those found in Europe (Hale et al., 2003).

PBDEs are also found in the indoor environment, including indoor air and house dust. Indoor air concentrations appear to be significantly higher than outdoor air concentrations, with one study showing indoor concentrations fifty times higher than the outdoors (Wilford et al., 2004b). PBDEs in house dust in North American have been found at levels ranging from 170-170,000 ng/g, with average concentrations of 4,600-12,000 ng/g. Typically BDE-209 is found at the highest concentration in house dust, with BDE-47 and BDE-99 the other major contributors to the total PBDEs in this media.

Potential Risks to Humans

The Potential Risk Section consists of summaries of two risk assessments from the scientific literature (Hays and Pratt, 2006; McDonald, 2005) and a risk assessment conducted by the TSG for this report. The TSG used a Margin of Exposure (MOE) approach to compare congener-specific human body burdens to estimate animal body burdens for specific congeners including Deca-BDE. Specifically, an MOE is calculated by dividing the estimated animal body burden LOAEL by the human tissue levels. Estimates of animal body burdens were calculated from the LOAELs reported in several animal toxicity studies for each of the following PBDE congeners: BDE-47, -99, -153 and -209. The calculation used to estimate the body burden LOAEL is presented. Human tissue levels used to generate the MOEs were the lowest median, the highest median and the highest body burden concentrations from the studies reviewed for this report. The uncertainties associated with the approach are identified. An MOE of 300 or greater is identified as posing a minimal level of risk to humans based on the information cited in the report. A significant concern for highly exposed individuals to BDE-47, -99, and -153 was identified based on the estimated ranges of MOEs. Similarly, a minimal level of risk was identified for highly exposed individuals considering BDE-209 alone. A range of MOEs was also estimated for total PBDEs suggesting a significant level of risk and concern for exposures to all PBDEs combined.

Regulatory and Legislative Action

<u>Michigan</u>

A MDEQ staff report recommends that Penta-, Octa-, and Deca-BDEs be placed on the CMR; the TSG PBDE Subcommittee supports that recommendation. The CMR is a list of substances which pose an environmental concern. All facilities with a non-sanitary wastewater discharge are required, by law, to report annually on their use and discharge of chemicals on the CMR.
House Bill 4406, was signed into law as Public Act 562 in 2004, and became effective January 3, 2005. Beginning on June 2, 2006, a person shall not manufacture, process, or distribute a product or material containing more than 1/10 of 1% of Penta-BDE. Senate Bill 1458, is a similar bill that addresses Octa-BDE; it was also signed into law in 2004 and became Public Act 526.
House Bill 5573, which proposes to ban Deca-BDE in a similar fashion, was introduced on January 24, 2006.

<u>Other States, the EPA, and Related Information</u>

California was the first state to ban the manufacture and commercial distribution of products containing more than 1/10 of 1% of Penta- or Octa-BDE. Bills to ban or regulate products containing PBDEs have also been adopted in Hawaii, New York, Illinois, Maryland, Oregon, and Maine. The EPA issued a draft

Significant New Use Rule for Penta- and Octa-BDE on December 6, 2004. The EPA has included PBDEs in the High Production Volume Evaluation and Testing Programs and also in a pilot program for the Voluntary Children's Chemical Evaluation Program. The main United States manufacturer of Penta- and Octa-BDE voluntarily ceased production of Penta- and Octa-formulations at the end of 2004. Replacement chemicals must be adequately tested to assure they will not present unacceptable risks to human health and the environment. In 2006 the EPA also released the PBDE Project Plan.

Europe

In early 2003, the European Union (EU) adopted a directive, which banned the marketing and use of Penta- and Octa-BDE in all consumer products beginning August 15, 2004. In addition, a separate Europe-wide ban under the Restriction on Hazardous Substances, which has a specific focus on electronics, will eliminate all PBDEs in electronics by 2006. A risk assessment on Deca-BDE conducted by the EU is being evaluated to determine if Deca-BDE should be exempt from the electronics ban.

Conclusions and Recommendations

The updated conclusions and recommendations focus on Deca-BDE, since Penta- and Octa-BDEs were banned in 2006. Various concerns and uncertainties related to Deca-BDE are summarized, including its neurodevelopmental toxicity, significant potential for human exposures, and detectable levels in various biota including humans. The first recommendation is to support a legislative ban on Deca-BDE rationale is provided and includes various uncertainties and concerns, such as increasing trends of other PBDE congeners in humans, limited data on human tissue concentrations particularly in children, significant exposure potential for children, the potentially significant breakdown of Deca-BDE into the more toxic, lower brominated congeners, among others. The remaining recommendations are: investigate the efficacy of the legislative bans on Penta- and Octa-BDE; develop criteria when adequate toxicity studies are available and/or EPA completes the draft RfDs; pursue development of educational materials aimed at reducing exposures in children; investigate the safety of replacements for PBDEs; pursue options for changing the United States chemical policy; and consider implementing some of the monitoring recommendations in the 2004 PBDE Draft Report.

