



# Washington State Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: *Final Plan*

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## Washington State Polybrominated Diphenyl Ether (PBDE) Chemical Action Plan: *Final Plan*

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## **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 multi-program, 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 was used 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 the 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. 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

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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.

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Automobile Manufacturing Auto Manufacturers Alliance Greg Dana

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## **Acronyms and Abbreviations**

ABS	acrylonitrile butadiene styrene
ATSDR	Agency for Toxic Substances and Disease Registry
BDE	brominated diphenyl ether
BFR	brominated flame retardant
CEPA	Canadian Environmental Protection Act
CPSC	Consumer Product Safety Commission
DOH	Washington State Department of Health
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
EPDM	ethylene-propylene terpolymer
EU	European Union
FOIA	Freedom of Information Act
HIPS	high-impact polystyrene
HIPS/PPO	high-impact polystyrene/polyphenylene oxide
IWGFM	Interagency Working Group on Fire and Materials
L&I	Washington State Department of Labor and Industries
LDPE	low-density polyethene
MSDS	Material Safety Data Sheets
NIOSH	National Institute for Occupational Safety and Health
PBDE	polybrominated diphenyl ether
PBDF	polybrominated dibenzofuran
PBT	persistent bioaccumulative toxin
PCB	polychlorinated biphenyl
POP	persistent organic pollutant
RoHS	Restriction on Hazardous Substances
SNUR	Significant New Use Rule
TSCA	Toxics Substances Control Act
THF	tetrahydrofuran
WEEL	Workplace Environmental Exposure Level

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## I. Introduction

This Final PBDE Chemical Action Plan (CAP) is a joint document of the Washington State Department of Ecology (Ecology) and Department of Health (DOH). The purpose of this document is to identify, characterize and evaluate uses and releases of the class of flame retardants known as polybrominated diphenyl ethers (PBDEs), and to recommend actions the state may take to reduce threats posed by PBDEs.

This chemical action plan was created at the direction of Governor Locke, in his January 2004 Executive Order. This Final CAP builds on the work of the *Interim PBDE CAP*, which was completed in December 2004. A multi-program, multi-agency effort, Ecology and DOH have consulted with external stakeholders at all stages of developing this plan. There have been two Advisory Committees, with some overlap in membership, and each with broad representation from business, recycling, environmental and consumer advocacy and local government interest. The first group met during the second half of 2004, to provide perspectives and knowledge on the wide range of topics covered by the PBDE CAP. The second Advisory Committee met between July and November of 2005, and focused more specifically on Deca-BDE and the alternatives assessment (conducted by DOH) and Cost Benefit Analysis (done by Ecology). While Ecology and DOH were interested in identifying areas of consensus among members, working towards consensus on issues or solutions was not an objective of the committees.

A detailed timeline describing the development of the PBDE CAP follows this Introduction.

The *Interim Plan* recommended that Ecology and DOH conduct additional research on Deca-BDE alternatives and the costs and benefits of a ban. This Final CAP includes the results of this work as well as an update of existing information. 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.

The *Interim CAP* focused on all three main types of PBDEs used in consumer products --Penta-BDE, Octa-BDE and Deca-BDE. With national and international agreement that the Penta-BDE and Octa-BDE mixtures should be banned, Ecology and DOH began focusing the remaining CAP work on Deca-BDE. Somewhere between 45 and 80% of the Deca-BDE currently used commercially is in TV casings -- the black plastic used to enclose the rear of the television. Given time and staffing constraints, it was decided that the alternatives assessment and the cost benefits analysis would focus on Deca-BDE use in TVs, although Deca-BDE does have other uses.

This Final CAP provides an extensive literature review and analysis of PBDEs, presenting what is currently known about the universe of PBDEs. Chapter II provides an introduction to PBDEs and discusses their purpose and uses. In Chapter III, the effects of PBDEs on human health and the environment is discussed. Chapter IV looks at the issue of Deca-BDE degradation. Chapter V is a detailed review by DOH of literature on alternatives to Deca-BDE in electronic casings, and Chapter VI is a cost benefits analysis on a ban on Deca-BDE conducted by Ecology. The

regulatory environment surrounding PBDEs is reviewed in Chapter VII, including information on the European Union, the U.S., and activities around the world. The last chapter presents Ecology and DOH's PBDE policy recommendations. The document concludes with appendixes containing supplemental information, including an extensive bibliography.

The Draft Final PBDE CAP was posted on-line December 1, 2005 for 30 days of public comment (until December 31, 2005). Following the public comment period, Ecology and DOH reviewed the recommendations and made some changes in light of comments received. A Responsiveness Summary on comments received will be posted on the web for review in late January or February, 2006.

**Note**: For purposes of this report, commercial mixtures are distinguished from homologues by upper and lower case designations. Commercial mixtures will be identified by capitalization of the first letter ("Deca-BDE," "Octa-BDE," and "Penta-BDE"). Lower case first letter designations (mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and deca-BDE) refer to homologues, that is, groups of molecules that have between one and ten bromine atoms. The terms "BDE-209" and "deca-BDE" are used synonymously.

If a sentence starts with "Deca-BDE" and refers to "deca-BDE," it has been notated as "Deca-BDE(209)," so that the reader will understand it refers to the homologue.

### **PBDE CAP Development Timeline**

### <u>2004</u>

- January Gov. Locke issues Executive Order #04-01
- 2004 Legislative Session Legislature provides \$83,000 in Supplemental Budget solely for development of PBDE CAP
- February staff person hired to write CAP; research begins
- March Internal Ecology/DOH PBDE Technical Committee formed, comprised of members from 6 different Ecology programs and from DOH's Office of Environmental Health Assessments – met bi-weekly
- June External PBDE Advisory Committee formed (met 5 times, through Dec. 2004)
- **October** Draft PBDE CAP published; public comment period Oct. 11 to Nov. 9; public meetings held in Seattle and Spokane
- December Interim PBDE CAP published

### <u>2005</u>

- **2005 Legislative session** Legislature allocated an additional \$187,000 to complete alternatives analysis and cost-benefits analysis on Deca-BDE
- May Ecology and DOH began alternatives assessment and cost-benefits analysis
- Summer/Fall Ecology/DOH PBDE Technical Committee met bi-weekly
- July External Deca-Alternatives External Advisory Committee formed (met 3 times, through Nov. 2005)
- December Draft Final PBDE CAP published; public comment period Dec. 1-31.
- **December** Internal Ecology/DOH End-of-Life Technical Committee formed. External PBDE End-of-Life Advisory Committee formed, with first meeting scheduled for January 31, 2006

### <u>2006</u>

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## **II.** Purpose and Description of PBDEs

**IN BRIEF:** PBDEs (Polybrominated Diphenyl Ethers) are chemicals added to consumer products so the products will not catch on fire or will burn more slowly if exposed to flame or high heat. PBDEs are added to plastics, upholstery fabrics and foams in such common products as computers, TVs, furniture and carpet pads. These chemicals are effective flame retardants as well as cost effective, hence their wide use.

There are three main types of PBDEs used in consumer products: Penta-BDE, Octa-BDE and Deca-BDE. Each has different uses and 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-BDE and Octa-BDE 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. Companies must find alternatives to Penta-and Octa-BDE, and Octa-BDE as well.

### **Purpose of PBDEs**

During the twentieth century, manufacturers began to replace traditional materials such as wood, metal, and wool with petroleum-derived products such as plastics and polyurethane foam. The new materials are more flammable and, once alight, combust more rapidly, allowing people less time to escape.<sup>1</sup>

Fires are a leading cause of death among children in the U.S. Each year more than 40,000 children ages 14 and under are injured by fires in the home, and in 2001, nearly 500 children ages 14 and under died as a result of a residential fire.<sup>2</sup> The elderly are also especially vulnerable to being injured or killed in fires. Strict U.S. fire safety regulations may be a reason that flame-retardants are used more here than in other countries.

Flame retardants reduce the likelihood that an item will ignite. They also slow the initial burn rate of a fire. This increases the amount of time before a possible "flash over," which is when all combustible materials in a room ignite, allowing occupants extra time to escape.<sup>3</sup>

### **Uses of PBDEs**

The global demand for PBDEs was estimated at almost 70,000 metric tons for 2001. Of world demand in 2001, North America used 44 percent of Deca-BDE, 40 percent of Octa-BDE, and 95 percent of Penta-BDE.<sup>4</sup> (See Table 1) Of the 165 million pounds of BFRs consumed in North America in 2001, about 35 percent were PBDEs, and 85 to 90 percent of that was Deca-BDE.<sup>5</sup> With the discontinuation of Penta and Octa-BDE production at the end of 2004, Deca-BDE now accounts for 100 percent of PBDE production.

PBDE Mixture	Americas	Europe	Asia	Other	Total
Deca-BDE	24,500 (44%)	7,600 (14%)	23,000 (41%)	1,050 (2%)	56,100 (100%)
Octa-BDE	1,500 (40%)	610 (16%)	1,500 (40%)	180 (5%)	3,790 (100%)
Penta-BDE	7,100 (95%)	150 (2%)	150 (2%)	100 (1%)	7,500 (100%)
Total	33,100 (49%)	8,360 (12%)	24,650 (37%)	1,330 (2%)	67,390 (100%)

Table 1. PBDE volume estimates: Total market demand by region in 2001 in metric tons (and by percent)

Source: Major Brominated Flame Retardants Estimates, BSEF, viewed at <u>http://www.bsef-site.com/docs/BFR\_vols\_2001.doc</u>, March 25, 2004.

In 2002, the total market demand for Deca-BDE was 65,677 metric tons; and in 2003, the demand for Deca-BDE was 56,418 metric tons.<sup>6</sup>

### **Specific applications**

Penta-, Octa-, and Deca-BDE have each been used for different purposes. The amount of PBDE in products differs depending on the product and the flame retardant chemical used, but typically ranges between 5 and 30% by weight.<sup>7</sup>

*Penta-BDE* has been used in unsaturated polyester, rigid and flexible polyurethane foams, epoxies, laminates, adhesives and coatings.<sup>8,9,10</sup> Typical end products containing Penta-BDE include mattresses, seat cushions and other upholstered furniture, and rigid insulation. The most common use (95-98%) of Penta-BDE was in polyurethane foam. This foam contains between 10 and 18% of the commercial Penta-BDE formulation (typically made up of 75% Penta-BDE and 25% aromatic phosphate esters).<sup>11,12</sup> Prior to the voluntary phase-out of Penta-BDE at the end of 2004, approximately 7.5% of the more than 2.1 billion pounds of flexible polyurethane foam produced each year in the U.S. contained the commercial Penta-BDE formulation. Most Penta-containing foam products were sold in California to meet the state's flammability standards for upholstered furniture.<sup>13</sup>

*Octa-BDE* has been used in acrylonitrile butadiene styrene (ABS), nylon, thermoplastic elastomers, and polyolefins.<sup>14</sup> Typical products containing Octa-BDE include housings for fax machines and computers, automobile trim, telephone handsets, and kitchen appliance casings. Approximately 95% of the commercial Octa-BDE formulation (made of Octa-BDE and antimony trioxide) was used as a flame retardant for ABS terpolymers.<sup>15</sup> The ABS products containing the Octa-BDE mixture include high-impact polystyrene (HIPS), polybutylene terephthalate, and polyamide polymers, all containing 12 to15% Octa-BDE formulation by weight.<sup>18</sup>

*Deca-BDE* is used in thermoplastic, elastomeric and thermoset polymer systems, including highimpact polystyrene (HIPS), high-impact polystyrene/polyphenylene oxide (HIPS/PPO), polybutylene terephthalate (PBT), nylon, polypropylene, low-density polyethene (LDPE), ethylene-propylene-diene rubber and ethylene-propylene terpolymer (EPDM), unsaturated polyester, and epoxy. Deca-BDE is also used in wire and cable insulation of all types, coatings and adhesive systems, including back-coatings for fabrics.<sup>19,20</sup> Examples of end products that use Deca-BDE include housings for televisions, computers, stereos, and other electronics, audiotape cassettes, and upholstery textiles. Deca-BDE formulations in various polymer mixtures make up 10 to 15% of the product by weight.<sup>21</sup>

In textiles, the amount of commercial Deca-BDE used varies considerably with the material. Some fabrics are estimated to contain 18 to 27% Deca-BDE by weight, while others use no Deca-BDE at all.<sup>22</sup> With the exception of the state of California, fire safety standards for residential upholstered furniture, carpets and bed clothes (comforters, pillows) do not require the use of flame retardant chemicals like Deca-BDE. Furniture used in commercial settings do have flammability standards that may necessitate the use of flame retardant chemicals.<sup>23,24</sup> Proposed fire safety regulations for residential upholstered furniture from the Consumer Product Safety Commission are expected to increase the use of flame retardant chemicals in textiles.<sup>25,26</sup> Deca-BDE is not used in clothing.

Four companies, listed in Table 2, are known to produce Deca-BDE.

Company	Product Name	Country
Albemarle Corporation	SAYTEX 102E	Richmond, Virginia, U.S.
Dead Sea Bromine (subsidiary Israel Chemicals LTD)	FR 1210	Israel
Great Lakes Chemical Corporation (now Chemtura Corporation)	DE-83R, DE-83	Middlebury, Connecticut, U.S.
Tosoh Corporation	Flamecut 110R	Japan

Table 2. Companies that produce deca-BDE

### Market changes

With the discontinuation of Penta- and Octa-BDE, manufacturers are actively identifying alternatives. Some companies, such as IKEA, have already phased out all PBDEs.<sup>27</sup> Another factor encouraging the development of alternatives is the fact that many governments and large corporations have developed green procurement guidelines that prohibit the use of PBDEs in electronic products.<sup>28</sup> As of mid-November 2005, a number of electronics manufacturers were phasing out all PBDEs, including Deca-BDE. Specific company policies (with a complete set of references) are listed in Appendix C. Electronics manufacturers phasing out PBDEs in some or all of their electronic products include:

Hewlett Packard	Sharp
Matsushita	Sony
Mitsubishi	ViewSonic
NEC	Xerox
Panasonic	
Samsung	
	Matsushita Mitsubishi NEC Panasonic

Out of 14 mattress manufacturers in Washington, 11 indicated they do not use any PBDEs. The following mattress companies, comprising 70% of the total mattress market, do not have Deca-BDE in their mattresses:<sup>29</sup>

Corsicana	King Koil	Select Comfort
Englander	Lady Americana	Serta
Int'l Bedding Corp	Restonic	Simmons
Kingsdown	Sealy	Tempur-Pedic

Examples of alternative flame retardants processes currently being utilized include:<sup>30</sup>

- Bromine-free circuit boards for TVs, VCRs and DVD players (Sony)
- Phosphorous-based flame retardants for printed circuit boards (Hitachi)
- Flame resistant plastic without Deca-BDE (Toshiba)
- Halogen-free low-voltage internal wires (Panasonic/Matsushita)
- Fire barrier technologies for mattresses (Serta)

### **PBDEs: Scientific Description**

Polybrominated diphenyl ethers (PBDEs) are a class of additive brominated flame retardants used in a variety of plastics and foams.

More than 175 flame retardant chemicals exist, in four major groups: halogenated organic (usually brominated or chlorinated), organophosphorous, nitrogen-based compounds and mixtures, and inorganic.<sup>31</sup> Brominated flame retardants (BFRs) are themselves a chemically diverse group, including diphenyl ethers, cyclic aliphatics, phenolic derivatives, aliphatics, phthalic anhydride derivatives, and others.<sup>32</sup>

BFRs are either reactive or additive. Reactive BFRs form covalent bonds with other ingredients in the plastics and foams to which they are added. Additive BFRs, including PBDEs, are mixed into plastics and foams but do not form chemical bonds. This makes additive BFRs much more likely to leach out of goods and products.<sup>33</sup>

The PBDE class includes 209 different theoretical forms, or "congeners," of the PBDE molecule. PBDEs are manufactured by the chemical reaction of bromine with diphenyl ether. A diphenyl ether molecule consists of two rings of six carbon atoms each, where one carbon on each ring is bound to the same oxygen atom. The amount of bromine and the time allowed for the reaction controls the extent of bromination on the diphenyl ether molecule. Congeners vary based on the number of bromines (1 - 10) attached to the two carbon rings and the position of the bromines on the rings. There appear to be fewer actual PBDE congeners in the commercial mixtures than the theoretical number possible, largely because many of the congeners lack stability and tend to

debrominate.<sup>34</sup> A diagram of deca-BDE, the PBDE with the maximum number of bromine atoms, is shown in Figure 1.

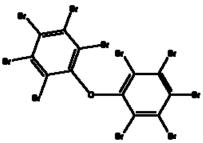


Figure 1: deca-BDE structure

Individual PBDE congeners are named BDE-1, BDE-2, BDE-3, and so on, through BDE-209, using the system developed by the International Union for Pure and Applied Chemistry (IUPAC) for numbering PCBs. Numbering is based on the number and position of bromines on the carbon rings. However, the numbering system does not intuitively communicate either the number of bromines or their position. Homologues are groups of PBDEs that have the same number of bromines. (See Table 3.)

Congener	Homologue	Primarily found in
BDE-47	tetra-BDE	General population, occupational human samples, marine mammals, birds, fish
BDE-99	penta-BDE	Penta-BDE commercial product, also high in human samples and biota (wildlife)
BDE-100	penta-BDE	
BDE-153	hexa-BDE	High in human samples and biota
BDE-154	hexa-BDE	
BDE-209	deca-BDE	Some occupational human samples, sediment, sewage sludge and house dust*

Table 3. PBDE congeners of particular interest

\* BDE-209 not widely analyzed for in general population samples<sup>35</sup>

The major commercial PBDE products consist mainly of penta-BDEs, octa-BDEs or deca-BDE, but contain other PBDEs. The general compositions of the commercial products are provided in Table 4.

Table 4. General composition of PBDE-based flame retardants given in percent of BDE congeners present<sup>36</sup>

	Congener Percent							
Commercial	tri-	tetra-	penta-	hexa-	hepta-	octa-	nona-	deca-
Product	BDE	BDE	BDE	BDE	BDE	BDE	BDE	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

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## III. Unintended Consequences: PBDEs, Human Health, and the Environment

**IN BRIEF:** PBDEs are being found in people, animals and the environment throughout the world. PBDEs are "additive" flame retardants, which means they are mixed into plastic and foams but are not chemically bound to consumer products. This makes it much more likely that PBDEs will leach out of products and be released into the environment over time. People are exposed to PBDEs in food, household dust and indoor air, although the contribution of each pathway remains unclear. Studies are looking at exposures in both the home and the workplace. Additional data is needed to better understand how people are exposed to PBDEs.

The highest levels of PBDEs in human tissues have been found in the U.S. and Canada, which used about 95 percent of the world's supply of Penta-BDE. Levels of PBDEs in human tissues (fat, blood and breastmilk) in the U.S. are 10 to 100 times higher than reported for Europe and Japan, and appear to be increasing.

Studies on lab animals show that exposure in the womb to PBDEs can impact the brain, affecting behavior and learning after birth and into adulthood. Animal studies have also shown that PBDEs can affect the thyroid and liver. Currently, the levels of PBDEs that cause these effects in animal toxicity studies are higher than the levels of PBDEs that most people encounter. In general, animal toxicity studies indicate that the PBDEs in Penta-BDE commercial products are more toxic than PBDEs in Octa- or Deca-BDE. Deca-BDE is the least toxic of the three forms, but there is growing concern based on several new studies that indicate Deca-BDE is likely to degrade into the more toxic PBDEs found in Penta- or Octa-BDE products. (See Chapter IV.)

Studies indicate that PBDEs are ubiquitous throughout the natural environment, in air, soil and sediments, and are building up in animals throughout the food chain. PBDEs have been found in peregrine falcon eggs, orca whales, harbor seals and fish. PBDEs have also been found in polar bears in the Arctic, which indicates that these chemicals can move great distances from where they are made and used. While PBDEs are the subject of increasing study, knowledge of environmental behavior, exposure and toxicity remains limited.

Once in the environment, PBDEs can last a long time depending on surrounding conditions such as the availability of water, organic compounds or sunlight. PBDEs, especially those with higher numbers of bromines such as deca-BDE, can break down into lower brominated PBDEs which are more bioaccumulative (that is, they build up more in animals). Pathways for PBDEs from products to the environment are not well understood, but PBDEs may be released at the time of disposal. For example, the processing of electronics for recycling or disposal of electronics into landfills may release PBDEs into the environment.

### **PBDEs and Human Health**

### Human exposure to PBDEs

### **PBDEs in human tissues**

PBDEs have been measured in a variety of human tissues, including blood, fat, and breast milk collected from people around the world. Some of the earliest available data on PBDEs in human tissue comes from studies in Sweden. Between 1972 and 1997, PBDE levels in the breast milk of Swedish women increased exponentially, doubling every 5 years (Figure 2).<sup>37</sup> Companies and branches of government in Sweden began voluntary PBDE phase-outs starting in early 1990, and total PBDE levels in Swedish women's breast milk fell about 30 percent between 1997 and 2000, from a high of about 3.7 ng/g of milk fat to 2.62 ng/g fat.<sup>38</sup>

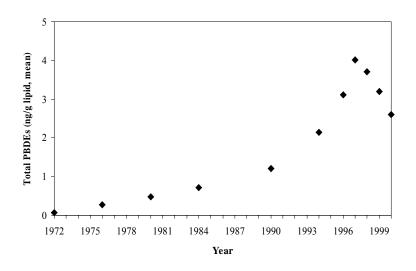


Figure 2. PBDEs in Swedish breast milk, 1972-2000.<sup>39,40</sup>

### Highest levels in U.S.and Canada

The highest levels of PBDEs in human tissues collected from the general public have been found in the U.S. and Canada.<sup>41,42,43,44,45,46</sup> Figure 3 shows the mean levels of total PBDE congeners found in the U.S. and Canada, compared to Swedish breast milk levels during the same time. Levels of PBDEs in human tissues in the U.S. are between 10-100 times higher than levels reported for Europe and Japan. One reason for the higher levels of PBDEs in U.S. and Canadian tissue samples may be that North America has used about 95% of the world's supply of the Penta-BDE commercial product.<sup>47,48</sup> While levels in Japan and some European countries appear to have begun decreasing recently, levels in the U.S. appear to be increasing.<sup>49,50,51</sup> In contrast, levels of another group of persistent environmental contaminants that were banned in the 1970s, PCBs, have been decreasing. Currently, U.S. levels of PBDEs in human tissue samples are similar to or greater than levels of PCBs.<sup>52,53</sup>

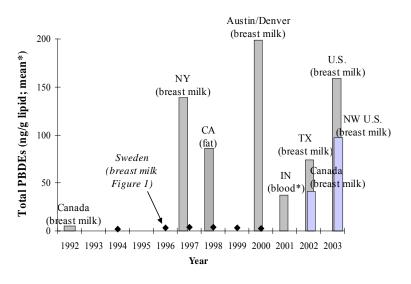


Figure 3. PBDEs in Breast Milk and Fat Samples Around the World<sup>54</sup> \*Note: all total PBDE values are means, except levels for data from Indiana (IN) which are a median.

#### Variability of PBDE levels in tissues

There is a wide range of PBDE levels in tissues, including some people with very high tissue levels (high-end) compared to the average tissue levels among all people tested.<sup>55</sup> For example, a study in Texas reported levels of total PBDEs measured in breast milk ranging from 6 to 419 nanograms/gram lipid with an average of 74.<sup>56</sup> A more recent study found even higher levels of PBDEs. Concentrations of total di- through hexa- PBDEs in adipose tissue collected in New York City ranged from 17 to 9630 ng/g lipid with a mean of 399 ng/g lipid.<sup>57</sup> This wide variability is seen in tissue samples from the U.S. and from other countries.<sup>58,59</sup> The reasons for the large variability in tissue levels and why some people have high-end exposures to PBDEs are not known. Additional research is needed to understand this phenomenon. There is some concern that people with very high levels of PBDEs are at or near exposures that may cause health impacts.<sup>60</sup>

#### PBDE levels in people are due to recent exposures

Studies of PBDE levels in people indicate that exposure to PBDEs is a recent phenomenon. For example, some studies have compared characteristics of PBDE exposures to the well-studied exposure characteristics of PCBs. These studies indicate that there are differences in routes and timing of human exposures between PCBs and PBDEs. People are mainly exposed to PCBs through diet, and age has been shown to be a predictor of PCB levels in human tissues.<sup>61</sup> Levels of PCBs and PBDEs were not correlated in a study that measured both in breast milk, i.e. the levels of these compounds were not both high in the same individuals.<sup>62</sup> Additionally, a study of PBDEs in adipose tissue of women in California found that the levels of PBDEs were not correlated with age.<sup>63</sup> Studies in Sweden and Norway have also found that PBDE tissue levels were not correlated with age.<sup>64,65</sup> This suggests that exposures to PBDEs have occurred recently, i.e. PBDEs have not accumulated in older people over time, as has been seen with PCBs.

*Penta-BDE congeners generally are the highest PBDE concentrations found in human tissue* In general, BDE-47 is the PBDE congener reported at the highest concentration in human tissues analyzed from the general population and in wildlife including fish, birds, and marine mammals. BDE-47 is the second most abundant congener in the Penta-BDE commercial mixtures (BDE-99 is the most abundant). Differences in uptake and excretion between Penta-BDE congeners may account for BDE-47 being found at the highest levels even though it is not the most abundant congener in the Penta-BDE products.<sup>66</sup> Penta-BDE-associated congeners, BDE-99, -100 and -153, have also been detected at higher levels than other PBDE congeners in general population samples. Recent reports from the Faroe Islands found BDE-153, instead of BDE-47, as the most abundant PBDE congener in breast milk samples and in children's blood serum.<sup>67,68</sup> Faroe Island residents consume more seafood, including pilot whale, than does the average U.S. citizen. The difference in congener levels suggests differences in dietary sources and other exposure pathways.

### Findings on Deca-BDE

BDE-209, the primary congener in Deca-BDE, had not been routinely included in earlier general population studies mainly because it was not suspected to build up in human tissues and it can be difficult to measure. More recent studies report BDE-209 in general population samples of breast milk, at levels on average 40-50 times lower than BDE-47.<sup>69,70</sup> Occupational studies have found BDE-209 as a dominant congener in some workers (see section on Workplace Exposures). BDE-209 has generally been found as the dominant congener in sediments and sewage sludge that is land applied (biosolids).<sup>71</sup> BDE-209 has been found as a main congener, along with BDE-47 and BDE-99, in indoor air in homes and workplaces, and in house dust samples.<sup>72</sup> BDE-209 has been found in fish and other food.<sup>73</sup>

### Human Exposure Pathways to PBDEs - General Population

PBDEs have been detected in foods, house dust and indoor air.<sup>74,75,76,77</sup> There is a fair amount of data available on how nursing infants and some workers are exposed to PBDEs. However, how much exposure in the general population can be attributed to each of these sources is currently an area of active research.<sup>78,79</sup> Early studies indicated that food was likely the main source of exposure to PBDEs after PBDEs were found in food. Structural similarities between PBDEs and PCBs also suggest that food would be the main source of exposure to PBDEs since food is the primary source of human exposure to PCBs. However, more recent studies indicate that indoor dust may be a greater contributor to human exposures than food, especially for infants and toddlers.<sup>80,81</sup> Two recent Canadian reports estimate that 80 to 90% of a toddler's daily average intake of PBDEs comes from dust.<sup>82,83</sup> These studies also suggest that food is the main source of PBDEs intake for most adults, except for individuals who may encounter very high dust levels.

### Food

An earlier analysis of multiple exposure sources (air, water, food, and dust) by Health Canada estimated diet as the main route of exposure to PBDEs for adults in the general public.<sup>84</sup> However, dust was identified as the main source of exposure for 0-6 month old infants who were not breastfed, indicating that the contribution of different PBDE sources to total exposure can vary with age-related behaviors. A recent study based on food and air measurements, also from Canada, estimated that 96% of a person's total intake of PBDEs was through diet, however this

study did not include household dust exposures.<sup>85</sup> A study in the U.K. that evaluated PBDEs in indoor air and diet estimated that 93% of a person's total daily intake of PBDEs came from food.<sup>86</sup> A recent study among urban anglers in New York and New Jersey investigated the contribution of intake of locally caught fish to blood PBDE levels. This study found that consumption of locally caught fish did not appear to be a major contributor to PBDE exposures in this population.<sup>87</sup>

#### Breast milk

Recent assessments have shown that nursing infants are mainly exposed to PBDEs through breast milk.<sup>88,89</sup> In an analysis by Health Canada, breast-fed 0-6 month old infants were identified as having the greatest exposures of all age groups, with 92% of their exposure coming from breast milk.<sup>90</sup> Studies of PBDE levels in maternal and cord blood indicate that prenatal exposure to PBDEs occurs.<sup>91,92</sup> While the levels of PBDEs in breast milk are of concern and will likely be monitored further by researchers, health agencies including DOH continue to recommend breastfeeding as the best choice for feeding infants.<sup>93</sup> Breast milk contains factors that boost the immune system and develop brain tissue, and may well protect the infant from the effects of prenatal exposure.

#### Levels in different types of foods

There are some recent data on levels of PBDEs in food in the U.S. (Table 5). Two studies tested mainly foods of animal origin bought at grocery stores in Texas or California. The highest concentrations of total PBDEs were found in fish. These studies, however, used small sample sizes, especially for diary products, meat and poultry. In another study, the U.S. Department of Agriculture (USDA) collected meat and chicken fat products from nine grocery stores nationwide finding PBDEs levels in these samples to be highest in chicken and pork fat.

Studies in Texas and California of store-bought food, including fish, meat and dairy products, reported higher levels of PBDEs than similar studies in Japan and Spain.<sup>94,95</sup> USDA testing of meat indicated that PBDEs in pork and chicken were higher in the U.S. compared to levels reported in Europe, but that PBDE levels in beef were similar.<sup>96</sup> Studies in the U.S. and other countries report that fish contain the highest PBDE levels of different foods tested.<sup>97,98,99</sup> A study in Sweden reported that increasing blood plasma levels of PBDEs were associated with increasing intake of fatty fish (mainly salmon and herring).<sup>100</sup> A study in Japan found higher PBDE levels in breast milk from women who had higher dietary intake of fish and shellfish.<sup>101</sup>

### Fish still part of a healthy diet

While some of the higher levels of PBDEs have been detected in fish, DOH continues to encourage people to eat a variety of fish as part of a healthy diet. Fish are an excellent source of protein and beneficial fatty acids. Currently, there are no fish consumption advisories in Washington State related to PBDEs. Choosing fish low in PCBs and mercury and preparing fish and meats in ways that reduces fat will also reduce the levels of PBDEs. For additional information on the health benefits of eating fish and existing fish consumption advisories and recommendations, please visit DOH's "Fish Facts" website at <u>http://www.doh.wa.gov/fish</u>.

#### Need for additional data

Additional data on PBDEs in a variety of foods (including foods not derived from animal products) are needed to provide a complete picture of possible dietary exposures to PBDEs. A person's dietary intake of PBDEs will depend on the amounts and types of food they eat. For

example, a recent study in the U.K described lower PBDE dietary intakes among people who ate vegan (non-animal based) diets compared to those who ate animal products.<sup>102</sup>

Tuote e. Let		L5 III 1000 II0III (	ine 0.5., Japan and	Europe.		
Location (date)	Type of sample	PBDE congeners	Food (Sample size)	Total PBDE Concentration, ppt wet weight,	Ref.	
(uale)	sample			except where noted <sup>a</sup>		
Texas (2003)			Fish (9)	Median 1725; range 8.5–3078		
			Meat (9)	Median 283; range 0.9-679		
	Grocery	13 total including	Dairy products (9)	Median 31.5; range ND -1373	103	
	stores	BDE-47, 99, 100,	Soy formula (1)	16.9		
		153, 154, 209	Eggs (1)	73.7		
			Calf liver (1)	115	1	
California (2003 and 2004)		25 total including	Fish, wild (8)	Range 255 – 4955	1	
	Grocery		Fish, farmed (5)	Range 506 – 3063	104	
	stores	BDE-47, 99, 100,	Meat (3)	Range 164 – 379		
	510105	153, 154, 209	Fowl (6)	Range 196 – 2516		
			Bacon (11)	Mean 296; range ND – 7831;		
		BDE-28, 47, 99, 153, 154, 183. 209	Bacon (11)	BDE-209 ND		
Nine U.S. cities (2001)	Grocery		Chicken fat (17)	Mean 1593; range 86 – 8965; mean BDE-209 1845	105	
	stores	data given separately.	Steak fat (11)	Mean 165; range ND – 586; BDE-209 ND		
		separatory.	Pork fat (9)	Mean 1282; range 17 – 7831; mean BDE-209 1913		
			Eich & challfich (0)		├	
	Grocery stores	BDE-47, 99, 153, 154, 183	Fish & shellfish (8)	Mean 333.9 <sup>a</sup>	-	
			Meat (15)	Mean 109.2 <sup>a</sup>	106	
			Eggs (2)	Mean 64.5 <sup>a</sup>		
Spain (2000)			Milk (2)	Mean 16.9 <sup>a</sup>		
			Dairy products (2)	Mean 47.9 <sup>a</sup>		
			Fats and oils (3)	Mean 587.7 <sup>a</sup>		
	500105		Fruits (6)	Mean 5.8 <sup>a</sup>		
			Cereals (4)	Mean 35.7 <sup>a</sup>		
			Pulses (2)	Mean 10.7 <sup>a</sup>		
			Tubers (2)	Mean 7.4 <sup>a</sup>		
			Vegetables (8)	Mean 7.9 <sup>a</sup>		
Japan (2001)	Grocery	BDE-28, 47, 99,	Fish (16)	Median 1400; range 17.7-1720		
			Shellfish (2)	Median 52; range 43 – 61	107	
	stores	100, 153, 154	Meat (3)	Range 6.25 – 63.6		
			Vegetables (3)	Range 38.4 – 134		
U.S., U.K.,	Eist Comme	43 congeners	Salmon, farmed	Median 2500 (approx.); range 500 –		
Norway, and Norway and and fish		including BDE-28,	(153)	4000 (approx.)	108	
Canada (2001		47, 99, 153, 154,	Q - 1	Median 150 (approx.); range 100 –		
and 2002)	suppliers	183	Salmon, wild (45)	4200 (approx.)		
Sweden (1999)	Grocery	BDE-47, 99, 100,	Diary Products (sample size not provided)	Mean 360 ppt (lipid basis)	109	
	stores	153, 154	Meat Products	Mean 360 ppt (lipid basis)		
			Eggs	Mean 420 ppt (lipid basis)	1	
Europe (inc. North Sea and Baltic Sea) (various years)	Not provided	BDE-47 only or various congeners	Herring (Sample size not provided)	Range 17,000 – 528,000 ppt (lipid basis) total PBDEs; Range 9,000 – 100,000 ppt (lipid basis) BDE-47 only.	110	
Scotland and Belgium (1999 and 2001)	Fish markets	BDE-28, 47, 71, 75, 66, 99, 100, 153, 154	Salmon, farmed and wild (13)	Range 1,100 – 85,200 ppt (lipid basis)	111	

Table 5. Levels of PBDEs in food from the U.S., Japan and Europe.

ppt = parts per trillion; ND = non-detectible; Ref = Reference <sup>a</sup> Mean values are assumed because actual method of calculation is unclear from the report.

### <u>House dust</u>

PBDEs have been detected in dust from homes and other buildings. Studies have identified mainly Penta-BDE associated congeners and BDE-209 in dust. House dust sampled from 10 homes across the U.S. found that BDE-47, BDE-99 and BDE-209 were found in the highest concentrations.<sup>112</sup> Another recent study of household dust from 16 U.S. homes found that Penta-BDE congeners (BDE-47, -99 and -100) and BDE-209 accounted for most of the total PBDEs detected.<sup>113</sup> A study of dust in Parliament buildings from eight European countries identified BDE-209 as the predominant congener.<sup>114</sup> Computer wipe samples collected from 16 offices around the U.S. detected PBDEs, with BDE-209 found as the predominant congener, although levels of Penta-BDE congeners were not reported.<sup>115</sup>

PBDEs are found in higher levels in house dust in the U.S. than in Europe. The contents of vacuum bags were used to assess household dust exposures to PBDEs in a total of 20 U.S. and German homes.<sup>116</sup> This study found that BDE-47, BDE-99 and BDE-209 were present in the highest concentrations and that U.S. samples were approximately 50 times higher than samples from Germany. Household dust collected in Massachusetts had 5-10 times higher levels of PBDEs than levels reported for Germany and the U.K.<sup>117</sup>

It is currently unclear what sources or behaviors are responsible for the levels of PBDEs found in dust. Studies have not found correlations between levels of PBDEs in house dust and characteristics of the house such as the year of construction, type of flooring or the number of home electronics.<sup>118,119</sup>

### <u>Indoor Air</u>

Higher PBDE levels have been found in indoor air than in outdoor air. A study in Canada used organic window films as a measure of ambient air levels of PBDEs both indoors and outdoors.<sup>120</sup> In general, PBDEs in indoor films were 1.5-20 times higher than outdoor films. Exterior window films in urban areas had approximately 10 times higher PBDE levels than in rural areas. BDE-209 was the predominant congener detected in the indoor and outdoor organic window films. A study in the U.K. measured Penta-BDE congeners (BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154) inside homes and offices and in outdoor air.<sup>121</sup> Indoor levels were reported to be 120-150 times higher than outdoor levels. Workplaces were found to have approximately eight times higher concentrations of PBDEs than homes. (See Workplace discussion below.) A recent study of 74 homes in Ottawa, Canada found that indoor air levels of total PBDEs (BDE-17, -28, -47, -99, -100, -153, -154) were approximately 50 times higher than outdoor air levels.<sup>122</sup>

Studies report that indoor air levels vary widely between homes and within buildings. For example, the study of Ottawa homes reported a thousand-fold difference between the lowest and highest total PBDE concentrations.<sup>123</sup> The study from the U.K. reported that total PBDE levels varied from 100 to 15,000 pg/m<sup>3</sup> within different rooms of one building at a university. The reason for the variability in PBDE indoor air levels is not well understood, but is likely related to the presence of PBDE containing products as well as other factors including ventilation and activities that can liberate PBDEs. The U.K. study reported that PBDE levels in indoor air increased with an increasing number of electrical appliances (including computers) and with increasing numbers of polyurethane foam chairs. In the Ottawa study, the highest indoor air

PBDE levels were in homes that had recently been paint stripped and insulated, had new windows installed, received new carpets or had new electronics.

For additional information on PBDEs in indoor and outdoor air, refer to the section on "PBDEs and the Environment," later in this chapter.

### Human Exposure Pathways to PBDEs – Workplace

Occupational studies of PBDE exposures have mostly been conducted in Sweden. These studies suggest that workers engaged in electronics recycling, or the manufacture or disposal of PBDE-containing products, may be exposed to PBDEs in the workplace. The highest concentrations of PBDEs in air were found in an electronics recycling facility; elevated PBDE levels were also found in the blood of electronic dismantlers. Blood tested from these workers contained Penta-, Octa- and Deca-BDEs. More research on workplace exposures is needed.

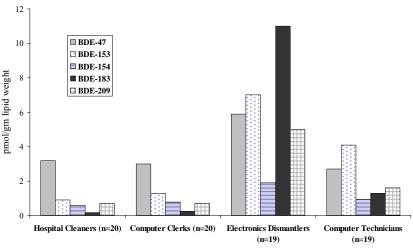
### <u>Air</u>

PBDEs have been detected in air samples taken from a variety of workplaces (an electronics recycling plant, a factory assembling printed circuit boards, a computer repair facility, and offices equipped with computers).<sup>124</sup> The highest PBDE concentrations in air were found at the electronics recycling plant, where products such as computers, printers, TVs, and microwave ovens were dismantled and the plastic components shredded. PBDEs, especially Deca-BDE, are used in some plastic components of electronics. BDE-183 and BDE-209 were the most abundant congeners detected at the electronics recycling plant, while BDE-47 was the most abundant congener detected in air sampled from other workplaces. PBDEs were mostly associated with airborne particles. However, the airborne BDE-209 levels at the electronics recycling plant were more than 25,000 times lower than the Workplace Environmental Exposure Level (WEEL) of 5 mg/m<sup>3</sup> set by the American Industrial Hygiene Association.<sup>125</sup> For comparison, the Washington State occupational exposure limit for PCBs is 1 mg/m<sup>3</sup> as an 8-hour time-weighted average. There are currently no occupational exposure limits for PBDEs in Washington State.<sup>126</sup>

### <u>Blood</u>

A Swedish study evaluated the PBDE levels in the blood of three occupational groups: workers at an electronics recycling facility, hospital cleaners and computer clerks. Workers who dismantled electronics at a recycling facility had higher blood levels of PBDEs than hospital cleaners and computer clerks (control groups).<sup>127</sup> The PBDE congeners found in the workers' blood were different in these three occupational groups. BDE-47 was the congener detected at the highest levels in the blood of the two control groups; however, BDE-183 and BDE-209 were detected at high levels in the blood of the electronics dismantlers (Figure 4). Computer technicians had higher PBDE levels in their blood compared to hospital cleaners and computer clerks, but not as high as in electronics dismantlers.<sup>128</sup> In the computer technicians, BDE-153, BDE-183 and BDE-209 contributed more to the total PBDEs measured in blood compared to the two control groups. A recent follow-up study reported a reduction in blood levels of BDE-183 and BDE-183 and BDE-209 among electronics dismantlers following workplace changes such as upgrading the ventilation system and moving some equipment outside.<sup>129</sup> However, PBDE blood levels of electronics dismantlers.

A recent study found elevated levels of Deca-BDE among workers in rubber manufacturing and handling.<sup>130</sup> Specifically, this study evaluated exposures to Deca-BDE from its use in the production of some flame-retarded rubber. The deca-BDE levels in the blood of the rubber workers were 15-fold higher than the comparison group (slaughterhouse workers). Octa- and nona-BDEs were also elevated in the rubber workers' blood.



Sources: Sjodin et al., 1999 and Jakobsson et al., 2002.

Figure 4. Serum PBDE levels in four occupational groups (Sweden)

#### Estimates of human daily intake of PBDEs

Several studies have estimated the daily intake of PBDEs for people in different countries (Table 6). While many of these estimates have primarily focused on diet, more recent estimates include exposures from air and occupational exposures. Several estimates of human exposures identify infants and children as the most highly exposed groups.<sup>131,132</sup>

Daily PBDE intake	Country	Age	Sources of	PBDE congeners	Ref.
(mg/kg-bw i/day)	-	-	exposure		133
0.0000007	Sweden	adult infant (0-6 mo.)	food	47, 99, 100, 153, 154	
	0.00001 <sup>a</sup> Sweden		breast milk	47, 99, 100, 153, 154	134
0.00000062 <sup>b</sup> (0.044 μg/day)	Canada	adult	food	28, 47, 99, 100, 153, 154	135
0.00000019 – 0.000003 <sup>b</sup> (0.013-0.213 µg/day)	The Netherlands	adult	food	28, 47, 99, 100, 153, 154	136
0.00000140000011 <sup>b</sup> (0.097-0.082 µg/day)	Spain	adult	food	Sum of tetra- to octa-BDEs	137
0.00000059 <sup>b</sup> (0.041 μg/day)	Sweden	adult	food	47, 99, 100, 153, 154	138
0.0000013 <sup>b</sup> (0.091 μg/day)	U.K.	adult diet, air, occupational		47, 99, 100, 153, 154	139
0.00000073 <sup>b</sup> (0.051 μg/day)	Canada	infant	breast milk	Sum of tri-BDEs to hepta-BDEs	140
0.00000043 <sup>b</sup> (0.030 μg/day)	Canada	adult	diet, air, occupational	Sum of tri- to hepta-BDEs	141
0.0002 -0.0026	Canada	0-6 mo., 0.5-4, 5-11, 12-19, 20-59, 60+ yrs.	air, water, food, breast milk, and dust	Sum of (tetra- to deca-BDEs)	142
0.000355 (U.S) 0.000011 (Germany)	U.S. and Germany	nursing infants	breast milk	17, 28, 47, 66, 77, 85, 99, 100, 138, 153, 154, 183, 209	143
max 0.000004 (child); max 0.000003 (adult)	U.S. (CA)	children (<18 yrs) and adults	food (fish, meat, fowl)	Sum of (mono- to deca-BDEs)	144
0.00004-0.0009	U.S.	<1 yr, 1-2 yrs, 3-5 yrs.	multiple pathways	Penta-BDE congeners	145, 146
0.000014 - 0.000054 °	U.S.	adult women	back-calculated from tissue levels	Total; mostly 47, 99, 100, 153, 154	147

Table 6. Estimates of PBDE daily human intake for different countries.

Notes: mg/kg, milligram per kilogram bodyweight per day; µg/day, microgram per day; Ref., reference

<sup>a</sup> Calculated from value in cited reference using an assumed 7.5 kg bodyweight for infant.

<sup>b</sup> Calculated from value in cited reference using an assumed 70 kg bodyweight for adult.

<sup>c</sup> Calculated from value in cited reference using an assumed 62 kg bodyweight for adult woman.

## **Toxicity of PBDEs**

Information on the possible health impacts of PBDEs comes primarily from animal toxicity studies. In general, these studies indicate that Penta-BDE commercial products, and specific PBDE congeners found in these products, are more toxic than Octa-BDE and Deca-BDE (i.e. Penta-BDE produces adverse effects in animals at lower levels than Octa-BDE or Deca-BDE). Table 7 shows the doses (milligrams PBDE per kilogram of bodyweight per day: mg/kg/day) at which health effects were observed in animal studies, demonstrating the differences between PBDE products. An overview of health effects associated with each of the three commercial products (Penta-BDE, Octa-BDE and Deca-BDE) is provided below (and see Table 7). Several recent reports and articles provide reviews of available PBDE toxicity studies and are recommended as sources of additional background information.<sup>148,149,150,151,152</sup> (Potential human

health impacts were evaluated as part of the cost-benefit analysis; for additional information, see also Chapter VI.)

#### Penta-BDE

Animal toxicity studies have been used to evaluate commercial Penta-BDE products (consisting of a mixture of PBDE congeners -- see Table 4) and the predominant congeners in the commercial product (BDE-47 and BDE-99). Based on available studies, the toxicity endpoints of greatest concern are adverse effects on neurobehavioral development, reproduction, thyroid hormone disruption and possibly liver toxicity. The most sensitive toxic effects (i.e. effects that occur at the lowest dose) associated with Penta-BDE congeners appears to be developmental neurotoxicity and developmental reproductive effects. Impacts on brain function (including changes in behavior, learning and memory) have been observed in rodents exposed to Penta-BDE products either in the womb (*in utero*) or soon after birth (post-natally). Some of these effects persisted and worsened into adulthood. The lowest dose that produced developmental neurotoxic effects in these studies is 0.8 mg/kg.<sup>153,154,155</sup>

Exposure to Penta-BDE commercial products and BDE-99 has been shown to decrease thyroid hormone levels in rodents exposed *in utero* and after birth at doses of 1 mg/kg.<sup>156</sup> Adequate thyroid hormone levels are necessary for normal brain development *in utero* and post-natally.<sup>157</sup> In humans, the critical time of rapid brain growth occurs during the final trimester of pregnancy and extends after birth until the age of two years.<sup>158</sup> However, similar impacts on thyroid hormone levels have not been observed in humans and scientists are continuing to evaluate the relevance of rodent studies for predicting human health hazards. Penta-BDE may also impact other hormone systems, with estrogen-like activity being one possible mechanism.<sup>159</sup> Recent animal studies report impacts on both male and female reproduction, occurring at doses as low at 0.06 mg/kg.<sup>160,161</sup> Effects seen in these studies include changes in both male and female reproductive systems.

No animal cancer studies have been conducted on the commercial Penta-BDE product or the congeners present in the commercial mixture. Penta-BDE has been found to be negative in several mutagenic tests. Various congeners present in Penta-BDE mixtures display dioxin-like activity (binding to the aryl hydrocarbon receptor (AhR)). PBDE congeners display binding affinities that are 2-to-5 orders of magnitude lower than 2,3,7,8-TCDD (tetrachlorodibenzo-paradioxin; 2,3,7,8-TCDD).<sup>162</sup>

The Agency for Toxic Substances and Disease Registry (ATSDR) has established several Minimal Risk Levels (MRLs – defined below) for lower PBDEs:

- intermediate inhalation exposure (0.006 mg/m3 based on endocrine effects)
- acute oral (0.03 mg/kg/day)
- oral intermediate exposure (0.007 mg/kg/day based on endocrine effects),
- chronic oral exposure (0.0008 mg/kg/day based on liver toxicity).<sup>163</sup>

Evaluations sponsored by the Great Lakes Chemical Corporation through EPA's Voluntary Children's Chemical Evaluation Program included toxicity assessment which produced toxicological values based on thyroid effects (0.04 mg/kg/day) and developmental effects (0.07 mg/kg/day).

Note: A *Minimal Risk Level* – MRL -- is an ATSDR estimate of daily human exposure to a hazardous substance at or below which that substance is unlikely to pose a measurable risk of harmful (adverse), noncancerous effects. MRLs are calculated for a route of exposure (inhalation or oral) over a specified time period (acute, intermediate, or chronic). MRLs should not be used as predictors of harmful (adverse) health effects.

## **Octa-BDE**

Octa-BDE and/or congeners present in the commercial mixture have been shown to be neurotoxic <sup>164</sup> and are able to disrupt the endocrine system (thyroid hormone levels) in animals.<sup>165</sup> Fetal toxicity has been identified as a sensitive toxic endpoint in rat and rabbit studies involving Octa-BDE.<sup>166</sup> Exposure in the womb resulted in bone malformations and decreased fetal weight in rat and rabbit offspring beginning at doses of 2 mg/kg with fetal death occurring at higher doses. Liver changes were also observed in animal studies following exposure to Octa-BDE products at 10 mg/kg or higher.<sup>167,168</sup>

Available toxicological studies were reviewed as part of the EPA's Voluntary Children's Chemical Evaluation Program and calculated toxicity values for three non-cancer endpoints:<sup>169</sup>

- 1. reproductive/developmental effects (0.09 mg/kg/day based on decreases in maternal and fetal body weights);
- 2. thyroid effects (0.09 mg/kg/day based on decreases in thyroid hormone (T4) levels and thyroid hyperplasia); and
- 3. liver enzyme induction (0.003 mg/kg/day = IRIS RfD value) (RfD = Reference Dose).

## Deca-BDE (BDE-209)

BDE-209 is a large molecule and is generally considered to be less toxic than less-brominated congeners. Indeed, most of the concern about BDE-209 is driven by its potential to degrade in the environment to less-brominated congeners. (The degradation of Deca-BDE is discussed in detail in Chapter IV and Appendix D.) In the past, researchers had thought that the molecule's size would prevent it from being absorbed into the body.<sup>170</sup> However, recent studies indicate that BDE-209 is partially absorbed from the gut of rats and has been found in human tissue samples, indicating that some absorption occurs.<sup>171</sup>

Results from animal studies provide some evidence of toxic effects associated with exposure to BDE-209 including neurotoxicity,<sup>172,173</sup> thyroid hyperplasia, liver toxicity and carcinogenicity at high doses. The results of some of these studies have been questioned because of statistical design, relevance of animal test results for predicting human health hazards (e.g. relevance of thyroid effects in animals) and the high dose levels used in the animal cancer study. ATSDR has established a Minimal Risk Level for deca-BDE (oral intermediate exposure (10 mg/kg/day based on developmental effects)).<sup>174</sup>

Associated PBDE product	PBDE congener or product	Endpoint	Duration/time of exposure (animal)	Lowest Observed Effects Level (mg/kg/day)	Ref.
	BDE-47	Developmental neurotoxicity	1 day/post-natal day 10 (rat)	0.8	175
Penta-BDE	Penta product	Decreased thyroid hormone (exposure during development)	15 days/gestational days 6-20 (rat)	1.0	176
	BDE-99 Developmental reproductive effects		1 day/ gestational day 6 (rat)	0.06	177
Octa-BDE	Saytex 111(Octa- BDE commercial product)	Fetotoxicity	13 days/ gestational days 7-19 (rat)	2-5	178
	Octa-BDE product	Liver changes	28 days and 13 weeks (rabbit)	10	179;180
	BDE-209	Developmental neurotoxicity	1 day/post-natal day 3 (mouse)	20.1	181
Deca-BDE	Deca-BDE Thyroid changes, liver and kidney effects and fetal death		30 days (rat)	80	182
	Deca-BDE	Cancer	103 weeks (rat and mouse)	1120 - 3200	183

Table 7. Lowest observed effect levels in PBDE animal toxicity studies.

Notes: mg/kg/day = milligram of PBDE per kilogram of bodyweight per day; Ref = Reference.

## Issues with Predicting Human Effects from Animal Studies

# Comparing the Levels of PBDE Effects from Animal Studies to Estimates of Human Exposure

Environmental health agencies, including the U.S. EPA, rely on both animal and human toxicity studies to establish various criteria for the protection of human health. One important criterion is determining the level (for a given chemical) below which adverse human health effects are not expected. These so called "safe doses," as derived by EPA, are known as oral reference doses (RfDs). In order to provide adequate protection for human health, toxic effects levels observed in animals or humans are divided by uncertainty (or safety) factors to give the lower, and more protective RfD. Factors of 10 to 10,000 are typically used to account for uncertainties when using animal toxicity data to derive an RfD. A nearly identical process is used by ATSDR to set Minimal Risk Levels (MRLs). It is the RfD, not the toxic effect level itself, that should be used to estimate whether or not exposure to a contaminant in the environment represents a potential health risk. The magnitude of the risk can be inferred by the degree to which the RfD is exceeded. Background information on safety factors and the derivation of RfDs can be found in several U.S. EPA guidance documents.<sup>184,185</sup>

The levels at which toxic effects have been observed in animal studies for Penta-BDE congeners (Table 7) are between 10 to 1,000,000 times higher than estimates of daily human intake of total

PBDEs (Table 6). Estimates of adult intake based on multiple sources of exposure have yielded higher intakes compared to estimates based on food intake only. For example, recent daily intake estimates based on diet, air and other sources range from 0.0002 – 0.0026 mg/kg/day for total PBDE (tetra to deca-BDE congeners) and 0.00004 – 0.0009 mg/kg/day for Penta-BDE congeners. This intake estimate for Penta-BDE congeners is between about 60 to 1,500 times lower than the lowest effect level reported from animal studies for BDE-99 of 0.06 mg/kg/day. This indicates that at least one study has predicted human intakes of Penta-BDE within the range of RfDs or MRLs that could be derived from existing animal studies. Newly emerging research will better define appropriate toxicity studies and human exposure estimates upon which new RfDs and MRLs can be derived.

## Studying the Build-up of PBDEs in the Body

PBDEs can build up in the body and remain stored there for years. The term "biological halflife" refers to how long it takes the body to excrete half of an accumulated amount.<sup>186</sup> Different PBDEs have different half-lives.<sup>187</sup> For BDE-47 and BDE-153, human half-lives of 2 to 26 years have been predicted, respectively.<sup>188</sup> BDE-209 has a much shorter half-life, estimated to be about two days to one week in people, while the half-life estimated for BDE-183 is three months.<sup>189,190</sup> Half-lives of tetra-, penta- and hexa-BDEs in rats are much shorter than for people, ranging from about 19 to 119 days.<sup>191</sup>

Many of the rodent toxicity studies described above, especially the studies evaluating developmental toxicity, involve exposing rodents to PBDEs for durations of a single day to weeks. However, people are most likely exposed to PBDEs continually from many sources resulting in a build-up of many PBDEs over time. Therefore, the toxic effects levels presented in Table 7 are not directly comparable to most of the human exposure estimates presented in Table 6 because of differences in half-lives and exposure durations between rodents and people.

Body burden (i.e. accumulated amount of PBDEs in the body) is a better measure than daily intake when comparing rodent and human exposures. Body burdens will vary depending on the type of PBDE, the amount and duration of exposure, as well as on individual differences in absorption, metabolism and excretion. One recent report suggests that after adjusting for PBDE body burdens between rodents and humans, high-end human exposures appear to be approaching toxic effects levels observed in animal studies, mainly for Penta-BDE associated congeners.<sup>192</sup> A follow-up report suggests that the estimated daily intakes of women at the high end (95th percentile) of exposures currently exceed effects levels observed in animal studies for the most sensitive health endpoint (reproductive changes).<sup>193</sup>

## **PBDEs and the Environment**

PBDEs were first detected in the environment in 1981 in the River Viskan, downstream from a textile manufacturing plant southwest of Stockholm.<sup>194,195</sup> Subsequent studies, primarily in Europe, North America, and Japan, indicate that PBDEs are ubiquitous in sediment and biota, and that their levels appear to be increasing rapidly. Levels detected in the U.S. tend to be much higher than those detected in similar media in Europe or Japan. While PBDEs are the subject of

increasing study, knowledge of environmental behavior, exposure, and toxicity remains limited. Specific data on the presence of PBDEs in Washington State is also limited.

## Air

PBDEs have been detected in air, both outdoor and indoor. Strandberg et al. found that PBDEs were widely distributed in the air over the Great Lakes region and could be transported to rural remote regions from urban areas through the atmosphere.<sup>196</sup>

#### Indoor Air

Many sources of PBDEs are found indoors, resulting in elevated levels of PBDEs in indoor air. Indoor contaminants are less prone to photo-degradation and atmospheric dilution, increasing their persistence. Indoor contaminants have been suggested as a possible source for PBDEs found in humans and breast milk. Butt et al. found that indoor levels of PBDEs in Southern Ontario were 1.5 to 20 times greater than outdoor levels on a site-by site basis. They suggest that indoor air may serve as a significant source of PBDEs to outdoor air.<sup>197</sup>

#### House dust

Four studies have been identified that examined PBDEs in household dust in the U.S. Rudell et al. measured tetra- and penta-BDE in residential dust in five houses on Cape Cod, Massachusetts, with 90<sup>th</sup> percentile concentrations ranging from 0.7 to 4.1  $\mu$ g/g dust.<sup>198</sup>

In 2004, Sharp and Lunder measured concentrations of 13 BDE congeners in dust samples from 10 houses across the U. S. Results varied widely between houses, from 614 to 16,366 ppb (parts per billion) for total PBDEs. One house was treated separately because the study participant had used her vacuum to clean up polyurethane foam residues when she removed carpet padding, two mattress pads, and an uncovered foam cushion from her home. Her sample contained 41,203 ppb total PBDEs. Three congeners, BDE-47, -99, and -209, accounted for 90 percent of the PBDEs by weight. BDE-47 and -99, major components of Penta-BDE; each accounted for 24 percent on average. BDE-209 accounted for an average of 42 percent of the samples. Levels of BDE-209 averaged 2,394, ranging from less than 400 ppb to 7,510 ppb.<sup>199</sup>

Initial studies by Stapleton et al. measured 14 congeners in 16 household dust samples from the Washington, D.C. area. Total BDE concentrations ranged from 310 ng/g dry mass to 30,140 ng/g dry mass.<sup>200</sup>

A more recent study by Stapleton in 2005 examined the degradation of BDE-209 in house dust following exposure to natural sunlight. This study concluded that PBDEs, primarily BDE-209, are susceptible to photolytic degradation, via debromination, following exposure to UV light. Samples of house dust spiked with BDE-209 were sealed in UV plastic cuvettes and placed outdoors in direct sunlight for a total of 90 hours. As a control, samples of house dust in UV cuvettes were kept indoors and wrapped in aluminum foil during the exposure period. Over the 90-hour sunlight exposure, the concentration of BDE-209 in the house dust decreased by almost 30 percent. This decrease coincided with an increase in the concentration of nona-, octa-, and hepta-brominated congeners. A mass balance calculation suggests that 83% of the BDE-209 loss was due to debromination into less brominated congeners. The remaining 17% of the BDE-209

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loss could not be accounted for, suggesting that a portion of BDE-209, or its degradation products, are lost to volatilization processes and/or the formation of unknown products.<sup>201</sup>

## Sediment

PBDEs have been detected in sediment and soil in North America. Song et al. took sediment cores in 2001 and 2002 in Lake Superior at six locations away from lakeshores. In contrast to recent declining or level-off trends in PCB fluxes, the sedimentary records of PBDEs generally show a significant increase in recent years. Excluding BDE-209, concentration of total PBDEs ranged from ranged from 0.5 to 3 ng g<sup>-1</sup>. Concentrations of BDE-209 were about an order of magnitude higher than the sum of the other congeners, comprising 83 - 94 percent of total PBDEs measured in the sediments.<sup>202</sup> Rayne et al. measured PBDE concentrations ranging from 2.7 to 91  $\mu$ g/kg in 11 surficial sediments collected in 2001 from several sites along the Columbia River system in Southeastern British Columbia.<sup>203</sup>

## **Biota**

Animal species appear to vary widely in their ability to metabolize or accumulate specific PBDE congeners. Wolkers et al. examined congener-specific accumulation and prey-to-predator transfer of 22 PBDEs in polar cod, ringed seal, polar bear and beluga whale. PBDE congeners 47, 99, and 100 were dominant in all species studied. The pattern in the ringed seal was somewhat simpler than that of the polar cod, with PBDE 47 being more than 90% of the total PBDEs. Beluga whales, which feed on prey similar to that of ringed seals, showed higher PBDE levels and a more complex PBDE pattern than ringed seals. And in polar bears, only one congener was detected.<sup>204</sup>

Buck measured total PBDEs in bald eagle eggs collected along the Lower Columbia River in Washington and Oregon states at 446 to 1,206  $\mu$ g/kg wet weight.<sup>205</sup>

## Freshwater fish

In 2000, Ecology analyzed 16 freshwater fish samples from various locations in Washington State. Concentrations of total PBDEs ranged from 1.4  $\mu$ g/kg (wet weight) in remote Douglas Creek rainbow trout to 1,250  $\mu$ g/kg in mountain whitefish from the Spokane River. The highest concentrations were found in areas draining urbanized watersheds (Spokane, Yakima and Snake Rivers); concentrations were much lower in undeveloped watersheds (Douglas Creek, Rock Island Creek, and Soleduck River). Results for the latter three watersheds probably represent background for PBDEs in local freshwater fish. Tetra and penta isomers were the major congeners present, in ratios similar to the commercial formulation Penta-BDE. There appeared to be substantial inter-species differences in the ability of the fish to metabolize PBDEs, with relatively low accumulation by large-scale suckers and carp relative to rainbow trout and mountain whitefish.

#### Whales

Rayne et al. measured PBDEs in orcas from three communities from the northeastern Pacific Ocean, including Puget Sound and Georgia Basin. Communities sampled included northern residents, southern residents, and transients. Total PBDE levels were 2 to 10 times greater than those reported for sperm whales from the North Atlantic and pilot whales in the North Sea. The PBDE levels were compared to total PCB levels. Unlike total PCB levels, no significant age-related relationships were observed for total PBDE concentration. Reasons for this difference are unknown and are confounded by the effects of increasing PBDE production levels over the past 20 years, potentially different environmental stability as compared to PCBs, and the unknown influence of lifetime exposure to PBDEs. With PBDE concentrations only 1 to 2.5 orders of magnitude less than total PCB concentrations in orcas in the northeastern Pacific, the authors stated that PBDEs must be considered as one of the potentially dominant organohalogen (that is, organic halogen compounds) contaminants in aquatic biota.<sup>207</sup>

#### PBDE levels increasing

Temporal trends indicate increasing levels of PBDEs in animals. Ikonomou et al. measured the blubber of Arctic male ringed seals over the period 1981 to 2000. Mean total PBDE concentrations increased exponentially from approximately 0.6  $\mu$ g/kg lipid in 1981 to 6.0  $\mu$ g/kg lipid in 2000.<sup>208</sup> Between 1989 and 1998, PBDE concentrations in tissue from harbor seals in San Francisco Bay doubled every 1.8 years.<sup>209</sup> Lebeuf et al. measured PBDEs in blubber from beluga whales in the St. Lawrence Estuary in Canada for the period 1988 to 1999. Total PBDEs increased exponentially over the period, with a doubling period of no longer than three years.<sup>210</sup>

Table 8 summarizes PBDEs measured in North American biota.

Organism Location; year		Total PBDEs	Reference	
	Biota measured in Pacific Northwe	st		
Dungeness crab hepatopancreas	West coast, Canada; 1993 - 1995	4.2 – 480 μg/kg lipid	211	
Bald eagle egg	Lower Columbia River, Washington and Oregon, 1994 - 1995	446 – 1,206 μg/kg ww	212	
Heron egg	British Columbia; 1983 - 2000	1.308 – 288 μg/kg ww	213	
Orca blubber	Northeastern Pacific Ocean; 1993 - 1996	87 – 1,620 μg/kg lipid	214	
Mountain whitefish (muscle)	Columbia River, British Columbia; 1992 - 2000	0.726 – 131 µg/kg ww	215	
Rainbow trout		297 µg/kg ww		
Mountain whitefish	Spokane River, Washington; 1999	1250 µg/kg ww	216	
Largescale sucker		105 µg/kg ww		
	Biota measured in other areas of North A	merica		
Murre egg	Northern Canada; 1975 - 1998	0.442 – 2.93 μg/kg ww	217	
Fulmar egg	Northern Canada; 1975 - 1998	$0.212 - 2.37 \mu g/kg ww$		
Herring gull egg	Great Lakes; 1981 - 2000	9.4 – 1544 μg/kg ww	218	
Beluga whale blubber	Canadian Arctic	81.2 – 160 μg/kg lipid	219	
Beluga whale blubber	St. Lawrence Estuary, Canada, 1988 - 1999	17.2 – 935 μg/kg lipid	220	
	Lake Ontario; 1997	95 μg/kg ww		
Lake trout	Lake Erie; 1997	27 μg/kg ww	221	
Lake Hout	Lake Superior; 1997	56 μg/kg ww		
	Lake Huron; 1997	50 μg/kg ww		
Carp Virginia; 1998 - 1999		1140 μg/kg ww	222	

#### Table 8. Measured concentrations of PBDEs in North American biota

ww = wet weight

#### Bears

Christensen et al. investigated persistent organic pollutant (POP) concentrations, including PBDEs, in connection with the eating patterns in two feeding groups of grizzly bears in Western Canada. One group, referred to as "maritime grizzlies," residing predominately along the Coast Range, consume a diet high in salmon. The maritime grizzly bears carried more POPs and a very different group of contaminants than "interior" grizzlies that lived predominantly on a plant diet. The differing feeding habits provided an unique opportunity to dissect pathways of exposure to a variety of bioaccumulating global contaminants. The study concluded that the maritime grizzly population's diet is similar to that of other top predators in that they are exposed to more global bioaccumulating contaminants than interior grizzlies. On the other hand, the interior grizzlies are storing more PBDEs, especially the heavier PBDE congeners (BDE-209). The study suggests that the atmospheric transport of BDE-209 is greater than predicted.<sup>223</sup>

#### Soils and earthworms

Sellstrom et al. analyzed for PBDEs in soils and earthworms located at three research stations and two farms in Sweden that were amended with sewage sludge. Sewage sludge amendment at the research stations increased concentrations of all BDE congeners 2- to 13- fold, with the highest increases for BDE-209. Concentrations 100- to 1000-fold higher were seen in soils at the two farms. BDE-209 was the predominant congener in all soils.<sup>224</sup> The sum of the PBDE concentrations in worms ranged from 3.1 to 38,000 ng/g lipid weight and were correlated to soil

concentrations, including octa- and deca-BDEs. Biota-soil accumulation factors declined in the following order: tetra-BDE > penta-BDE > hexa-BDE > octa-BDE > nona-BDE > deca-BDE, and ranged from 0.3 to 2 for the octa- and deca-BDEs. Thus, higher-brominated PBDEs, including BDE-209, are bioavailable from soils and accumulate in earthworms, presenting an exposure pathway into the terrestrial food web. High levels found at one farm, 20 years after the last use of PBDEs, indicate high persistence of PBDE in soils, including BDE-209. No evidence of photolytic debromination of BDE-209 in soils was seen.<sup>225</sup> This result is inconclusive as it was only one soil sample and the test was only 21 days long, yet it does illustrate the complexity of PBDE degradation. More tests are needed.

## Long-range transport

Swedish and Dutch scientists measured atmospheric deposition of PBDEs in the Baltic Sea for the first time in research published in January 2004. Measurements were taken from an island in the central basin of the Baltic Sea far from human settlement; deposition of PBDEs would therefore be the result of long-range transport through the atmosphere. The research compared deposition of PBDEs to the better documented deposition of PCBs. The atmospheric deposition of PBDEs was decreasing.

BDE-209 comprised the largest percentage of PBDEs detected, with BDE-47 and BDE-99 representing the next most abundant congeners.

Concentrations of total PBDEs were highly correlated with concentrations of total PCBs, suggesting similar atmospheric transport mechanisms. More detailed regression analysis showed similar regression slopes for total PCBs, BDE-47 and BDE-100, with a different regression slope for BDE-209. The researchers suggest that BDE-209 has different underlying atmospheric transport processes and/or sources than PCBs, BDE-47, and BDE-100. BDE-47 and BDE-100 both originate from the commercial Penta-BDE formulation, which has been phased out in the European Union. The researchers hypothesize that BDE-47 and BDE-100 may originate from secondary sources, where they have accumulated in the environment, such as sediment or soil, while BDE-209 still has primary sources, namely new products containing Deca-BDE. The difference in PBDE congeners reflects the change in usage of commercial PBDE formulations.

BDE-17, a tri-brominated congener, was also detected in air on the Baltic Sea island. It has not been detected in air at source areas, such as electronics recycling facilities and highly urbanized environments. The researchers believe BDE-17 is a breakdown product from atmospheric debromination processes, possibly from BDE-209.<sup>226</sup>

PBDEs have been identified in polar cod, ringed seal, polar bear and beluga whale.<sup>227</sup> PBDE concentrations in Canadian beluga whales increased between 1982 and 1997. PBDEs appear to be increasing in marine mammals and may surpass PCBs as the most prevalent pollutant in arctic habitats.<sup>228</sup>

## **Products Containing PBDEs at End-of-Life**

Pathways for PBDEs from products to the environment are largely unknown. Some of the substance is likely released at the time of disposal. Potential pathways for PBDEs from three generic product types - electronics, automobiles, and upholstered furniture - are illustrated in Figures 5 through 7. Not all electronics, automobiles or upholstered furniture contain PBDEs, but PBDEs are used in all three types of products. The product types were chosen to show the wide variety of possible pathways. The volume of PBDEs released to the environment at any point illustrated below is unknown.

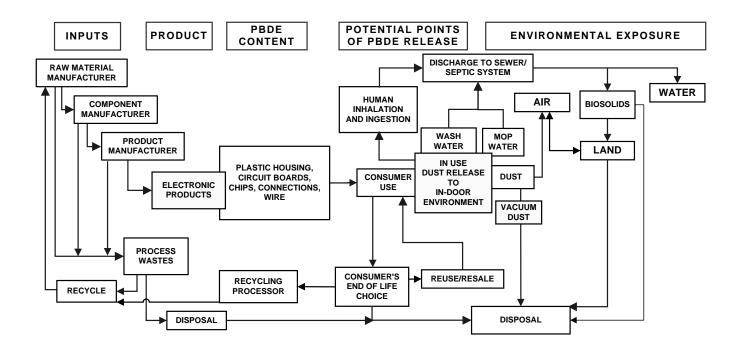


Figure 5. Electronic products and potential PBDE pathways to the environment

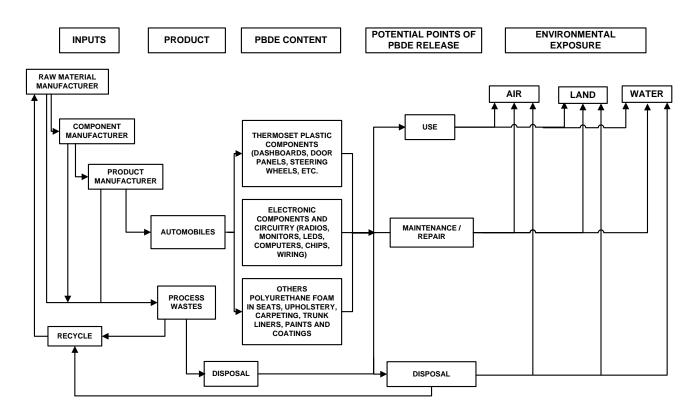


Figure 6. Automobiles and potential PBDE pathways to the environment

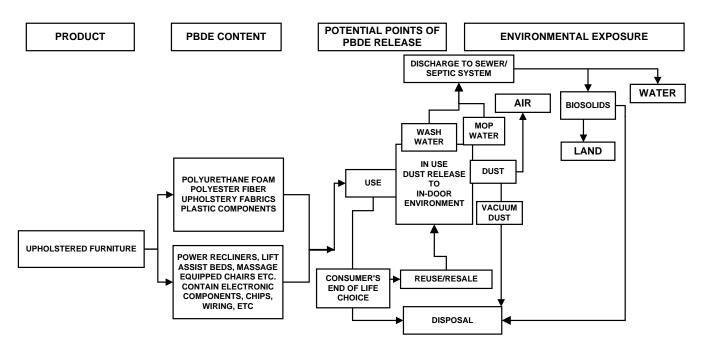


Figure 7. Upholstered furniture and potential PBDE pathways to the environment

Most products containing PBDE are long lived. Automobiles, for example, have a life expectancy of 12 years. Building materials can last 100 years or more. Electronics tend to become obsolete before they wear out, but many remain in storage rather than being discarded.

Waste composition information available for the state of Washington indicates that as much as 6.5 percent, or 360,000 tons annually, of the discarded municipal solid waste stream could be products containing PBDEs. Commercial products can be comprised of as much as 30% PBDEs.<sup>229</sup> (See Table 9.)

Waste category	Percent of total municipal solid waste
Plastics/other materials	2.5%
Electronics	0.3%
Furniture/mattresses	1.4%
Carpet and carpet pad	2.3%
Total percent of waste that may contain PBDEs	6.5%

Table 9. Waste composition analysis for the state of Washington, 2003

## **Electronics Recycling**

Electronics recycling facilities may represent a source of PBDEs to the surrounding environment. Concentrations of ambient PBDEs outside and inside an electronics recycling facility in Southern Ontario were approximately 4.4 and 22 times higher, respectively, than outdoor and indoor ambient PBDEs in Toronto.<sup>230</sup> Workers in a Swedish electronics recycling facility were found to have blood levels of five PBDE congeners that were significantly higher than those found in a control group.<sup>231</sup>

## Landfills

The vast majority of solid waste in Washington is landfilled. With the exception of products diverted for recycling, such as electronics, most products containing PBDEs are probably landfilled in Washington.

Auto fluff is waste that is left over after metals have been separated from shredded scrap cars and other consumer products. A large percentage of auto fluff is made up of plastic and foam, which may or may not contain PBDEs.

Auto fluff, in addition to being generally disposed of in landfills as part of the municipal solid waste stream, is used extensively at the Pierce County Recycling, Composting & Disposal LLC dba LRI Landfill in Tacoma as a daily cover layer over waste. A landfill generally offers a controlled environment for disposal; for example, any PBDE-contaminated liquid that leaches out would be collected and piped off for treatment. Common treatments include recycling the leachate back into the landfill or sending the leachate to a sewage treatment plant. However, the

effectiveness of leachate treatment with respect to PBDEs, and the risks posed by PBDEs in the landfill environment, remain unknown.

## Formation of Polybrominated Dioxins and Furans

Aside from the direct release of PBDEs into the environment, disposal of PBDE-containing substances raises concern about the formation of polybrominated dioxins (PBDDs) and polybrominated furans (PBDFs). Most of these concerns relate to combustion of PBDE-containing plastics and foams that could result in the formation of polybrominated dioxins and furans. Some natural processes also result in formation of such compounds. Chlorinated dioxins and furans have been extensively studied because of their possible carcinogenic and other systemic effects in humans, and brominated dioxins are suspected to have similar effects.<sup>232</sup>

Halogenated dioxins and furans (including brominated ones) form during combustion of halogenated compounds. Formation depends on the availability of halogenated compounds, combustion temperatures in the range of 400 to 1,000°F, and the presence of particles whose surfaces catalyze the reactions.<sup>233</sup>

Dioxins and furans can form during combustion from chlorine-, bromine- or fluorine-ion containing salt and the elements carbon, hydrogen and oxygen, or hydrocarbons, or result from the degradation of halogen-containing compounds (such as plastics, halogenated pesticides and phenols). Photochemical reactions involving UV light and some biological processes may also form dioxins and furans. (See Chapter IV, Degradation of Deca-BDE.)

For all industrial and natural processes that create dioxins, it would be logical to expect dioxins to be present in all products or materials created by the process to the extent such products or materials actually contain organic matter. Accordingly, it would be logical to expect that all residues from combustion processes creating dioxins also contain dioxins. Where dioxins are created during plastic manufacturing, products containing these plastics should be expected to contain dioxins.<sup>234</sup> On the other hand glass and metals containing virtually no organic matter should not be expected to contain dioxins.<sup>235</sup>

## **Municipal Waste Incinerators**

Washington State has one operating municipal waste incinerator, in Spokane. The minimum operating temperature for the Spokane incinerator is 982 C (1800 F) for a 15-minute average and not below 871 C (1600 F) for any reading, as given in WAC 173-434-160. Combustion of plastics containing PBDEs may be an ongoing source of small amounts of brominated dioxins and furans.

## **Biosolids and Sewage Sludge**

Biosolids are sewage sludges processed for land application. PBDEs have been detected in biosolids and sewage sludge in the U.S. and Europe. Hale et al. examined biosolid samples from Virginia, Maryland, New York and California and found significant amounts of tetra-, penta-, and hexa-BDEs with relative contributions that match the commercial formulation of

Penta-BDE. Total concentration was  $1,100 - 2,290 \ \mu\text{g/kg}$  dry weight. The study's authors suggest that this indicates the input was high and consistent, regardless of the region of origin and irrespective of pretreatment application. While penta-BDE congeners were fairly consistent across samples, concentrations of deca-BDE varied widely among U.S. biosolids analyzed.<sup>236</sup> Washington State does not monitor PBDEs in biosolids.

Washington State has five sewage sludge incinerators, located in Anacortes, Bellingham, Edmonds, Lynnwood, and Vancouver. A few smaller communities also send biosolids to these cities to be incinerated. In Washington, the U.S. EPA has the authority to permit sludge incinerators for their emissions. The criteria for sewage sludge incinerators are located in Title 40 of the Code of Federal Regulations, Part 503 ("40 CFR 503") which establishes standards for sewage sludge applied to the land, placed on a surface disposal site (such as a landfill or designated sludge disposal lagoon) or incinerated. Specific requirements for minimum temperatures are not included.

## **Other Burn Facilities**

Ecology is not aware of any facility that specifically burns only plastics or foam. Some wood boilers at pulp mills burn some plastics (mostly polyethylene and some PVC, that is, polyvinyl chloride or vinyl), when the plastic is a contaminant in wood wastes fuel. Boiler temperature is not subject to legal regulation but would typically be in the 1200° to 1800°F range.

## **Episodic Fires**

Episodic fires may be a source of release for PBDDs and PBDFs. A furniture factory, store or even an apartment house blaze may release more PBDDs or PBDFs than an incinerator because of the uncontrolled combustion/pyrolyzing nature of the event.

## Ash Reuse

Chapter 173-306 WAC includes provisions for allowing the reuse of municipal incinerator ash rather than sending ash to landfills. If brominated dioxins and furans were present in substantial quantities, this could be a pathway for release to the environment.

# **IV. Degradation of Deca-BDE**

**IN BRIEF:** Considerable scientific research on the degradation of deca-BDE has been conducted in recent years. (Refer to the scientific literature documented in Appendixes D and E.) Existing studies focus on both how deca-BDE breaks down (by exposure to light, through biological degradation, and others), as well as what the composition of degradation products is. Studies have used a wide range of media (sediments, sewage sludge, and water) and conditions (aerobic, anaerobic, sunlight, UV light, etc.). The degradation of deca-BDE has been evaluated in detail in both laboratory studies<sup>237</sup> and in environmental samples.<sup>238</sup>

In laboratory tests, deca-BDE was found to degrade to lower PBDE species, that is, PBDEs with fewer bromines.<sup>239</sup> The relevancy of these results to conditions deca-BDE may experience in the environment has been questioned. Many of these concerns are legitimate and can only be addressed with additional research. As with many laboratory tests, conditions were often exaggerated in order to determine chemical degradation and dynamics within a useful time period. However, the main difference between laboratory studies and the fate of deca-BDE in the environment is thought to be the rate at which these reactions occur. Therefore, the laboratory results provide valuable information to support the concern that deca-BDE breaks down in the environment.

Ecology and DOH also reviewed many, if not all, of the same technical articles included in the European Union Risk Assessment and its two updates, and have monitored scientific progress since the Interim CAP was published. The Bromine Science and Environmental Forum (BSEF) provided extensive scientific data, which was also carefully reviewed. While further research is needed, Ecology and DOH believe the following conclusions are appropriate:

- 1. Deca-BDE undergoes degradation. The most common path in laboratory studies is the debromination of deca-BDE to lower PBDE species. Other degradation products have been found in some studies, including brominated dioxins, phenols and dibenzofurans. The negative impact these degradation products have upon human health and the environment is unquantified, but the abundance of studies that document negative impacts makes this a matter of considerable concern.
- 2. Debromination of deca-BDE occurs through light exposure (both UV radiation and direct sunlight) and biological activity. These pathways lead to a variety of degradation products.
- 3. The rate of debromination has been determined in laboratory studies. Further work is needed to determine the debromination rate under environmental conditions. Degradation in the environment occurs more slowly. This phenomenon is consistent with whar occurs to halogenated compounds with similar chemical structure, and is supported by knowledge of standard chemical processes.
- 4. Deca-BDE will continue to be a source of lower brominated diphenyl ethers and other degradation products for some time.

<u>Note</u>: The terms "degradation" and "debromination" have similar meanings in the context of this chapter. "Debromination" is the most common degradation process Deca-BDE undergoes: when it degrades, it loses bromine atoms.

## Methods of breakdown: degradation processes

## **Photolytic Degradation**

Photolytic degradation occurs when the energy from light is used to break chemical bonds. In the case of PBDEs, light (sunlight or UV radiation alone) can cause the molecule to debrominate (that is, lose a bromine atom). A number of studies have demonstrated that photolytic degradation of PBDEs does occur, and that it can occur in a variety of circumstances including those that mimic environmental conditions.

In one study the degradation of deca-BDE was evaluated using several solvents, including those more typically found in the environment.<sup>240</sup> For example, in addition to subjecting deca-BDE to both sunlight and UV radiation with a range of organic solvents, tests were conducted on deca-BDE in water both with and without humic acids (as would be found in the environment). Deca-BDE(209) was found to degrade via debromination under all test conditions. Control samples were used in all tests and degradation did not occur in the absence of light.

Sellstrom's work demonstrated that deca-BDE degrades relatively quickly when subjected to light.<sup>241</sup> These studies took place in a hydrogen-rich environment provided by organic solvents, and there was concern that the solvent used was affecting the degradation rate. As part of a later study, Sellstrom analyzed a single sample of biosolids-amended farm soil but was unable to reproduce earlier laboratory results which indicated photolytic degradation of deca-BDE occurs.<sup>242</sup> These latter results need to be treated with caution as they represent only one sample and were conducted over a relatively short period of time (21 days). Other evaluations have been conducted for much longer periods of time, such as 40 to 238 days.

Another study was conducted in water ("aqueous media") with the addition of naturally occurring organics, such as humic acid.<sup>243</sup> These studies proved that similar degradation occurred in aqueous media as with the organic solvents although at a slower rate. A study was also conducted on household dust samples which were spiked with deca-BDE and subjected to sunlight for a total of 90 hours.<sup>244</sup> Deca-BDE was observed to degrade to lower congeners along with other, unidentified products. No degradation was observed in control samples not subjected to sunlight. Additional studies are being conducted by the author to expand upon the conclusions of this study and to address concerns raised with the analytical method.

#### **Biological Degradation**

In addition to photolytic degradation, PBDEs can also degrade via biological mechanisms including microbial degradation. Microbial degradation was examined in a 2005 study by Gerecke et al. An analysis of the inputs and outputs from a sewage plant anaerobic digester indicated deca-BDE degraded to octa- and nona-BDEs.<sup>245</sup> The analyses were conducted both with and without organic compounds that are believed to facilitate the degradation process. Deca-BDE(209) degraded in both tests. Degradation was observed to occur at a slower rate in the samples without the organics. Control samples were also used and exhibited no degradation under sterilized conditions, demonstrating the occurrence of biologically-driven degradation. These results confirmed data from other laboratory studies reported in the same article.