European Union **2002**

Citation: "European Union Risk Assessment Report bis(pentabromophenyl) ether EC: 214-604-9" **2002** pp 294. Web address: < http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/decabromodiphenyletherreport013.pdf>

OVERALL RESULTS OF THE RISK ASSESSMENT

CAS Number: 1163-19-5
EINECS Number: 214-604-9
IUPAC Name Bis(pentabromophenyl) ether

Environment

Conclusion (i) There is a need for further information and/or testing.

This conclusion applies to the risk of secondary poisoning from all sources of decabromodiphenyl ether. The current PEC/PNEC approach indicates that there is no risk of secondary poisoning. The PEC/PNEC ratios are much less than 1 (in fact below 10-5) for the commercial decabromodiphenyl ether product. It is possible that the current PEC/PNEC approach for secondary poisoning may not be appropriate in terms of both the PEC and the PNEC, and could underestimate the risk. This issue needs further investigation.

Two possible areas for further work are as follows:

- A more widespread monitoring project to determine whether the finding in top predators (including birds' eggs) is a widespread or localised phenomenon, and trends (if possible).

- Further toxicity testing. The existence of a mammalian toxicity data set means that testing could be considered on birds (e.g. an avian reproduction test (OECD 206), with appropriate tissue analysis). Overall, the benefit of further vertebrate testing is open to question due to expected difficulties in achieving sufficiently high exposures. This leaves the toxicity issue with some unresolved uncertainty.

A second aspect of the concern for secondary poisoning is that although the substance is persistent, there is evidence that it can degrade under some conditions to more toxic and bioaccumulative compounds. The current database is inconclusive on this point, and further work could be done as follows:

- An investigation of the rate of formation of degradation products under environmentally relevant conditions over a suitably prolonged time period (e.g. years) - for example, an extended monitoring programme to determine trends in degradation product levels in various environmental compartments. This could be coupled with analysis of the parent compound to detect whether it is building up in the environment or has achieved equilibrium. A controlled field study (or studies) might be the way forward, with controlled continuous input of the substance and regular monitoring of other components.

- Further toxicological work on the non-diphenyl ether degradation products, to determine if they pose a hazard or risk.

There is a high level of uncertainty associated with the suitability of the current risk assessment approach for secondary poisoning and the debromination issue. The combination of uncertainties raises a concern about the possibility of long-term environmental effects that can not easily be predicted. It is not possible to say whether or not on a scientific basis there is a current or future risk to the environment. However, given the persistent nature of the substance, it would be of concern if, once the further information had been gathered, the analysis indicated a risk to predators, since it could then be difficult to reduce exposure. In summary, although it is concluded that further information should be gathered in order to refine the risk assessment, in light of:

• the persistence of the substance,
• the time it would take to gather the information and
• the fact that there is no guarantee that the studies would provide unequivocal answers, consideration should be given at a policy level about the need to investigate risk management options now in the absence of adequate scientific knowledge.

[N.B. A number of technical experts from EU member states consider that this uncertainty is sufficient to warrant risk reduction measures directly (*conclusion (iii)*) based on the information currently provided in this assessment.]

The possible long-term increase in levels as a result of releases from waste sites might need to be considered further in any future revision of this risk assessment report.

Conclusion (**ii**) There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied already.

This applies to the environmental assessment of risks to the aquatic (surface water, sediment and wastewater treatment plants), terrestrial and atmospheric compartments by the conventional PEC/PNEC approach for decabromodiphenyl ether itself from all sources.

Human health

<u>Human health toxicity</u>

Workers
Conclusion (**ii**) There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied already.

Consumers
Conclusion (**ii**) There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied already.

Humans exposed via the environment
Conclusion (**ii**) There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied already.

Combined exposure
Conclusion (**ii**) There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied already.

Human health (risks from physico-chemical properties)
Conclusion (ii) There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied already.

Results of discussion at the policy level

Following the agreement of the risk assessment conclusions reached on a technical basis as presented in this report, Member States noted the uncertainties expressed regarding the risk characterization for secondary poisoning (Section 3.3.4). They also noted the conclusion that further information would be required to remove these uncertainties and refine the risk assessment. Member States were concerned that it would take a significant time to gather the information and that the resulting refined risk assessment could then indicate a risk to predators.