The same authors also attempted to quantify deca-BDE degradation using inlet and outlet samples from an anaerobic digester operating in a wastewater treatment facility. Although an increase in possible degradation products was observed, deca-BDE degradation could not be confirmed.

#### **Other Degradation Processes**

Other degradation processes for PBDEs have been identified. Studies were conducted in water using a variety of reducing agents including iron, iron sulfide and a solution of sodium sulfide.<sup>246</sup> (A "reducing agent" is a chemical which provides electrons to another compound as part of a reaction.) These tests were conducted to determine if the catalysts could be used to decontaminate deca-BDE polluted sites. The data showed that deca-BDE degrades rapidly to lower brominated compounds, including many of the components of Penta-BDE. For example, over the full 40 days of the experiment, deca-BDE was found to degrade into BDE-47, -99, -100, -153 and -154, all of which are found in Penta-BDE.<sup>247</sup> After 14 days, Deca-BDE concentrations were reduced as much as 90% for iron, 33% for sodium sulfide and 2% for iron sulfide. Some concern was raised about the presence of these reducing agents in the environment and the validity of comparing these test results to the fate of deca-BDE in the environment.

Additional studies are needed in this area to better approximate conditions actually experienced in the natural environment, including the impact of small particles upon how light is absorbed, adsorption of the deca-BDE onto small particles and the presence of less favorable hydrogen donors.

## **Degradation Products**

In addition to the methods of breakdown, it is also important to understand what the breakdown products are in order to assess their toxicity. One hurdle which complicates deca-BDE degradation studies in the environment is the large amount of PBDE congeners already present from the commercial production and use of Penta- and Octa-BDEs. It is often difficult to determine contributions from deca-BDE degradation because of the large background concentrations from other PBDE mixtures. In addition, purified compounds to use as standards for many PBDE congeners do not exist and little is known about other possible degradation pathways, which makes identification of degradation products difficult.

In laboratory tests where deca-BDE was subjected to direct sunlight, the debromination reactions continued to lower substituted PBDEs (tri, tetra and penta-BDEs).<sup>248</sup> Very little degradation was found to include the mono- and di-BDEs. In one study, the degradation of deca-BDE was monitored in detail.<sup>249</sup> Deca-BDE was found to degrade to nona- and octa-BDE congeners. One nona-BDE congener (BDE-208) increased in concentration by more than ten-fold (from below the quantitation limit to 0.15 nmole/bottle). A second nona-BDE (BDE-207) increased more than six-fold (from 0.024 to 0.16 nmole/bottle). Similarly, the amount of octa-BDE congeners increased from below the quantitation limit to 0.21 nmole/bottle. In all of these studies, the concentration of deca-BDE decreased.

The same study evaluated the degradation of two nona-BDE congeners (BDE-206 and 207) separately from deca-BDE.<sup>250</sup> Both nona-BDE congeners were found to debrominate to octa-BDEs. Insufficient tests were done to obtain a degradation rate for these compounds. Another study conducted experiments with di-, tri-, tetra- and penta-BDEs.<sup>251</sup> All were found to undergo debromination although the debromination rate was found to decrease with decreasing number of bromines.

Another recent study evaluated the degradation of deca-BDE in house dust.<sup>252</sup> When subjected to a total of 90 hours of direct sunlight, the deca-BDE in the samples lost approximately 30% of its total mass and a corresponding increase was found in nona-, octa- and hepta-brominated congeners. Evaluation of the mass balance for the reaction indicated that 17% of the total mass could not be accounted for. The author suggested this was due to the generation of unknown compounds and/or loss due to evaporation.

These findings agree with the chemistry of other compounds with high electron densities (as deca-BDE has). In compounds such as these, bromine radicals (bromine atoms that, due to presence of an unpaired electron, are extremely reactive and exist only for a short period of time) typically exit the compound with a minimal impact upon the electron density of the remaining structure. Electron density is an evaluation of the amount of electrons present in a compound. Deca-BDE(209) has a high electron density due to the presence of ten bromine atoms. Bromine atoms have a large number of electrons (35) compared with carbon (6) and oxygen (8). Deca-BDE(209), therefore, has 430 total electrons. The exit of one bromine radical has a small impact on the relative number of electrons in the compound (the nona-BDE congeners have 396 electrons for an 8% reduction in electron density from deca- to nona-BDE). The percentage reduction increases with each bromine removal.

As more bromine radicals exit the compound, subsequent debromination reactions occur at a slower rate. The rate of debromination would be highest (fastest) for electron-rich compounds such as deca-BDE and would decrease with each subsequent debromination. The debromination rate would be lowest (slowest) for compounds such as mono- and di-BDE as these compounds have the lowest electron density of any of the PBDEs. This agrees with laboratory studies which indicate deca-BDE is chemically susceptible to debromination reactions.<sup>253</sup>

Many studies were able to account for only a percentage of the total degradation products, usually within 40 to 50 percent.<sup>254</sup> Several reasons were proposed including: 1) insufficient standard availability for all 209 PBDEs which prevented identification of all PBDEs created in the degradation process, 2) generation of other compounds for which no standard exists, 3) formation of bound (non-extractable) deca-BDE residues, and 4) imprecision in the analytical procedures used.

Evidence exists for reaction pathways other than debromination and replacement of bromine with hydrogen. Degradation products have been observed in which methoxy (CH<sub>3</sub>-O- or methanol based) and exothy (CH<sub>3</sub>CH<sub>2</sub>-O- or ethanol based) groups have replaced one of the bromine atoms forming oxygenated PBDEs. Other compounds containing oxygen are also theorized. Additional studies have indicated the presence of brominated dibenzofurans,<sup>255</sup>

brominated phenols,<sup>256</sup> and potential brominated dioxins.<sup>257</sup> However, the exact structure and composition of many of the decomposition products remain unknown.

Studies have demonstrated that deca-BDE degrades relatively quickly when subjected to light.<sup>258</sup> (Refer to the earlier section in this chapter on photolytic degradation.) These studies took place in a hydrogen-rich environment provided by organic solvents, and there has been some concern voiced that the solvent used was affecting the degradation rate. Additional studies have been conducted in water with the addition of naturally occurring organics such as humic acid.<sup>259</sup> These studies proved that similar degradation products were produced in both water and organic solvents, although the aqueous degradation occurs at a slower rate.

In addition, attempts were made to determine whether deca-BDE degradation could be observed from soil and sediment samples taken in the vicinity of facilities either using or producing deca-BDE.<sup>260</sup> Core samples were analyzed to determine if any deca-BDE degradation could be measured over time. The results of this study were inconclusive. The samples indicated a wide range of PBDEs including many of the congeners thought to be deca-BDE degradation products. However, no statistically significant relationship could be identified between deca-BDE and possible degradation products. Therefore, no conclusion on the degradation of deca-BDE could be obtained. It was suggested that the manufacture and release of substantial amounts of Penta-and Octa-BDE may have masked any deca-BDE degradation products and would make determination of deca-BDE degradation in the environment difficult, if not impossible to determine.

#### Uncertainty

Research has shown that deca-PBDE degrades. Considerable uncertainty remains, however, about the exact degradation products and the relative ratios in which these products are formed. Laboratory studies have shown degradation of deca-PBDE into lower congeners including the congeners found in the Penta, Octa and Deca-BDE commercial mixtures. Many of these same studies indicate, however, that other degradation products are also formed including congeners not commonly found in the commercial mixes. Due to lack of standards for all 209 PBDE congeners and the emphasis placed upon the congeners found in the commercial mixes, research often has not attempted to identify all degradation products. Research has shown that products other than PBDEs are formed from the degradation of deca-BDE. The most commonly mentioned are brominated phenols where a bromine atom is replaced by an alcohol (OH) group. Others degradation products often mentioned in the scientific literature are methyl (CH3), ethyl (CH2CH3) and brominated dioxins and furans. The lack of knowledge about the toxicity of these unidentified congeners and degradation products increases the concern of additional impacts to human health and the environment.

#### In conclusion

Concern has been raised that deca-BDE will remain a long-term source of lower substituted PBDEs.<sup>261</sup> Potential degradation products include other PBDEs such as lower brominated congeners found in Penta-BDE which have been proven to have a greater environmental impact and are known to bioaccumulate, biomagnify and have greater toxicity. As it has been shown that deca-BDE does degrade readily under laboratory conditions, deca-BDE will also degrade in the environment with time. Therefore it is likely deca-BDE will remain a constant source of lower substituted PBDEs and other degradation products over time.

<u>Note</u>: All references to "deca-BDE" in this chapter refer to the compound, not the commercial mixture. Occasionally grammatical demands have required the "D" to be capitalized, in which case "(209)" was added to clarify that the reference was to the compound.

## V. Alternatives

**IN BRIEF:** This chapter looks at alternatives to the use of PBDEs. PBDE flame retardants can be replaced in three ways:

- a different flame retardant can be substituted in a given material (i.e. plastic or foam);
- a different flame retardant in a different type of plastic or foam can be substituted; or
- a product can be redesigned so that its very structure eliminates the need for flame retardants.

Since production of Penta-BDE and Octa-BDE has been largely phased out on both a national and international level, this chapter focuses primarily on Deca-BDE. During calendar year 2005, the Washington State Department of Health (DOH) did an extensive review of existing literature to determine if safer, effective alternatives to Deca-BDE exist. DOH's alternatives assessment considered only those chemicals currently marketed and available to work in the same plastics and products as Deca-BDE, while still providing adequate fire protection.

For their review, DOH focused on evaluating alternatives to Deca-BDE used in electronic enclosures. Electronic enclosures were selected because somewhere between 45 and 80% of Deca-BDE in the U.S. is used in TV enclosures (the black plastic that encloses the rear of a TV). DOH focused on alternatives to replace Deca-BDE for use in combination with two plastics: high impact polystyrene (HIPS) and HIPS/PPO (high-impact polystyrene/polyphenylene oxide).

HIPS was selected because it is already in wide use: it is an inexpensive, lightweight plastic that is very compatible with Deca-BDE and other brominated (halogenated) flame retardants. HIPS/PPO was selected because it provides the option of being used in combination with nonhalogenated flame retardants. Therefore, the DOH review looked at different flame retardants available to replace Deca-BDE in HIPS, and at different flame retardants available for HIPS/PPO, that can also be used in electronic enclosures. Other types of plastics used in electronic enclosures, as well as design changes, were not evaluated.

The DOH review resulted in 11 possible alternatives to Deca-BDE: seven halogenated and four non-halogenated alternatives. DOH evaluated the persistence, bioaccumulation and toxicity of Deca-BDE and each alternative. A main aspect of DOH's evaluation included determining whether the alternatives were currently on Ecology's list of Persistent, Bioaccumulative Toxins (PBTs), or met the criteria for being a PBT.

The results of the alternatives assessment show that two alternatives are currently on Ecology's PBT List. Other alternatives were found to have persistent, bioaccumulative and toxic properties that may qualify them as PBTs. Some of these lacked sufficient information for determining whether they meet all the PBT criteria. A few alternatives do not appear to be either persistent or bioaccumulative, but lack sufficient toxicity information. Two of these are promising non-halogen alternatives, RDP and BAPP. However, there is currently insufficient information available to fully assess them.

Additional research is needed. DOH will continue to collect information on alternatives to Deca-BDE, and is pursuing the use of computer modeling to better assess the toxicity, persistence and bioaccumulation potential of RDP and BAPP.

Detailed toxicity profiles for Deca-BDE and Deca-BDE alternatives are in Appendix F.

## **Alternatives to PBDEs: Penta- and Octa-BDE**

Four documents that evaluate chemical flame retardants were initially identified.<sup>262,263,264,265</sup> Three focused on alternatives to the larger class of brominated flame retardants, as opposed to considering the merits of using other brominated flame retardants as alternatives to PBDEs.

## Penta-BDE

Alternative flame retardants for Penta-BDE are listed by substrate in Table 10. Ecology and DOH have not examined the human health or environmental impacts of these alternatives. The U.S. EPA Design for the Environment, completed an alternatives assessment for Penta-BDE which was released in September 2005.<sup>266</sup>

## Table 10. Alternative flame retardants for Penta-BDE by substrate (except where indicated, based on Danish Action Plan, 2001, and Prioritization of Flame Retardants for Environmental Assessment, U.K. Environment Agency, 2003)

Substrate (material, or matrix, in which the flame retardant is used)	Products in which the substrate is used in flame retardant quantity	Alternative flame retardants in commercial materials	Alternative materials: Non-flammable or containing halogen-free flame retardants
Ероху	<ul> <li>Printed circuit boards</li> <li>Electronic component encapsulation</li> <li>Technical laminates</li> </ul>	<ul> <li>Reactive nitrogen and phosphorus constituents</li> <li>Ammonium polyphosphate</li> <li>Aluminium trihydroxide</li> </ul>	• Polyphenylene sulphide
Unsaturated polyester	<ul> <li>Technical laminates</li> <li>Plastic parts in transportation</li> </ul>	<ul> <li>Ammonium polyphosphate</li> <li>Aluminium trihydroxide</li> <li>Dibromostyrene<sup>267</sup></li> <li>Tetrabromophthalic Anhydride Based Diol<sup>268</sup></li> <li>Tetrabromophthalic Anhydride<sup>269</sup></li> <li>Bis (Tribromophenoxy) ethane<sup>270</sup></li> </ul>	None identified
Rigid polyurethane foam	• Insulation of cold- storage plants/freezing rooms, pipes, etc.	<ul> <li>Ammonium polyphosphate</li> <li>Red phosphorus</li> <li>Tetrabromophthalate Diol<sup>271</sup></li> <li>Tetrabromophthalic Anhydride Based Diol<sup>272</sup></li> <li>Bisphosphate<sup>273</sup></li> </ul>	• Some applications: mineral wool or other technical solutions
Flexible polyurethane foam	<ul> <li>Furniture</li> <li>Components in transportation</li> </ul>	<ul> <li>Ammonium polyphosphate</li> <li>Melamine</li> <li>Reactive phosphorus polyols</li> <li>Tetrabromophthalic anhydride derivative<sup>274</sup></li> <li>Phosphorous-Bromine<sup>275</sup></li> <li>Reofos NHP (halogen-free phosphorus flame retardant)<sup>276</sup></li> <li>Bisphosphate<sup>277</sup></li> </ul>	None identified
Laminates		• Triaryl phosphate isopropylated <sup>278</sup>	None identified
Adhesives		<ul> <li>Tetrabromophthalate diol<sup>279</sup></li> <li>Tetrabromophthalic anhydride based diol<sup>280</sup></li> <li>Hexabromocyclododecane<sup>281</sup></li> <li>Reomol® TOP<sup>282</sup></li> <li>Bis (Tribromophenoxy) ethane<sup>283</sup></li> </ul>	None identified
Coatings		<ul> <li>Tetrabromophthalate Diol<sup>284</sup></li> <li>Tetrabromophthalic anhydride based diol<sup>285</sup></li> <li>Hexabromocyclododecane<sup>286</sup></li> <li>Triaryl phosphate<sup>287</sup></li> <li>Bis (Tribromophenoxy) ethane<sup>288</sup></li> </ul>	None identified

## Octa-BDE

Alternative flame retardants for Octa-BDE are listed by substrate in Table 11. Ecology and DOH have not evaluated the human health or environmental impacts of these alternatives.

Table 11. Alternative flame retardants for Octa-BDE by substrate (except where indicated, based on Danish Action Plan, 2001, and Prioritization of Flame Retardants for Environmental Assessment, UK Environment Agency, 2003)

Substrate (material, or matrix, in which the flame retardant is used)	Products in which the substrate is used in flame retardant quantity	Alternative flame retardants in commercial materials	Alternative materials: Non-flammable or containing halogen-free flame retardants	
ABS	• Housings for electronic products	<ul> <li>Tetrabromobisphenol A<sup>289,290</sup></li> <li>Triaryl phosphate<sup>291</sup></li> <li>Triaryl phosphates butylated<sup>292</sup></li> <li>Bisphosphate<sup>293</sup></li> <li>Bis (Tribromophenoxy) ethane<sup>294</sup></li> <li>Phenoxy-terminated carbonate oligomer of tetrabromobisphenol A<sup>295</sup></li> <li>No non-halogenated alternatives identified in commercial use</li> </ul>	• PC/ABS blends or PPE/PS blends with organic phosphorus compounds	
Synthetic textiles• Furniture, textiles• Components in transportation• Protective clothing		<ul> <li>Reactive phosphorus constituents</li> <li>Hexabromocyclododecane<sup>296</sup></li> </ul>	None identified	
Thermoplastic elastomers		• Bis (Tribromophenoxy) ethane <sup>297</sup> •Tribromophenyl allyl ether <sup>298</sup>	None identified	
Polyolefins		<ul> <li>Polypropylene-dibromostyrene<sup>299,300</sup></li> <li>Dibromostyrene<sup>301</sup></li> <li>Tetrabromobisphenol A bis<sup>302</sup></li> <li>No non-halogenated alternatives identified in commercial use</li> </ul>	None identified	

## **Deca-BDE Alternatives**

Deca-BDE can be used in many different polymers. (A *polymer* is a large molecule formed by the combination of many similar smaller molecules.) DOH research to identify and evaluate Deca-BDE alternatives focused on alternatives for use in combination with two polymers, high impact polystyrene (HIPS) or HIPS/polyphenylene oxide (HIPS/PPO blend). Deca-BDE/HIPS is primarily used in televisions; specifically the black plastic used to enclose the rear of a TV. TV enclosures are reported to account for approximately 45-80% of the Deca-BDE use in the U.S.,<sup>303,304</sup> and therefore DOH's research focused on alternatives for use in TV enclosures. Other polymers or design changes have not yet been evaluated.

DOH used three main sources of information to identify Deca-BDE alternatives:

- 1. Survey of electronics companies
- 2. Existing reports
- 3. Flame retardant product information from chemical manufacturers

#### 1. Survey of electronics companies

Beginning in June 2005, Ecology began contacting electronics manufacturers to ask them about their use of flame retardants and their use of alternatives to Deca-BDE. Information was collected via telephone interviews and via email. Each manufacturer was asked a common set of questions developed by Ecology and DOH (Appendix A). Many companies contacted did not provide information.

#### 2. Existing reports

A number of reports, including many from Europe and the U.S., address the use of flame retardants and alternatives to brominated flame retardants. The reports used by DOH to identify alternatives to Deca-BDE are listed at the end of this chapter.

#### 3. Flame retardant product information from chemical manufacturers

Information on flame retardant products marketed by their manufacturers for use in HIPS or HIPS/PPO was collected from information posted on chemical manufacturer's websites, including:

- Great Lakes Chemical Corporation (now Chemtura)
- Akzo Nobel (now Supresta)
- LG Chemical Limited
- Hexion Specialty Chemicals Inc. (which includes Resolution Performance Products)
- Clariant GmBH
- Albemarle Corporation.

## Identified Alternatives to Deca-BDE in electronic enclosures

DOH initially compiled a list of alternatives that could replace Deca-BDE in high impact polystyrene (HIPS) used in TV enclosures, as well as alternatives to Deca-BDE in HIPS/PPO blends. The latter have been marketed as substitutes for brominated HIPS resins, and this option

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opens up the possibility of non-halogen substitutes.<sup>305</sup> The possibility of non-halogen substitutes for use in HIPS/PPO is confirmed by information from Great Lakes Chemical (now Chemtura).<sup>306</sup> However, Great Lakes Chemical also reports that changes in processing conditions are required for HIPS/PPO and these changes are associated with higher costs.

The following list of alternatives is divided between halogenated and non-halogenated alternatives. All alternatives listed are currently marketed or reportedly used as flame retardants in electronics and are therefore identified as feasible and effective flame retardants. For each alternative, the resource used to identify it as an alternative is specified. (The reports mentioned without endnote reference are listed at the end of this chapter.) Several of these alternatives can also be used in other polymers including acrylonitrile-butadiene-styrene (ABS) and polycarbonate/ABS blends (PC/ABS).

#### Halogen-containing alternatives:

- Bis(pentabromophenyl)ethane (also called ethane-1,2-bis (pentabromophenyl) or decabromodiphenylethane; CAS# 84852-53-9).
   This chemical is marketed as SAYTEX 8010 by Albemarle Corp. and Firemaster 2100 by Great Lakes Chemical Corp. for use in HIPS. It can also be used in ABS, PC/ABS and HIPS/PPO polymers.<sup>307</sup> This alternative is mentioned in the 2000 German report.
- 1,2-bis(tetrabromophthalimido) ethane (CAS# 32588-76-4). This chemical is marketed as SAYTEX BT-93 and BT-93W by Albemarle Corp. for use in HIPS. It can also be used in ABS, PC/ABS and HIPS/PPO polymers.<sup>308</sup> This alternative is mentioned in the 2000 Danish report.
- Tetrabromobisphenol A epichlorohydrin polymer (EPON resin 1163 (CAS# 40039-93-8)).

This product is made by Hexion Specialty Chemicals (under Resolution Performance Products) and marketed as Starex® by Cheil Industries, Korea. This brominated epoxy resin is reportedly used by one electronics manufacturer as their alternative to Deca-BDE. The chemical is produced from tetrabromobisphenol A and epichlorohydrin. This alternative is not mentioned in reports from Europe or the U.S. (e.g. EPA, CPSC).

- 4. Bis(tribromophenoxy)ethane (CAS# 37853-59-1) This chemical is marketed as FF-680 by Great Lakes Chemical Corp. for use in HIPS, but is typically used in ABS.<sup>309</sup> It is mentioned in the 2000 Danish BFR report but was determined to have no or very few data in their preliminary screening.
- 5. Hexabromocyclododecane (HBCD) (CAS# 3194-55-6 and 25637-99-4) This chemical is marketed as SAYTEX HP-900 and 9006L by Albemarle Corp. and SP-75 and CD-75P by Great Lakes Chemical Corp. for use in HIPS. The primary use of this flame retardant is in polystyrene foam insulation materials and not HIPS.<sup>310</sup> This alternative is included in the 2000 German and Danish reports, and the CPSC and NAS reports related to textiles.

- 6. Tetrabromobisphenol A (TBBPA) (CAS# 79-94-7) This chemical is marketed as SAYTEX CP-2000 by Albemarle Corp. and BA-59P by Great Lakes Chemical Corp. for use in HIPS. It was identified in the 2000 German, 2000 Danish and 2003 U.K. reports. Use of tetrabromobisphenol A in HIPS is included in an analysis of waste TV sets in Japan.<sup>311</sup> The main use of TBBPA is in printed wiring boards with some use in ABS polymers.<sup>312</sup>
- 7. Tetrabromobisphenol A bis(2,3-dibromopropyl ether) (CAS# 21850-44-2) This chemical is marketed as SAYTEX HP-800A, HP-800AG, and HP-800AGC by Albemarle Corp.; PE-68 by Great Lakes Chemical Corp. for use in HIPS; and in product 403AF by LG Chem with use in fire retarded HIPS. However, this flame retardant is mainly used in other polymers including polypropylene.<sup>313</sup> This chemical is not mentioned in any of the reviewed reports.

#### Non-halogen alternatives:

- 8. Resorcinol bis(diphenylphosphate) (RDP) (CAS# 57583-54-7 and 125997-21-9) This flame retardant is identified in the Lowell Center report<sup>314</sup> as a non-halogen alternative to Deca-BDE for use in HIPS/PPO. RDP is currently marketed as FyrolflexRDP by Akzo Nobel, and Reofos RDP by Great Lakes Chemical Corp. This alternative was mentioned in the 2000 German and Danish reports.
- 9. Bisphenol A diphosphate (BAPP, BPADP) or bisphenol A bis(diphenyl phosphate) (BDP) (CAS# 181028-79-5 and 5945-33-5) This flame retardant is identified in the Lowell Center report<sup>315</sup> as a non-halogen alternative to Deca-BDE for use in HIPS/PPO. This flame retardant is currently marketed as Reofos BAPP by Great Lakes Chemical Corp., Fyrolflex BDP by Akzo Nobel and NcendX P-30 by Albemarle Corp. It can be used in HIPS, HIPS/PPO and PC/ABS polymers.<sup>316</sup> This chemical was not included in any other existing reports.
- 10. Diphenyl cresyl phosphate (CAS# 26444-49-5)

This flame retardant is manufactured as Kronitex CDP by Great Lakes Chemical Corp., Phosflex CDP by Akzo Nobel, and Transol by Chemiehandel GmbH.<sup>317</sup> This chemical is reported in the Lowell Center report<sup>318</sup> as an alternative to Deca-BDE in PC/ABS applications. It is unclear if this alternative can be used in HIPS or HIPS/PPO in electronic enclosure applications. This chemical is not mentioned in any of the existing European reports on flame retardants. It is manufactured by Bayer AG, FMC Process Additives and TRANSOL Chemicals.<sup>319</sup>

11. Triphenyl phosphate (TPP) (CAS# 115-86-6)

This chemical is marketed as Reofos TPP by Great Lakes Chemical Corp. and Phosflex TPP by Akzo Nobel. TPP is a constituent of products containing RDP at approximately <5-6% for use in HIPS/PPO and PC/ABS. This chemical was included in the Lowell Center report<sup>320</sup>, the Danish report (2000), the CPSC/NAS reports on upholstered furniture and in EPA's recent analysis of alternatives to Penta-BDE.

#### Related chemicals:

- 12. Zinc Borate (CAS# 1332-07-6) This chemical is marketed as Firebrake ZB-467 by Great Lakes Chemical Corp.. for use in HIPS as a synergist in conjunction with brominated flame retardants. This chemical is mentioned in the 2000 Danish report on BFR alternatives and in the CPSC and NAS reports on textiles.
- Polytetrafluoroethylene (PTFE, also commonly called Teflon; CAS# 9002-84-0) PTFE is used in chlorine and bromine-free polycarbonate resins at approximately 0.3% as an anti-drip agent.<sup>321</sup>
- 14. Antimony trioxide (CAS# 1309-64-4)

Antimony trioxide is marketed as several different products by Great Lakes Chemical Corp. as synergists for use with brominated flame retardants (including Deca-BDE) in HIPS. These products include TMS/Timonox Red Star, Fireshield H/Thermoguard S and Microfine/Ultrafine.

#### Unknown or proprietary products:

One additional product was identified for use in HIPS, but it has not been possible to evaluate it due to lack of information on the specific chemicals included in this product:

• SAYTEX BC70HS (proprietary) – Marketed by Albemarle for use in HIPS.

# Evaluation of the persistence, bioaccumulation potential and toxicity of Deca-BDE and Deca-BDE alternatives (Table 12)

Information on the physical and chemical properties, persistence, bioaccumulation and toxicity of Deca-BDE, Deca-BDE alternatives and related chemicals was collected from a number of sources. These are listed at the end of this chapter.

Information on each alternative was compiled using a standard toxicity profile template. The template used for this report was developed based on several templates included in existing flame retardants reports.<sup>322,323,324,325</sup> Draft Toxicity Profiles for each alternative and related chemicals are provided in Appendix F.

Table 12 includes the toxicity, persistence and bioaccumulation data for each alternative, organized under the following column headings (for more detailed explanations, see Appendix G):

1. Deca-BDE/Alternative name: includes any synonyms and its identifying Chemical Abstract Service (CAS) number.

2. Product name: the names of commercial products which contain the alternative.

3. Use: information on the polymers in which the alternative is used. This assessment focuses on use of these alternatives in polymers for electronic enclosures. It is important to note that many of these flame retardants have uses in other products and materials not listed here.

4. Reactive or Additive: whether the chemical is used as an additive or reactive flame retardant.

5. Human Health Effects (Cancer hazard, Non-cancer effects, Mutagenicity): information from toxicity studies. Different potential human health effects (cancer, non-cancer effects, and mutagenicity) are ranked as low, medium or high (L, M or H) concern. The ranking of human health effects are based mainly on toxicity studies in laboratory animals since there is very little information on health effects in human studies for either Deca-BDE or the alternatives. In cases where there are no available toxicity studies for a health effect, NI (No/insufficient Information) is indicated instead of the L, M, or H rank.

6. A/M (Aquatic and Microbial ) Ecotoxicity (Acute, Chronic): Concern related to ecotoxicity (mainly aquatic toxicity) is ranked as low, medium or high (L, M, or H) depending on the results of toxicity studies.

7. Amount of toxicity information ("Amt. of tox. info"): a ranking for the amount of information available relative to toxicity and potential for human exposures. Ranked as Low, Medium or High (L,M,H).

8. Information on potential routes of exposure: whether there is information on potential routes of human exposure. Categories include Yes, No, or NI (No/insufficient Information).

9. Persistence/Bioaccumulation potential: indicates if the alternatives meet Ecology's PBT criteria for environmental persistence and bioaccumulation potential. Categories include Yes, No, or NI (No/insufficient Information).

10. PBT: whether the alternative meets Ecology's PBT criteria, listed as either Yes, No, or NI (No/insufficient Information).<sup>326</sup>

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					Human Health Effects		A/M Eco- toxicity		Informa- tion on potential				
	Deca and Alternative	Product name	Use	Reactive or Additive	Cancer hazard	Non- cancer effects	Muta- genicity	Acute or chronic	Amt of tox. info	routes of exposure	Persist- ence	Bioaccum Potential	PBT
Halo	ogen-containing												
1	Decabromodiphenyl ether (Deca-BDE) (CAS# 1163-19-5)	SAYTEX 102E, DE-83R	HIPS	Additive	L	М	L	L-H	M-H	Yes	Yes (PBDEs)	Yes (PBDEs)	Yes <sup>a</sup>
2	Bis(pentabromophenyl) ethane (CAS# 84852-53-9)	SAYTEX 8010, Firemaster 2100	HIPS,ABS, PC/ABS	Additive	L	L	L	L	L	Yes	NI (likely)	No	No
3	1,2-bis(tetrabromophthalimido) ethane (CAS# 32588-76-4)	SAYTEX BT- 93 and BT-93W	HIPS,ABS, PC/ABS	Additive	L	L	L	L	L	NI	NI (likely)	No	No
4	Tetrabromobisphenol A epichlorohydrin polymer (brominated epoxy resin) (CAS# 40039-93-8)	EPON Resin 1163, STAREX	HIPS, Polystyrene	?	NI	L (NI)	L (NI)	NI	L	NI	NI	NI	NI
5	Bis(tribromophenoxy)ethane (CAS# 37853-59-1)	FF-680	Mainly ABS	Additive	L	L	L	L-M	L	NI	Yes	Yes	No
5	Hexabromocyclododecane (HBCD) (CAS# 3194-55-6 and 25637-99-4)	SAYTEX HP- 900, -9006L, SP-75, CD-75P	Polystyrene foam	Additive	L (NI)	NI	L	L-H	L	Yes	Yes	Yes	Yes <sup>a</sup>
7	Tetrabromobisphenol A (TBBPA) (CAS# 79-94-7)	SAYTEX CP- 2000, BA-59P	ABS, HIPS	Additive in HIPS	L	М	L	M-H	М	Yes	Yes	Yes	Yes <sup>a</sup>
8	Tetrabromobisphenol A bis(2,3- dibromopropyl ether)(CAS# 21850-44-2)	SAYTEX HP- 800A, -800AG, -800AGC, PE- 68, 403AF	Polyprop- ylene	Additive	М	L	Н	NI	L	NI	NI	Yes	NI
Non	-halogen										•		
9	Resorcinol bis (diphenylphosphate) (RDP) (CAS# 57583-54-7 and 125997-21-9)	FyrolflexRDP, Reofos RDP	HIPS/PPO, PC/ABS	Additive	NI	L	L	M-H	L	NI	No	No	No
10	Bisphenol A diphosphate (BAPP, BPADP) or Bisphenol A bis(diphenyl phosphate) (BDP) (CAS# 181028-79-5 and 5945-33-5)	Reofos BAPP FyrolflexBDP, NcendX P-30	HIPS/PPO, PC/ABS	Additive	NI	L	L	L-M	L	NI	Yes	NI	NI
11	Diphenyl cresyl phosphate (DCP) (CAS# 26444-49-5)	Kronitex CDP Phosflex CDP	Maybe HIPS/PPO	Additive	NI	М	L	M-H	L-M	Yes	Yes	Yes	Mayb (NI)
12	Triphenyl phosphate (TPP) (CAS# 115-86-6)	Reofos TPP Phosflex TPP	HIPS/PPO, PC/ABS	Additive	L	L-M	L	M-H	L-M	Yes	No	No	No
Rela	ted chemicals												
13	Zinc Borate (CAS# 1332-07-6)	Firebrake ZB- 467, -112, -237, -100	Synergist for use in HIPS	Additive	NI	L	NI	M-H	L	Yes	NI	NI	NI (un- likely
14	Polytetrafluoroethylene (PTFE) (CAS# 9002-84-0)		anti-drip agent	?	NI	Н	NI	NI	М	Yes (if heated)	NI	NI	NI
15	Antimony trioxide (CAS# 1309-64-4)	TMS/Timonox Red Star,	Synergist w/ BFRs	Additive	L-M	L	M-H	L-M	M-H	Yes	NI	NI	Mayb (NI)

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## **Legend/Notes for Table 12**

Deca-BDE evaluated as compound itself, and as breakdown products including Penta-BDE and Octa-BDE congeners.

HIPS = high impact polystyrene

- HIPS/PPO = high impact polystyrene/polyphenylene oxide
- ABS = acrylonitrile-butadiene-styrene
- PC/ABS = polycarbonate/ABS blends
- NI No Information/insufficient information
- BFR = brominated flame retardants

Ranking of H = high, M = medium, L = low concern based on available information: Ranking is based on EPA report on penta-BDE alternatives<sup>327</sup>

<sup>a</sup> Chemical is currently on Ecology's PBT List (Chapter 173-333 WAC, Persistent Bioaccumulative Toxins)

## Results

DOH has identified a total of eleven possible alternatives to Deca-BDE for use in electronic enclosures, mainly to replace Deca-BDE use with HIPS. Of these eleven alternatives, seven contain bromine (halogen-containing) and four are halogen-free. DOH also identified three related chemicals that are used in conjunction with different alternatives as either synergists or anti-drip agents.

The following is a brief description of the toxicity, persistence and bioaccumulation potential for each alternative and Deca-BDE. Detailed (draft) Toxicity Profiles for each chemical are in Appendix F. (References to Ecology's PBT List or criteria refer to the criteria laid out in Chapter 173-333 WAC, the Persistent Bioaccumulative Toxins rule for environmental persistence, bioaccumulation potential and toxicity.)<sup>328</sup>

1. Decabromodiphenyl ether (Deca-BDE) (CAS# 1163-19-5)

There are several animal toxicity studies of Deca-BDE evaluating its potential to cause cancer and other health effects including neurodevelopmental effects. Based on these studies, Deca-BDE represents a low-to-high concern for human health and aquatic toxicity. Recent studies indicate that people can be exposed to Deca-BDE via food and indoor dust. Half-life information for Deca-BDE in water and other media indicate that it is persistent in the environment. Deca-BDE shows a moderate tendency to bioaccumulate into organisms. However, the main concern around Deca-BDE is its potential to breakdown to lower brominated forms of PBDEs that have greater toxicity and greater potential to bioaccumulate. Deca-BDE is classified as a PBT under Ecology's PBT criteria.

2. Bis(pentabromophenyl) ethane (CAS# 84852-53-9) (SAYTEX 8010)

There are few toxicity studies available on bis(pentabromophenyl) ethane. Toxicity studies are reported by one of its manufacturers (Albemarle Corp.) but documentation for these has not yet been obtained for evaluation. Toxicity values provided by Albemarle Corp. indicates that this chemical has low toxicity concern. One study in Sweden indicated potential occupational exposures to this chemical.<sup>329</sup> SAYTEX 8010 is expected to be persistent because it is a large halogenated compound, but there is no data on its half-life in water or other media with which to quantitatively evaluate its potential environmental persistence. Bis(pentabromophenyl) ethane shows a low tendency to bioaccumulate into organisms. This chemical does not meet Ecology's PBT criteria due to low bioaccumulation potential and low toxicity based on limited toxicity information.

3. 1,2-bis(tetrabromophthalimido) ethane (CAS# 32588-76-4) (SAYTEX BT-93)

There are few toxicity studies available on 1,2-bis(tetrabromophthalimido) ethane. Toxicity studies are reported by one of its manufacturers (Albemarle Corp.) but documentation for these has not yet been obtained for evaluation. Toxicity values provided by Albemarle Corp. indicates that this chemical has low toxicity concern. There is no information on potential human exposures to this chemical. SAYTEX BT-93 is expected to be persistent because it is a large

halogenated compound, but there is no data on its half-life in water or other media with which to quantitatively evaluate its potential environmental persistence. 1,2-bis(tetrabromophthalimido) ethane shows a low tendency to bioaccumulate into organisms. This chemical does not meet Ecology's PBT criteria due to low bioaccumulation potential and low toxicity based on limited toxicity information.

4. Tetrabromobisphenol A epichlorohydrin polymer (brominated epoxy resin) (CAS# 40039-93-8)

There are very few toxicity studies available on Tetrabromobisphenol A epichlorohydrin polymer. Toxicity values provided in an MSDS for this compound indicate low toxicity concern for mainly acute exposures. No information was found on several health impacts of interest including reproductive and developmental toxicity. No information on aquatic toxicity (ecotoxicity) was found. There is some indication of possible mutagenicity concern based on testing of a related compound, but more information is needed for the chemical itself. There is no information on potential human exposures to this chemical. There is no available information with which to evaluate this chemical's environmental persistence or bioaccumulation potential. There is insufficient information on this chemical to evaluate whether it meets Ecology's PBT criteria.

5. Bis(tribromophenoxy)ethane (CAS# 37853-59-1)

Toxicity testing for bis(tribromophenoxy)ethane has been conducted by Great Lakes Chemical Corp. Results from these tests are reported by Great Lakes Chemical Corporation in reports submitted to EPA's High Production Volume Challenge program. These reports provide summaries of the toxicity studies. Further documentation of these studies is not easily available. These toxicity studies indicate low toxicity concern for this chemical. There is no information on potential human exposures to this chemical. The chemical shows a tendency to persist in the environment and to bioaccumulate into organisms. This chemical meets Ecology's criteria for persistence and bioaccumulation, but does not meet Ecology's PBT criteria due to low toxicity based on limited toxicity information.

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

There is a moderate amount of information on HBCD available in the published medical literature and from companies that make it. HBCD is included in Ecology's PBT list indicating that it meets Ecology's criteria for environmental persistence, bioaccumulation potential and toxicity.<sup>330</sup>

7. Tetrabromobisphenol A (TBBPA) (CAS# 79-94-7)

There is a moderate amount of information on TBBPA available in the published medical literature and from companies that make it. TBBPA is included on Ecology's PBT List indicating that it meets Ecology's criteria for environmental persistence, bioaccumulation potential and toxicity.<sup>331</sup>

## 8. Tetrabromobisphenol A bis(2,3-dibromopropyl ether)(CAS# 21850-44-2)

Tetrabromobisphenol A bis(2,3-dibromopropyl ether has few available toxicity studies. It is ranked as a medium-to-high concern for cancer and mutagenicity based on its structural similarity to a known carcinogen. There is no information on aquatic toxicity or potential human exposures. The chemical shows a tendency to bioaccumulate into organisms. There is no data on this chemical's half-life in water or other media with which to evaluate its potential environmental persistence. This chemical meets Ecology's PBT criteria for toxicity and bioaccumulation potential, but there is insufficient information with which to evaluate persistence.

9. Resorcinol bis (diphenylphosphate) (RDP) (CAS# 57583-54-7 and 125997-21-9)

RDP is one of the more promising alternatives. Most of the available toxicity testing for RDP has been conducted by two of its manufacturers, Great Lakes Chemical Corp. and Albemarle Corp. Results of these toxicity studies indicate low toxicity concern for this chemical for humans and medium toxicity concern for aquatic organisms. There are no animal cancer studies available for this chemical and there is no information on potential human exposures. The chemical does not show a tendency to persist in the environment and does not indicate a tendency to bioaccumulate into organisms based on some limited data. While this chemical does not appear to meet Ecology's criteria for persistence and bioaccumulation, information on toxicity is limited. Additional toxicity information is being pursued by Ecology and DOH using QSAR (Quantitative Structure Activity Relationship) modeling.

10. Bisphenol A diphosphate (BAPP, BPADP) or Bisphenol A bis(diphenyl phosphate) (BDP) (CAS# 181028-79-5 and 5945-33-5)

BAPP is one of the more promising alternatives. All available toxicity testing for BAPP has been conducted by two of its manufacturers, Great Lakes Chemical Corp. and Albemarle Corp. Results from these tests are available in reports by the companies that provide only summaries of the toxicity studies. Results of these toxicity studies indicate low toxicity concern for this chemical for humans, and low to medium toxicity concern for aquatic organisms. There are no animal cancer studies available for this chemical and there is no information on potential human exposures. The chemical does show a tendency to persist in the environment. There is some conflicting information regarding its ability to bioaccumulate into organisms. There is insufficient information on this chemical to evaluate whether it meets Ecology's PBT criteria.

#### 11. Diphenyl cresyl phosphate (DCP) (CAS# 26444-49-5)

Toxicity studies on DCP indicate a medium concern for human health and aquatic toxicity. There are no animal cancer studies available for this chemical. There is some information on human exposures, primarily in the workplace. The chemical shows a tendency to persist in the environment and to bioaccumulate into organisms. This chemical is on the borderline of meeting Ecology's criteria for bioaccumulation and toxicity based on limited toxicity and bioaccumulation. 12. Triphenyl phosphate (TPP) (CAS# 115-86-6)

Toxicity studies on TPP indicate mostly low concern for non-cancer human health effects and medium-to-high concern for aquatic toxicity. There is some information on estimated human exposures from use of TPP. The chemical does not show a tendency to persist in the environment and does not indicate a tendency to bioaccumulate into organisms. This chemical does not meet Ecology's PBT criteria due to low persistence, low bioaccumulation potential and low toxicity based on limited toxicity information.

#### Conclusions

Based on a review of available information, there do not appear to be any obvious alternatives to Deca-BDE that are less toxic, persistent and bioaccumulative and have enough data available for making a robust assessment. It is clear from this exercise that there is much more data available on Deca-BDE than for any of the alternatives. Two of the alternatives with a moderate amount of data, hexabromocyclododecane and tetrabromobisphenol A, are on Ecology's PBT list, indicating that they present a hazard to the environment and human health. Other alternatives do not appear to meet Ecology's PBT criteria, indicating that they are less of a concern, but it is difficult to draw definitive conclusions based on incomplete data sets for these chemicals. DOH will continue to collect information on alternatives to Deca-BDE and is pursuing the use of computer modeling to assess toxicity and environmental fate for two of the most promising alternatives, RDP and BAPP.

# Additional Information on Deca-BDE and Alternatives: Production and Tracking (Table 13)

In addition to environmental fate and toxicity information on alternatives to Deca-BDE, DOH collected other types of information on each alternative. Table 13 provides production information and information related to whether the alternative is currently part of an existing tracking or evaluation program. This information was collected for the U.S. and other countries (mainly the EU) where available. The purpose of collecting and summarizing this type of information is to illustrate other data gaps in information about alternatives, such as information on their production, use and tracking mechanisms.

Table 13 shows that information on the total years of production for alternatives is unavailable. This appears to be mainly due to confidential proprietary information. It is also difficult to find estimates of the volume of production or estimated use for many of the alternatives. Table 13 also shows that there is little information on emissions data for these chemicals (TRI data) and that many alternatives are not included in EPA's High Production Volume program, which would be a source of toxicity and other information. Most alternatives identified are not included in existing U.S. environmental or biomonitoring programs for tracking their potential

buildup in animal or human tissues. Table 13 also illustrates that there is limited tracking and evaluation information available for alternatives in Europe.

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<ol> <li>Deca-BDE (CAS# 1163-19-5)</li> <li>Bis(pentabromophenyl) ethane (CAS# 84852-53-9)</li> <li>1,2-bis(tetrabromophthalimido)</li> </ol>	1970's	24.500			4? Section 8?	NHANES	program? <sup>332</sup>
(CAS# 84852-53-9)		24,500 metric tons (U.S2001) (>1,000,000 lbs)	2003; 827,428 lbs total release	Yes	Yes / Yes	CDC, began in 2004	Yes, USACE ERED
3 1 2-bis(tetrabromophthalimido)		Confidential**	No	No	No <sup>333</sup>	No	No
ethane (CAS# 32588-76-4)		Confidential** (>1,000,000 lbs- 1994)	No	Yes	No / Yes Section 8	No	No
4. Tetrabromobisphenol A epichlorohydrin polymer (CAS# 40039-93-8)		108,000 tons (World-2000)	No	No	No / No	No	No
5. Bis(tribromophenoxy)ethane (CAS# 37853-59-1)		16,710 tonnes (World-2001) (>1,000,000 lbs)	No	Yes	Yes / Yes	No	No
6. Hexabromocyclododecane (HBCD) (CAS# 3194-55-6 / 25637-99-4)		12,200 tons (2002) (>1,000,000 lbs)	No	Yes	No?	Nominated for 2004 CDC NHANES	No
7. Tetrabromobisphenol A (TBBPA) (CAS# 79-94-7)		60,000 tonnes (World 1999) (>1,000,000 lbs)	2003; 643,250 lbs total release	Yes	Yes / Yes	Nominated for 2004 CDC NHANES	No
8. Tetrabromobisphenol A bis(2,3- dibromopropyl ether) (CAS# 21850- 44-2)		1500 Total EU tonnage <sup>334</sup>	No	No	Yes / Yes	No	No
9. Resorcinol bis (diphenylphosphate) (RDP) (CAS# 57583-54-7 and 125997-21-9)		1500 Total EU tonnage <sup>335</sup>	No	Yes (CAS# 125997- 21-9)	No /No	No	No
10. Bisphenol A diphosphate (BAPP, BPADP, BDP) (CAS# 181028-79-5 and 5945-33-5)		Not available.	No	No	No / No	No	No
11. Diphenyl cresyl phosphate (DCP) (CAS# 26444-49-5)		Confidential** (>1,000,000 lbs)	No	No	No / Yes Section 8	No	No
12. Triphenyl phosphate (TPP) (CAS# 115-86-6)		Confidential**	No	Yes	Yes / Yes	No	No

 Table 13A. Additional production and tracking information on Deca-BDE alternatives and related chemicals.

#### Table 13A. (con't) Additional production and tracking information on Deca-BDE alternatives and related chemicals.

	Chemical	Year of initial production/ or total years of production	Volume of production/or estimated use	TRI reporting? Volume (most recent year available)	EPA HPV?	Subject to TSCA: Section 4? Section 8?	Part of a national biomonitoring program? i.e. CDC NHANES	Part of a national environmental monitoring program? <sup>336</sup>
	Related Chemicals							
13.	Zinc Borate (CAS# 1332-07-6)		1000 Total EU tonnage <sup>337</sup>	No	No	No / No	No	No
14.	Polytetrafluoroethylene (PTFE) (CAS# 9002-84-0)		Confidential**	No	No	No / No	No	No
15.	Antimony trioxide (CAS# 1309-64-4)		~4,720 metric tons (2003) (>1,000,000 lbs US)	2003; 13,157,168 (includes other antimony compounds) <sup>338</sup>	Yes	No / Yes Section 8	No	EPA drinking water monitoring (antimony)

(Legend follows, page 60.)

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Table 13B         Additional production and tracking information on Deca-BDE alternatives and related chemicals.	Table 13B Additional	roduction and tracking information on Deca-BDE alternatives and related che	micals.
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	Chemical	EU	IUCLID Data	EU	European Priority List?	Other Assessments / Risk	International
		EINECS?	Sheet? (year)/ OECD SIDS (year)	HPV?	EU Risk Assessment Status	Assessments?	Biomonitoring?
	Deca-BDE (CAS# 1163-19-5)	Yes	Yes, IUCLID (2000)	Yes	Yes/ Risk Assessment updates released May 2004, August 2005 (UK and France)		Yes, Swedish biomonitoring program
	Bis(pentabromophenyl) ethane (CAS# 84852-53-9)	Yes	No	No	No	UK Risk Assessment prending – expected 2006	
	1,2-bis(tetrabromophthalimido) ethane (CAS# 32588-76-4)	Yes	Yes, IUCLID (2000)	Yes	No	France - PBT Assessment	
	Tetrabromobisphenol A epichlorohydrin polymer (CAS# 40039-93-8)	No	No	No	Yes/ Currently underway (UK)		
	Bis(tribromophenoxy)ethane (CAS# 37853-59-1)	Yes	No	No	No		
	Hexabromocyclododecane (HBCD) (CAS# 3194-55-6 / 25637-99-4)	Yes	Yes, IUCLID (2005)	Yes	Yes/ Draft 2004, update pending (Sweden)		
	Tetrabromobisphenol A (TBBPA) (CAS# 79-94-7)	Yes	Yes, IUCLID (2000)	Yes	Yes/ Draft 2005 (UK)		
	Tetrabromobisphenol A bis(2,3- dibromopropyl ether) (CAS# 21850-44-2)	Yes	No	No	No	Netherlands Risk Assessment – expected 2006	
	Resorcinol bis (diphenylphosphate) (RDP) (CAS# 57583-54-7 and 125997- 21-9)	Yes	No	No	No	UK Risk Assessment pending – expected 2006	
	Bisphenol A diphosphate (BAPP, BPADP, BDP) (CAS# 181028-79-5 and 5945-33-5)	No	IUCLID (2004)/ OECD SIDS (2002, Japan)	No	No	Australia NICNAS (2005)	
	Diphenyl cresyl phosphate (DCP) (CAS# 26444-49-5)	Yes	Yes, IUCLID (2000)	Yes	No	UK Risk Assessment pending – expected 2006	
	Triphenyl phosphate (TPP) (CAS# 115-86-6)	Yes	Yes, IUCLID (2000)	Yes	No	UK Risk Assessment pending – expected 2006; EPA Penta alternatives assessment (2005)	
	Related Chemicals	1		-		1	
	Zinc Borate (CAS# 1332-07-6)	Yes	No	No	No	Norway -conducted data assessment	
	Polytetrafluoroethylene (PTFE) (CAS# 9002-84-0)	No	No	No	No		
	Antimony trioxide (CAS# 1309-64-4)	Yes	Yes, IUCLID (2000)	Yes	Yes/ Early stage in risk assessment (Sweden)	Sweden doing EU Health & Enviro. Review – expected 2006	
(Lege	end, next page.)	•		·	· · · · · · · · · · · · · · · · · · ·		

### Legend: Tables 13A + B

\*\* According to all records found, the manufacturers for this substance are keeping the production of this chemical confidential, and therefore no precise numbers could be obtained.

CDC NHANES = The Centers for Disease Control and Prevention; the National Health and Nutrition Examination Survey

EINECS = European Inventory of Existing Commercial Chemical Substances

HPV = High Production Volume programs (EPA and EU)

IUCLID = International Uniform Chemical Information Database. IUCLID data sets and other information under the EU available at: <u>http://ecb.jrc.it/</u>

NICNAS = National Industrial Chemicals Notification and Assessment Scheme, Australia Department of Health and Aging. List of chemicals with information available at: <u>http://www.nicnas.gov.au/publications/CAR/NEW/CARSORT.ASP?infReq=30</u>

OECD SIDS = Organization for Economic Cooperation and Development, Screening Information Data Set – voluntary international testing program for developing base level test information on approximately 600 poorly characterized international HPV chemicals (SIDS available at: <a href="http://www.inchem.org/pages/sids.html">http://www.inchem.org/pages/sids.html</a>)

TRI = EPA's Toxic Release Inventory

USACE ERED = U.S. Army Corps of Engineers; Environmental Residue Effects Database. Information about this database is available at: <u>http://www.battelle.org/Environment/publications/EnvUpdates/Special2000/article2.html</u>

The following reports and information sources were used and referenced in the Deca-BDE alternatives assessment.

Reports used to identify alternatives to Deca-BDE:

- Consumer Product Safety Commission (CPSC) Staff Exposure and Risk Assessment of Flame Retardant Chemicals in Residential Upholstered Furniture, 2001.
- Danish Environmental Protection Agency, 1999. Brominated Flame Retardants, Substance Flow Analysis and Assessment of Alternatives.
- Danish EPA, 2000. Alternatives to brominated flame retardants screening for environmental and health data.
- Danish EPA, 2000. Brominated flame retardants; toxicity and ecotoxicity.
- Environmental research plan of the German Federal Ministry for the Environment, Nature Conservancy and Nuclear Safety, 2000. Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals. Research report 297 44 542.
- EPA, 2005. Environmentally preferable options for furniture fire safety, low-density furniture foam. Final released 09/05. Available at <u>www.epa.gov/dfe</u>.
- The Lowell Center for Sustainable Production, University of Massachusetts Lowell, 2005. Decabromodiphenylether; an investigation of non-halogen substitutes in electronic enclosure and textile applications.
- National Academy of Sciences (NAS), 2000. Toxicological risks of selected flameretardant chemicals.
- The Swedish Chemicals Inspectorate, 2005. Survey and technical assessment of alternatives to Decabromodiphenyl ether (decaBDE) in plastics. KEMI Report No. 1/05.
- U.K. Environment Agency, 2003. Prioritization of flame retardants for environmental risk assessment.

Sources of information and evaluation for the persistence, bioaccumulation and toxicity of Deca-BDE alternatives

- 1. Existing flame retardant reports.
- 2. Material Safety Datasheets (MSDSs) provided by chemical and electronics manufacturers.
- 3. National Library of Medicine Medline and Toxline Databases (searchable databases of published literature). Available at: <u>http://www.nlm.nih.gov/</u>.
- European Chemical Substances Information (ESIS), an online EINECS information system of the European Inventory of Existing Commercial Chemical Substances (EINECS). Available at: <u>http://ecb.jrc.it/esis/esis.php?PGM=ein</u>.
- 5. Information obtained from EPA via a Freedom of Information Act (FOIA) request of toxicity studies on Deca-BDE alternatives submitted under TSCA. Request submitted by Department of Ecology to EPA, 01/05.
- 6. QSAR (toxicity) modeling (by Accelrys Inc.).
- 7. EPIWIN model by Syracuse Research Corp. (<u>http://www.syrres.com/esc/epi.htm</u>)
- 8. EPA's PBT Profiler. (http://www.epa.gov/oppt/pbtprofiler/)
- 9. EPA's High Product Volume program. Information available at: <u>http://www.epa.gov/chemrtk/volchall.htm</u>

- 10. Australia's Department of Health and Aging, National Industrial Chemicals Notification and Assessment Scheme (NICNAS). Available at: <u>http://www.nicnas.gov.au</u>.
- 11. Chemical manufacturers who make Deca-BDE and other flame retardants (Akzo Nobel (Supresta), Albemarle Corp., Great Lakes Chemical Corp. and Clariant).
- 12. Chapter 173-333 WAC, Persistent Bioaccumulative Toxins rule, Washington State
- 13. General internet searches of pertinent information.

# **VI. Cost Benefit Analysis**

**IN BRIEF:** A cost-benefit analysis (CBA) is a tool used to assess the total expected costs vs. the total expected benefits of a course of action. Ecology evaluated the potential costs (first to Washington business, and then to the individual) with the human health benefits associated with a statewide ban on the use of deca-BDE in electronic casings. The focus of deca-BDE in electronic enclosures was chosen because most production of Penta- and Octa-BDE has already stopped, and the predominant use of deca-BDE in the U.S. is in electronic enclosures (TVs and computers). Ecology developed two different approaches to evaluate the potential costs; the potential health benefits were then examined against the costs.

Under the first approach ("Business Model"), Ecology attempted to develop estimates of overall costs to Washington business, to compare with overall benefits. A key component of this approach was a survey questionnaire sent to Washington wholesalers and retailers. The limited response to the survey questionnaire (despite the fact that, in addition to the e-mail survey, each non-responder was contacted at least twice by phone) prevented Ecology from developing estimates of overall costs to Washington business.

Under the second approach ("Individual Model"), Ecology attempted to estimate the average lifetime expenditures for TVs and computer monitors. This model estimated the average benefits to individuals, which was then used to estimate the minimum price increase for electronic purchases that would make costs outweigh the benefits. This approach to costs yielded more definitive information than the Business Model. Meanwhile, however, Ecology was finding that there was a high degree of uncertainty surrounding the estimates of potential health effects. When this uncertainty was combined with the fact that a safer, effective alternative to Deca-BDE has not yet been identified, Ecology concluded that both approaches to the cost-benefit analysis had limited utility to inform decisions on whether or not to phase-out deca-BDE.

This chapter is organized into four main sections:

- <u>Business Model</u>: This section provides a brief summary of this model and Ecology's efforts to develop information on business costs.
- <u>Individual Model</u>: A brief summary of this model is provided, including details on how estimates of lifetime expenditures for TVs and computer monitors were developed.
- <u>Potential Health Benefits</u>: The methods and assumptions used to estimate potential social benefits associated with banning the use of deca-BDE in those products are discussed.
- <u>Uncertainty and Variability</u>: This section summarizes the sources of uncertainty that complicated Ecology's efforts to estimate costs and benefits, and ultimately limited the utility of these comparisons to help inform a choice of strategies.

Additional information on Ecology's methods and assumptions are included in Appendix H.

## **Business Model**

The Business Model was designed to produce estimates of overall costs to Washington business and overall human health benefits. This methodology would answer the question, "What are the total costs of a ban on deca-BDE and how do those costs compare with potential societal benefits associated with such a ban?" The Business Model required three steps:

- Estimate the costs to Washington business associated with a ban on the use of deca-BDE in TVs and computer equipment.
- Estimate the potential social benefits associated with a ban on TVs and computer monitors containing deca-BDE.
- Compare estimates of potential social benefits with the overall costs to business.

The primary mechanism for developing cost estimates was a survey questionnaire sent to Washington wholesalers and retailers. Many affected businesses did not complete the questionnaire, which hindered Ecology's ability to develop overall cost estimates. (This is discussed in more detail below.) In the end, the uncertainties were too great for the Business Model to yield useful information. Therefore a second approach (the Individual Model) was developed, for which cost data was more likely to be available.

The following sections provide a brief overview of Ecology's methodology for estimating costs to business. The methods and assumptions used to estimate potential social benefits are discussed separately.

## Approach to Estimate Costs to Washington Business

Ecology used a simple model to estimate costs to Washington business, summarized in Figure 8 (below). A multi-step process was used; those steps are briefly described below. Key assumptions associated with each step are summarized in Appendix H, Tables H-1 through H-4.

		ing Č	ure 8: Costs to Washington Business ected Sales x % Price Increase
Where:			
Tot	al Affected Sales	=	the share of sales that would have to be replaced by deca-free product
% F	Price Increase	=	expected percentage price increase

- 1. **Identification of affected sales**: The first step in the Business Model was to determine product focus; electronic housings were selected (see Appendix H, Table H-1). The next step was to identify affected sectors; these were determined to be Washington manufacturers, wholesalers, retailers, and consumers. Since it was not possible to separate out the share of loss to each sector, assumptions were made about how each sector functions (see Appendix H, Table H-2).
- 2. **Conducting a survey:** Ecology concluded that wholesalers and retailers would be most affected by a ban. Ecology surveyed Washington wholesalers and retailers of selected industries (identified by the North American Industry Classification Code, NAICS). The survey was designed to elicit data for use in estimating the percentage of sales of PBDE-containing products affected by a deca-BDE ban. Out of 307 entities surveyed:
  - o 176 did not sell televisions or other electronic equipment.
  - 103 could not be reached after a minimum of two attempts (out-of-business, couldn't get through, wouldn't respond, bankrupt, duplicates, etc.).

Of the remaining 28, only seven companies returned the survey. The lack of response from those affected, and in particular from large companies, had the effect of creating selection bias. This rendered the assessment of total affected sales questionable at best. (Refer to Appendix B for a more detailed look at the survey process.)

- 3. **Price increases associated with use of products without deca-BDE:** The Business Model also required a determination of the amount (percentage) that costs would increase if companies were required to shift to products that did not contain deca-BDE. The assumptions used were that:
  - Some of the companies that had removed deca-BDE from their production lines would continue to produce PBDE-free products, even though the European Union (EU) has exempted deca-BDE from its ban. Currently, about 57% of TVs and 95% of computer products are PBDE-free (see Appendix H, Table H-3).
  - Some companies may postpone or reverse the transition to deca-BDE-free products. (The shift to deca-BDE-free products was prompted in part by the original EU ban and in part by the market shift away from cathode-ray tubes, CRTs. CRTs often contain deca-BDE.)

A wide range of values have been reported regarding what the final price increase would be. The Lowell report<sup>339</sup> estimates the materials-based cost shift between 1.5 percent and 2.5 percent of the final product prices for televisions, although it may not fully cover the costs. Personal conversations with four manufacturers of finished products currently making deca-BDE-free products estimated the increase at between 5 and 15 percent.<sup>340</sup> Another company indicated a price increase of less than 0.5%.<sup>341</sup> Ecology finally estimated the cost increase between 5 to 15 percent for the final product (finished products and components of finished products). This is despite the fact that the plastic itself may increase in price by more than 50

percent and despite the fact that the price of the alternative itself may be doubled. However, some manufacturers say the material is not the only basis for the cost shift, and cite greater energy, down time and form retooling. Thus there is a difference between the expected cost shift and the expected price shift, although there may be no difference between the expected cost shift and a diminishment of the expected price reduction. The latter is very difficult to quantify from market data.

## **Individual Model**

The Individual Model was designed to answer the question, "What price increase created by a ban would be high enough to offset the potential health benefits resulting from reduced exposure to deca-BDE and its breakdown products?" The Individual Model included three steps:

- Estimate average individual lifetime expenditures associated with the use of deca-free products.
- Estimate potential societal benefits associated with reduced use of TVs and computer monitors containing deca-BDE.
- Compare estimates of potential benefits and average individual lifetime expenditures in order to identify a breakeven price increase.

## Average Individual Lifetime Expenditures

Ecology used a simple model to estimate average individual lifetime expenditure on electronic products (TVs and computer monitors). A simplified version of the model is summarized in Figure 9.

		Figure 9
	Fo	rmula for Estimating Average Lifetime Expenditures
1	ime per	person = PV[(# TVs)(price of TVs)St + (# computers) (price of monitors)(Sm)]
Where:		
PV	=	Present value factor
#TVs	=	Average number of TVs purchased by average person in a lifetime
#monitors	=	Average number of computer monitors purchased by average person in a lifetime
TV price	=	Estimated cost of a new television
Monitor pric	ce =	Estimated cost of a new computer monitor
Sm & St	=	The share of monitors or TVs affected

Average individual lifetime expenditures were estimated based on (1) the estimated price of products, (2) the estimated lifespan of products and (3) the rate at which the products are turned

over in the home. Future expenditures were discounted to obtain the present value. (Refer to Appendix H, Table H- 5 for the complete formula.)

## **Breakeven Price Increase**

Ecology compared the average health benefits for individuals (discussed in the next section) to estimates of average lifetime expenditures for TVs and computer monitors (see Appendix H, Table H-14). The "breakeven price increase" is defined as the price increase that is equal to the estimated social benefit gains associated with phasing-out the use of TVs and computer monitors containing deca-BDE. The breakeven price increase (expressed as a percentage of the average individual lifetime expenditures) is calculated as follows:

% Price increase = Lifetime Benefits per Person / Lifetime Electronics Expenditures

This model depends on the identification of at least one safer, effective alternative to Deca-BDE. It is also highly sensitive to the uncertainty surrounding quantification of health benefits. This level of uncertainty, combined with the lack of an identified safer, effective alternative to Deca-BDE, prevented Ecology from being able 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.

## **Potential Health Benefits**

There are several categories of benefits associated with measures to reduce or phase-out the use of deca-BDE. Table 14 (next page) identifies the four broad categories of benefits typically considered by economists, and provides brief descriptions of specific benefits in each category. Ecology recognized that it might not be possible to determine a monetary value for all benefits identified in Table 14. Consequently, Ecology focused on human health benefits.

Table 14           Potential Benefits of Reducing/Phasing-Out deca-BDE				
Benefit Category	Description			
Human Health Benefits	Reduced mortality, reduced illness			
Amenity Benefits	No identified improvements in taste, odor or visibility			
<b>Ecological Benefits</b>				
• Direct Benefits	Reduced food contaminations (market) and reduced impacts on recreation and aesthetics (non-market)			
• Indirect-Use Benefits	Ecosystem health and services (e.g. biodiversity)			
<ul> <li>Non-Use Benefits</li> </ul>	Existence and bequest values; values of a clean environment			
Remediation Benefits	Reductions in future cleanup costs such as dredge disposal costs, biosolids management costs, etc.			

#### Key assumptions behind evaluation of human health benefits

Direct data on the human health effects of PBDEs (and deca-BDE in particular) are limited. In order to estimate potential human health benefits, Ecology made a number of assumptions, summarized in Appendix H, Tables H-6 through H-10. Key assumptions include:

- <u>Animal-to-human extrapolation</u>: Information on potential health impacts comes primarily from animal toxicity studies. A key underlying assumption is that results from rodent bioassays are a predictor of risks to human health. This approach and assumption has been consistently used by state and federal environmental agencies, and expert scientific review panels, over the last forty years.
- <u>High-to-low dose extrapolation</u>: Animal studies are typically conducted using exposure levels that are much higher than current or projected human exposure levels. A key underlying assumption is that results from high exposure levels can be extrapolated to the lower exposure levels commonly encountered by human populations. This approach and assumption has also been consistently applied by state and federal environmental agencies and expert review panels over the last several decades.
- <u>Chemical-to-chemical extrapolation</u>: The EPA<sup>342</sup> has concluded that the existing toxicology database for deca-BDE is "quite extensive." However, EPA identified several data gaps:

- (1) information on deca-BDE's potential to degrade to other substances in the environment;
- (2) a prenatal test in a second species and a two generation reproductive study that would serve to evaluate impacts of thyroid toxicity on reproductive success and fetal development; and
- (3) a neurotoxicity screening battery and a development neurotoxicity study.

Given these data gaps, Ecology decided to use toxicity information for other PBDEs (Pentaand Oct-BDE) and polychlorinated biphenyls (PCBs) as "proxies" or "surrogates" for deca-BDE when estimating potential health benefits. Ecology believes that toxicity information from Penta-BDE, Octa-BDE and PCBs can be used to provide a plausible upper bound on the toxicity of deca-BDE given:

- (1) the structural similarities between the two classes of chemicals, as well as structural similarities to thyroid hormones;
- (2) evidence suggesting that deca-BDE can breakdown to less-brominated PBDEs; and
- (3) both classes of chemicals have been shown to cause chronic damage to organs, changes in thyroid hormone levels, affect signaling in nerve cells, and cause spatial learning impairment and irregular movement in mice exposed early in life.

#### General approach used to estimate human health benefits

Ecology used a simple model to estimate human health benefits, summarized in Figure 10 (below). Ecology used a multi-step process to develop estimates of potential health benefits. Each of those steps is briefly described below. Key assumptions associated with each step are summarized in Appendix H, Tables H-6 through H-10.

Figure 10 Health Benefit Model					
Estimated		th benefits/year = (Exposure) * (Toxicity) * (Population) * (Valuation) Estimated health benefits/year = $\Delta X * (\beta * CF) * N * V$			
Where:					
ΔΧ	=	Estimated exposure to deca-BDE for various population groups (current and projected) (mg/kg/day);			
β	=	Health risk factor relating changes in exposure to changes in health endpoint of concern (mg/kg/day) <sup>-1</sup> );			
CF	=	Conversion factor to account for differences in absorption between deca-BDE and surrogate chemicals (if any);			
N	=	Population at risk (i.e. estimated number of people exposed to deca- BDE (current and projected);			
V	=	Estimated benefit associated with health impact (\$/health impact).			

The seven-step process to generate estimates of potential health benefits was as follows:

1. <u>Hazard Assessment</u>: Ecology began the assessment by identifying the types of health effects that might result from exposure to deca-BDE (health endpoints). These are summarized in Table 15 (below). Ecology also identified the health endpoints for which available scientific information provided a basis for preparing quantitative estimates of health benefits.

Table 15 Health Endpoints Considered in Benefits Assessment					
Quantifiable	Non-Quantifiable				
<ul> <li>Effects on Development Due to Reduced Maternal Thyroid Hormone</li> <li>Systemic Effects Related to Reduced Thyroid Hormone</li> <li>Effects on Neurobehavioral Development</li> <li>Liver Cancer</li> </ul>	<ul> <li>Immune System Effects</li> <li>Liver Damage</li> <li>Hearing Impairment (via thyroid hormone reduction)</li> <li>Cardiovascular Effects (via thyroid hormone reduction)</li> </ul>				

- 2. <u>Dose-Response Relationships</u>: Ecology reviewed the scientific literature and EPA guidance materials to identify information on the relationships between exposure levels and health impacts. Four main approaches were used to characterize dose-response relationships:
  - Linear extrapolation from the lower 95th percent confidence limit on the benchmark dose (*BMDL*) calculated from animal studies involving exposure to Penta- and Octa-BDE. This approach was used to estimate the dose-response relationship for thyroid-related health impacts. Key assumptions include:
    - Maternal levels of thyroxine (T4) are a measure of thyroid hormone homeostasis. A 20% reduction in T4 levels is an indicator of hypothyroidism in rodent bioassays;
    - Linear extrapolation from the BMDL provides a reasonable method for extrapolating from high to low exposures;
    - Dose-response information for Penta- and Octa-BDE mixtures provides a reasonable basis for evaluating the health risks associated with deca-BDE/breakdown products; and
    - The probability of adverse effects in the developing fetus/pregnant mother can be estimated based on relationships between maternal hypothyroidism and specific health endpoints (e.g. reduction in IQ scores, low birth weight, hypertension).
  - Linear extrapolation from the lower 95<sup>th</sup> percent confidence limit on the benchmark dose (BMDL) calculated from studies on PCB exposures. This approach was used to develop a dose-response relationship for impacts on neurological development. Key assumptions:

- PCBs provides a reasonable basis for evaluating the health risks associated with deca-BDE/breakdown products;
- Scores on Intelligence Quotient (IQ) tests provide a measure of cognitive development;
- Dose-response information provides a reasonable basis for estimating the relationship between PCB exposure and IQ scores;<sup>343</sup> and
- Dose-response relationships for PCBs need to be adjusted to take into account the relative absorption of PCBs and deca-BDE.
- *Cancer slope factor developed for PCBs*: The range of EPA slope factors developed for different PCBs mixtures was used as surrogate values for deca-BDE/breakdown products. Key assumptions:
  - Dose-response information for PCBs provides a reasonable basis for evaluating the health risks associated with deca-BDE/breakdown products;
  - The EPA slope factors are reasonable estimates for evaluating cancer risks associated with PCB exposure;
  - Dose-response relationships for PCBs need to be adjusted to take into account the relative absorption of PCBs and deca-BDE; and
  - 80% of people developing liver cancer in a given year will die of the disease in that year.
- Slope of the line resulting from a linear extrapolation from the TD50 (dose estimated to induce tumors in 50% of experimental animals) to zero: Ecology used the slope of the line resulting from a linear extrapolation from a TD50 value calculated from the NTP<sup>344</sup> to estimate a cancer slope factor for deca-BDE. Key assumptions include:
  - Linear extrapolation from a TD50 provides a reasonable approach for estimating a cancer slope factor that is similar to estimates using the multistage model;<sup>345</sup>
  - Neoplastic lesions/liver hyperplasia can progress to malignant forms of cancer;
  - The NTP study results provide a reasonable basis for estimating a TD50;<sup>346</sup> and
  - 80% of people developing liver cancer in a given year will die of the disease in that year.
- 3. <u>Exposure Assessment</u>: Ecology considered two approaches for estimating human exposure.

The first approach (used by Health Canada in their evaluation of PBDEs<sup>347</sup>) involves four steps. First, identify exposure pathways (e.g. breast milk, house dust). Next, estimate contaminant levels in various media (e.g. dust, water, breast milk). Thirdly, estimate contact rates (e.g. dust ingestion rates) for different population or age groups. And finally, use that information to estimate human exposure in terms of a daily intake (ug/kg/day).

The second approach<sup>348</sup> (which Ecology chose to use) involves using information on lipid normalized concentrations (expressed in terms of ug/glipid) of deca-BDE in serum and breast milk, fraction body fat, body weights, half-life of deca-BDE in the human body and

the fraction of ingested deca-BDE absorbed into the body to estimate daily intakes (ug/kg/day). Key assumptions included:

- This approach provides a reasonable basis for estimating daily intakes (ug/kg/day);
- Monte Carlo simulation can be used to factor in the variability in exposure parameters. The median, mean, and 95th percentile values from the calculated distribution provide low, mid-range and high exposure estimates;
- Information on lipid normalized blood and breast milk concentrations from other parts of the U. S. can be used to estimate concentrations in Washington;
- The EPA Exposure Assessment Guidelines<sup>349,350</sup> provide point estimates and distributions for key exposure parameters (e.g. body weight) that are applicable to the Washington population; and
- Exposure reductions will occur over a 1-18 year period as existing TVs and computers are replaced with products that do not contain deca-BDE.

Exposure estimates are based on levels of deca-BDE in blood and breast milk and do not take into account levels of other PBDEs that might result from the breakdown of deca-BDE. Consequently, calculated intake values may underestimate overall exposure related to the use of deca-BDE.

- 4. <u>Populations at Risk</u>: For purposes of this evaluation, Ecology assumed that all Washington residents may be exposed to deca-BDE because of the widespread presence of TVs and computers at home and at work. However, the population at risk varies with the health effect. For example, pregnant women were considered to be the population-at-risk when estimating the risks of impacts on neurological development in the developing fetus resulting from reductions in maternal thyroid hormone levels. All Washington residents were considered to be the population at risk when estimating systemic health effects related to reduced thyroid levels and liver cancer.
- 5. <u>Health Benefits Estimates</u>: Ecology integrated the information on toxicity/dose response, exposure and number of people exposed into the health benefit model (Figure 10) to estimate potential health impacts associated with exposure to deca-BDE and its breakdown products. The health outcomes considered in the CBA are cancer, thyroid-related effects and reductions in IQ scores. (See Appendix H for details, Tables H-6 through H-10.)
- 6. <u>Benefit Valuation</u>: Ecology estimated the dollar values associated with the potential human health benefits by multiplying estimates for various health impacts (e.g., reduction in IQ points) by the standard costs for those impacts (e.g. amount of lost income associated with each IQ point loss). (See Appendix H, Table H-11) Monetary evaluations come from existing analyses, quality-of-life impact literature and the Health Care Authority. (See Appendix H, Table H-12) The annual cost per thyroid treatment is \$7,940 based on direct billings to the Health Care Authority. Billings do not reflect all losses due to illness. The dollar values used to generate these estimates are more likely to underestimate the benefit than overestimate the values. The value of life was estimated to be \$4 million. The value of an IQ point was estimated to be \$14,500.

7. <u>Present Value Estimates</u>: Once the value of all the disorders was obtained, the present value of an 82-year lifetime of effects was estimated. The general model used to prepare present value estimates is shown in Figure 11. Appendix H, Table H-13 includes more detailed information and assumptions used to prepare present value estimates.

		Figure 11 Present Value Estimate of Health Benefits
		$\mathbf{B} = (\mathbf{W})(\mathbf{\%} \operatorname{deca})(\mathbf{R})(\mathbf{D})$
Whe	ere:	
В	=	Annual benefit summed over an 82-year life span using present value as the basis. This involves discounting future years more than the current year.
W	=	Value of reduced PBDE-related illnesses
% deca	ι =	% of deca in electronic housings
R	=	Percent reduction factor to describe the impact of delayed replacement of PBDE-laden electronic housings
D	=	Percent reduction factor to describe the impact of delayed onset of illness after exposure

## **Limitations Due to Uncertainty and Variability**

Ecology efforts to finalize the cost-benefit analysis were hindered by three factors:

- (1) limited information on health effects, exposures and conditions (e.g. uncertainty<sup>351</sup>);
- (2) differences in sensitivity to deca-BDE, exposures and business responses to changing regulatory requirements (e.g. variability<sup>352</sup>), and
- (3) emerging information on toxicity, exposure and economic issues.

These hurdles are created in part by disclosure issues and by uncertainty in available scientific information and current and future economic conditions. Given these limitations, it is important to recognize that there is a high degree of uncertainty surrounding estimated expenditures and health benefits and those estimates are highly sensitive to assumptions on future economic conditions, exposure and health risks.

Ecology believes that these sources of uncertainty and variability complicate the interpretation and use of the study results. There is uncertainty in the medical outcomes that may overstate impacts. In response to the uncertainty surrounding available data, Ecology generally used conservative assumptions for the economic values used to estimate health benefits and, consequently, actual benefits may be higher than estimated values. Important sources of uncertainty and variability include the following:

• Uncertainty on the toxicity and costs associated with alternatives to deca-BDE.

- Nature and extent of deca-BDE degradation.
- Use of dose-response information from lower-brominated PBDE mixtures and/or PCB mixtures to evaluate health risks associated with deca-BDE/breakdown products:
- Significance of reductions in T<sub>4</sub> levels observed in rodent studies in terms of predicting human health risks.
- Intra-individual variability in thyroid hormone levels and sensitivity to predicted reductions.
- Shape of the dose-response curve at low levels of exposure (including the presence/absence of a threshold for adverse effects in a heterogeneous population):
- Current and projected changes in deca-BDE uses and environmental levels.
- Variability in environmental concentrations of deca-BDE and its potential degradation products.
- Intra-individual variability in exposure and factors that influence exposure.

# **VII. PBDEs and the Regulatory Environment**

**IN BRIEF:** Industry voluntarily ceased manufacture of Penta and Octa-BDE in December 2004. U.S. EPA followed this action with a proposed Significant New Use Rule (SNUR) that will require notification of, and evaluation by, EPA of any new use of Penta or Octa-BDE.

The EPA is developing a rule to complement a national flammability standard for residential upholstered furniture under consideration by the Consumer Product Safety Commission. The rule would require notification to, and review by, the EPA of Deca-BDE and 15 other flame retardant chemicals or categories of chemicals likely to be used on furniture fabrics.

Several U.S. states and the European Union have taken action on PBDEs, including manufacturing bans on Penta and Octa-BDE. Actions on Deca-BDE have not included restrictions on manufacturing.

The following section provides an overview of existing regulatory requirements and proposed actions governing PBDEs at the state, federal and international levels. Activities other than those identified below may also exist.

## Washington State Overview

Only one Washington State regulation was identified that pertains to PBDEs, WAC 173-303-100, Dangerous Waste Regulations, Persistence Criteria. The regulation describes methods for determining whether a solid waste is a dangerous waste based on toxicity and/or persistence. Persistent constituents are defined as chemical compounds which are either halogenated organic compounds (HOC), or polycyclic aromatic hydrocarbons (PAH). PBDEs are HOCs. Under these criteria, many products containing PBDEs would probably be considered dangerous waste at end-of-life.

## **Federal Overview**

## **Toxics Release Inventory**

Deca-BDE is the only one of the commercial PBDE formulations for which reporting is required for the U.S. EPA's Toxic Release Inventory (TRI). TRI is a publicly available EPA database that contains information on toxic chemical releases and other waste management activities reported annually by certain covered industry groups as well as federal facilities. This inventory was established under the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) and was expanded by the Pollution Prevention Act of 1990. Covered industry groups and federal facilities that dispose of more than 10,000 pounds of Deca-BDE annually are required to report how much they discard. Only one facility in Washington has reported on the use of Deca-BDE under TRI. The company operating the facility, Matsushita, has stated an intent to phase out the use of all PBDEs.

## **Toxic Substances Control Act**

In November 2003, the Great Lakes Chemical Corporation (now Chemtura) agreed to phase out use of Penta and Octa-BDE by the end of 2004. On December 6, 2004, EPA proposed a Significant New Use Rule (SNUR) under Section 5 of the Toxics Substances and Control Act (TSCA) requiring manufacturers and importers to notify EPA at least 90 days before commencing the manufacture or import of Penta-BDE or Octa-BDE on or after January 1, 2005. The required notice would provide EPA with the opportunity to evaluate any intended new use and associated activities and, if necessary, to prohibit or limit that activity before it occurs. The proposed rule would not prohibit the import of products containing Penta-BDE or Octa-BDE (e.g., mattresses, upholstered furniture).

All three PBDE formulations must be tested for dioxin and furan contamination under EPA's 1987 TSCA Section 4 Dioxin/Furan Test Rule (Title 40 of the Code of Federal Regulations, Part 766 ("40 CFR 766")).

EPA is also developing a rule under TSCA to complement a national flammability standard for residential upholstered furniture under consideration by the Consumer Product Safety Commission (CPSC). The rule would require notification to, and review by, EPA of 16 flame retardant chemicals or categories of chemicals, including Deca-BDE, identified by CPSC and industry as likely to be used to flame retard fabrics on furniture in order to comply with such a standard.<sup>353</sup>

## **Other Federal Activities**

Industry-sponsored risk assessments for Penta-, Octa- and Deca-BDE were developed through EPA's Voluntary Children's Chemical Evaluation Program (VCCEP). VCEPP is an EPA effort to work with chemical manufacturers to provide more data on the potential health risks to children associated with certain chemical exposures. In September 2005, following review of the VCEPP documents, EPA requested manufacturers to voluntarily provide additional data on the fate and transport of Deca-BDE along with reproductive toxicity tests for Penta and Octa-BDE.<sup>354</sup>

In addition to VCEPP, EPA is sponsoring and conducting their own research on PBDEs within the Office of Research and Development. This research is aimed at determining PBDE levels in children, house dust, food, and breast milk; developmental and reproductive toxicity of PBDEs; and the environmental fate of PBDEs upon release or after disposal and incineration of electronic equipment.<sup>355</sup>

EPA has also drafted a PBDE Project Plan, expected to be published in early 2006. This Project Plan will provide information on EPA's overall approach to PBDEs, including the current scientific understanding of PBDEs and ongoing or planned activity by EPA and the federal government to research and address the potential risks from PBDEs. The Project Plan will describe EPA's four objectives and the key activities undertaken to achieve those objectives. EPA's principal objectives are: 1) assess substitutes for pentabromodiphenyl ether and

octabromodiphenyl ether; 2) assess and evaluate decabromodiphenyl ether; 3) assess risks of pentabromodiphenyl ether and octabromodiphenyl ether; and 4) track developments concerning other brominated flame retardants of interest.<sup>356</sup>

EPA is currently re-assessing toxicity data for PBDEs in order to update existing reference doses and/or cancer assessments on their Integrated Risk Information System (IRIS). The new assessment is expected to be released in 2006.<sup>357</sup>

The furniture manufacturing industry and EPA's Design for the Environment Program have initiated a partnership to explore a variety of approaches to achieve environmentally sound fire protection. Approaches include identifying and evaluating environmentally preferable flame retardants and identifying and evaluating technological barriers to sustainable design as well as alternative formulations for foam.<sup>358</sup>

The Interagency Working Group on Fire and Materials (IWGFM), formed in 1993, is a group of federal scientists and engineers from over 40 agencies that implements coordinated, long-range, national research efforts to understand the fire and thermal behavior of materials and develop advanced materials with improved performance.<sup>359</sup> IWGFM objectives are:

- Develop uniform test procedures for fire performance evaluation of materials for consideration by government agencies
- Provide a mechanism to coordinate and communicate among government/ industry/ university research activities
- Analyze current research, development and technology in light of present and projected national needs
- Advance defense/ civilian agency dual-use objectives
- Promote research and development of advanced fire-safe materials by strengthening the case for more government and industrial funding.