Furthermore, increasing levels in the environment and the possible formation of more bioaccumulative and toxic compounds via degradation could occur while the data were being gathered. Consequently Member States agreed that emission reduction measures should be considered without delay for the sources of this exposure. In the light of this agreement, a risk reduction strategy for this substance will be developed in parallel to the performance of the proposed testing listed under the conclusion (i) in Section 3.3.4. Depending on the strategy adopted, the further testing might have to be adjourned in the interests of animal welfare and cost versus benefit unless expert advice is provided which indicates that tests may be relevant to the controls

<u>European Union</u> (Final Environmental Draft) 2004

Citation: "Update of the Risk Assessment of bis(pentabromophenyl) ether (decabromodiphenyl ether) (Final Environmental Draft)" 2004 pp 122. Web address: <http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/ADDENDUM/decabromodiphenylether_add_013.pdf>

OVERALL RESULTS OF THE RISK ASSESSMENT

CAS Number: 1163-19-5
EINECS Number: 214-604-9
IUPAC Name: Bis(pentabromophenyl) ether

Environment

(x) **i)** There is a need for further information and/or testing.

This conclusion applies to the PBT assessment. Decabromodiphenyl ether is likely to be very persistent (vP), but not bioaccumulative nor toxic in the marine environment according to the criteria presented in the Technical Guidance Document. However, the PBT assessment is complicated by data available on the:

- Widespread occurrence of the substance in top predators (e.g. birds and mammals, including terrestrial species) and the Arctic;
- Neurotoxic effects and uptake of the substance by mammals in laboratory studies; and
- Possible formation of more toxic and accumulative products such as lower brominated diphenyl ether congeners and brominated dibenzofurans in the environment.

This means that the available assessment methodology might not be applicable to this substance. As a minimum there is a continued need to monitor environmental contamination for a suitable time period for both the substance and (if possible) its more toxic and bioaccumulative degradation products. The monitoring options are outlined in a report (available on request from the rapporteur), but matrices will include estuarine sediment, bird of prey tissues and sewage sludge samples at least. Any programme should be reviewed at suitable time points to decide if further action is necessary.

The fact that the additional work will take some years to deliver results led to a further examination of the evidence presented in this updated assessment at the policy level in May 2004 to review whether precautionary risk management is still considered necessary. The outcome is reported below.

[The original assessment noted that the possible long-term increase in levels as a result of releases from waste sites might need to be considered further in any future revision. Methods are still not available to enable this to be done, so this statement is still valid.]

(x) **ii)** There is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied already.

This conclusion applies to the assessment of surface water and sediment (freshwater and marine), waste water treatment plants, the terrestrial compartment, the air compartment and secondary poisoning for all life cycle stages using the PEC/PNEC assessment approach.

Results of further discussion at the policy level (May 2004)

The Competent Authorities agreed that the voluntary emission reduction programme proposed by Industry should be implemented in parallel with the collection of further data as described above. Industry will be required to provide progress updates in a series of interim reports delivered at suitable intervals. Depending on the success of the programme in reducing emissions, and the results of the further scientific investigations, the need for more formal risk reduction measures might be reviewed at a later date.

European Union (Update of Human Health Risk Assessment) 2005

Citation "Update of the Risk Assessment Addendum of Bis(pentabromophenyl) Ether (Decabromodiphenyl Ether) (Human Health Draft)" 2005 pp 45. Web address: <http://www.cleanproduction.org/library/Deca%20Health%20Update.doc>

OVERALL RESULTS OF THE RISK ASSESSMENT

Cas N° : 1163-19-5
EINECS N° : 214-604-9
IUPAC name : Bis(pentabromodiphenyl)ether (Decabromodiphenyl ether)

Human Health

Workers

Conclusion (i): There is a need for further information and /or testing.

A conclusion (i) applies to the human health part (section 4.1.2.10.5) because an appropriate NOAEL cannot be derived from the available neurotoxicity study. New data is consequently expected namely a developmental neurotoxicity study before this part of the risk characterisation can be filled.

Consumers
Conclusion (ii):
There is at present no need for further information and/or testing and for risk reduction measures beyond those which are being applied already.

This conclusion was reached in the risk assessment report because consumer exposure was considered negligible. However, consumers may be exposed to DBDPE released from consumer products (electronic equipment and fabrics). Exposure is not yet quantified in this report but will be considered when further information about the neurotoxic developmental effects become available.

Humans exposed via the environment

Conclusion (i) applies to the risk characterisation for human exposed via the environment.

- Although no risk has currently been identified, additional information are needed on current concentrations of decabromodiphenyl ether in humans due to the remaining uncertainties on DecaBDPE exposure. Consequently, a suitable bio-monitoring programme, including breast milk, and a trend analysis over a certain time period, are required.
- In order to complete the risk assessment for developmental neurotoxicity an appropriate NOAEL should be derived for this endpoint. A developmental neurotoxicity study is consequently expected.