## **Other States: Overview**

## California

In August 2003, the California State Legislature passed <u>AB 302</u>, which prohibits, on and after January 1, 2008, a person from manufacturing, processing, or distributing in commerce a product containing more than one-tenth of 1% Penta-BDE or Octa-BDE, by mass.<sup>360</sup> In 2004, the California State Legislature passed into law AB 2587, which moves the date of the California ban from 2008 to June 1, 2006.<sup>361</sup>

As required by AB 302, in June 2004 the Senate Office of Research submitted a report entitled "Polybrominated Diphenyl Ethers (PBDEs): Potential Hazards from Deca-BDE and Unresolved Issues from AB 302" to the President Pro Tempore of the Senate and the Senate Environmental Quality Committee. The report stated that, based on the "likely potential harm to humans posed by Deca-BDE and the known human exposures to this chemical, it does not appear that human

exposure to Deca-BDE is occurring at a level that is likely to be unsafe for human health or development." The report concluded that, at this time, it would be premature to add Deca-BDE to the list of banned PBDEs contained in AB 302.<sup>362</sup>

The report went on to state that, because of inherent problems in extrapolating from rodent studies to human effects and the limited data on human exposure, it was not possible to say that Deca-BDE does not pose a danger to human health. Rather, the data available does not conclusively show that there is a danger to human health at this time. While the potential breakdown of Deca-BDE is mentioned in the body of the report, potential breakdown products are not referenced in the conclusion or its rationale.<sup>363</sup>

The report recommends that California's Office of Environmental Health Hazard Assessment set a reference dose for Deca-BDE based on the level in human tissue that would represent an unsafe level. It also recommends that the state create a breast milk monitoring program.<sup>364</sup>

#### Proposed Legislation:

In June 2005, the California Assembly passed AB 263, which imposes civil penalties of a minimum of \$10,000 for violating the existing statutory ban on Penta-BDE and Octa-BDE, scheduled to start June 1, 2006, on the manufacture, processing or commercial distribution of any product containing any significant amount of pentabrominated diphenyl ether (Penta-DBE) or Octa-DBE.<sup>365</sup>

#### Connecticut

#### Proposed Legislation:

In June 2005, the Connecticut State Senate passed SB785. This bill prohibits the sale of the penta and octa mixtures of polybrominated diphenyl ethers and requires study of the relevant risk assessments relating to the deca mixtures of polybrominated diphenyl ethers. SB785 passed from the Senate to the House on June 4, 2005, where it awaits further action.<sup>366</sup>

#### Hawaii

In June 2004, Hawaii enacted HB2013/SD2/CD1, which prohibits the manufacture, processing, or distribution of a product or flame-retarded part of a product containing more than 0.1% by mass of Penta-BDE, Octa-BDE, or any other chemical formulation that is part of these classifications, on or after January 1, 2006.<sup>367</sup>

#### Illinois

In July 2005, Illinois HB2572 was signed into law. The new law creates the Brominated Flame Retardant Prevention Act and provides that effective January 1, 2006 a person may not manufacture, process, or distribute in commerce a product, or a flame-retarded part of a product containing more than one-tenth of 1% of Penta-BDE or Octa-BDE by mass. The law includes exemptions for the sale of used penta- or octa-containing products by businesses, charities, or private parties; the distribution of original equipment replacement service parts manufactured

prior to January 1, 2006, and for the processing of recyclables containing Penta- or Octa-BDE in compliance with applicable state and federal laws. The law does not restrict a manufacturer, importer, or distributor from transporting products containing PBDEs through the state or from storing PBDEs in the state for further distribution.<sup>368</sup>

The law also requires that by January 2, 2006, the Illinois Environmental Protection Agency shall submit to the General Assembly and the Governor a report that reviews the latest available scientific research to address certain issues related to the effects of Deca-BDE. The Illinois Department of Public Health is required to submit by February 28, 2006 a report to the General Assembly and the Governor a report that reviews the Illinois Environmental Protection Agency's Deca-BDE study.<sup>369.</sup>

#### Maine

In April 2004, Maine enacted legislation [PL 2003, c 629] to reduce contamination from PBDEs. Section 1 of the bill prohibits the sale of products that contain more than 1% Penta-BDE or Octa-BDE beginning January 1, 2006. Section 2 expresses the intent of the Legislature to reduce risks associated with Deca-BDE either by implementing risk management measures or by prohibiting the sale of products that contain more than 1% Deca-BDE beginning January 1, 2008, provided a safer, nationally available alternative is identified. To assist the Legislature in deciding which if either of these strategies to pursue, the Department of Environmental Protection is required to review emerging information on PBDEs and other BFRs, including information on alternatives to Deca-BDE, and report annually to the Legislature's Committee on Natural Resources beginning January 5, 2005.<sup>370,371</sup>

## Maryland

In May 2005, the State of Maryland enacted <u>HB83</u>, which prohibits, on or after October 1, 2008, the manufacture, processing, sale, or distribution in the State of a product or flame-retardant part of a product that contains more than a specified amount of Penta- or Octa-brominated diphenyl ether. In addition, the law also requires that on or before January 8, 2007, the Maryland Department of Environment must report on the use of Deca-BDE and recommend restrictions on its use and sale.<sup>372</sup>

## Massachusetts

Bills H  $2275/\underline{S}$  1268 relate to alternatives to the use of toxic chemicals. PBDEs are included on the list of chemicals to be phased out. The bills were heard in September 2003 in the Joint Committee on Natural Resources and Agriculture and were eligible for Executive Session.

Deca-BDE is subject to the Massachusetts Substance List.<sup>373</sup>

## Michigan

On January 3, 2005, Michigan enacted HB 4406, and SB 1458, Public Acts 562 and 526 respectively, which amend Michigan's Natural Resources and Environmental Protection Act.<sup>374</sup> The laws ban, as of June 1, 2006, the manufacture, process, or distribution of products or materials containing more than 1/10 of 1% of penta-BDE. The law includes exemptions for original equipment manufacturer parts, or the processing of recyclables containing Penta- or Octa-BDE in compliance with applicable state and federal laws. SB 1458 also authorizes the Michigan Department of Environmental Quality to establish a PBDE advisory committee to review scientific information gathered on PBDEs, specifically on Deca-BDE. Should new information indicate a significant risk for human health and the environment, the Department will advise the legislature of the risk for possible action.<sup>375</sup>

#### **New Jersey**

Deca-BDE is subject to the New Jersey Right to Know Hazardous Substance List (1 percent reporting limit).<sup>376</sup>

### **New York**

In August 2004, New York enacted A 10050/S 7621, which prohibits the manufacture, process, or distribution of brominated flame retardants, specifically penta- and octa-BDE, but does not prohibit the use or sale of such products. The bill also establishes a Task Force on Flame Retardant Safety to study the risks associated with Deca-BDE and the availability, safety and effectiveness of alternatives to Deca-BDE.<sup>377</sup>

## Oregon

In 2005, the Oregon legislature approved SB 962, a bill to phase out the use of Penta-BDE and Octa-BDE. The legislation also included a provision to study the effects of Deca-BDE.<sup>378.</sup>

#### Pennsylvania

Deca-BDE is subject to the Pennsylvania Environmental Hazard List.<sup>379</sup>

## **International Overview**

## **European Union**

The European Union (EU) currently has two main laws which regulate the market and use of PBDEs in Europe. Directive 2003/11/EC of February 6, 2003, passed by the European Parliament and European Council, banned the marketing and use of Penta-BDE and Octa-BDE as of August 15, 2004.<sup>380</sup> In January 2003, the European Parliament and the Council of the European Union passed Directive 2002/95/EC, "Restriction of Certain Hazardous Substances to Electrical and Electronic Equipment" (RoHS), which lists the substances which are to be phased out of electrical and electronic equipment by July 1, 2006. The list includes Polybrominated Diphenyl Ether (PBDE) flame retardants, among them Penta-, Octa-, and Deca-BDE.

The Directive also called for an evaluation of applications for Deca-BDE to establish whether the Directive should be amended, i.e., certain applications of Deca-BDE should be exempted from the ban.

In parallel, within the framework of the Existing Substances Regulation (793/93 EEC), a comprehensive risk assessment on Deca-BDE is being carried out by France and the U.K. on behalf of the EU. The human health risk assessment was to be completed by France and the environmental risk assessment by the U.K.

In February 2004, France completed the Human Health Draft of the Draft Update Risk Assessment for Deca-BDE. This portion of the risk assessment drew one conclusion on Deca-BDE, with regard to neurotoxicity. The Draft Update concluded that there is at present no need for further information and/or testing or for risk reduction measures beyond those which are being applied already.<sup>381</sup>

In May 2004, the U. K. completed the Final Environmental Draft of the Draft Update Risk Assessment for Deca-BDE. It concluded that there is need for further information and/or testing with regard to the assessment of Deca-BDE to be persistent, bioaccumulative, and toxic. The study also concluded that further information and testing are necessary to monitor the possible formation of more toxic and bioaccumulative products that may result from the degradation of Deca-BDE. However, the study concluded that further risk reduction measures are not currently necessary for Deca-BDE.<sup>382</sup>

In March 2005, the Scientific Committee on Health and Environmental Risks (SCHER), a committee of physicians and professors who serve an advisory role to the European Commission, released their opinion on the May 2004 Environmental Risk Assessment completed by the U.K. Although the SCHER states that the update is well done, they disagree with the recommendation that risk reduction measures are not currently necessary. The SCHER concludes that,

*Emissions of DeBDE [Deca-BDE] to the environment may constitute serious problems in the future. If formation of lower brominated, bioaccumulating substances take place this process can go on for a very long time and there are no possibilities to stop it. The previous scientific committee (CSTEE<sup>383</sup>) said that the* 

uncertainties in the fate of Deca-BDE warrant risk reduction measure. Today there is further evidence for degradation of this substance to potentially harmful compounds and SCHER also strongly recommends risk reduction measures (conclusion iii).<sup>384</sup>

Following the release of the SCHER opinion in March 2005, the European Commission Joint Research Center authored a second update to the May 2004 Environmental Risk Assessment. While disagreeing with the conclusion of the SCHER that further risk reduction measures are necessary, the report incorporates the SCHER's recommendations for a regular review of any new information relating to Deca-BDE.<sup>385</sup> The report does discuss the need for further study of Deca-BDE, particularly the debromination of Deca-BDE to lower PBDE congeners which it cites as of "high concern" and notes that, "many of these substances [lower PBDE congeners] are considered to be "persistent, bioaccumulative, and toxic (PBT) or very persistent and very bioaccumulative (vPvB)."<sup>386</sup>

On April 19, 2005, the Technical Adaptation Committee for the RoHS Directive (a committee formed to make decisions on unresolved issues of the RoHS) met to vote on a draft Decision by the European Commission to continue to exempt Deca-BDE from the RoHS Directive. Prior to the vote, some member states questioned whether an exemption was appropriate due to continuing doubts regarding the environmental and human health impacts of Deca-BDE.<sup>387</sup> Nevertheless the vote proceeded and the Draft Decision passed, although the vote fell short of a qualifying majority of 72.3% and was passed on to the European Parliament for scrutiny, and to the European Council of Ministers for decision on June 6, 2005.

The European Parliament, upon receiving the Draft Decision, questioned on formal and procedural grounds whether the Commission had exceeded its implementing powers, and on substance charged the Commission with ignoring findings of the May 2004 Environmental Risk Assessment and the March 18, 2005 SCHER opinion. On June 21, 2005, Parliament's Committee on the Environment, Public Health and Food Safety then proceeded by voting in favor of a resolution calling for the European Council of Ministers to oppose the Draft Decision unless the Commission reconsidered the exemption of Deca-BDE.<sup>388</sup> The European Parliament followed suit on July 6, 2005 with the plenary adoption of the same resolution.<sup>389</sup> Despite the objections of members of the European Parliament, the Council of Ministers voted in favor of the exemption on September 2, 2005, although a qualifying majority was not achieved to immediately adopt the exemption, and hence the final decision fell upon the Commission.<sup>390</sup> The Draft Decision to exempt Deca-BDE was then forwarded back to the Commission, adopted, and published on October 13, 2005.<sup>391</sup> The exemption of Deca-BDE will remain in effect for 5 years, although it can be "unexempted" on the basis of a proposal by the Commission to be adopted by the Council of Ministers. Because of the uncertainty surrounding Deca-BDE, the EU will continue to review new data and studies on Deca-BDE and the Commission may propose an outright ban or specific use restrictions which may include the RoHS exemption in the future.

On January 9, 2006 the European Parliament published its intent to challenge the Commission's decision to exempt Deca-BDE from the RoHS Directive (Commission Decision 2005/717/CE) to the European Court of Justice.<sup>392</sup> The European Parliament joins Denmark in challenging the exemption of Deca-BDE, which criticizes the Commission for not considering possible safer

alternatives to Deca-BDE.<sup>393</sup> It is not known when the cases will be heard at the Court of Justice.

# Contacts between the Departments of Ecology and Health Communication and the European Commission

Much of the proceedings of the European Union are closed sessions, meaning that official transcripts are unavailable to the public. As a result, interpretations vary in how different branches of EU government have responded to the exemption of Deca-BDE from the RoHS. Throughout this process, Ecology and DOH has kept in contact with Robert Donkers, Environment Counselor at the Delegation of the European Commission to the U.S. in Washington , D.C. He has articulated that the Commission and the UK as the lead member state for the Deca-BDE file will continue to monitor Deca-BDE closely and the Commission may propose to introduce an across the board ban for Deca-BDE or propose to withdraw the exemption in the future if new findings arise that show Deca-BDE, or its products, to be too harmful to humans or the environment.

### Australia

Australia published an assessment of PBDEs in June 2001, conducted under its National Industrial Chemicals Notification and Assessment Scheme (NICNAS). The assessment recommended that, due to identified health and environmental effects of concern with some PBDEs, the lack of adequate data on others and their wide use, a full risk assessment be considered when hazard data is available from international assessments. The assessment further recommended that, on the basis of known hazards for specific PBDEs, material safety data sheets and other hazard communication materials be revised to reflect the information on hazards already available.<sup>394</sup> In June 2005, NICNAS listed Deca-BDE as a Priority Existing Chemicals and will undergo a full risk assessment, including an assessment of the degradation products of Deca-BDE, in particular octa- and penta-BDE.<sup>395</sup> The government is also conducting risk assessments on a number of chemical alternatives to Deca-BDE.

## Canada

Deca-BDE is listed on the Domestic Substances List<sup>397</sup> which includes substances that were, between January 1, 1984, and December 31, 1986, in Canadian commerce, used for manufacturing purposes, or manufactured in or imported into Canada in a quantity of 100 kg or more in any calendar year. The purpose of the List was to define what was "New to Canada;" it currently contains about 23,000 substances.<sup>398</sup>

In February 2004, Environment Canada released a Draft "Environmental Screening Assessment Report on Polybrominated Diphenyl Ethers (PBDEs)" for Public Comment. The draft proposes that PBDEs, including tetra-BDE, penta-BDE, hexa-BDE, hepta-BDE, octa-BDE, nona-BDE and deca-BDE, be considered "toxic" under section 64 of the Canadian Environmental Protection Act of 1999 (CEPA 1999). It further proposes that consideration be given to adding tetra-BDE, penta-BDE, and hexa-BDE to the Virtual Elimination List under CEPA 1999 and that that PBDEs, including tetra-BDE, penta-BDE, hexa-BDE, hepta-BDE, octa-BDE, nona-BDE, and deca-BDE, be considered as "Track 1" substances under the Toxic Substances Management Policy.<sup>399</sup>

The Virtual Elimination List is compiled by the Canadian Ministers of Environment and Health. The Ministers must specify the level of quantification for each substance on the List and, having done so, must prescribe the quantity or concentration of the substance that may be released into the environment either alone or in combination with any other substance from any source or type of source.<sup>400</sup> A "Track 1" substance is one that has been determined to be persistent, bioaccumulative, toxic and primarily the result of human activity and subsequently targeted for virtual elimination from the environment. This objective will be achieved by addressing sources of release to the environment or by removing or managing the substance if it is already in the environment.

In February 2004, Health Canada released a "Screening Assessment Report- Health: Polybrominated Diphenyl Ethers (PBDEs) [Tetra-, Penta-, Hexa-, Hepta-, Octa-, Nona- and Deca- Congeners]". The report also proposes that, principally on the basis of environmental considerations, PBDEs as a group be considered "toxic" as defined in Section 64 of CEPA 1999.<sup>402</sup>

## China

In 2002 China's Ministry of Information began drafting regulations entitled the "Management Methods for the Prevention and Control of Pollution from Electronics Information Products" (Methods). Among other chemicals, the Methods ban PBDEs in electronic information products. The list of products covered is still under development, as are standards for maximum tolerated thresholds and labeling requirements.<sup>403</sup> The regulations are often referred to as the "China RoHS" because they incorporate the substance regulations of the European Union's RoHS Directive, including those for PBDEs.<sup>404</sup> China's draft regulations differ from the RoHS however, in a series of requirements for the labeling of the toxic-substance content, material-content, recyclability, "safe-use", and point-of-origin of products manufactured and imported into China.<sup>405</sup>

## Denmark

The Danish Environmental Protection Agency published an "Action Plan for Brominated Flame Retardants" in 2001 to serve as the foundation for future regulation of brominated flame retardants in Denmark. The action plan states as one of its short-term objectives the phase-out of PBDEs. The plan outlines seven areas of activity to accomplish its objectives, including international regulation, international cooperation, national initiatives, build-up of knowledge, standardization, information activities and the support of cleaner production.<sup>406</sup> On January 2, 2006, the Danish government announced that it will challenge the European Union's exemption of Deca-BDE from the RoHS Directive to the European Court of Justice.<sup>407</sup> The government argues that the European Commission, in its decision to exempt Deca-BDE from the RoHS, failed to consider alternatives to Deca-BDE.<sup>408</sup> The Danish government joints the European Parliament in challenging the exemption (see European Union, above).

## Germany

Deca-BDE is not used on a voluntary basis in Germany by association-bound companies in the plastics and textile industry.<sup>409</sup> In 1989, the Chemical Industry Association and the Association of the Plastics Producing Industry, in a statement to the Federal Government, voluntarily agreed to discontinue the production and further use of PBDEs.<sup>410</sup>

#### Norway

On July 29, 2005, Norway notified the World Trade Organization of the Norwegian Deca-BDE Action Plan adopted by the government which bans from its market any product or substance that contains more than 0.1% Deca-BDE by mass.<sup>411</sup> Norway cites the SCHER (European Commission Scientific Committee on Health and Environmental Risks) report in its rationalization for adopting the regulation. The action plan which controls Deca-BDE in the market went into effect in August 2005.

#### Sweden

In May 2004, Sweden commissioned the national chemicals inspectorate, KemI, to draft plans for banning Deca-BDE, in advance of EU actions on Deca-BDE. KemI is considering a national ban on all brominated flame retardants and is examining risks associated with a number of other substances.<sup>412</sup> The recent EU exemption of Deca-BDE from the RoHS Directive will affect the government's support of a national ban, although the Swedish Chemicals Inspectorate has spoken out in opposition of the exemption of Deca-BDE from the EU RoHS.<sup>413</sup>

#### Switzerland

The Swiss Parliament's Rule for the Reduction of Risks in the Use of Certain Extremely Dangerous Substances, Process, and Objects (Chemical Risk Reduction Rule, Chem RRV) directs that as of July 1, 2006, new objects in electro and electronic instruments (as defined by guidance 2002/95 EG), in lighting for the home, and in replacement parts containing more than 0.1% Deca-BDE may not be brought into commerce, unless no alternatives are available.<sup>414</sup> Exemptions to this rule are included for medical instruments, and certain security and control instruments, and for objects brought into commerce before July 2006.<sup>415</sup>

## **United Kingdom**

The U.K. Environment Agency is currently conducting national risk assessments for chemicals that are possible alternatives to Deca-BDE, or are used with chemical alternatives, but have not yet been investigated at the international level (such as an EU risk assessment). Assessments are pending for a number of chemicals including Triphenyl phosphate (TPP), Diphenyl cresyl phosphate (DCP), and Resorcinol bis-diphenyl phosphate (RDP). Assessments will be published as they are completed.<sup>416</sup> The U.K. is also coordinating with the Organization for Economic Cooperation and Development (OECD) on production of an Emission Scenario Document (ESD)

for plastic additives, a major sector of the industry for PBDEs and other flame retardants. The ESD would describe the source, production, process, pathways, and use patterns of plastic additivies with the aim of quantifying emissions and concentration of a particular chemical into the environment.<sup>417,418</sup>

## OECD

The Organization for Economic Cooperation and Development (OECD) is made up of 30 member countries, including the U.S., and has active relationships with about 70 other countries.<sup>419</sup> As part of the OECD's Risk Reduction Programme, a risk assessment of PBDEs, along with two other flame retardants, polybrominated biphenyls and tetrabromobisphenol A, was published in 1994. This led producers of PBB and PBDE to enter into a voluntary agreement with the OECD in 1995 to minimize the risk of production spills and for the industry to refrain from producing other PBDEs than those already on the market. Joint meetings between OECD and the industry oversee industry's implementation of the commitments.<sup>420</sup>

## **OSPAR Commission**

The OSPAR Commission is made up of the countries that have ratified or approved the Convention for the Protection of the Environment of the North-East Atlantic (the "OSPAR Convention"). As of 2001, Belgium, Denmark, Finland, France, Germany, Ireland, Iceland, Luxembourg, Netherlands, Norway, Portugal, Sweden, Switzerland, and the United Kingdom had ratified the Convention, and the European Union and Spain had approved it. In 1998, the OSPAR Commission placed PBDEs on its "List of Chemicals for Priority Action."<sup>421</sup> An OSPAR Commission background document on PBDEs was reviewed by Sweden in 2001. The next full review of this document is not planned before 2008.<sup>422</sup>

## **POPS Treaty**

The Stockholm Convention on Persistent Organic Pollutants (POPs) is a global treaty to protect human health and the environment from persistent organic pollutants. The Convention outlines measures to reduce or eliminate releases from the intentional production and use of 12 chemical substances to be taken by nation states that become members of the Convention. PBDEs are not included. The Convention was adopted by a Conference of Plenipotentiaries on May 22, 2001, and entered into force on May 17, 2004, following ratification by 50 nations.<sup>423</sup>

The U.S. has signed the Stockholm Convention, but has not yet ratified it. A bill to implement the Convention in the U.S., S. 1486, was introduced by Senators Chafee and Jeffords on July 29, 2003, and reported from the Committee on Environment and Public Works by Senator Inhofe with amendments on April 29, 2004. Under S. 1486, if the "Conference of Parties," the organization of nations that have signed the Stockholm Convention, decides to add a chemical substance to the 12 initially covered, the U.S. will not automatically adopt the change. Instead, the EPA administrator will follow an independent process to determine whether and how the chemical substance will be restricted in the U.S.. On April 29, 2004, the bill was placed on the Senate Legislative Calendar under General Orders.<sup>424</sup> Ratification of the treaty would likely

require amendments to both the Toxic Substances Control Act and the Federal Insecticide, Fungicide, and Rodenticide Act to meet the treaty obligations.<sup>425</sup>

Jim Willis, the head of the United Nations Environment Programme chemicals division, told Reuters that "brominated flame retardants are a possibility (for addition to the list) as are many other chemicals."<sup>426</sup> In May 2005 at the Conference of the Parties of the Stockholm Convention, both the European Union and Norway proposed Penta- and Octa-BDE be added to the list of POPs chemicals.<sup>427,428</sup> This page is purposely left blank for duplex copying

# **VIII. Policy Recommendations**

**IN BRIEF:** This section lists the key findings, policy options, recommendations and rationale for each of four areas of action proposed by Ecology and DOH. The areas of action are:

- Products containing PBDEs at end-of-life
- Source control
- Minimizing human exposure
- Monitoring and research

# **Products Containing PBDEs at End-of-Life**

#### **Key Findings**

PBDEs are found in a vast number of consumer products, with a correspondingly vast potential for continued human exposure. Under Chapter 173-303 WAC, Dangerous Waste Regulations, Persistence Criteria, most products containing PBDEs would probably be considered hazardous waste at end-of-life. Currently, these products are handled by the solid waste system. Many products containing PBDEs, particularly electronics, are recycled or could be recycled, which conserves valuable resources. It is unknown whether the current system for disposing of and recycling products containing PBDEs adequately protects human health and the environment.

#### **Policy Options**

- Identify products containing PBDEs that may be entering the waste stream, along with the estimated percent of PBDEs in the product.
- Examine known information about potential pathways of PBDEs from products to the environment. Evaluate and recommend the most effective methods for preventing PBDEs from entering the environment.
- Create effective and practical methods to dispose of products containing PBDEs that is consistent in hazardous waste, solid waste, water quality, and toxic cleanup regulations.
- Create a "special waste" designation that is consistent in the hazardous waste, solid waste, water quality, and toxic cleanup regulations to isolate PBDEs and remove them from the waste stream. This could include chronic, sub-lethal criteria for designation.
- Remove foam and other materials with Penta-BDE and Octa-BDE from the recycling stream unless the recycling or processing activity safely handles and removes the PBDEs, and workers are adequately protected.
- Require separation of electronics containing brominated flame retardants during disposal.

- Ban the resale of designated products containing polyurethane foam, such as upholstered furniture.
- Establish a voluntary program with charities, reuse organizations, and businesses to minimize the resale of upholstered furniture containing polyurethane foam. Financing would be provided by the bromine industry to charities to properly dispose of foam containing items that are "dumped" on them, whether or not they are accepted by the charity.
- Restrict the disposal of products containing PBDEs to landfills that do not release leachate into the environment or to waste water treatment plants.
- If it is determined that disposal of existing PBDE containing materials are not safely handled in most available landfills or incineration facilities, require the bromine industry to establish and finance a collection, transportation and proper disposal system for the state.
- Require manufacturers that continue to use Penta-BDE and Octa-BDE in products sold to the general public (as opposed to specialty industries, such as aeronautics) to establish and finance a proper disposal system for their products.
- Place a tax on products sold in Washington State that contain PBDEs to fund a public information campaign and proper collection and disposal system. The tax should be adequate to cover all related costs to the public and private sector.
- No action.

#### Recommendations

Ecology should establish a process (to begin upon completion of this CAP) to evaluate and determine appropriate disposal and recycling practices for products containing PBDEs, including potential financing options. Ecology will involve appropriate stakeholders in this process, including, but not limited to, local government, private waste haulers and landfill operators, recyclers, manufacturers, environmental advocates, and human health advocates. Ecology anticipates that this may require a rule revision of Chapter 173-303 WAC, outlining recommended methods for recycling and disposal. As part of the evaluation, Ecology will:

- 1. Identify known information about potential pathways of PBDEs at end-of-life. Both PBDE releases to the environment and occupational exposure to workers would be examined at waste collection facilities, recycling facilities, waste disposal facilities, manufacturers using PBDEs and service industries such as carpet installers and upholsterers.
- 2. Through a literature search and limited product testing, characterize PBDE content of products along high-priority exposure pathways.
- 3. Establish where monitoring of PBDEs associated with end-of-life, including biosolids, leachate, and incinerator emissions, is warranted and, if so, for what purposes.

#### Rationale

Currently, not enough is known about the environmental and relative cost impacts of disposal practices for products containing PBDEs. In particular, the reuse and recycling of products containing PBDEs conserves valuable resources. Additional study is required before well-founded recommendations can be made. If special handling, recycling or disposal of products or wastes containing PBDE is required, adequate financing mechanisms will need to be identified.

# **Source Control**

# Penta-BDE and Octa-BDE

# **Key Findings**

The only U.S. manufacturer of Penta- and Octa-BDE, Great Lakes Chemical Corporation (now Chemtura), phased out production of both products at the end of December 2004. Penta- and Octa-BDE have been phased out in most international markets as well. Both Penta-BDE and Octa-BDE have a guaranteed shelf life of six months, so new products containing Penta-BDE and Octa-BDE theoretically will not be produced past June 2005.

On December 6, 2004, U.S. EPA issued a draft Significant New Use Rule (SNUR) for Penta-BDE and Octa-BDE. This proposed rule would require manufacturers and importers to notify EPA at least 90 days before commencing the manufacture or import of Penta-BDE or Octa-BDE on or after January 1, 2005. The required notice would provide EPA with the opportunity to evaluate any intended new use and associated activities and, if necessary, to prohibit or limit that activity before it occurs. The proposed rule would not prohibit the import of products containing Penta-BDE or Octa-BDE (e.g., mattresses, upholstered furniture). The comment period for the SNUR closed February 4, 2005. EPA plans to finalize the SNUR in early 2006.

# **Policy Options**

- Ban the import and use of Penta-BDE and Octa-BDE in Washington State.
- Ban the sale of new products containing Penta-BDE and Octa-BDE in Washington State with a phase-in period, allowing existing stock to be sold.
- Ban the sale of new products containing Penta-BDE and Octa-BDE in Washington State with a phase-in period, allowing existing stock to be sold. Allow recycled PBDE content of foam to be no more than 0.5% by mass, where the sole source of the PBDE can only be from recycled foam. This level of recycling might be permitted for a few years such as until 2010, after which content would be reduced to less than 0.1% by mass.
- Require labeling of new products containing Penta-BDE and Octa-BDE; the label should identify the PBDE formulation.

- Identify which Washington manufacturers use Penta-BDE and Octa-BDE in their products.
- No action.

# Recommendation

The Washington State Legislature should ban the manufacture, distribution (but not transshipment) or sale of new products containing Penta-BDE and Octa-BDE in Washington State by July 2006. The ban may include an exemption for the use of recycled material containing Penta-BDE and Octa-BDE in new products, pending further review. The ban should include an exemption for products where no alternative for Penta-BDE or Octa-BDE is available. The ban would not include the reuse of products containing Penta-BDE or Octa-BDE (for example, the sale of used cars or upholstered furniture).

# Rationale

Currently, there is no provision that would prevent a manufacturer, either domestic or foreign, from reintroducing Penta-BDE and Octa-BDE on the market. Penta-BDE and Octa-BDE are known persistent, bioaccumulative toxins, found in increasing concentrations in environmental media and humans. A ban on the manufacture, distribution, or sale of new products containing Penta-BDE and Octa-BDE would be consistent with similar laws in the European Union, California, Hawaii, Illinois, Maryland, Maine and New York. Such a ban also would provide a disincentive to manufacturers from reintroducing these products. This should have little or no impact on manufacturers since they are already using alternatives for these chemicals in order to comply with the EU ban and the discontinuation of supplies to the U.S. A temporary exemption for the use of recycled material containing Penta-BDE and Octa-BDE in new products is recommended until it can be determined that disposal is preferable.

# Deca-BDE

# **Key Findings**

Globally, Deca-BDE has become the most used PBDE product and is the only PBDE product currently in production. Recent scientific evidence suggests that Deca-BDE breaks down into more bioaccumulative and potentially toxic compounds. The amount of Deca-BDE in use, the expected increase in its use, and its expected breakdown in the environment argue that Deca-BDE use should not be allowed to increase and should be decreased.

Consumer electronics (primarily televisions) currently account for approximately 45 to 80 percent of Deca-BDE use. In preparation for the European Union's Restriction on Hazardous Substances (RoHS) ban on Deca-BDE, most major consumer electronics manufacturers announced that they had phased out or planned to phase out, the use of Deca-BDE. These manufacturers included: Apple, Brother, Daikin, Dell, Hewlett Packard, Matsushita, Panasonic, Samsung, Sharp, Sony, and Xerox. Since the EU exempted Deca-BDE from this ban in October, 2005, it is unknown how many of these firms will continue to use alternatives to Deca-BDE.

During 2005, Ecology and DOH pursued two lines of inquiry regarding Deca-BDE. An extensive survey of the available literature on Deca-BDE alternatives and an analysis of the costs and benefits were both inconclusive. A lack of data about the chemical alternatives and disclosure issues hampered the effort of the process. Few electronics manufacturers would share their use of alternatives or cost data with the state, either due to concerns about confidentiality or because it was not in their best interest to do so.

At the same time, the market for Deca-BDE is expected to shift and grow in response to two proposed national flammability standards for residential upholstered furniture and mattresses under consideration by the U.S. Consumer Product Safety Commission (CPSC). (See Appendix I) Sixteen flame retardant chemicals or categories of chemicals – including Deca-BDE – have been identified by CPSC and industry as likely to be used to flame retard fabrics on furniture in order to comply with the proposed standard. EPA is developing a rule to complement this standard, which would require notification to and review by EPA of flame retardants used by upholstery fabric manufacturers. With this rule, EPA may or may not restrict the use of Deca-BDE. Deca-BDE is also identified as useable by CPSC staff to meet the proposed mattress flammability standard. If Deca-BDE is banned for these uses now, prompting manufacturers to choose another flame retardant from the start, it would eliminate a potential new source of Deca-BDE in the environment without forcing manufacturers to incur costs for redesign or retooling to replace Deca-BDE later. However, no other state in the U.S. has banned Deca-BDE.

Because Deca-BDE is present in so many products, it would be nearly impossible to capture or control it in all products. Therefore, it was necessary to evaluate the effectiveness of a potential ban by examining the types of Deca-BDE containing products individually. Ecology and DOH conducted an in-depth review of the literature concerning alternatives to Deca-BDE for electronic enclosures. This effort focused on alternatives that had been identified as feasible (i.e. the product could be manufactured using the alternative AND could meet fire safety standards). To date, no clearly safer alternative for these products has been identified. The results of the alternatives assessment show that two alternatives are currently on Ecology's PBT list, and other alternatives were found to have persistent, bioaccumulative and toxic properties that may qualify them as PBTs. A few alternatives do not appear to be either persistent or bioaccumulative, but lack sufficient toxicity information. Two of these are promising non-halogen alternatives, RDP and BAPP. However, there is currently insufficient information available to fully assess them.

# **Policy Options**

- Ban the import and use of Deca-BDE and the sale of new products containing Deca-BDE in Washington State with a phase-in period, allowing existing stock to be sold.
- Ban the import and use of Deca-BDE and the sale of products containing Deca-BDE for applications where alternatives are available.
- Ban the import and use of Deca-BDE and the sale of products containing Deca-BDE for applications where known, safer alternatives are available.

- Examine the implications and logistics of a ban on products containing Deca-BDE to maximize benefits while minimizing negative impacts, including possible impacts on fire safety.
- Re-examine known information on the health and environmental impacts of Deca-BDE, along with the availability of safe alternatives, on a regular basis (e.g., annually) to determine if a ban, restricted use, or other actions are warranted.
- Identify which Washington manufacturers use Deca-BDE in their products.
- No action.

# Recommendations

The Washington State Legislature should ban the manufacture, distribution (but not transshipment) or sale of new products containing Deca-BDE provided that safer alternatives are identified or upon the emergence of additional evidence of Deca-BDE harm. The legislature should also provide funding to Ecology and DOH to continue to evaluate alternatives to Deca-BDE. If safer alternatives are not found in a reasonable time, Ecology and DOH should work with stakeholders to develop incentives/disincentives to encourage manufacturers to identify and develop safer alternatives or product design changes that eliminate the need for PBDEs.

# Rationale

Ecology and DOH believe that the benefits of reducing Deca-BDE use in Washington are likely to be significant to both public health and the environment. The most prudent course of action is to take steps now to reduce the use of Deca-BDE, despite the uncertainty of the data. However, two of the alternatives to Deca-BDE are included in the list of PBTs in the rule (Chapter 173-333 WAC). Care must be taken not to drive manufacturers to flame retardants that are as bad, if not worse, than Deca-BDE. Ecology and DOH will continue to evaluate the toxicity, persistence and bioaccumulation characteristics of alternatives.

# **U.S. Chemical Policy**

# Background

The Toxic Substances Control Act (TSCA) is the key statute around which U.S. chemical policy is formulated. It provides the framework by which EPA regulates new and existing chemicals to ensure the protection of human health and the environment. TSCA was signed into law by President Gerald Ford on October 11, 1976. Shortly after the law was signed, EPA Administrator Russel E. Train said that TSCA is "one of the most important pieces of preventative medicine legislation ever passed by Congress." Train went on to say that the current problem of toxic environmental contamination is that "we know so little - so abysmally little - about these chemicals".<sup>429</sup>

Under TSCA, EPA gathers information on the potential risks to human health and the environment posed by new and existing chemical substances and mixtures. EPA's TSCA Inventory currently contains over 82,000 existing chemicals; of which 3,000-4,000 are produced in excess of one million pounds per year and so are considered high-production volume (HPV) chemicals.<sup>430,431</sup>

TSCA requires testing information to be submitted in the form of Premanufacture Notices (Section 5) on all new chemicals, or proposed new uses of chemicals, prior to their introduction in to commerce. If the information is judged inadequate, EPA can require further testing, limit or prohibit manufacture. Such actions must be based on "an unreasonable risk of injury to health or the environment" or concern that the substance would "enter the environment in substantial quantities or there is or may be significant or substantial human exposure to the substance". Since 1979, approximately 150 Premanufacture Notices submitted for new flame retardant chemicals have been reviewed by EPA.

For chemicals already in commerce prior to TSCA implementation in 1979, such as PBDEs, EPA must promulgate a rule (Section 4) in order to obtain test data. The burden of using Section 4 to obtain data on the more than 60,000 chemicals that existed prior to TSCA has generally led EPA to rely on voluntary data submission as exemplified by the HPV Challenge Program. This program is a voluntary effort by industry to submit data on approximately 3,000 HPV chemicals. If such data suggests that an existing chemical poses "an unreasonable risk of injury to health or the environment," EPA can promulgate a rule under Section 6 to restrict production and use provided it is the least burdensome option that will adequately protect human health and the environment.

Criticism of TSCA implementation began almost immediately with a review by the General Accounting Office (GAO) in 1980 that noted EPAs slow response in beginning chemical review. Subsequent GAO reports from that time through the most recent review released in June 2005 have outlined numerous problems facing EPA in its implementations of TSCA.<sup>6,432,433,434,435,436,437,438,439,440,441,442</sup> Central to the theme of these reviews is the truly massive task that faces EPA in dealing with the more than 80,000 chemicals that are on the TSCA Inventory, the large majority of which were in commerce prior to TSCA. GAO's most recent report as well as other reviews have outlined important drawbacks in the statute and implementation by EPA.<sup>6,443,444,445,446,447,448</sup>

The criticisms outlined in these recent examinations of TSCA focus around EPA's ability to get and use data. Efforts to evaluate alternatives to Deca-BDE by DOH support these criticisms. DOH considered only those chemical alternatives to Deca-BDE that are feasible in terms of availability, fire safety and cost. Some of these chemical alternatives looked promising based on very limited data, but DOH found that there was insufficient information available to conclude that any such alternatives were better than Deca-BDE (see Chapter V, Alternatives Assessment).

While comments on this finding from the External Advisory Committee were varied, some acknowledgment was made that TSCA could be improved. Frustration was also noted from some members regarding the inability of Ecology and DOH to acknowledge a preference for those alternatives to which many companies have switched, e.g. RDP (resorcinol

bis(diphenylphosphate)). (External Advisory Committee meeting – Meeting Notes: October 25, 2005)

# **Key Findings**

Permitted use of chemicals for which little data has been collected points to significant flaws in U.S. law for regulating existing chemicals. In addition, EPA's ability to provide public information on chemical production and risk is hindered by strict confidential business information (CBI) provisions of TSCA.

This dilemma is clearly illustrated in the struggle to identify alternatives to Deca-BDE that will have a minimal impact on the environment and human health. Because so few studies on each of the alternatives have been conducted and because much of the information collected is not readily available, an adequate evaluation of alternatives to Deca-BDE was made difficult. Even basic information about chemical alternatives, such as production volumes and the number of years the chemical has been in commerce were not publicly available.

TSCA creates a disadvantage for:

- manufacturers, who cannot make fully informed decisions about the products they use;
- retailers, who are unaware of environmental and health implications of the products they sell;
- consumers, who cannot make fully informed purchasing decisions;
- industries dependent on a healthy environment, such as fishing and whale watching, whose "products" may be adversely impacted by chemical contamination; and
- regulators, who lack necessary information on product safety.

Local governments, primarily responsible for municipal waste disposal and recycling, bear increased costs when products discovered to be hazardous are disposed. Environmental protection agencies within state governments (e.g. Ecology) are spending considerable funds to clean up contaminated sites and sediments. State and local health departments must evaluate exposure pathways (e.g. fish consumption and indoor exposure) in order to provide advice on ways to reduce exposure.

# Recommendations

Ecology and DOH will actively seek opportunities to work with other states and interested parties to contribute to the national dialogue regarding needed improvements to U.S. chemical policy, with a goal of developing and advocating practical solutions. As a first step, Ecology participated as a member of the organizing committee for the Stakeholder Summit on Framing a Future Chemicals Policy, organized by the Lowell Center for Sustainable Production, which took place in April 2005.

# Rationale

Change in national chemical policy must occur at the federal level. However, Ecology and DOH can work to facilitate and participate in a process to develop solutions.

# **Minimizing Human Exposure**

# State Purchasing

# **Key Findings**

Executive Order 04-01 states that the Department of General Administration's Office of State Procurement shall make available for purchase and use by all state agencies equipment, supplies, and other products that do not contain persistent, toxic chemicals unless there is no feasible alternative. In circumstances where a product that does not contain persistent, toxic chemicals is not available, preference shall be given to the purchase of products that contain the least amount of persistent, toxic chemicals.

# **Policy Options**

- Specify that goods purchased through state contracts should not contain PBDEs.
- Specify that bidders on state contracts should disclose which PBDE formulations, if any, are used in products.
- No action.

#### Recommendations

Consistent with Executive Order 04-01, restrict the state's purchase of PBDEs in appropriate contracts.

• General Administration should prefer products that do not contain Deca-BDE.

# Rationale

Alternatives are available for many, but not all, applications of Deca-BDE. Alternatives are available for all applications of Penta and Octa-BDE, as neither product has been produced since December, 2004.

# **General Public**

# **Key Findings**

Human health risks are associated with exposure to PBDEs, though pathways and levels necessary to result in harm are not clearly understood.

# **Policy Options**

• The DOH should develop recommendations for the general public to reduce PBDE exposure.

- Direct the bromine industry, at its expense, to provide best management practices and a public information campaign on how to reduce human and environmental exposure.
- No action.

#### Recommendation

DOH should develop methods and materials for health education about PBDEs. DOH should develop and implement a strategy to communicate with health care providers about PBDEs and provide guidance appropriate for both the general public and health care providers concerning reduction of exposure to contaminants in the environment, including PBDEs. This strategy will include information on the benefits of breastfeeding and the benefits of eating fish as part of a healthy diet.

#### Rationale

Levels of PBDEs measured in people in the U.S. vary widely but are consistently much higher than levels found in people outside of the U.S. and Canada. Several potential routes of exposure exist. Humans appear to be exposed primarily through eating PBDE contaminated foods and through indoor air and household dust. Though PBDEs are used in many consumer products, individuals cannot easily identify which products contains PBDEs. PBDEs differ from many other environmental pollutants because they are associated with several sources and because it is so difficult for individuals to identify how they might be exposed.

PBDEs accumulate in the body over time. Levels in women build up prior to conceiving a child and can be passed on to the child during fetal development and through breast milk. Because of this, public health education will focus on young women and their health care providers.

Currently, there are uncertainties about the relative contribution of different sources of PBDEs to total exposure and why some people have higher than average levels. Efforts to develop strategies to reduce human exposures will need to rely on continual monitoring of the research literature related to PBDEs. Public health recommendations for exposure reduction and educational strategies to communicate those recommendations will be revised to reflect new information as needed.

# **Occupational Exposure**

# **Key Findings**

Workers may be exposed to PBDEs in computers and electronics. A Swedish study showed that workers who dismantle and discard electronics at a recycling plant are exposed to PBDEs. PBDE exposure was also found in computer technicians, although at lower levels than for those in the recycling plant. The source of the exposure is thought to be dust from plastic components. Reducing the amount of PBDE-containing dust at the recycling plant led to reductions in workers' PBDE plasma levels. Another Swedish study found elevated PBDE levels in workers manufacturing or handling rubber. Occupational exposure to PBDEs has been implicated in a 2003-2004 study conducted in New York. Although appropriate occupational exposure studies have not yet been conducted, it is reasonable to assume that workers may also be exposed to PBDEs during the manufacture and recycling/disposal of polyurethane foams treated with these flame-retardants.

# **Policy Options**

- To minimize occupational exposure to PBDEs, develop recommendations for employers and employees stating that exposure to PBDE-containing dusts should be controlled using standard industrial hygiene controls. (*At the time of this writing, L&I has already developed recommendations.*) Make employers and employees in potentially high exposure industries aware of the resources available from L&I to assist them in controlling exposure to PBDE containing dusts. L&I would focus on the most significant workplace exposures, which are likely associated with the manufacture and recycling/disposal of foams and plastics, rather than the office environment. There are no legally enforceable occupational exposure limits for PBDEs; however, L&I would apply the existing regulation for nuisance dust, i.e., particulates not otherwise regulated.
- No action.

#### Recommendation

• To minimize occupational exposure to PBDEs, develop recommendations for employers and employees stating that exposure to PBDE-containing dusts should be controlled using standard industrial hygiene controls. (*At the time of this writing, L&I has already developed recommendations.*) Make employers and employees aware of the resources available from the L&I to assist them in controlling exposure to PBDE containing dust. There are no legally enforceable occupational exposure limits for PBDEs; however, apply the existing regulation for nuisance dust, i.e., particulates not otherwise regulated. This process should be informed by the proposed study to 1) identify industrial processes that generate high levels of PBDE-containing dust or fume and 2) conduct biological monitoring for PBDEs in high-exposure workers.

#### Rationale

In the Swedish electronics recycling plant, dust control had a significant impact on PBDE exposures. Exposure was reduced when the shredder was moved away from the workers, the ventilation system was upgraded and cleaning procedures were improved. Therefore, recommending standard industrial hygiene controls to reduce exposures is warranted.

# **Monitoring and Research**

# **Key Findings**

Current regulations do not require monitoring for PBDEs in Washington State. As a result, very little data exist on PBDEs specific to Washington. While sampling of human tissue and laboratory animal studies indicate a risk to human health, a lack of knowledge persists regarding exposure pathways. Additional information needs include:

- Environmental monitoring data to establish baselines and monitor trends.
- Biomonitoring to establish baselines and monitor trends.
- Public awareness and perspectives on PBDEs.
- Magnitude and pathways for potential occupational exposure.
- Levels of occupational exposure to establish baselines and monitor trends.
- Deca-BDE debromination in various environments.
- The fate of PBDEs in the landfill environment.
- Alternative, non-brominated flame retardants, including their current presence in the environment and biological organisms, including people, to establish a baseline for future studies.
- Product design and other solutions to chemical fire retardants.

Research and monitoring efforts are typically conducted in coordination with other government agencies and research institutions to maximize efficient use of resources.

# **Policy Options**

- Bring together regional government agencies and research institutions involved in environmental monitoring and research to develop a multi-media monitoring program for PBDEs.
- Establish a biomonitoring program that includes examination of PBDEs in blood and breast milk to monitor trends and identify at-risk populations.
- Devise a sampling strategy to determine the relative contributions of PBDEs from various products and processes. This would include an evaluation of environmental releases from manufacturing processes (e.g., foams) in addition to recycling and disposal operations. This study could be funded via legislative request similar to the study conducted on metals in fertilizers.

- A two-phase workplace exposure study in collaboration with CDC. This study could be funded jointly by Ecology, CDC, and potentially NIOSH, with some logistical support provided by L&I. Once Washington State workplaces with the greatest potential for PBDE exposures have been identified, the following study could be conducted in a two-phased approach.
  - Phase 1 Air and surface sampling for PBDEs to determine the magnitude of potential exposures via the inhalation, dermal, and ingestion routes. If this evaluation suggests that there is a potential for exposure, proceed to Phase 2.
  - Phase 2 Biomonitoring of workers who are potentially exposed to PBDEs in the workplace.
- Test biosolids, leachate and incinerator emissions for PBDEs. Top priorities may include biosolids used for food production and leachate from the Pierce County Recycling, Composting & Disposal LLC dba LRI Landfill in Tacoma, which uses auto fluff for daily cover.
- Require the bromine industry or manufacturers of products containing PBDEs to finance monitoring and research through direct financing or a tax on products containing PBDEs.
- In collaboration with other government agencies and research institutions, conduct research on the following issues:
  - The fate of PBDEs in the landfill environment, with particular attention to Deca-BDE debromination.
  - Deca-BDE debromination in various environments as a result of UV light exposure and metabolic processes, with particular attention to biosolids.
  - Alternative, non-brominated flame retardants, including current presence in the environment and biological organisms, including people, to establish a baseline for future studies.
  - Product design and other solutions to fire retardant needs.

#### Recommendations

# Human Health Monitoring

- DOH should coordinate with federal agencies on existing national biomonitoring of PBDEs.
- DOH should explore whether additional regional biomonitoring is needed. Additional funding to support this effort would be required.

- DOH should research public awareness and perspectives to assure correct message development and environmental health communications strategy. This research is necessary to minimize unintended consequences of information delivery.
- DOH and L&I should implement a two-phase workplace exposure study in collaboration with CDC. Once Washington State workplaces with the greatest potential for PBDE exposures have been identified, the following study could be conducted in a two-phased approach.
  - Phase 1 Air and surface sampling for PBDEs to determine the magnitude of potential exposures via the inhalation, dermal, and ingestion routes. If this evaluation suggests that there is a potential for exposure, proceed to Phase 2.
  - Phase 2 Biomonitoring of workers who are potentially exposed to PBDEs in the workplace.

# Environmental Monitoring

- Ecology has developed a monitoring program for PBDEs in the environment. Ecology should evaluate whether further sampling for Deca-BDE alternatives is needed.
- Ecology should determine whether additional sampling for PBDEs at landfills, recycling facilities, sewage treatment facilities or other areas is needed.

# Research

Encourage other government agencies and research institutions to conduct research on the following issues:

- Deca-BDE debromination in various environments.
- The fate of PBDEs in the landfill environment.
- Alternative, non-brominated flame retardants, including their presence in the environment and biological organisms, including people, to establish a baseline for future studies.
- Product design and other solutions to chemical fire retardants.
- A better characterization of how people in the U.S. are being exposed to PBDEs. This should include further monitoring of PBDEs in U.S. foods, identifying sources and levels of PBDEs in homes and other buildings, and identifying behaviors that contribute to PBDE levels in human tissues.

# **Appendixes**

Appendix A	Survey Of Manufacturers
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# Appendix A: Survey of Manufacturers

# Deca-BDE Alternative Assessment Questions for Industry Users

Company Name:	
Contact Name/#:	
Date Surveyed:	
Surveyed By:	

- 1. Does your company use polybrominated diphenyl ether (PBDE) flame retardants in the manufacture of any of your products? If yes, can you tell us which products specifically? (*If they do not know, we will ask who their plastics supplier is to try to get to someone who does know.*)
- 2. If the answer to #1 is "Yes," does your company use the penta, octa, or deca forms of PBDE?
- 3. Has your company evaluated using alternatives to Deca-BDE? If "No," why not?
- 4. Is your company using an alternative to Deca-BDE or are you planning on using an alternative to Deca-BDE? Which alternative(s) was selected? What products will Deca-BDE alternatives be used in?
- 5. If the answer to #4 is "No," is there a time line for replacing Deca-BDE in your manufacturing process?
- 6. If the answer to #3 is "Yes," do all the alternatives identified by your company appear on the attached list? Did your company reject any alternatives? Which ones and why?
- 7. If Deca-BDE alternatives that your company uses or knows about do not appear on the attached list, will you share that information with Ecology so we can update our list of possible alternatives?
- 8. What, if any, information are you lacking to complete your evaluations of Deca-BDE alternatives?
- 9. Do any of the Deca-BDE alternatives you have identified require changes in other production materials or equipment in order for your company to use them? Would you be willing to answer some additional specific questions regarding production changes? How many product lines have you made or will you be making adjustments to? What is the net increase in your costs, if any? What is the percentage change in the price of your product, if any?

- 10. Is/was end-of-life recyclability of your products a consideration when thinking about the impacts of using alternatives to Deca-BDE? If "Yes," how do the Deca-BDE alternatives you have identified affect the end-of-life recyclability of your products? What is the recyclability percentage of products with Deca-BDE alternatives?
- 11. As Ecology and Health started their assessment of Deca-BDE alternatives we realized we are lacking some basic information. We have a couple of questions to see if you can help us fill those needs. First, do you have any information on the amount of the alternative fire retardant remaining in the plastic at the end-of-life of your products?
- 12. Secondly, do you have any information on toxicity testing of the alternative fire retardant you are using (or considering using)? Could we call you or someone else if we have any follow-up questions regarding toxicity of the Deca alternatives you are using?
- 13. Are there other questions we should be asking?

# Appendix B: Survey of Wholesalers and Retailers

Ecology did a survey of retailers and wholesalers in order to better define the share of the market that might be affected by a ban. Ecology contacted 307 companies in the following SIC sectors:

- 5045 Computer and Computer Peripheral Equipment and Software Merchant Wholesalers
- 5064 Radio, Television and Other Electronics Stores
- 5065 Other Electronic Parts and Equipment Merchant Wholesalers
- 5311 Department Stores (except Discount Department Stores)
- 5331 All Other General Merchandise Stores
- 5399 Warehouse Clubs and Supercenters
- 5731 Radio, Television and Other Electronics Stores
- 5961 Electronic Shopping, Electronic Auctions, Mail Order Houses

	5045	5064	5065	5311	5331	5399	5731	5961	Row totals
No tv or comp 1-4	2	16	13	9	15	17	13	16	101
No tv or comp 5-9	7	2	7	2	7		4		29
No tv or comp 10-19	3	5	4	6	3	1			22
No tv or comp 20-49	4	2	1	6	2		1		16
No tv or comp 50-99			1	2					3
No tv or comp 100-249				1					1
No tv or comp 250-499	2			1					3
No tv or comp 1,000-4,999				1					1
Never got through	27	2		5	1	7	15	7	64
Refusal								1	1
Phone disconnected	11		3	1		4	9	5	33
Bankruptcy					1			2	3
Duplicates				2					2
Surveys sent	13		1	4			9	1	28
Surveys received	3		1				3		
Column totals	69	27	30	40	29	29	51	32	307

# Survey results by SIC sector

- 57 percent indicated there is no possible impact
- 33 percent were disconnects, refusals, bankruptcy, duplicates etc.
- 9 percent indicted there was a possible impact and received a password and link to the electronic portion of the survey
- 25 percent of those receiving a password responded

# **Small Numbers Problem**

Despite the sample size, the survey suffers because so few companies indicated they would have an impact.

- Only 28 companies indicated a possible impact.
- Of these, only 7 responded to the survey.
- The range in this minimal response was from no impact to 100 percent impact.
- The largest number of companies reporting a level of impact in any sector was 3.

What this means is:

- Ecology knows a large share of each sector would have no impact, but . . .
- Ecology doesn't know the level of sales affected for those who currently sell product with PBDE in it.
- Given the small number of responses, the addition or removal of a single response changes the upper value in one sector by nearly an order of magnitude.
- The list of manufacturers providing PBDE-free product has changed since the European Union (EU) decision.
- Finally, Ecology may have a handle on the impact to smaller companies; however, only one affected company with employment over 50 responded. As a group, the companies which had more than 50 employees were more likely to be affected. Thus there is a possibility of extreme selection bias, based on non-response, in the results.

# Survey Management

The survey was run as follows:

The questions were designed to cover electronic housings but to focus on TVs and other consumer electronic housings. The target was data on sales to consumers rather than to businesses. The verbal response to the first question helped to narrow down the number of companies that might have any impact:

"Do you sell televisions or other electronic equipment?"

The respondents who said "no" were automatically allocated to zero impact. The respondents who said "yes" were asked if they would be willing to fill out an electronic survey.

Respondents who answered "yes" were asked to participate in the survey and were given a pass code. A follow-up email gave them the electronic address of the survey.

# Questionnaire

1. Do you sell televisions or other electronic equipment? Yes No										
1. Do you sen elevisions of other electionic equipment? Tes into										
2. What perc	entage of your sale	es are televisions?								
1	percent of your TV	sales are TVs ma	de by one or mo	ore of the compa						
listed below?										
Dell	Hitachi	HP	Moto							
NEC	Panasonic	Samsung	Shar							
Sony	Royal Philips El	ectronics	Tosh	iba						
3a. What p	entage of your sale percentage of your	electronic equipm	·	- /						
3a. What p from the foll	percentage of your owing companies l	electronic equipm isted below?	ent sales (not in	cluding TVs) co						
3a. What p	percentage of your	electronic equipm	·	- /						
3a. What p from the foll Apple	bercentage of your owing companies l Brothers Hitachi	electronic equipm isted below? Canon	ent sales (not in Compaq	cluding TVs) co Daikin						
3a. What p from the foll Apple Dell	bercentage of your owing companies l Brothers Hitachi	electronic equipm isted below? Canon HP	ent sales (not in Compaq IBM	cluding TVs) co Daikin Intel						
3a. What p from the foll Apple Dell Matsushita	bercentage of your owing companies l Brothers Hitachi Motorola Sony	electronic equipm isted below? Canon HP NEC	ent sales (not in Compaq IBM Panasonic	cluding TVs) co Daikin Intel						
3a. What p from the foll Apple Dell Matsushita Sharp Royal Philip	bercentage of your owing companies 1 Brothers Hitachi Motorola Sony s Electronics	electronic equipm isted below? Canon HP NEC Toshiba	ent sales (not in Compaq IBM Panasonic Xerox	cluding TVs) co Daikin Intel						
3a. What p from the foll Apple Dell Matsushita Sharp Royal Philip Please help u	bercentage of your owing companies l Brothers Hitachi Motorola Sony	electronic equipm isted below? Canon HP NEC Toshiba	ent sales (not in Compaq IBM Panasonic Xerox or small.	Daikin Daikin Intel Samsung						

The list of companies with no PBDE has shifted due to the EU decision to exempt Deca-BDE. However, the survey was already largely complete by that time.

#### **Selection of Respondents**

- 1. Potentially affected sectors were identified using data from Department of Revenue on Gross Business Income.
- 2. The NAICS crosswalk to SIC codes was used to list SIC codes.
- 3. The detailed definitions of the SIC codes were reviewed and some were eliminated. The remaining sectors were selected for the survey.
- 4. Companies within Workforce Explorer from the correct SIC codes were identified.
- 5. The companies were selected using a random number table.
- 6. Each person who agreed to fill out the survey received a randomly generated nonrepeating number to write into the response so Ecology knew the correct SIC code and the company still had anonymity. This also allowed Ecology to track any tendency of large or small businesses to skip responding and identify potential selection bias in the sample.

2002							
Code	SIC	2002 NAICS title	# Firms	Tota	al Gross	me	an Gross
334111	3571	Electronic Computer Manufacturing	23	\$	216,963,226	\$	9,433,184
334112		Computer Storage Device Manufacturing	5	\$	261,221,188	\$	52,244,238
334113	3575	Computer Terminal Manufacturing	5	\$	2,629,331	\$	525,866
334119		Other Computer Peripheral Equipment					
	3577	Manufacturing	29	\$	769,280,628	\$	26,526,918
334310		Audio and Video Equipment Manufacturing	29	÷	107,356,225	\$	3,701,939
334417	3678	Electronic Connector Manufacturing		\$	507,225	\$	169,075
334419	3679	Other Electronic Component Manufacturing	24	\$	238,582,227	\$	9,940,926
423430	5045	Computer and Computer Peripheral Equipment and Software Merchant Wholesalers	463	s	4,073,022,083	s	8,797,024
423690	5065	Other Electronic Parts and Equipment Merchant Wholesalers	644	s	2.705.278.531	s	4.200.743
424610		Plastics Materials and Basic Forms and		-			
	5162 & 5199	Shapes Merchant Wholesalers	111	s	390.161.275	s	3.514.966
425110	many + 5045, 5064	Business to Business Electronic Markets	20	\$	13,879,286	\$	693,964
443112	5064 & 5731	Radio, Television, and Other Electronics Stores	634	S	1,181,897,426	s	1.864.192
443120		Computer and Software Stores	1,763	S	1.918.632.365	S	1.088.277
452111		Department Stores (except Discount					
	5311	Department Stores)	17	\$	2,055,430,012	\$1	20,907,648
452112	5311	Discount Department Stores	7	\$	1,353,020,411	\$1	93,288,630
452910		Warehouse Clubs and Supercenters	25	\$	4,626,783,518	\$1	85,071,341
452990		All Other General Merchandise Stores	416	\$	3,965,909,449	\$	9,533,436
454111	5961	Electronic Shopping	894	\$	3,259,747,378	\$	3,646,250
454112	5961	Electronic Auctions	29	\$	602,890	\$	20,789
454113		Mail-Order Houses	441	\$	356,267,394	\$	807,863
532210	7359	Consumer Electronics and Appliances Rental	66	\$	71,946,730	\$	1,090,102
811212	7378, 7629, 7699	Computer and Office Machine Repair and Maintenance	552	\$	121,751,952	\$	220,565

# Appendix C: Companies Phasing out PBDEs

Company	Policy	Source	Date viewed
Apple Computer	No PBDEs in mechanical plastic parts heavier than 25-50g and none in the base material for the iMac 20" (11/21/03)	"Environmental Attributes" http:// <u>www.apple.com</u> ,	4/27/04 and 4/30/04
Brother Industries Ltd	PBDEs prohibited in product when concentration is 100ppm or more	Brother Green Procurement Standard <u>http://www.brother.com</u> ,	5/14/2004
<u>Canon</u>	Abolished the use of PBDEs 10 years ago	Survey	8/11/05
Daikin Industries	Plans to phase out PBDEs by the end of March 2006	"Environmental Assessment of Our Products" http://www.daikin.com/data /environment/pdf03/report2 003_5.pdf	4/28/2004
Dell Computer Corp.	Dell has phased out PBDEs from its products. The company's goal is to phase out all other brominated flame retardants in desktop, notebook, and server chassis plastic parts by year-end 2004.	http://www.dell.com	3/10/2004
Eizo Nanao Corporation	Plastics do not contain brominated or chlorinated flame retardants.	http://www.eizo.com Eco- Products 2004	5/17/2004
Ericsson	Does not use PBDEs.	http://www.ericsson.com, "ECO Declaration"	4/27/2004
Hewlett Packard	Prohibits use of PBDEs. They have restricted the use of PBDEs for over 10 years	"RoHS" Position Statement, http://www.hp.com/hpinfo/ globalcitizenship/environm ent/pdf/leadposition.pdf Survey	10/1/2004
<u>Matsushita</u>	Intends to phase out all PBDEs by March 2005.	Matsushita Electronic Components Group Chemical Substances Management Guidelines, <u>http://panasonic.co.jp/maco/</u> <u>en/environment/pdf/kagaku</u> <u>kanri.pdf</u> ; pers. comm., D. Swanson	6/3/2004
Mitsubishi Electric	Eliminate the use of PBDEs by December 31, 2005.	Environmental Sustainability Report 2004, http://global.mitsubishielect ric.com/company/environ/p df/Report_2004e2.pdf	7/26/2004
<u>NEC</u>	Goal of eliminating PBDEs by the end of FY 2005.	NEC Corporate Profile, <u>http://www.nec-</u> <u>lcd.com/english/profile/envi</u> <u>ronment_energy.html</u>	10/1/2004

Company	Policy	Source	Date viewed
Panasonic	ROHS compliant, at posting, Deca-BDE was subject to a ban in the near future.	http://www.panasonic.com/i ndustrial/components/pdf/p a003.pdf	9/6/2005
Philips Electronics Ind. (Taiwan) Ltd., CED	2002/95/EC requires the substitution of various heavy metals (lead, mercury, cadmium, hexavalent chromium) and brominated flame retardants (PBB and PBDE) in new electrical and electronic equipment put on the market from 1 July 2006.	http://www.cft.philips.com/	7/26/2004
Samsung Electronics Co. Ltd.	PBDEs will be banned in all applications. As of May 2004, threshold limit was under development.	Position Paper of Samsung Electronics with regard to the use and phase out of certain substances when appropriate. http://www.samsung.co.uk/	7/26/2004
Sharp Corporation	Use of PBDEs in its products except in CTV for the U.S.	"Parts/Materials Contained Chemical Substance Investigation Manual (for Business Partners)," July 2003, p. 6. http://www.sharp.co.jp	4/29/2004
Sony Corporation	Sony will not accept parts from suppliers containing PBDEs except for parts made by dies that were made prior to January 2003. This exemption applies only to bodies of displays and TV sets to be shipped to non-European countries. As of January 1, 2005, parts whose dies were made in 2003 or later must not contain PBDEs.	Management Regulations for the Environment- Related Substances to be Controlled Which are Included in Parts and Substances, 3rd ed., p. 9, www.sony.com	4/29/2004
<u>TOTOKU Electric Co.,</u> <u>Ltd.</u>	Totoku has developed lead-free wires that do not contain halogens. It intends to manufacture lead- free, halogen-free wires that satisfy UL standards.	"Environmentally friendly type electric wires"	5/5/2004
ViewSonic Corporation	ViewSonic has taken steps with its manufacturing partners to eliminate halogen and bromide-related flame retardant chemicals, particularly in CRT products. Specific model numbers are not provided by the company.	"Quality and Environment"	5/5/2004
<u>Xerox</u>	Goal to eliminate use of PBDEs in all products introduced in FY 2004.	"Activities in 2002" http://www.fujixerox.co.jp/ eng/ecology/report2003/200 3e_12.pdf	10/1/2004

Updated: November 30, 2005

# Appendix D: Degradation of PBDEs

A number of studies have shown that PBDEs are subject to some degree of degradation under a variety of laboratory conditions. Portions of the section below on photolytic degradation, along with the conclusions on photolytic degradation presented in the body of the *Interim CAP*, were reviewed in writing by A. Bergman (Stockholm University), L. Birnbaum (U.S. EPA), J. de Boer (Netherlands Institute for Fisheries Research), C. deWit (Stockholm University), R. Hale (Virginia Institute of Marine Science), R. Hites (Indiana University), and B. Jansson (Stockholm University). Additionally, the section in the *Interim CAP* was discussed at length by phone with C. Jafvert (Purdue University). The sections on biological and non-biological degradation and the recent scientific publications not included in the *Interim CAP* were not reviewed externally.

#### **Photolytic degradation**

Norris et al. found that both Deca-BDE and Octa-BDE were photodegraded in xylene by reductive debromination with half lives of 15 hours and 40 hours respectively when exposed to UV light. Stepwise photoreduction led to the formation of a variety of lower brominated diphenyl ethers and brominated biphenyls. An initial study performed on Deca-BDE dissolved in octanol and exposed to UV light showed Deca-BDE to decompose with a half-life of four hours. Degradation products for this study were not reported. In an attempt to model more environmentally relevant conditions, they also exposed Deca-BDE in water to natural sunlight for three months and found that it degraded. Breakdown products were not identified, though they appeared not to be mono-, di-, or tri-brominated diphenyl ethers.

Watanabe and Tatsukawa examined photolysis of Deca-BDE in a mixture of hexane, benzene, and acetone exposed to UV light and natural sunlight. After 16 hours of exposure to UV light, they identified tri- to octabrominated diphenyl ethers and polybrominated dibenzofurans (PBDFs) with 1 to 6 bromine atoms as the major degradation products. PBDFs appeared to form as secondary products from debrominated diphenyl ethers, but not directly from Deca-BDE.<sup>450</sup>

Jafvert and Hua examined photochemical reactions of BDE-209 when precipitated onto hydrated surfaces, including quartz glass, silica particles (sand), and humic acid-coated silica particles. When adsorbed to sand and exposed to sunlight for 84 hours, approximately 80 percent of the initial amount of BDE-209 was recovered. The concentration of BDE-209 was similar in the exposed samples and in control samples kept in the dark. The authors concluded that little or insignificant photodegradation had occurred. They pointed out that light does not penetrate beyond a few millimeters into the sand and, therefore, only BDE-209 close to the exposed surface is exposed to light. When adsorbed to humic acid-coated sand and exposed to sunlight for 96 hours, approximately 88 percent of BDE-209 remained on the sand.

Jafvert and Hua adsorbed BDE-209 to quartz tubes containing humic acid solution and exposed the tubes to sunlight for 72 hours. After 72 hours, approximately 70 percent of the BDE-209 remained. BDE-209 appeared to transform quickly within the first 24 hours, after which the concentration remained relatively steady. In contrast, the accumulation of bromide ion was

nearly linear after the first 12 hours, implying the production of the bromide ion continued after the loss of the parent compound, BDE-209, slowed. HPLC analysis of samples did not indicate large peaks of lower brominated diphenyl ether congeners, except possibly nona- or octa-BDE congeners.

Jafvert and Hua suggested that the apparent absence of organic products in their experiments using reagent grade water could be due to condensation polymerization within the precipitated deca-BDE. The initial reaction in photolysis of deca-BDE is agreed to be the cleavage of a carbon-bromine bond. Because the deca-BDE was precipitated onto a solid and placed in water, a hydrogen donor was not readily available. Following the initial reaction, the authors proposed that the nonabrominated aryl radical instead reacted with another nonabrominated aryl radical, forming a macromolecule that was not detected. When humic acid solution was used instead of reagent grade water, the degradation products were altered because the humic acid acted as a reducing agent and a hydrogen source.<sup>451</sup>

Ohta et al. examined the degradation of Deca-BDE in toluene and a mixture of toluene, ethanol and water (1:3:6) under UV light, tungsten light and sunlight. Deca-BDE completely decomposed in toluene after 40 minutes. By 60 minutes, mono- to nona-BDEs were observed. In sunlight, after 24 hours, tri- to nona-BDEs had been observed. Decomposition products appeared to be temporarily concentrated in two kinds of hepta-BDE. The authors thought the concentration of hepta-BDE could be a result of the difference in intensity between the UV light and natural sunlight. They performed an additional experiment exposing BDE-209 to tungsten light where two hepta-BDEs were also observed, one identified as BDE-183.<sup>452</sup>

As reported in the European Union's Update of the Risk Assessment of Bis (pentabromophenyl) ether (decabromodiphenyl ether), Palm et al. performed an in-depth investigation on the photodegradation of BDE-209. The first series of experiments determined the UV spectrum of BDE-209 in toluene, dichloromethane, tetrahydrofuran (THF), methanol, and ethanol. The spectrum obtained was similar in all solvents used and showed a weak absorption band above 290 nm, which is in the range of the solar spectrum at ground level. The spectrum of BDE-209 in THF was also compared to those of BDE-47, other brominated diphenyl ethers. As the number of bromine atoms per molecule decreases, overlap of the absorption spectra with light of wavelength >290 nm is reduced, implying a reduced susceptibility for photodegradation in the environment.<sup>453</sup>

Palm et al. also examined the degradation of BDE-209 under filtered (300 nm) xenon lamps in toluene, dichloromethane, and a mixture of hexane, benzene and acetone (8:1:1). The half-life in all three solutions was about 0.5 hours. Reductive debromination was found to occur, with all three nona-BDE congeners forming, which further reacted to form six congeners of octa-BDE, which reacted to form two major hepta-BDE congeners, along with several minor hepta-BDE congeners. Traces of hexa-BDE congeners were then formed. Mass balance calculations showed that degradation products identified accounted for 75 percent of BDE-209 in the study. Products from the remaining 25 percent were not identified.

Palm et al. examined BDE-209 in toluene under natural sunlight for two days in July, which resulted in the complete disappearance of BDE-209. Degradation products identified at the end

of the exposure period included three nona-BDE isomers, several octa-BDE congeners, several hepta-BDE congeners with two isomers dominating, a group of hexa-BDE isomers with a single congener dominating, and a group of penta-BDE congeners. Similar results were obtained by examining BDE-209 in THF under a sunlamp for 84 hours. With the longer exposure, tri-BDE and tetra-BDE congeners were also observed but not identified. The gas chromatographic pattern for the experiment did not resemble those found in the Octa-BDE or Penta-BDE congeners found in the Octa-BDE and Penta-BDE products implies that the lower brominated PBDEs found in the environment are not derived from the photolysis of Deca-BDE.

Palm et al. exposed BDE-209 in THF to a polychromatic light source and determined the halflife to be 1.9 minutes. Degradation products included three nona-BDE isomers, three octa-BDE isomers, and several hepta-BDE isomers, lower brominated congeners and brominated dibenzofurans. Seventeen percent of the degradation could not be explained. A separate experiment was performed to confirm the presence of mono-, di-, tri-, and tetrabromodibenzofurans. Higher brominated furans were not found, though it was indicated that their presence may have been masked by the formation of equivalent brominated diphenyl ethers formed in higher amounts. By changing the light source in this experiment from  $\lambda > 280$  nm to light using a cut-off filter at 320 nm, the half-life for BDE-209 was found to increase by 26 minutes and the pattern of nona-BDE congeners formed changed. The authors concluded that the product distribution depends on the light source used.

Palm et al. adsorbed BDE-209 onto silicon dioxide and placed this in suspension in water. The test suspension was then exposed to polychromatic light for 45 minutes. Around 45 percent of the BDE-209 was found to have degraded after 45 minutes. Details of degradation products were not available, but the test report indicated that brominated furans were formed.<sup>454</sup>

Söderstrom et al. examined debromination time trends and half-lives of BDE-209 in toluene and on silica gel, sand, sediment and soil. All samples were exposed to UV light, and samples on soil, sand, and sediment were additionally exposed to outdoor sunlight. BDE-209 degraded in all five matrices, though at different rates. Half-lives in toluene and on silica gel were less than 15 minutes following continuous exposure. The half-life for BDE-209 on sand exposed to UV light was 12 hours; the half-life for BDE-209 on sand exposed to sunlight was 37 hours. Exposure to sunlight was not continuous, while the exposure to UV light was. The authors calculated that the irradiance over the outdoor exposure approximated 13 hours of continuous exposure, comparable to UV light results. The half-life for BDE-209 exposed to UV light on soil was between 150 and 200 hours. BDE-209 exposed to sunlight on sediment and soil showed irregular degradation; the half-life for soil was not reported. The half-life for sediment was estimated as 80 hours for discontinuous sunlight and 30 hours for continuous sunlight.<sup>455</sup>

Söderstrom et al. explained the difference in half-lives by pointing to the differences in surface structure and chemical composition of the matrices. The smooth surfaces of silica gel and sand allow greater exposure to UV light, while the porous nature of sediment and soil enables the BDE-209 to be adsorbed into the particle where it is shielded from UV radiation. In addition, the authors suggest that organic carbon contained in sediment and soil could no covalently bind with

BDE-209, possibly increasing half-lives both by physically shielding the molecule from UV radiation and by stabilizing the molecule as a result of the chemical bond.

While the matrix used impacted rate of degradation, Söderstrom et al. found consistent degradation pathways across matrices. Degradation appeared to be, at least initially, a stepwise debromination process. As BDE-209 disappeared, nona- to hexa-BDEs were formed. After the peak formation of hexa-BDEs, only small amounts of lower brominated compounds were formed with a discontinued mass balance. Tetra-BDFs, penta-BDFs, and hexa-BDF were identified in soil and sand samples, but no PBDFs were identified on the other matrices. BDE congeners that were identified as degradation products on all matrices included BDE-128, -154, x-183, -206, -207, and -208. In addition, two unknown hexa-BDEs, one unknown hepta-PBDE, and four unknown octa-BDEs were formed. BDE-47, -99, -100, and -153 were found only on some matrices. Too few samples were analyzed for PBDFs to draw conclusions about exposure times and matrix dependence.<sup>456</sup>

Eriksson et al. examined the photodegradation rates and products of 15 individual PBDEs, including BDE-209. Photolysis of BDE-209 was measured in methanol/water (4:1), pure methanol, THF, water, and water containing humic substances. With the exception of water, photolysis of deca-BDE in all other media measured resulted in an almost identical set of products, though in water containing humic substances a higher proportion of penta-BDFs was observed. Each of the three nona-BDEs were formed and produced a number of octa-BDEs, although the major products were different for each nona-BDE congener. Hepta- and hexa-BDEs and mono- to penta-BDFs were also formed. The UV degradation products of two hepta-BDEs, BDE-190 and BDE-183, and three hexa-BDEs, BDE-155, BDE-154, and BDE-139 were also identified. The substances followed the same trend of consecutive debromination with the exception that tri- and tetra-BDEs were also observed as products from the latter reactions. The authors found that the total area under the HPLC chromatogram decreased by approximately 15% after most of the BDE-209 had decomposed. They suggested that this could be due to the formation of PBDFs or uncharacterized products. Some minor peaks in the mass chromatogram could not be characterized as PBDE or PBDF congeners. One such peak was consistent with a methoxylated tetrabromodibenzofuran.<sup>457</sup>

Eriksson et al. found that the photolytic reaction rate was 700 times greater for BDE-209, the congener with the fastest reaction rate, than for BDE-77, the congener with the slowest reaction rate. Lower brominated congeners generally degraded more slowly than higher brominated congeners. They attributed much of the difference to the fact that higher brominated diphenyl ethers absorb UV light at longer wavelengths. They also found more subtle differences within groups with the same number of bromine substituents. Photolysis rates for tetra-BDE through hepta-BDE congeners were faster for congeners with a fully brominated ring. However, for congeners with less than fully brominated rings, the impact of structural parameters on degradation rate was unclear. The reaction rate was also dependent on the solvent such that the reaction rate in the methanol/water solution was consistently about 1.7 times lower than in pure methanol and two to three times lower than in THF.

Eriksson et al. also attempted to measure the photolytic degradation rate and breakdown products of BDE-209 in pure water. The BDE-209 disappeared from solution, but no degradation

products were found. The authors suggest this may have been due to adsorption to glass walls rather than chemical transformation, given the extremely low water solubility,  $< 1 \mu g/L$ , of BDE-209.<sup>458</sup>

Bezares-Cruz et al. examined the reaction rate and products of solar degradation of BDE-209 in hexane under a range of solar wavelengths. They reported that the range of wavelengths where both the molar absorptivity of BDE-209 and the solar irradiance flux are significant occurs between 300 and 350 nm. They found that upon solar irradiation, BDE-209 reductively dehalogenated to other PBDEs. During 34 hours of irradiation, PBDEs from nona- to tribromodiphenyl ethers were observed. In total, 43 PBDEs were detected, and 21 were identified by matching them to available congener standards. BDE-47 and BDE-99 were among the congeners identified. In additional experiments, BDE-156, -184, -191, -197, -206, and -207 dissolved in hexanes were exposed individually to solar radiation for reactivity and product analysis. Comparable appearance of less substituted PBDEs was observed in all cases, with greatest reactivity apparent for those congeners fully substituted in all ortho- positions. Whether this was a result of higher quantum yields of molar absorptivities of those congeners was unknown.<sup>459</sup>

Rahm et al. evaluated the degradation pathways for PBDEs and attempted to quantify the susceptibility of highly substituted PBDEs to nucleophilic substitution and hydrolysis. The study determined that, as bromine is electron withdrawing and a good leaving group, highly brominated PBDEs are very susceptible to nucleophilic aromatic substitutions and that the rate decreased with each bromine removal. Although the study did a good evaluation of the susceptibility of PBDEs for degradation, concerns have been raised that the study did not evaluate how readily these substitution reactions would occur outside the laboratory.<sup>460</sup>

Sellström et al. conducted a study of the effects of sewage sludge application of higher brominated PBDEs on soils and the impact this application has upon earthworms. The authors collected soils from research stations and farms to which sewage sludge had been applied or had been flooded with stream soils downriver from plants using PBDEs and evaluated the ability of earthworms to absorb PBDEs. In addition to their evaluation of adsorption by earthworms, the authors subjected BDE-209 laced soil from a single farm to artificial UV-light for up to 21 days as a follow-up to their earlier laboratory work which proved photolytic debromination. Although no data is provided in the paper to support their determination, the authors indicate that '... no evidence of photolytic breakdown was seen.' No raw data from their analyses was provided. As an aside, the authors did determine that deca-BDE can be absorbed by earthworms and therefore can enter the food chain increasing the exposure to higher tropic level organisms.<sup>461</sup>

Stapleton evaluated the degradation of deca-BDE in house dust subjected to sunlight. The author used household dust provided by the National Institute of Standards and Technology which consisted of dusted collected primarily from home vacuums and a few motels and hotels. The dust was treated with dichloromethane to extract any PBDE contaminants. The dust was allowed to dry removing any remaining solvent and tested prior to deca-BDE addition to verify removal of any contaminants. The cleaned dust was spiked with deca-BDE, placed in to sealed glass cuvettes and subjected to UV light for a total of 90 hours of direct sunlight. When not exposed to sunlight, the cuvettes were wrapped in aluminum foil and stored at room temperature until the

next period of exposure. Blanks containing the cleaned dust without any deca-BDE addition were subjected to the same regime.

After 90 hours of exposure, deca-BDE was found to decrease by almost 30% and leading to an increase in nona-, octa- and hexa-BDE congeners. Upon conducting a mass balance evaluation, the author concluded that 83% of the deca-BDE loss was due to debromination and formation of lower PBDE congeners. 17% of the deca-BDE loss could not be accounted for. The author theorized the loss was due either to volatilization and/or the formation of unknown degradation products. The author concluded that '*The formation of lower brominated BDE congeners through debromination of BDE 209 leads to potentially more persistent and toxic products.*' Additional studies are being done at longer periods of time and with different dust matrices to address some concerns raised with the study.<sup>462</sup>

# **Biological transformation of PBDEs**

Several studies indicate the potential for PBDEs to break down as a result of biological processes.

Kierkegaard et al. exposed rainbow trout to food amended with the commercial Deca-BDE formulation for 16, 49, and 120 days with an exposure of 7.5 - 10 mg/kg body weight/day.BDE-209 concentrations in muscle increased from <0.6 ng/g of fresh weight to 38 (±14) ng/g after 120 days. Several hexa- to nona-BDEs were observed, which increased in concentration with exposure length. The authors suggested that these could originate from metabolism of BDE-209 or selective uptake of minor components of the commercial formulation. Following a depuration period, BDE-209 concentrations declined significantly, but concentrations of some of the lower brominated congeners were unaffected.<sup>463</sup>

Stapleton et al. exposed juvenile carp to food amended with BDE-209 for 60 days with an exposure concentration of 940 ng/day/fish. During the following 40 days, the fate of BDE-209 was monitored. No net accumulation of BDE-209 was observed, though seven apparent breakdown products, identified as penta- to octa-BDEs, accumulated over the exposure period.<sup>464</sup>

La Guardia et al. collected samples near a plastics related facility and evaluated the levels of PBDEs (from tetra to deca-BDE) to see if degradation of deca-BDE could be observed in the field. Samples were also taken from waste treatment plant including samples from input to and output from the plant. The study found PBDEs in samples from the effluent of the waste treatment plant, surface water, sediment and fish from stream receiving effluent from the waste treatment plant. It was not possible to prove conclusively that deca-BDE degradation contributed to the PBDEs found.<sup>465</sup>

Gerecke et al. evaluated the degradation of deca-BDE in sewage sludge subjected to anaerobic conditions. Freshly digested sewage sludge samples from a facility in Switzerland were spiked with known concentrations of deca-BDE along with one of 5 organic compounds which were described as 'primers', i.e. organic compounds which might facilitate the degradation process. Additional samples were also spiked with two nona-BDEs, specifically BDE-206 or BDE-207 and sterilized controls were used. The samples were kept in the dark for a total of 238 days and

special care was taken to prevent any exposure to light. Gas was produced in all samples except the sterile controls which indicated microbial action was taking place.

In the experiments with 'primers', the concentration of deca-BDE was found to decrease by about 30 percent. No degradation was observed in the controls. In addition, the researchers evaluated possible degradation products and found two of the nona-BDEs (BDE-206 and BDE-207) and a number of octa-BDEs were formed in the samples. The amount of BDE-208 (a third nona-BDE) was observed to increase by more than a factor of 10.

The authors also looked at the mass balance of the reaction and compared the amount of deca-BDE that disappeared with the amount of nona- and octa-BDEs formed. The known degradation products accounted for only about 17% of the mass of deca-BDE which disappeared. The authors theorized that either unknown degradation products were formed and/or some of the deca-BDE was so strongly absorbed to particulate matter that it could not be subsequently removed.

The authors also conducted the same studies but eliminated the 'primers' mentioned above. The study found the same degradation process occurred, although at approximately half the rate of the samples with "primers." The experiments which began with the two nona-BDEs (BDE-206 and BDE-207) were also found to degrade to octa-BDEs. The study did not determine a rate constant for the degradation of nona-BDEs but provided information which indicated that the third nona-BDE, BDE-208, also undergoes similar debromination processes.

Lastly, based on the amounts and types of deca-BDE degradation products, the authors found that a preference for bromine removal from the meta- and para- positions was indicated although loss from the ortho- position was not clearly ruled out.<sup>466</sup>

Gerecke et al. also carried out a preliminary study to determine if deca-BDE could be found to degrade in a full-scale anaerobic digester from the same sewage treatment plant in Switzerland as used in the previous study. Samples were collected from the inlet and outlet of the digester and analyzed for PBDEs. Residence time in the digester was 28 days, only a fraction of their earlier laboratory study. Comparing the outlet values to the inlet, the data indicated that two of the nona-BDEs (BDE-208 and BDE-207) increased relative to the third (BDE-206), similar to what was observed in the laboratory studies. Because the residence time was only 28 days, deca-BDE degradation could not definitively be attributed as the cause for the increase in nona-BDE concentrations.<sup>467</sup>

# Non-biological transformation of PBDEs

Keum and Li conducted extensive laboratory tests using zero-valent iron, iron sulfide or a solution of sodium sulfide as a catalyst to spur the degradation of deca-BDE. The authors were not intending to approximate environmental conditions but were evaluating the use of these catalysts to facilitate remediation of deca-BDE contaminated sites. Samples containing deca-BDE and iron or iron sulfite were incubated at 30° C on a rotary shaker for up to 40 days. Controls were also prepared and subjected to the same experimental conditions. Extracts were removed from the test container at regular intervals and analyzed for a wide range of PBDEs.

The results were evaluated extensively and only a brief summary is provided here. The tests using zero-valent iron led to a 90% reduction of deca-BDE and the formation of a wide range of lower substituted PBDEs. However, based on a mass balance evaluation, 40-50% of the mass could not be found. In addition, the test results suggested there was a preference for bromine removal from the ortho- and meta- positions rather than the para-.

The experiments with iron and sodium sulfides exhibited the same deca-BDE degradation process as for the zero-valent iron but at a much slower rate. Similar lower substituted PBDEs were formed in all tests. The authors indicated that debromination occurs via a stepwise reaction, i.e. deca-BDE degraded to nona-BDE, nona-BDE to octa-BDE, octa-BDE to hexa-BDE, etc. Hydroxylated degradation products were not found during the analysis of samples.<sup>468</sup>

# Appendix E: References on Degradation

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
				(if known)			
2004	Agrell, C.	PBDES at a solid waste incineration plant I: Atmospheric Concentrations	Atmos. Environ.	Europe	air	Investigated atm. deposition (wet & dry) at municipal solid waste incineration plant w/electronics recycling. Deca found at all sites & higher at landfill than reference site	
2004	Baker, J	BDEs in the sediments, porewater, & biota of the Chesapeake Bay, USA	Organohalogen Compounds	US	sediment	Highest conc found downstream of a waste water treatment plant ranging from 9.000 ug/kg just below plant to 2,400 ug/kg 6 km downstream. Deca accounted for 99.7% of PBDEs found	
2004	Bezares-Cruz, J.	Solar Photo- decomposition of decabromodiphenyl Ether: Products and Quantum Yield	Environ. Sci. Technol.	USA	degradation	Deca in hexane degrades in minutes via solar radiation, debrominates to other PBDEs ranging from nona to tri-BDE, total 43 PBDEs detected, 21 known congeners	Significant impact of solvent on reaction rate
2004	Bezares-Cruz, J.	Solar Photodecomposition of decabromodiphenyl ether: Products and Quantum Yield	Environ. Sci. Technol.	U.S.	degradation, photochemical	Deca found to degrade rapidly on exposure to sunlight, concentration reduced to 5% of the initial after 45 minutes exposure in October and to <1% of the initial concentration after 30 minutes exposure in July. Over 40 PBDE degradation products were apparent in	The substance was found to be stable in dark controls over this period. The degradation reaction was found to follow first order kinetics.

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
						the experiments with deca, with over 21 of these having identical chromatographic retention times to known PBDE congeners.	
2005	Blais J.M.	Artic seabirds transport marine-derived contaminants.	Science	Artic	air	Decabromodiphenyl ether is undergoing long-range transport to polar regions.	Most probably via the atmosphere, but other mechanisms could be involved.
2005	Blake, A.	The next generation of POPs: PBDEs & lindane	Int'l POPs Elimination Network Report	World	food	Chicken eggs collected from around world. 12 composite samples tested and deca found in all samples. Deca also dominant congener in most samples.	Eggs collected near hazardous waste & municipal solid waste incinerators, waste dumps, and near petroleum and chemical plants. Results may be worst case.
2004	Blanchard, P	Atmospheric PBDEs conc at Canadian IADN Sites: abstract	Abstract from 3rd Int'l Workshop on BFRs	Canada	air	Air & precip samples analyzed for deca. Aver deca conc in air was 1.8 pg/m3 and precip 5 to 9 ng/L.	
2004	Burreau, S.	Biomagnification of PCBs and PBDEs studies in pike (Esox lucius), perch (Perca fluviatilis) and roach (Rutilus rutilus) form the Baltic Sea	Chemosphere	Sweden	biota	Deca found in 3 of 8 roach, 12 of 33 perch & 4 of 25 pike samples. Evaluated conc and trophic level and found no correlation so no indication of biomagnification.	Large conc of deca found in blank (up to 20% of sample conc) so the data should be used cautiously
1992	Chem. Inspection & Testing Institute	Biodegradation and bioaccumulation data of existing chemicals based on the CSCL Japan	Japan Chem Ecol-Toxic and Information Centre	Japan	degradation, aerobic	Deca incubated with activated sludge from several sources over 2 week period. No degradation was seen.	Length of time of study short compared with environmental conditions.

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2001	de Boer, J.	Polybrominated diphenyl ethers in the aquatic environment	RIVO Report, C023/01		degradation, anaerobic	Unlikely that significant amounts of lower brominated diphenyl ethers formed in sediment unless at a very slow rate.	
2000	de Wit, C.	Brominated Flame Retardants	Swedish Environmental Protection Agency Report 5065	Sweden	degradation, anaerobic	No deca degradation observed in anaerobic in sediment samples after 4 months. One sample continued for 2 years and showed no change.	Details on the work is not provided.
2004	de Wit, C.	Brominated flame retardants in the Arctic-an overview of spatial and temporal trends	Organohalogen Compounds	Canada	biota	Deca not found in samples from ringed seals	
2004	Eljarrat, E.	Occurrence & bioavailability of PBDEs & hexabromocyclododecane in sediment & fish from the Cinca River, a tributary of the Ebro River (Spain)	Environ. Sci. Technol.	Spain	biota	23 fish samples, from 2 upstream and 2 downstream sites. Liver & muscle samples analyzed but no deca found. Deca found in sediments from same areas.	Detection limit was 2-19 ng/kg
2004	Eljarrat, E.	Occurrence & bioavailability of PBDEs & hexabromocyclododecane in sediment & fish from the Cinca River, a tributary of the Ebro River (Spain)		Spain	sediment	Deca concentrations ~20 times higher immediately after industrial town compared with upstream samples	
2005	Environmental Defense	Toxic Nation: A Report on Pollution in Canadians	Private publication	Canada	blood	Sampled blood from 11 volunteers for 88 chemicals including 5 PBDEs (not deca). PBDEs found in most volunteers, BDE-47 found in 10 of 11. Two samples had all 5.	

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2004	Eriksson J.	Photochemical decomposition of 15 PBDE congeners in methanol/water.	Environ. Sci. Technol.	lab	degradation, photochemical	Degradation of decabromodiphenyl ether in the methanol/water system was found to occur by consecutive debromination down to hexabromodiphenyl ethers.	The experiments using water-only were reported to be very difficult to carry out, and it is possible that the disappearance seen could have resulted from adsorption to the glass wall since no degradation products were apparent in these experiments.
2001	Eriksson, J.	Photodecomposition of brominated diphenyl ethers in methanol/water	Poster: 2nd Int'l Workshop on Brominated Flame Retardants	Sweden	degradation	Deca degradation in methanol: water (80:20) mixtures subjected to fluorescent light. Deca degraded readily w/half-life of approx. 30 minutes. Degradation products included lower PBDEs and polybrominated furans. Deca degradation leads to build up of lower brominated diphenyl ethers.	Similarity of results to environmental conditions unclear as methanol/water mixtures not typical.
2004	Fabrellas, B.	Presence of PBDEs in Spanish sewage sludges: Important contribution of deca-BDE	Organohalogen Compounds	Spain	sewage sludge	Deca 93-99% of PBDEs found. Highest conc. from area w/mainly textile manufacturing facilities.	
2005	Gabrielson, G.W.	Organic pollutants in norther fulmars (Fulmarus glacialis) from Bjornoya	SPFO Report, Norw. Pollution Control Authority	Norway	biota	15 liver samples (6 female, 9 male) tested. Deca found in one sample at 206 ug/kg wet wt.	No detection limit given.
2004	Gabrielson, G.W.	Halogenated organic contaminants & metabolites in blood & adipose tissues of polar bears (Ursus maritimus) from Svalbard	SPFO Report, Norw. Pollution Control Authority	Norway	biota	Samples of adipose tissues from 15 bears analyzed and deca was not found in any samples.	Detection limit was 1 ug/kg wet weight

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2001	Gallet, G.	Two approaches for extraction and analysis of brominated flame retardants (BFR) and their degradation products in recycled polymers and BFR containing water	Poster: 2nd Int'l Workshop on Brominated Flame Retardants	Sweden	degradation, hydrolysis	Deca placed in sealed vials containing water at pH 5 or 7 for six weeks at 100 degrees C. No change in deca concentrations suggesting deca stable to hydrolysis.	
2005	Gerecke A.C.	Anaerobic degradation of decabromodiphenyl ether.	Environ. Sci. Technol.	Switzerland	degradation, sewage sludge	The amount of decabromodiphenyl ether was found to decrease by around 30% after 238 days incubation in the experiments with primers. No significant degradation of decabromodiphenyl ether was seen in the sterile controls.	The study indicates that the microbial community in the experiment were able to degrade halogenated compounds. The study also investigated the amounts of several lower brominated congeners present at various times in the study.
2004	Gerecke A.C.	Formation of lower brominated congeners by anaerobic degradation of decabromodiphenyl ether in sewage sludge.	Abstract from 3rd Int'l Workshop on BFRs	Switzerland	degradation, sewage sludge	The amount of decabromodiphenyl ether was found to decrease by around 30% after 238 days incubation in the experiments with primers. No significant degradation of decabromodiphenyl ether was seen in the sterile controls.	The study indicates that the microbial community in the experiment were able to degrade halogenated compounds. The study also investigated the amounts of several lower brominated congeners present at various times in the study.
2004	Gouin, T.	Conc of Deca-PBDE in air from Southern Ontario: Evidence for particle- bound transport	Abstract from 3rd Int'l Workshop on BFRs	Canada	air	Air samples from spring and winter, 115 km NE of Toronto. Deca conc. ranged from nd to 105 pg/m3 with average 19 pg/m3. Deca mainly associated w/particulate fraction	

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2004	Hamm, S.	PBDEs in sewage sludge & effluents of sewage treatment plants from a central region of Germany	Organohalogen Compounds	Germany	sewage sludge	Samples from 8 municipal plants. Deca found to be 43- 79% of PBDEs in sludge, 33-58% in effluent suspended solids	
2004	Hayakawa, K	PBDEs, PBDD/Fs, & MoBPXDD/Fs in atmosphere & bulk deposition in Kyoto, Japan	Organohalogen Compounds	Japan	soil	Deca found in soil, air and wet & dry deposition at Kyoto Univ.	
2004	Hirai, Y	Atmospheric emission of BDE-209 in Japan	Organohalogen Compounds	Japan	soil	Deca found in 25 of 30 samples tested. No info on whether due to sludge application or atm deposition	
2004	Hites, R. A.	Global assessment of PBDEs in farmed and wild salmon	Environ. Sci. Technol.	US	biota	Around 700 samples tested, deca not found in any. Deca was found in the fish food for farmed salmon.	Detection limit of 0.1 ug/kg wet wt
2004	Huwe, J	PBDEs in meat samples collected from supermarkets across the US	Abstract from 3rd Int'l Workshop on BFRs	US	food	Meat & poultry samples from 9 cities analyzed. Deca not found in bacon (11) or beef fat (9) but found in chicken (17) and pork (11).	High conc of deca found in lab blank so data should be used with caution.
2001	Jafvert, C.	Letter to Wendy Sherman, American Chemical Council Brominated Flame Retardant Industry Panel		USA	degradation	Deca degradation on humic acid-coated sand in two replicates evaluated and data on 43 congeners provided. Subjected to 72 hour sunlight exposure. Data suggests hexa- and hepta-BDE congeners generated although no clear identification of nona- and octa-BDEs could be determined	Evaluation rough. Also low sample size and high variability impacts results.

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2001	Jafvert, C.	Photochemical Reactions of Decabromodiphenyl Oxide and 2,2',4,4'- Tetrabromodiphenyl Oxide	Final Report to EU	USA	degradation	Deca degradation on quartz glass and silica particles (sand), humic acid-coated silica particles and glass surfaces in contact with water subjected to artificial and natural light. 10% degradation on spiked sand within 12 hours.	Degradation also observed in controls so suggested no debromination occurred. Significance of findings questionable.
2001	Jafvert, C.	Photochemical Reactions of Decabromodiphenyl Oxide and 2,2',4,4'- Tetrabromodiphenyl Oxide	Final Report to EU	USA	degradation	Deca degradation on humic acid-coated sand indicated 12% reduction of deca after 96 hours. Dark controls showed fluctuation but no loss.	Tetra- or penta-BDE not found.
2001	Jafvert, C.	Photochemical Reactions of Decabromodiphenyl Oxide and 2,2',4,4'- Tetrabromodiphenyl Oxide	Final Report to EU	USA	degradation	Deca absorbed onto quartz tubes containing humic acid solution subjected to natural sunlight. 30% degradation after 72 hours followed by plateauing of degradation. Only nona- and octa-BDE found although not all degradation products identified.	Dark controls used but no change observed.
2001	Jafvert, C.	Photochemical Reactions of Decabromodiphenyl Oxide and 2,2',4,4'- Tetrabromodiphenyl Oxide	Final Report to EU	USA	degradation	Solar radiation of deca in quartz tubes without humic acid present. Degradation found at a greater rate than with humic acid. 71% degraded after 72 hours. 50% of degradation products not identified. No lower PBDEs found other than octa- and penta-BDE. Increased degradation may be due to lack of humic acids to absorb radiation.	Dark controls used but no change observed.

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2001	Jafvert, C.	Photochemical Reactions of Decabromodiphenyl Oxide and 2,2',4,4'- Tetrabromodiphenyl Oxide	Final Report to EU	USA	degradation	Deca degradation in Rayonet reactor using artificial light (2 lamps). Controls and dark controls also run. 69% degradation occurred within 60 hours. 27% of degradation products unaccounted for.	
2001	Jafvert, C.	Photochemical Reactions of Decabromodiphenyl Oxide and 2,2',4,4'- Tetrabromodiphenyl Oxide	Final Report to EU	USA	degradation	Deca degradation in Rayonet reactor using artificial light (4 lamps). Controls and dark controls also run. Increased amount of deca in test to determine degradation products. Deca found to degrade more slowly. Significant amount of deca remained after 240 hours. Possibly lower PBDEs observed but speciation not done.	
2004	Jaspers, V.	Brominated flame retardants and organochlorine pollutants in eggs of little owls (Athene noctua) from Belgium	Environ. Pollut.	Belgium	biota	40 owl eggs collected and analyzed for PBDEs mainly lower brominated congeners. Of the few, unspecified tested for deca, only one egg had deca at 17 ug/kg lipid.	Detection limit was 8 ug/kg
2004	Johansson, I.	Levels & trends of past 20 yrs of PBDEs in mussels from the Seine estuary, France	Abstract from 3rd Int'l Workshop on BFRs	France	biota	Used archived, frozen samples from 1982-2003. Samples were cleaned (to remove intestinal tract contamination) and shelled prior to storage. Data reported for 11 yrs & conc peaked in 1999 (.96 ug/kg).	
2004	Kajiwara, N.	Geographical distribution and temporal trends of	Abstract from 3rd Int'l	Japan	biota	41 blubber samples from 7 species from 1990-2001	Detection limte of 0.5 ug/kg lipid

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
		PBDEs in cetaceans from Asian waters	Workshop on BFRs			tested and deca was not found in any samples.	
2005	Keum and Li	Reductive debromination of PBDEs by zerovalent iron.	Environ. Sci. Technol.	lab	degradation, abiotic	The experiments with iron sulfide and sodium sulfide showed transformation of decabromodiphenyl ether to lower brominated congeners but at a slower rate than found with zero valent iron.	Although the degradation rate was slower with sodium sulfide, the congener profile of the degradation products was found to be similar to that obtained with zero valent iron.
2004	Khan, N.	Determination of PBDEs & other halogenated components in sediments collected in Pakistan	Abstract from 3rd Int'l Workshop on BFRs	Pakistan	sediment	Deca found in 1 of 5 freshwater sediment samples from Indus river and in all other samples (estuarine & oceanic sediments.	
2004	Kierkegaard, A.	Identification of the flame retardant deca-PBDE in the environment	Environ. Sci. Technol.	Netherlands	sediment	Found deca in sediments.	
2004	Kilemade, M.	An assessment of the pollutant status of surficial sediment in Cork Harbour in the SE of Ireland w/particular reference to PAHs	Mar. Pollut. Bull.	Ireland	sediment	Deca not detected in any intertidal surficial samples (top 1-2 cm)	
2005	Klamer, H. J. C.	A Chemical & Toxicological Profile of Dutch North Sea Surface Sediments	Chemosphere	Netherlands	sediment	Deca found in southern North Sea surface sediment samples at 1-32 ug/kg dry weight.	
2004	Knoth, W.	Occurrence & fate of PBDE in sewage sludge from municipal waste water treatment plants	Organohalogen Compounds	Germany	sewage sludge	Samples from all stages of eleven POTWs. Found ppm conc. of deca & no indication of any change in bromination pattern during treatment process	

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2004	Kokic, T. M.	Paper biosolids and manure: an investigative approach regarding levels of PBDES	Abstract from 3rd Int'I Workshop on BFRs	Canada	sewage sludge	Various biosolid sources (paper, paper compost, & animal manure). Compared ratio of PBDEs in the two paper sources and deca was lower in the compost results compared with the non-composted suggesting deca degradation w/time (only suggested, not proven). No info on source of deca in paper	
2004	Kolic, T. M.	BDE levels: A comparison of tributary sediments versus biosolid material	Organohalogen Compounds	US	sediment	Deca found in stream sediments @ 6.9-400 ug/kg & biosolids @ 310-2,000 ug/kg.	
2004	Kolic, T. M.	Paper biosolids and manure: an investigative approach regarding levels of PBDES	Abstract from 3rd Int'l Workshop on BFRs	Canada	sewage sludge	Suggests degradation of deca during biosolids decomposition/composting process could be an explanation for the changes in the relative ratios of congeners seen in composted and uncomposted biosolids.	Authors note that further work is needed to test this hypothesis.
2004	Kosterhaus, S. L.	Polybrominated diphenyl ethers (BDEs) in sediment, pore water, & infaunal invertebrates along a spatial gradient in an urban estuarine river receiving wastewater effluent in Baltimore Maryland USA	Abstract from 3rd Int'l Workshop on BFRs	US	sediment	Deca found in sediments down river from waste water treatment plant. Levels ~2,400-9,000 ug/kg dry wt. Conc. Decrease farther downstream from plan. Deca accounts for most of PBDEs in samples (93-99%)	

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2004	La Guardia, M. J.	Environmental debromination of decabrominated diphenyl ether.	Abstract from 3rd Int'l Workshop on BFRs	USA	degradation	Decabromodiphenyl ether and other congeners were found in these samples, but it was not possible to determine conclusively if their presence was related to possible degradation of deca.	Samples collected close to plastics-related facility. Concentrations in water in excess of the water solubility of deca & probably reflect deca adsorbed onto suspended matter.
2004	La Guardia, M. J.	Organic contaminants of emerging concern in land- applied sewage sludge (biosolids)	J. Resid. Sci. Technol.	US	sewage sludge	Samples taken from POTWs using different stabilization techniques. Deca found in all samples at conc. Ranging from 85 to 4,890 ug/kg dry wt.	
2004	Leonards, P.	Species-specific accumulation & biostranformation of PBDEs and HBCDD in two Dutch Food Chains	Abstract from 3rd Int'l Workshop on BFRs	Netherlands	biota	6 fish species tested (unknown # of samples) and deca found in 24% analyzed ranging from 1.9 to 17 ug/kg lipid.	
2004	Lichota, G.	Endangered Vancouver Island marmots: sentinels of atmospherically delivered contaminants to British Columbia, Canada	Environ. Toxicol. Chem.	Canada	biota	Single female tested for PBDEs. Deca found to be dominant PBDE present (approx. 67% of total).	Low analytical recoveries may have impacted results.
2004	Lopez, D.	A preliminary study on PBDEs and HBCDD in blood and mil from Mexican women	Abstract from 3rd Int'l Workshop on BFRs	Sweden	human milk		
2004	Lopez, D.	A preliminary study on PBDEs and HBCDD in blood and milk from Mexican women	Abstract from 3rd Int'l Workshop on BFRs	Mexico, Sweden	human milk and blood	Decabromodiphenyl ether was found at similar levels in Mexican women and Swedish women.	
2004	Luksemburg, W.	PBDEs, PCDD/Fs & PCBs in fish, beef, and fowl purchased in food markets in Northern California	3rd Int'l	US	food	Wide range of types of meat purchased. Deca found in all wild and farm fish, fowl and scallops tested. Deca was not found in grain-fed beef or ground deer but found in	Results available only in abstract form. Some of results near quantitation limit which may indicate a blank problem so data should be used

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
						free-range beef.	cautiously.
2004	Luksemburg, W.	PBDEs, PCDD/Fs & PCBs in fish, beef, and fowl purchased in food markets in Northern California	Organohalogen Compounds	US	food	Data on add'l products from results in abstract. Deca not found in fish (2) and chicken (1) sample but found in many other fish (4), beef (2) and poultry (2) products.	
2004	McCrindle, R.	Native & mass labeled [13C14] deca-BDE: Characterization and use in determination of deca- BDE in sewage sludge	Organohalogen Compounds	Canada	sewage sludge	Deca found in 10 samples of sewage sludge from 6 locations, ranging from 0.47- 1.8 mg/kg	
2004	McPherson, A.	BFRs in dust on computers: The case for safer chemicals and better computer design	Clean Production Action	US	dust	Wipe samples from CPUs & monitors of new & old computers. 16 samples analyzed and deca found in all ranging from 2.1 to 213 pg/cm2. Nona- & octa-BDE found and high correlation found between these two and deca.	
1974	Norris, J. M.	Toxicological and Environmental Factors involved in the selection of decabromodiphenyl oxide as a fire retardant chemical	J. Fire Flamm. Combust. Toxicol.		degradation	Subjected deca to degradation in simulated and natural light and a range of solvents including octanol, xylene and water. Found to degrade with half- lives of 4 and 15 hours, depending upon conditions.	
2004	North, K. D.	Tracking PBDE releases in a wastewater treatment plant effluent, Palo Alto, CA	Environ. Sci. Technol.	US	sewage sludge	Deca found both in sludge (aver. 1,183 ug/kg) & effluent (aver. 1.73 mg/L). Effluent conc may be related to suspended solids and	

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
						deca absorbed onto particulates. Calc ~0.9 kg total PBDEs released to San Francisco bay per year with deca ~ 6% of total	
2004	Northwest Environment Watch	Flame retardants in the bodies of Pacific Northwest residents. A study on toxic body burdens.	Northwest Environment Watch	Pacific Northwest	human milk	Decabromodiphenyl ether was found to be present in 24 of the 40 samples.	Area included Montana, Oregon, Washington and British Columbia
2004	Nylund, K.	Bromerade Flamskyddsmedlel in avsloppslam	Swedish Environ. Prot. Agency Rpt	Sweden	sewage sludge	50 plants, pooled samples from one month, deca found in all samples from 6 - to 1,000 ug/L.	
2004	Ohta, S.	Characterization of Japanese pollution by PBDES, TBBPA, PCDDs/DFs, PBDDs/DFs and PXDD/DFs observed in the long-term stock- fishes and sediments	Abstract from 3rd Int'l Workshop on BFRs	Japan	sediment	Deca found in all 17 samples, highest from area containing many chemical factories.	
2004	Ohta, S.	Levels of PBDEs, TBBPA, TBPs, PCDDs/DFs, PCDDs/DFs and PBDDs/DFs in human mil of nursing women and diary milk products in Japan.	Organohalogen Compounds	Japan	human milk	The actual concentration of decabromodiphenyl ether present in the samples is unclear.	The results are only displayed graphically.
2001	Ohta, S.	Contamination levels of PBDEs, TBBPA, PCDDs/DFs, PBDDs/DFs and PXDDs/DFs in the environment of Japan	Organohalogen Compounds	Japan	degradation	Deca decomposition in organic solvents/organic solvent mixtures at various light sources. Reductive debromination occurred including degradation of products.	

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2004	Okazawa, T.	Congener-specific data of PBDEs in pine needles	Organohalogen Compounds	Japan	biota	Samples from 10 sites collected in 1999. PBDEs found in all samples with deca 90% of total present. Deca was also found at a control site.	No QA details given
2002	Olsman, H	Formation of dioxin-like compounds as photoproducts deca-BDE during UV-irradiation	Organohalogen Compounds		degradation	Deca dissolved in toluene. Lower PBDEs produced as well as some potential dioxins.	Dioxins only suggested by activity during bioassay. No structural identification.
1997	Orn, U.	Synthesis of polybrominated diphenyl ethers and metabolism of 2,2',4,4'-tetrabrom [14C]diphenyl ether	Licentiate Thesis, Dept. of Environ. Chem., Stockholm University	Sweden	degradation	Deca dispersed as thin layer on sand debrominate when subjected to sunlight. When water added to sand, brominated phenols also found.	Few details on study available.
2005	Oros, D. R.	Levels & Distribution of PBDEs in water, surface sediments, & bivalves from the San Francisco estuary	Environ. Sci. Technol.	US	sediment	Deca found in 32 of 33 surface water samples but not in any of 48 sediment samples. Highest conc. found near POTW output	
2004	Osako, Masahiro	Leaching of Brominated flame retardants in leachate from landfills in Japan	Chemosphere	Japan	leachate	nd to 4000 pg/L for raw leachate, nd for treated leachate, no deca results, higher values in newer landfills, highest conc w/highest organics	
2004	Paepke, O	PBDEs in fish samples of various origins	Organohalogen Compounds	Germany	food	10 fish samples purchased from German markets and analyzed for deca. Deca found in 50% of fish sampled ranging from 0.04 - 2.79 ug/kg lipid.	Only edible parts of fish used in samples.

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2003	Palm, W-U	Environmental photochemistry of deca- BDE: UV spectra, photolysis and photochemistry of PBDES in organic solvents and adsorbed on particles in air and in aqueous suspension (including a feasibility study on OH reactivities in an aerosol smog chamber facility)	Report for the Bromine Science and Environmental Forum		degradation	Amt of photolytic energy absorbed decreases w/successive debromination. Deca degraded in all test conditions. Degradation products were not similar to commercial octa and penta mixtures. Tested to determine if furans produced by degradation of deca. Low substituted furans found. Concludes deca degrades via successive debromination. Deca in air suspensions found to degrade but much slower than in solutions.	Higher brominated furans not found but may be due to presence of equivalent PBDEs formed in higher amounts.
2004	Parsons J.	Reductive debromination of decabromodiphenyl ether (BDE 209) by anaerobic sediment microorganisms.	Organohalogen Compounds	Western Scheldt	degradation, sediment	A decrease in the concentration of decabromodiphenyl ether in sediment was seen over the first two months incubation.	Results displayed graphically. There are some uncertainties with this test that are not clearly explained in the paper.
2004	Raff, J.	PBDEs in Mississippi River suspended sediment	Organohalogen Compounds	US	sediment	PBDEs found at 32 sites. Deca estimated to be 96.8% of total. Calculated ~8 tonnes of PBDEs discharged into Gulf of Mexico in 2002	
2005	Rahm S.	Hydrolysis of environmental contaminants as an experimental tool for indication of their persistency.	Environ. Sci. Technol.		nucleophilic substitution	Concluded as bromine groups are electron- withdrawing, and bromide is good leaving group, fully brominated deca susceptible to nucleophilic aromatic substitutions which decreases with decreasing	Not possible to ascertain whether such substitution reactions would occur in the environment.

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
						degree of bromination.	
2004	Rayne, S.	PBDEs, PBBs, and PCNs in three communities of free-ranging killer whales (Orcinus orca) from the Northeastern Pacific Ocean	Environ. Sci. Technol.	US	biota	Blubber from 39 killer whales (age 1-69 yrs old) collected between 1993- 1996 were tested for PBDES. 13 PBDEs found in all samples out of 37 tested.	No info on which 37 PBDEs tested & no indication deca was one.
2004	Sawal, G.	Polybrominated diphenyl ethers in sediments from the River Elbe, Germany	Abstract from 3rd Int'l Workshop on BFRs	Germany	sediment	Deca dominant & averages about 78% of total PBDEs in sample. 3 samples from Czech Rep showed same but others were mostly lower congeners (70% tetra- to hexa-BDE)	
2001	Schaefer, E. C.	Potential for biotransformation of radiolabelled decabromodiphenyl oxide (DBDPO) in anaerobic sediment	Wildlife International Ltd	USA	degradation, anaerobic	Sediment and water collected from river. Used 14C labeled deca and similarly labeled glucose used as a control. Deca found to be stable over conditions of test.	
2004	Schecter, A	PBDE contamination of US food	Environ. Sci. Technol.	US	food	32 food samples (canned milk, baby food , milk powder, fish, meat , eggs, cheese, ice cream, sausage, butter & margarine) tested for PBDEs. Fish had highest conc of PBDEs followed by meat products. Deca dominant congener in calf liver, soy instant formula, cheese and margarine.	Results displayed graphically so hard to determine exact deca conc in all samples. Similar work also reported in Organohalogen Compound and Abstract at 3rd Intl Workshop on BFRs

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2004	Schlaback, M	Brominated flame retardants in Drammens River & the Drammensfjord, Norway: abstract	Abstract from 3rd Int'l Workshop on BFRs	Norway	sediment	Deca found in all samples. The highest level found in the fjord was from a site near a pier used for shipping auto fluff	Fish also collected but no results provided.
2005	Sellstrom, U.	Personal communication	EU deca risk addendum, Aug 2005	Sweden	soil	Deca present at 2,400 ug/kg dry wt in farm soil sampled in 2000 that received sewage sludge land applied in 1978 & 1982 from PBDE using textile industry source.	Continued sludge application might therefore lead to a potential build-up in soils.
2005	Sellstrom, U.	Effect of Sewage-Sludge application on Concentrations of Higher- Brominated Diphenyl Ethers in Soils and Earthworms	Environ. Sci. Technol. Advance publication	Sweden	soil	Took soil from 3 research stations and 2 farms which have had sewage sludge applied. Evaluated transport of deca and found to deca bioavialble from soils and accumulating in earthworms, presenting an exposure pathway into terrestrial food web. Found no evidence of photolytic debromination of deca from 1 soil sample.	No data provided on debromination study. Only one sample and standard tested and only for 21 days.
1998	Sellstrom, U.	Photolytic debromination of decabromodiphenyl ether (DeBDE)	Organohalogen Compounds	Sweden	degradation	Deca in a range of media, dissolved in toluene or as thin layer on silica gel, sand, soil or sediment. Samples subjected to simulated and natural light. Toluene samples debrominate successively with half-life less than 15 minutes. Debromination also occurred in sand although at slower rate, half-life 35-37 hours.	No 2,2',4,4'- tetrabromodiphenyl ether (common in the environment) found in samples. Long-term composition of degradation products unclear.

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2004	Sjodin, A.	Conc of PBDEs in household dust from various countries - inhalation a potential route of human exposure	Organohalogen Compounds	Germany/U S	air	Samples from vacuum cleaner bags, 10 each from US & Germany. US conc.: 120-21,000 ug/kg, Germany:<5-410. Determined to be statistically significant.	Another study in 2003 reported higher conc for Germany & no difference between two
2003	Soderstrom, G	Photolytic debromination of decabromodiphenyl ether (BDE 209)	Environ. Sci. Technol	Sweden	degradation	Degradation in toluene, silica gel, sand, soil or sediment. Deca degradation in all media w/half-life of 15 mins in toluene. Similar for non-organic media. Reductive brominating step wise to hexa and lower PBDEs. Compounds other than PBDEs formed including brominated dibenzofurans.	No furans found in silica gel experiments. Though furans degraded quickly under test conditions when compared with more environmentally relevant experiments.
2004	Song, W.	PBDEs in the sediments of Great Lakes 1: Lake Superior	Environ. Sci. Technol.	US	sediment	Core samples from 2001 & 2002. Deca conc. decreased rapidly w/depth. Accounted for 83-94% of total PBDEs. 73-135 kg/yr calc. added to lake. Increase noted from 1970's onwards with increasing trend still apparent in 2002	
2004	Sorensen, P. B.	Persistent organic pollutants (POPs) in the Greenland environment- Long-term temporal changes and effects on eggs of a bird of prey	Tech Rpt, Ministry of Environ., Denmark	Greenland	biota	36 egg samples from 1986- 2003 were analyzed and deca was found in all samples (3.8-250 ug/kg lipid w/median 11 ug/kg). Time trend analysis suggested levels increasing w/time.	Falcons winter in Central & South America so results are not due solely to conc in Greenland

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2005	Stapleton, H.	Degradation of deca in House Dust Following Sunlight Exposure	Environment Agency	USA	degradation	House dust spiked with deca placed in ampules and subjected to 200 hours of sunlight exposure. Found degradation to nona-, octa-, and hepta-BDEs. Mass balance accounted for 83% of bromine/ Remaining balance lost due to volatilization or formation of unknown products	Is conducting a second series of tests and increasing sunlight exposure to 200 hours. Will also attempt to address issues raised in 1st study, i.e. whether removal of organic carbon along with background PBDEs affected results and use of organic solvent affected PBDE particlization & adsorption.
2005	Stapleton, H.	Polybrominated Diphenyl Ethers in House Dust and Clothes Dryer Ling	Environ. Sci. Technol.	USA	dust	Collected dust and dryer lint samples from homes and analyzed for PBDEs. Found PBDEs in every sample with penta and deca dominating.	
2004	Stapleton, H.	Measurement of PBDEs in environmental matrix standard reference materials	Organohalogen Compounds	US	biota	Deca was not found in whale blubber, and fish & mussel tissue used as std reference mtls	Detection limit 1.0 ug/kg wet wt.
2004	Stapleton, H.	Measurement of PBDEs in environmental matrix standard reference materials	Organohalogen Compounds	US	dust	Deca found at 2,505 and 2,230 ug/kg dry mass in two samples of house dust used as standard reference mtls in US	
2004	Stapleton, H.	Measurement of the flame retardants PBDEs and HBCDD in house dust	Organohalogen Compounds	US	dist	17 samples using handheld vacuum. Aver deca 160 to 8,700 ug/kg with mean 2,100. Deca comprises 10- 86% of total PBDEs found. Tried to correlate to known PBDE sources. No correlation found.	Could be same results reported in 3rd Int'l Workshop on BFRs by same author. Conclusions similar.

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2004	Stapleton, H.	PBDE measurements in household dust	Abstract from 3rd Int'l Workshop on BFRs	US	dust	16 samples using handheld vacuum. Deca found in all samples ranging between 83 to 8,750 ug/kg and comprised 4 to 90% of PBDEs found.	
2004	Takasuga, T	Accumulation of chlorinated and brominated persistent toxic substances (PTS) and their relationship to testosterone suppression in Norway rats from Japan	Organohalogen Compounds	Japan	biota	Rat liver samples from samples taken from urban (2), rural (2), landfill (1) and island (1) locations were analyzed and PBDEs found in all samples. Deca accounted for large percentage of PBDEs (4 to 83% of total). Rats thought to be good indicators of human exposure.	Two method blanks also analyzed and no PBDEs found.
2004	Takasuga, T	Impact of fermented brown rice with Aspergillus oryzae (FEBRA) intake and concentration of polybrominated diphenylethers (PBDEs) in blood of humans from Japan.	Chemosphere	Japan	human blood	Decabromodiphenyl ether was detected in 102 samples out of 156 samples collected from nine married couples in Japan over a two year period.	
2004	Tasaki, T.	Substance flow analysis of brominated flame retardants and related compounds in waste TV sets in Japan	Waste Management	Japan	Use, degradation	Evaluated deca in TV casings. Deca peak expected in 2009 even though non-BFRs used after 2006, Br conc in plastics expected to increase until 2020	

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2004	ter Schure, A. F. H.	PBDEs at a solid waste incineration plant II: Atmospheric deposition	Atmos. Environ.	Sweden	air	Collected wet and dry deposition and air samples from island in Blatic Sea. Found deca in all samples. Yearly deposition estimated to be 166 kg/yr	
2004	Tomy, G.	Hexabromocyclododecane (HBCD) isomers and BDE congeners in fish from Lake Winnepg, Manitoba (Canada)	Abstract from 3rd Int'l Workshop on BFRs	Canada	biota	Identified a hexabrominated diphenyl ether.	This congener may be present in some other commercial PBDEs, or indeed could be formed from the degradation/ metabolism of PBDEs other than decabromo- diphenyl ether in the environment.
2004	Tomy, G.	Hexabromocyclododecane (HBCD) isomers and BDE congernes in fish from Lake Winnepg, Manitoba (Canada)	Abstract from 3rd Int'l Workshop on BFRs	Canada	biota	Deca found in all fish sampled and dominant PBDE in walleyee, perch, burbot & whitefish. Suspected metabolite of deca (one of the hexa- BDEs) found in all fish.	Not clear if metabolite from deca or present in other PBDE formulations.
2001	Tysklind, M.	Abiotic transformation of polybrominated diphenyl ethers (PBDEs): Photolytic debromination of deca- BDE	2nd Int'l Workshop on Brominated Flame Retardants	Sweden	degradation	Continuation of Sellstrom's work. Half-lives in sediment and soil 100 and 200 hrs, respectively.	
2005	US PIRG	The Right Start: The Need to Eliminate Toxic Chemicals From Baby Products	US PIRG	US	general		
2004	Verreault, J.	New and established organohalogen contaminants and their metabolites in plasma and eggs of glaucous gulls from Bear Island	SPFO Report, Norw. Pollution Control Authority	Norway	biota	109 plasma (57 male & 52 female) & 32 egg samples collected from gulls, 89 analyzed for deca. Deca found in 15% of egg (23.2- 52.5 ug/kg wet wt) & 30% (202-1,055 ug/kg lipid)of	Report cautions on use of deca results as deca found unstable during analysis leading to high det limit of 2.73 ug/kg wet wt.

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
						plasma samples.	
2005	Verslycke, T. A.	Flame retardants, surfactants & organotins in sediment & mysid shrimp of the Scheldt estuary (the Netherlands)	Environ. Pollut.	Netherlands	sediment	Deca found both in sediments & shrimp.	
2005	Verslycke, T. A.	Flame retardants, surfacts & organotins in sediment & mysid shrimp of the Scheldt estuary (the Netherlands)	Environ. Pollut.	Netherlands	biota	Deca present in all shrimp samples from 3 sites in river estuary ranging from 269 to 600 ug/kg lipid	Digestive tract was not cleared before analysis so deca may have been in digestive track.
2004	Vieth, B.	PBDE levels in human milk: The situation in Germany and potential influencing factors-a controlled study	Organohalogen Compounds	Germany	human milk	143 samples divided between omnivores & vegetarians/vegans, 93 analyzed to date. Deca found in 40% of the samples. No difference could be observed based on diet.	
2004	Voorspoels, S	PBDEs in sediments from a polluted area in Europe: The Belgian North Sea, the Western Scheldt estuary & tributaries: abstract	Abstract from 3rd Int'l Workshop on BFRs	Europe	sediment	Deca found in most samples & most abundant (95% of total in estuary and 52 to 95% of total in freshwater tributary). Found correlation between deca & lower congeners in 2 of 3 sites	
2005	Wang, D.	Gas chromatography/ion trap mass spec applied for the determination of PBDEs in soil	Com. Mass Spectrom.	Japan	soil	Deca found at 1,026 ug/kg in soil at an open electronics waste treatment site	
1998	Watanabe, I.	Formation of brominated dibenzofurans from the photolysis of flame retard- ant decabromodiphenyl	Bull. Environ. Contam. Toxicol.	Japan	degradation	Deca debrominated mainly to tri- to octa-BDE. Formation of brominated furans also found but no	

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
		ether in hexane solution by UV and sunlight				dioxins were detected. Both under UV and sunlight.	
1986	Watanabe, I.	Confirmation of the presence of the flame retardant decabromo- diphenyl ether in river sediment from Osaka, Japan	Bull. Environ. Contam. Toxicol.	Japan	degradation	Deca quickly decomposed to hexa- through nona-BDEs on exposure to sunlight.	No info provided on solvent used.
2004	Watanabe, K.	Brominated organic contaminants in the liver and egg of the common cormorants (Phalacrocorax carbo) from Japan	Environ. Sci. Technol.	Japan	biota	Ten liver and 10 egg samples tested and deca below detection limit in all samples. Two samples of fish eaten by birds also tested with same results.	No info provided on detection limit or details of method used.
2004	Wenning, R. J.	Levels of polybrominated diphenyl ethers (PBDEs) in the Hackensack River & Newark Bay, NJ, USA: abstract	Abstract from 3rd Int'l Workshop on BFRs	US	sediment	Deca found in all samples. Means were 60 ug/kg dry wt for surface and 30 ug/kg dry wt in buried samples.	
2005	Wilford, B.	Deca-BDE in UK Air: abstract only	Birmingham POPs mtg	UK	air	Deca found in air samples, appears associated with particulate phase.	
2005	Wilford, B.	Poster: An extensive study of PBDEs in indoor air & dust with comparison to outdoor levels	Environ. Canada/ Lancaster Univ.	Canada	air	Indoor air samples collected from homes in Ottawa using diffusive samplers, samples from family vacuums & 7 outdoor samples. Only dust analyzed for deca which was 40% of PBDEs found. Estimated human ingestion was mas of 17,300 mg/day.	
2004	WWF	Bad blood? A survey of chemicals in the blood of European Ministers.	WWF Report	UK	blood	14 Ministers from 13 European country tested. Deca found in 3 of 14 samples tested.	

Pub. Year	Main Author	Title	Journal	Country	Keyword (s)	Data of importance	Note:
2004	WWF	Contamination: the next generation. Results of the family chemical contamination survey.	WWF Report	UK	blood	Samples from members of 7 families in UK. Individuals tested include 3 generations between 9 & 88 yrs totalling 33 samples. Deca found in 7 of 33 samples including grandmother (1), parents (2) and children (4).	Attempt made to correlate deca conc with lifestyle, food, etc but no conclusions could be reached.
2005	WWF/ Greenpeace	A Present for Life: Hazardous Chemicals in Umbilical Cord Blood	WWF/ Greenpeace	UK	general		



# Appendix F: Toxicity Profiles for Deca-BDE, alternatives and related chemicals

Chen	nical [Common Trade name]	CAS #
1.	Decabromodiphenyl ether (Deca-BDE)	1163-19-5
	[SAYTEX 102e, DE-83R]	
2.	Bis(pentabromophenyl) ethane [SAYTEX 8010]	84852-53-9
3.	1,2-bis(tetrabromophthalimido) ethane [SAYTEX BT-93]	32588-76-4
4.	Tetrabromobisphenol A epichlorohydrin polymer	40039-93-8
	[EPON Resin 1163]	
5.	Bis(tribromophenoxy)ethane [FF-680]	37853-59-1
6.	Hexabromocyclododecane (HBCD)	3194-55-6 and
		25637-99-4
7.	Tetrabromobisphenol A (TBBPA)	79-94-7
8.	Tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPA-	21850-44-2
	DBPE)	
9.	Resorcinol bis (diphenylphosphate) (RDP)	57583-54-7 and
		125997-21-9
10.	Bisphenol A diphosphate (BAPP, BPADP) [Refofos BAPP,	181028-79-5
	NcendX P-30] and bisphenol A bis(diphenyl phosphate) (BDP)	and 5945-33-5
	[Fyrolflex BDP]	
11.	Diphenyl cresyl phosphate (DCP)	26444-49-5
12.	Triphenyl phosphate (TPP)	115-86-6
Relat	ed Chemicals	
13.	Zinc Borate	1332-07-6
14.	Polytetrafluoroethylene (PTFE) [Teflon]	9002-84-0
15.	Antimony trioxide	1309-64-4

## **Request for Information on these chemicals:**

Washington Department of Health is in the process of collecting physical/chemical property information and toxicity studies for these chemicals. Please send any additional information or references to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov



# **Deca-BDE** Alternatives Assessment

Name:	Deca-B	DE
Date Upo	dated:	11/21/05

#### **IDENTIFICATION**

CAS number:	1163-19-5
EINECS:	214-604-9
EINECS name:	
Molecular formula:	C12-Br10-O (EU Risk Assessment, 2002)
Known uses:	HIPS, Thermoplastic, polyesters, PA, textiles (Danish EPA, 2000).
Use (tonnage):	56,100 metric tons (BSEF)

Structural formula:



	(from ChemIDPlus)
EU classification annex:	
Synonyms	Decabromobiphenyl ether Decabromodiphenyl oxide bis(Pentabromophenyl)ether Trade Names: FR-1210 (Dead Sea Bromine Group), Saytex 102E (Albemarle, Corp), Great Lakes DE-83-R (Great Lakes Chemical Europe)
Additive or Reactive FR	Additive
Halogenated?	Yes (contains bromine)

Additional Information

### PHYSICO-CHEMICAL CHARACTERISTICS

Physical form	White to off-white crystalline powder (EU Risk Assessment, 2002).
Molecular weight	959.22 (EU Risk Assessment, 2002)
Boiling point/range (deg C)	425C (Danish EPA, 2000)
Melting point (deg C)	295-310C (Danish EPA, 2000)
Decomposition temp. (deg C)	425 deg C (HSDB)
Vapor pressure (mg Hg)	4.63 10-6 Pa (EU Risk Assessment, 2002)
Relative density	
Water Solubility (in water; g/L)	Water solubility < 0.1 ug/L (at 25 deg C) (EU Risk Assessment, 2002)
Partition coefficient (log Kow)	Log Kow = 12.1 (EPIWIN). Log Kow = 6.27 (measured) (EU Risk Assessment, 2002). LogKow = 6.77 (tetra-BDE), LogKow = 7.66 (penta- BDE), LogKow = 8.55 (hexa-BDE) (KowWin).
РКа	
Flammability	
Explosivity	
Oxidizing properties	
Mobility	Has been detected in airborne particulate matter collected near industrial sites that use it. (HSDB, 1993)

Additional Information

## HUMAN EPIDEMIOLOGICAL DATA

HUMAN				
Epidemiological studies	There is no human epidemiologic data relevant to carcinogenicity.			
Occupational studies	Exposed workers have developed thyroid hyperplasia (HSDB, 1995). Blood serum concentrations of decabromobiphenyl ether in hospital cleaners (n=20), computer clerks (n=20) and electronics dismantlers (n=19) ranged from <0.3 to 3.9, <0.3 to 8.0, and <0.3 to 9.9, respectively. (Sjodin, 1999) Decabromobiphenyl ether was present in nearly all blood serum samples collected during this study.			
Biomonitoring studies	Deca-BDE has been found in human tissue samples indicating that some absorption occurs. (Sjodin et al., 2003).			

#### Additional information:

Several studies have identified deca-BDE in blood and breastmilk (See PBDE Interim CAP for review). Deca-BDE has also been identified in food and household dust, indicating potential exposure routes (See PBDE Interim CAP for review). Deca-BDE has been measured in market basket food and indoor dust and these represent human exposure pathways (Schecter et al., 2004; Stapleton et al., 2005)

## TOXICOLOGICAL DATA

ACUTE	
Oral	Dow Product FR-300-BA, LD50 (rats, single dose, intragastric intubation) > 2000 mg/kg. LD50 (rats, single oral does in corn oil) > 5000 mg/kg. (EU Risk Assessment, 2002).
Dermal	Commercial product DE-83, LD50 (rabbits, neat under occlusive wraps for 24 hours, 14 day observation) > 2000 mg/kg. (EU Risk Assessment, 2002).
Inhalation	Commercial product DE-83, LC50 (rats, 1 hour, 2 or 48.2 mg/l in air, 14 day observation) > 48.2 mg/l. Eye squint and increased motor activity observed at highest dose (EU Risk Assessment, 2002).
Other	
Skin irritation	No irritation reported in rabbits after a single (500 mg) exposure for 24 hours (EU Risk Assessment, 2002).
Eye irritation	Deca-BDE produced mild reversible irritation of the eye in rabbits (EU Risk Assessment, 2002).
Respiratory tract irritation	Commercial product DE-83, LC50 (rats, 1 hour, 2 or 48.2 mg/l in air, 14 day observation) > 48.2 mg/l. Marked dyspnea was observed at both concentrations (EU Risk Assessment, 2002).
Skin sensitization	Penta and Octa commercial products did not demonstrate skin sensitization in guinea pig studies, indicating low concern for skin sensitization for Deca-BDE. Skin irritation (but not skin sensitization) was observed in 9/50 human volunteers from a 5% deca-BDE suspension in petroleum. Another study of human volunteers found no evidence of skin sensitization (EU Risk Assessment, 2002).
Inhalation sensitization	No information (EU Risk Assessment, 2002).
	SUBCHRONIC
Oral	DecaBDE: Mice (NTP, 14 day diet study) NOAEL = 100,000 ppm in food (approx. 25,000 mg/kg/day for females, 15,000 mg/kg/day for males). Mice (NTP, 13 week diet study) NOAEL = 50,000 ppm (approx. 11,000 mg/kg/day for females, 7,000 mg/kg/day for males). Rats (NTP, 14 day diet study) NOAEL = 100,000 ppm (approx. 7,500 mg/kg/day). Rats (28 day diet study) NOAEL = 1000 ppm (70 mg/kg/day for male, 80 mg/kg/day for female). Rats (30 day diet study) LOAEL = 1000 ppm (approx. 80 mg/kg/day), however low purity of test compound (only 77% deca-BDE). Rats (13 week diet study) NOAEL = 50,000 ppm (approx. 3800 mg/kg/day for females, 2800 mg/kg/day for males (EU Risk Assessment, 2002).
Inhalation	DecaBDE: Rats (intratracheal injection of 20 mg dust, observation for up to 556 days). No evidence of fibrosis or other proliferative response in lungs or regional lymph nodes (EU Risk Assessment, 2002).
Dermal	



#### GENOTOXICITY AND CARCINOGENICITY

Mutagenicity	Negative results in Salmonella mutagenicity tests (EU Risk Assessment, 2002)
Gene mutation	Deca-BDE is not mutagenic in mouse lymphoma L 5178 Y/TK +/- assay for gene mutation with or without metabolic activation. (EU Risk Assessment, 2002).
Chromosome abnormalities	Deca-BDE did not induce sister chromatid exchanges or chromosomal aberrations in Chinese hamster ovary cells in vitro. (EU Risk Assessment, 2002).
Other genotoxic effects	

Cancer review:

Mice and rats (NTP, 2 year carcinogenicity study, via diet): LOAEL (non neoplastic lesions in spleen and forestomach, and in liver and lymph nodes at higher dose) = 25,000 ppm (in rats equivalent to approx. 1100 mg/kg/day). (EU Risk Assessment, 2002).

Liver, pancreas and thyroid cancers have been reported in rodents at high doses (2500-5000 mg/kg) (NAS, 2000) U.S. EPA classified in Group D: insufficient evidence in humans and animals (U.S.EPA, 1995). IARC classification Group 3: not classifiable (IARC, 1991).

#### REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY

Reproductive toxicity	
Teratogenicity	Mice (single dose on post-natal day 3): LOAEL (neurobehavioral effects) = 20.1 mg/kg (Viberg et al., 2003).
Embryotoxicity	

Additional information

#### OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

Respiratory Tract	
Neurotoxicity	Developmental neurotoxicity (see above under Teratogenicity)

Other toxicity information:

Absorption/DistributionStudies in rats indicate that >10 - ~26% of oral doses of absorbed. Lower brominated PBDEs, which are potent degradation of Deca-BDE, are more readily absorbed (I	TOXICOKINETICS	
The highest tissue concentrations (lipid basis) following rats were found in blood plasma and blood-rich tissues and liver) (Morck et al., 2003). Main route of excretion	tial products from the (Birnbaum et al., 2004). Ing a single oral dose in a (adrenals, kidney, hear	

Washington State Department of Health	Deca-BDE Alternatives Assessment
Metabolic pathways/products	Metabolic products include hydroxylated metabolites, o-methylated metabolites and lower brominated PBDEs (Morck et al., 2003; Birnbaum et al., 2004).

Additional information:

**Human Biomonitoring Studies:** Studies of levels of PBDEs in human tissues have found Deca-BDE in the blood of workers (electronic dismantlers) and in the breastmilk of women in the general population indicating some degree of human absorption (Jakobsson et al., 2002; Schecter et al., 2003; Northwest Environmental Watch, 2004; See Interim CAP (2004) for further background)

#### ECOTOXICITY DATA

Algae	Algae EC50 (72 or 96 hours) > 1 mg/l (EU Risk Assessment, 2002).
Crustacean	Daphnia assay (21 days exposure): NOEC = 2 ug/l (solubility limit for Deca- BDE) (EU Risk Assessment, 2002).
Fish	Fish (killifish) LC50 (48 hours) > 500 mg/l (above water solubility limit). Fish (rainbow trout; 16, 49 or 120 day exposures) LOEL = $7.5 - 10$ mg/kg bodyweight/day (120 day exposures). (EU Risk Assessment, 2002).
Bacteria	Activated sludge microorganisms, NOEC .>= 15 mg/l (EU Risk Assessment, 2002).

Additional information

Bioaccumulative potential	Juvenile carp given DeBDE in feed contained no detectible amount of the parent compound, but several ethers containing five to eight bromines were found. (Stapleton et al., 2004).
BCF or BAF	BCF (Deca-BDE) = 3.16 (EPIWIN). BCFs of potential breakdown products: BCF = 32,000 (tetra-BDE), BCF = 8,100 (penta-BDE), BCF = 490 (hexa- BDE) (EPA PBT Profiler). BCF = $\sim$ 27,400 (for Penta commercial product, in carp) (EU Risk Assessment for Penta, 2000).
Half-life (include media)	For Deca-BDE, half-lives (estimated) in water: 180 days, in soil: 360 days, in sediment: 1600 days and in air: 460 days (EPA PBT Profiler). For hexa, penta and tetra congeners, half-lives (estimated) in water: 180 days, in soil: 360 days, and in sediment: 1600 days (EPA PBT Profiler).
Henry's Law Constant (atm- m <sup>3</sup> /mole)	>44 Pa m3/mole (estimated) (EU Deca Risk Assessment, 2002)
Degradability	Recent studies indicate that Deca-BDE can degrade to lower brominated PBDEs under various conditions and in fish (See Deca-BDE degradation write-up in main report).

## ENVIRONMENTAL FATE

Washington State Department of Health	Deca-BDE Alternatives Assessment
Degradation products	Recent studies indicate that Deca-BDE can degrade to lower brominated PBDEs under various conditions and in fish (See Deca-BDE degradation write-up in main report).
Aerobic biodegradation	(See Deca-BDE degradation write-up in main report).
Anaerobic biodegradation	(See Deca-BDE degradation write-up in main report).
Other	

Additional information

#### ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq 60$ days.	Half life of deca-BDE in water, soil or sediments > 60 days. Half-lives of lower brominated congeners also > 60 days.
2. Bioaccumulation/Bio-concentration factor: BCF or BAF $>$ 1000; or log K <sub>ow</sub> $>$ 5	Log $K_{OW} = 5.24$ ; BCF = 3.16. BCF of potential breakdown products, including penta-BDE, are substantially higher. EU risk assessment lists BCF for penta-BDE = 27,400.
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Developmental neurotoxicity studies in rodents; potential degradation to more toxic penta, octa- BDEs. Environmental eco system buildup and potential toxicity.
4. Is the chemical an Ecology PBT?	Yes, currently on Ecology PBT list as part of PBDEs.

Additional information

## HEALTH AND ENVIRONMENT SUMMARY

Deca-BDE Alternatives Assessment

## NOTES

Reports/other sources that contributed information:

Danish reports: Yes German report: Yes UK report: Yes Lowell report: Yes CPSC/NAS reports: Yes EPA Penta report: No EPA FOIA request: No EPA HPV: Yes EPA IRIS file: Yes Accelrys run: No EU Risk Assessment: Yes (France and UK)

#### SOURCES/REFERENCES

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- EU Risk Assessment Report for Deca-BDE, 2002. European Union Risk Assessment Report for bis(pentabromophenyl) ether (CAS No: 1163-19-5). Available at: <u>http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK\_ASSESSMENT/REPORT/decabromodiphenyletherreport013.pdf</u>
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- Viberg H, Fredriksson A, Jakobsson E, Orn U, Eriksson P. Neurobehavioral derangements in adult mice receiving decabrominated diphenyl ether (PBDE 209) during a defined period of neonatal brain development. *Toxicol Sci* 2003;**76**(1):112-20.

## Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov



Name:	1,2 – bis(pentabromophenyl)ethane (Tradename: SAYTEX 8010)	
Date Up	dated:	12/30/05

#### **IDENTIFICATION**

CAS number:	84852-53-9
EINECS:	284-366-9 (MITI 4-1735)
EINECS name:	
Molecular formula:	C14H4Br10
Known uses:	Styrenic polymers, engineering resins, wire & cable and elastomers. HIPS, technical resins, polyamide, polypropylene, casing materials, appliances, insulation foams, textiles, cables. A minimum of 12% is needed to achieve a V-O fire rating for high impact polystyrene. (IUCLID Dataset, 2005).
Use (tonnage):	EU tonnage= 2500 yr (UK report)

Structural formula: (not available)

EU classification annex:	
Synonyms	Ethane-1,2-bis(pentabromophenyl) Decabromodiphenyl ethane bis(pentabromophenyl)ethane 1,1'-(ethane-1,2-diyl) bis[pentabromobenzene], Saytex 8010 (contains approx. 98.5% of 1,2(bis)pentabromophenyl ethane) (IUCLID Dataset, 2005)
Additive or Reactive FR	Additive (German report, 2001)
Halogenated?	Yes (contains bromine)

Additional Information



#### PHYSICO-CHEMICAL CHARACTERISTICS

Physical form	white/powder (Albemarle Corp. 1999c)
Molecular weight	971.2
Boiling point/range (deg C)	
Melting point (deg C)	350-361° C
Decomposition temp. (deg C)	
Vapor pressure (mg Hg)	< 1 x 10-4 Pa at 20° C (German report, 2001)
Relative density	
Water Solubility (in water; g/L)	0.72 ug/L (<0.01% @ 25 deg C) (IUCLID Dataset, 2005).
Partition coefficient (log K <sub>ow</sub> )	Log Kow = 3.2 (German report, 2001). Log Kow = 3.55 (@ 25 deg C) (IUCLID Dataset, 2005).
РКа	
Flammability	Thermally Stable up to 300° C
Explosivity	
Oxidizing properties	
Mobility	
	•

Additional Information

#### HUMAN EPIDEMIOLOGICAL DATA

HUMAN		
Epidemiological studies		
Occupational studies		
Biomonitoring studies		

Additional information: The U.S. EPA has established a New Chemicals Exposure Limit (NCEL) for this chemical of 2.0 mg/m3, 8 hour time weighted average (IUCLID Dataset, 2005).

#### TOXICOLOGICAL DATA

ACUTE	
Oral	Rat LD50 > 5000 mg/kg (Albemarle Corp. MSDS; IUCLID Dataset, 2005).
Dermal	Rabbit LD50 > 2000 mg/kg (Albemarle Corp. MSDS; IUCLID Dataset, 2005).
Inhalation	
Other	

Washington State Department of Health	Deca-BDE Alternatives Assessme	
Skin irritation	Not irritating (rabbits, 500 mg for 4 hours, up to 72 hour observation period) (IUCLID Dataset, 2005).	
Eye irritation	Not irritating (rabbits, 100 mg/eye, up to 72 hour observation period) (IUCLII Dataset, 2005).	
Respiratory tract irritation		
Skin sensitization	Not a skin sensitizer (guinea pigs) (IUCLID Dataset, 2005).	
Inhalation sensitization		
	SUBCHRONIC	
Oral	<ul> <li>NOEL &gt;= 1250 mg/kg bw/day (rats, 28 day gavage study). (IUCLID Dataset 2005).</li> <li>NOAEL = 1000 mg/kg/day (rats, 90 day gavage study; 28 day recovery).</li> <li>Observed liver changes which resolved after recovery period. (IUCLID Dataset, 2005).</li> <li>Lack of toxicity is likely related to poor bioavailability due to its high molecular weight and low solubility. (Hardy, et al., 2002).</li> </ul>	
Inhalation	No data	
Dermal	No data	
	GENOTOXICITY AND CARCINOGENICITY	
Mutagenicity	Negative Ames tests, with and without metabolic activation. (IUCLID Dataset, 2005).	
Gene mutation		
Chromosome abnormalities	Negative in in vitro chromosome aberration test, with and without metabolic activation (with Chinese Hamster lung cells) (IUCLID Dataset, 2005).	
Other genotoxic effects		

Cancer review:

No studies available (German Report, 2001)

<b>REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY</b>	
Reproductive toxicity	
Teratogenicity	NOAEL > 1250 mg/kg bw (for maternal toxicity and teratogenicity; rats, gavage during gestational days 6-15). NOAEL > 1250 mg/kg bw (for maternal and teratogenicity; rabbits, gavage during gestational days 6-18). (IUCLID Dataset, 2005).
Embryotoxicity	

Additional information



#### OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

Neurotoxicity	Respiratory Tract	
	Neurotoxicity	

Other toxicity information:

TOXICOKINETICS	
Absorption/Distribution	Appears to be poorly absorbed following single oral dose in rats. However, poor solubility of test compound limited the results of the toxicokinetics study. (IUCLID Dataset, 2005).
Metabolic pathways/products	
Additional information:	

Additional information:

#### ECOTOXICITY DATA

Algae	EC50 (96 hours) > 110 mg/L. (IUCLID Dataset, 2005).
Crustacean	EC50 (48 hours; Daphnia magna) > 110 mg/L. (IUCLID Dataset, 2005).
Fish	NOEL = 110 mg/l (96 hours; fresh water fish, Oncorhynchus mykiss). (IUCLID Dataset, 2005).
Bacteria	

Additional information:

Low toxicity to sediment and soil dwelling organisms (IUCLID Dataset, 2005).

#### ENVIRONMENTAL FATE

Bioaccumulative potential	No detection of accumulation in food chains
BCF or BAF	BCF < 2.5 - < 25-34 (in fresh water fish, Oryzias latipes) (Hardy M., 2004. Environmental Toxicology and Chemistry, 23 (3): 656-661; IUCLID Dataset, 2005).
Half-life (include media)	
Henry's Law Constant (atm-m <sup>3</sup> /mole)	
Degradability	Moderate
Degradation products	

Aerobic biodegradation	
Anaerobic biodegradation	
Other	

Additional information

#### ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq$ 60 days.	Half-life in all media unknown, but is stable halogen.
2. Bioaccumulation/Bio-concentration factor: BCF or BAF > 1000; or log $K_{ow} > 5$	Log $K_{ow}$ = 3.2 and BCF < 1000; not detected in food web, low water solubility.
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Rat LD50> 5000mg/kg; Rabbit LD50>2000mg/kg, NOAEL = 1000mg/kg. Low toxicity.
4. Is the chemical an Ecology PBT?	No

Additional information:

There is no data concerning the occurrence of Saytex 8010 in indoor air, domestic dust, outdoor air, soil, water. (Leisewitz, 2000).

There is a recent report of the detection of decabromodiphenyl ethane in sewage sludge, sediment and workplace indoor air in Sweden. (Kierkegaard et al., 2004).

#### HEALTH AND ENVIRONMENT SUMMARY



Deca-BDE Alternatives Assessment

## NOTES

Reports/other sources that contributed information:

Danish reports: No German report: Yes UK report: Yes Lowell report: No CPSC/NAS reports: No EPA Penta report: No EPA FOIA request: Yes, but no studies included. EPA HPV: No EPA IRIS file: No Accelrys run: No EU Risk Assessment: No, but UK Risk Assessment pending, expected in 2006.

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#### Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov



# **Deca-BDE** Alternatives Assessment

Name:	SAYTEX BT-93 (1,2-bis(tetrabromophthalimido(ethane))	
Date Updated:		11-21-05

#### **IDENTIFICATION**

CAS number:	32588-76-4
EINECS:	251-118-6
EINECS name:	N,N'-ethylenebis(3,4,5,6-tetrabromophthalimide)
Molecular formula:	C18H4Br8N2O4
Known uses:	Flame retardant /for/use in polyolefins, high-impact polystyrene (HIPS), thermoplastic polyesters (PBT, PET,etc.), polycarbonate and elastomers. (Albemarle Corp., 2005).
Use (tonnage):	Listed as a HPV chemical. >1million pounds in 1990. (NLM, HSDB)

Structural formula:

	(from ChemIDPlus)
EU classification annex:	
Synonyms	Ethylene bis(tetrabromophthalimide)(EBTBP), Saytex BT-93, Bis(tetrabromophthalimido)ethane, Great Lakes CN-81
Additive or Reactive FR	Additive
Halogenated?	Yes (contains bromine)

Additional Information

Physical form	Off White Powder (NLM, HSDB)
Molecular weight	951.47 (NLM, HSDB)
Boiling point/range (deg C)	Temperatures in excess of 400C/752F may liberate toxic gases (Albemarle, Corp. MSDS, 2002)
Melting point (deg C)	456° C
Decomposition temp. (deg C)	
Vapor pressure (mg Hg)	2.5 X 10 <sup>-22</sup> mm Hg at 25° C (NLM, HSDB)
Relative density	
Water Solubility (in water; g/L)	In water, 3.0 X 10 <sup>-9</sup> mg/L at 25° C (NLM, HSDB)
Partition coefficient (log Kow)	$\log K_{ow} = 9.80 (NLM, HSDB)$
РКа	
Flammability	Not established (Albemarle, Corp. MSDS, 2002) ; Nonflammable (IUCLID Dataset, 2000)
Explosivity	Not explosive (IUCLID Dataset, 2000)
Oxidizing properties	
Mobility	

PHYSICO-CHEMICAL CHARACTERISTICS

Additional Information

## HUMAN EPIDEMIOLOGICAL DATA

HUMAN				
Epidemiological studies				
Occupational studies				
Biomonitoring studies				

Additional information:

Occupational exposure may occur through inhalation and dermal contact, however exposure would be expected to be minimal, since it is manufactured in a closed system. (NLM, HSDB)

## TOXICOLOGICAL DATA

ACUTE	
Oral	Not expected to be acutely toxic (Albemarle, Corp. MSDS, 2002; IUCLID Dataset, 2000), Oral LD50(rat) >5000mg/kg (Albemarle, Corp. MSDS, 2002)
Dermal	Not expected to be acutely toxic (Albemarle, Corp. MSDS, 2002). Dermal LD50(rabbit) > 2000 mg/kg (Albemarle, Corp. MSDS, 2002; IUCLID Dataset, 2000).

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Washington State Department of Health		Deca-BDE Alternatives Assessmen
Inhalation		xpected to be acutely toxic (Albemarle, Corp. MSDS, 2002). Rat inhalation >203 mg/L/1 hr (IUCLID Dataset, 2000).
Other		
Skin irritation	Not ir	ritating (Susan Landry, personal communication 11-14-05)
Eye irritation	Not ir	ritating (Susan Landry, personal communication 11-14-05)
Respiratory tract irritation		
Skin sensitization		
Inhalation sensitization		
		SUBCHRONIC
Oral	doses, test ar study,	y feeding study in Sprague Dawley rats fed ad libitum at increasing NOAEL>1%, no hematological or organ growth differences between ad controls (IUCLID Dataset, 2000). Repeat test with 90 day feeding no histopathological differences of statistical significance between test ad controls. (IUCLID Dataset, 2000).
Inhalation		y NOEL= 1% of diet in male Sprague Dawley mice (estimated: 1000 g/day) (NLM, HSDB)
Dermal		
	GENOTO	XICITY AND CARCINOGENICITY
Mutagenicity	Negative Ames assay in a variety of salmonella strains, with and without activation (IUCLID Dataset, 2000).	
Gene mutation		
Chromosome abnormalities		
Other genotoxic effects		
Cancer review:		

Cancer review:

Reproductive toxicity	
Teratogenicity	Sprague Dawley rats, given increasing doses once daily by gavage from gestation to days 6-15, NOEL: >1000mg/kg bw. Neither maternally toxic nor teratogenic when administered to pregnant rats at a dosage as high as 1000 mg/kg. (IUCLID Dataset, 2000). Repeated results in New Zealand white rabbits. (IUCLID Dataset, 2000).
Embryotoxicity	



#### Additional information

#### OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

Respiratory Tract	
Neurotoxicity	

Other toxicity information:

TOXICOKINETICS
----------------

Absorption/Distribution	
Metabolic pathways/products	

Additional information:

# ECOTOXICITY DATA

Algae	
Crustacean	
Fish	Oryzias latipes, 48 hr freshwater test demonstrated an LC50 > 500 mg/l. (IUCLID Dataset, 2000)
Bacteria	

Additional information

#### ENVIRONMENTAL FATE

Bioaccumulative potential	
BCF or BAF	Fresh water fish (Cyprinus carpio, 56 d test at 25° C, concentration 2mg/l BCF: <.3-1.3., 1982, according to MITI guidelines, conducted by Albemarle S.A. Bruxelles. Repeat test at .2mg/l had a BCF of <3.3. (IUCLID Dataset, 2000) An estimated BCF of 9 was calculated for ethylene bis(tetrabromophthalimide), using an estimated log Kow of 9.8 (Meylan et al., 1995) and a regression-derived equation. According to a classification scheme (Franke, 1994), this BCF suggests the potential for bioconcentration in aquatic

Washington State Department of Health		Deca-BDE Alternatives Assessment	
	very l The p	organisms is low, as would be expected given the size of this molecule and its very low estimated water solublilty of $3.0 \times 10^{-9}$ mg/L. (EPA, 2003). The potential for bioconcentration in aquatic organisms is low (SRC). BCF < $0.3 - < 3.0$ (Hardy, 2004).	
Half-life (include media)			
Henry's Law Constant (atm-m <sup>3</sup> /mole)			
Degradability	enviro days a	ene bis(tetrabromophthalimide) is expected to undergo hydrolysis in the onment due to the presence of amide groups. A 0% theoretical BOD in 28 at 25 deg C using an activated sludge inoculum and the Japanese MITI aggests that biodegradation in water may be slow. (EPA HPV, 2005).	
Degradation products	MSD: hydro	ogen bromide, hydrogen cyanide, oxides of nitrogen (Albemarle Corp. S, 2002) Ethylene bis(tetrabromophthalimide) is expected to undergo lysis in the environment due to the presence of amide groups; hydrolysis ides results in the formation of a carboxylic acid and an amine (Wolfe,	
Aerobic biodegradation	theore collec a cont 0% bi	ene bis(tetrabromophthalimide), present at 100 mg/L, reached 0% of its etical BOD in 28 days at 25 deg C using an activated sludge inoculum eted in Japan at 30 mg/L and the Japanese MITI test. Aniline was used as trol and degraded 67% after 7 days. (EPA HPV, 2005) odegradation after 14 days (100mg/L in activated sludge) (IUCLID et, 2000)	
Anaerobic biodegradation			
Other			

Additional information:

Ethylene bis(tetrabromophthalimide)'s production and use as a flame retardant in electrical and electronics components, wire and cable insulation, switches, and conductors may result in its release to the environment through various waste streams. If released to air, an estimated vapor pressure of 2.5X10-22 mm Hg at 25 deg C indicates ethylene bis(tetrabromophthalimide) will exist solely in the particulate phase in the ambient atmosphere. Particulatephase ethylene bis(tetrabromophthalimide) will be removed from the atmosphere by wet and dry deposition. If released to soil, ethylene bis(tetrabromophthalimide) is expected to have no mobility based upon an estimated Koc of 8.0X10+5. Volatilization from moist soil surfaces is not expected to be an important fate process based upon an estimated Henry's Law constant of 3.6X10-21 atm-cu m/mole. Ethylene bis(tetrabromophthalimide) is not expected to volatilize from dry soil surfaces based upon its estimated vapor pressure. A 0% theoretical BOD in 28 days at 25 deg C using an activated sludge inoculum and the Japanese MITI test suggests that biodegradation is not an important environmental fate process. If released into water, ethylene bis(tetrabromophthalimide) is expected to adsorb to suspended solids and sediment based upon the estimated Koc. Volatilization from water surfaces is not expected to be an important fate process based upon this compound's estimated Henry's Law constant. An estimated BCF of 9.5 suggests the potential for bioconcentration in aquatic organisms is low. Hydrolysis may be an important environmental fate process since this compound contains amide functional groups that hydrolyze under environmental conditions. Occupational exposure to ethylene bis(tetrabromophthalimide may occur through dermal contact with this compound at workplaces where ethylene bis(tetrabromophthalimide) is produced or used. (NLM HSDB)

Deca-BDE Alternatives Assessment

#### ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq 60$ days.	Potential PBT/vPvB, requires further data is halogenated stable compound
2. Bioaccumulation/Bio-concentration factor: BCF or BAF $> 1000$ ; or log K <sub>ow</sub> $> 5$	log K <sub>OW</sub> = 9.8; threshold =>5. BCF < $0.3 - 3.0$ (Hardy, 2004).
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Low toxicity for lab animals
4. Is the chemical an Ecology PBT?	No

Additional information

# HEALTH AND ENVIRONMENT SUMMARY

#### NOTES

Reports/other sources that contributed information:

Danish reports: Yes German report: No UK report: Yes Lowell report: No CPSC/NAS reports: No EPA Penta report: No EPA FOIA request: EPA HPV: Yes EPA IRIS file: No Accelrys run: No EU Risk Assessment: No

#### SOURCES/REFERENCES

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- NLM (National Library of Medicine), HSDB (Hazardous Substances Data Bank). Available at: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB
- 3. U.K. Environment Agency, 2003. Prioritization of flame retardants for environmental risk assessment. Available at:
- 4. Albemarle Corp., 2002. Material Safety Data Sheet, Saytex BT-93 Flame Retardant. Baton Rouge, LA.
- 5. IUCLID Dataset 32588-76-4, 2000. European Commission. Available at: <u>http://ecb.jrc.it/esis/esis.php?PGM=ein</u>.
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- 7. Hardy M., 2004. A COMPARISON OF THE FISH BIOCONCENTRATION FACTORS FOR BROMINATED FLAME RETARDANTS WITH THEIR NONBROMINATED ANALOGUES. Environmental Toxicology and Chemistry, 23 (3): 656-661).
- 8. Franke. Chemosphere 1994;29:1501-1514.
- 9. EPA. Estimation Programs Interface (EPI). ver. 3.11. U.S. EPA version for Windows, 2003.
- EPA High Production Volume (HPV) Challenge Program, 2005. The HPV Voluntary Challenge Chemical List. Robust Summaries and Test Plans. 1H-Isoindole-1,3(2H)-dione, 2,2'-(1,2-ethanediyl)bis(4,5,6,7tetrabromo-. Washington, DC: USEPA, Off Prevent Pest Tox Subst, Pollut Prevent Toxics.
- 11. Wolfe. Handbook of Property Estimation Methods for Chemicals. Boca Faton, FL: Lewis Pub, 2000: 314.
- 12. Danish EPA, 2000. Brominated flame retardants: toxicity and ecotoxicity.
- 13. Susan Landry, Albemarle Corp., 2005. Personal communication 11-14-05, comments on draft toxicity profile for Saytex BT-93 submitted via email. Documentation for comments pending.

# Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov



Name:	EPON Resin 1163 (brominated epoxy resin)		
Date Upo	dated:	11/9/05	

# **IDENTIFICATION**

CAS number:	40039-93-8
EINECS:	
EINECS name:	
Molecular formula:	
Known uses:	
Use (tonnage):	

Structural formula:

,C1 Br Βr но ЮH. Br Ъr H.C сu

н <sub>а</sub> с сн <sub>а</sub>	(from ChemIDPlus)
EU classification annex:	
Synonyms	Phenol, 4,4'-(1-methylethylidene)bis[2,6-dibromo-,polymer with (chloromethyl)oxirane (Hexion Specialty Chemicals MSDS, 2005). Produced from tetrabromobisphenol A and epichlorohydrin (Product Data Sheet, Resolution Performance Products, 2004). Tetrabromobisphenol A epoxy resin (Gardiner et al., 1992). Ingredient (15-25%) in STAREX® flame retardant HIPS VE-1877 (MSDS for STAREX®, printing date 06/02/2003).
Additive or Reactive FR	
Halogenated?	Yes

Additional Information



#### PHYSICO-CHEMICAL CHARACTERISTICS

D1 : 10	
Physical form	White course powder (Resolution Performance Products MSDS, 2004)
Molecular weight	
Boiling point/range (deg C)	110 deg C
Melting point (deg C)	59 – 69 deg C
Decomposition temp. (deg C)	
Vapor pressure (mg Hg)	3 PA @ 20 deg C
Relative density	1.81 (Hexion MSDS)
Water Solubility (in water; g/L)	
Partition coefficient (log Kow)	
РКа	
Flammability	
Explosivity	
Oxidizing properties	
Mobility	
Additional Information	

Additional Information

# HUMAN EPIDEMIOLOGICAL DATA

HUMAN	
Epidemiological studies	
Occupational studies	
Biomonitoring studies	

Additional information:

# TOXICOLOGICAL DATA

ACUTE	
Oral	Rat LD50 > 12 g/kg (Hexion MSDS for EPON Resin 1163-T-60, 2005). For tetrabromobisphenol A epoxy resin (a related compound): LD50 > 12,000 mg/kg. Rat LD50 > 5000 mg/kg (Gardiner et al., 1992).
Dermal	Rabbit LD 50 > 2 g/kg (Hexion MSDS for EPON Resin 1163-T-60, 2005). For tetrabromobisphenol A epoxy resin (a related compound): LD50 > 6000 mg/kg. Rabbit LD50 >2000 mg/kg (Gardiner et al., 1992).

Washington State Department of Health	Deca-BDE Alternatives Assessment

Inhalation	No data available (Hexion MSDS for EPON Resin 1163-T-60, 2005)
Other	
Skin irritation	For tetrabromobisphenol A epoxy resin (a related compound): Negligible skin irritation. Minimally irritating to rabbit skin (Gardiner et al., 1992).
Eye irritation	For tetrabromobisphenol A epoxy resin (a related compound): Negligible eye irritation. Mild irritation using Draize test method in rabbits (Gardiner et al., 1992).
Respiratory tract irritation	
Skin sensitization	For tetrabromobisphenol A epoxy resin (a related compound): Not found to be sensitizing in guinea pigs (Gardiner et al., 1992).
Inhalation sensitization	

# SUBCHRONIC

Oral	
Inhalation	
Dermal	

# GENOTOXICITY AND CARCINOGENICITY

Mutagenicity	For tetrabromobisphenol A epoxy resin (a related compound): mutagenic in S. typhimurium strain TA 100 without metabolic activation only, but not in strains TA 98, TA 1535, TA 1537 and TA 1538 (Gardiner et al., 1992).
Gene mutation	For tetrabromobisphenol A epoxy resin (a related compound): induced chromosomal aberration in cultured Chinese hamster ovary cells with and without metabolic activation. Did not induce morphological transformation in the BALB/C-3T3 cell system. Daily dermal doses of 1000 mg/kg for 5 days did not induce chromosomal aberrations in bone marrow of rats (Gardiner et al., 1992).
Chromosome abnormalities	
Other genotoxic effects	

Cancer review:

REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY	
Reproductive toxicity	
Teratogenicity	
Embryotoxicity	



Additional information

#### OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

Respiratory Tract	
Neurotoxicity	

Other toxicity information:

TOXICOKINETICS
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Absorption/Distribution	
Metabolic pathways/products	

Additional information:

# ECOTOXICITY DATA

Algae	
Crustacean	
Fish	
Bacteria	

Additional information

# ENVIRONMENTAL FATE

Bioaccumulative potential		
BCF or BAF		
Half-life (include media)		
Henry's Law Constant (atm- m <sup>3</sup> /mole)		
Degradability		
Degradation products		
EDON Degin 1162	1	71

Washington State Department of Health	Deca-BDE
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Aerobic biodegradation	
Anaerobic biodegradation	
Other	
Additional information	

ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq 60$ days.	unknown
2. Bioaccumulation/Bio-concentration factor: BCF or BAF $> 1000$ ; or log K <sub>ow</sub> $> 5$	unknown
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Not acutely toxic; few data in animals, none human, carcinogenicity untested
4. Is the chemical an Ecology PBT?	unknown

Additional information

#### HEALTH AND ENVIRONMENT SUMMARY



#### NOTES

Reports/other sources that contributed information:

Danish reports: No German report: No UK report: No Lowell report: No CPSC/NAS reports: No EPA Penta report: No EPA FOIA request: No EPA HPV: No EPA IRIS file: No Accelrys run: No EU Risk Assessment: Yes (currently underway by UK)

#### SOURCES/REFERENCES

- 1. Hexion Specialty Chemicals Material Safety Data Sheet (MSDS) #1441 for EPON<sup>™</sup> Resin 1163. Print date 07/01/2005.
- Hexion Specialty Chemicals Material Safety Data Sheet (MSDS) # 1725-5 for EPON<sup>™</sup> Resin 1163. Date 07/01/05.
- 3. Resolution Performance Products product data sheet for EPON<sup>™</sup> Resin 1161 and 1163-T-60. Re-issued date November 2004.
- 4. ChemIDPlus. Available at: http://chem.sis.nlm.nih.gov/chemidplus
- 5. National Library of Medicine, TOXNET.
- 6. Gardiner, TH, Waechter, Jr., JM, Wiedow, MA, and Solomon, WT. Glycidyloxy compounds used in epoxy resin systems: a toxicology review. Regulatory Toxicology and Pharmacology 1992; 15:S1-S77.
- MSDS for STAREX®, flame retardant HIPS VE-1877. Samsung Cheil Industries (Korea). Print data 06/02/2003.

# Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov

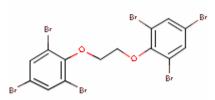


Name:	Bis (trib	romophenoxy)ethane
Date Upo	dated:	10/11/05

# **IDENTIFICATION**

CAS number:	37853-59-1
EINECS:	
EINECS name:	
Molecular formula:	C14H8Br6O2
Known uses:	Flame retardant for thermoplastics and thermoset resin systems.
Use (tonnage):	

Structural formula:



	(from ChemIDPlus)
EU classification annex:	
Synonyms	1,2-bis (2,4,6-tribromophenoxy)ethane; 1,1'-(1,2-ethanediylbis(oxy))bis(2,4,6-tribromo-benzene; FIREMASTER 680; TBE, FF-680.
Additive or Reactive FR	Additive (HSDB)
Halogenated?	Yes

Additional Information



#### PHYSICO-CHEMICAL CHARACTERISTICS

Physical form	White, crystalline powder (HSDB)
Molecular weight	687.68
Boiling point/range (deg C)	
Melting point (deg C)	224 deg C (HSDB).
Decomposition temp. (deg C)	
Vapor pressure (mg Hg)	2.4 x 10 <sup>-10</sup> mmg Hg at 25 dec C (HSDB)
Relative density	
Water Solubility (in water; g/L)	In water: < 1 mg/ml @ 19 deg C; In DMSO: < 1 mg/ml @ 19 deg C (HSDB) In water: 0.2 mg/L @ 25 deg C (ChemIDplus)
Partition coefficient (log K <sub>ow</sub> )	9.150 (ChemIDplus). Log Pow = 3.137 (Great Lakes Chemical Corp., 2002). Log Pow = 9.14 (modeled) (Great Lakes Chemical Corp., 2002). Log Kow = 9.15 (EPIWIN).
РКа	
Flammability	
Explosivity	Low sensitivity to ignition (Great Lakes Chemical Corp., 2002).
Oxidizing properties	
Mobility	
	-

Additional Information: Specific gravity = 2.58 (HSDB)

# HUMAN EPIDEMIOLOGICAL DATA

HUMAN	
Epidemiological studies	
Occupational studies	
Biomonitoring studies	

Additional information:

# TOXICOLOGICAL DATA

ACUTE	
Oral	Dog, LD50 > 10 gm/kg; rat, LD > 10 gm/kg (ChemIDplus)
Dermal	Rabbit, LD50 > 10 gm/kg (ChemIDplus). Rabbit, LD50 > 2000 mg/kg bw (Great Lakes Chemical Corp., 2002).

Washington State Department of Health	Deca-BDE Alternatives Assessment
Inhalation	Rat, LC50 > 36680 mg/m3/4 hours (ChemIDplus). Rat, LC50 > 13.08 mg/l for 4 hours (Great Lakes Chemical Corp., 2002).
Other	
Skin irritation	Rabbit (24 hour exposure), not-irritating. Rabbit (24 hour exposure), slightly irritating (Great Lakes Chemical Corp., 2002).
Eye irritation	Rabbit (0.1 g), not-irritating (Great Lakes Chemical Corp., 2002).
Respiratory tract irritation	
Skin sensitization	Human, not-sensitizing (Great Lakes Chemical Corp., 2002).
Inhalation sensitization	

# SUBCHRONIC

Oral	Rat (106 day feeding study), NOAEL = 729-874 mg/kg (males and females) (1% in diet), LOAEL = 8329 – 9362 mg/kg (10% in diet). Rat (28 day feeding study), NOAEL = 75.2-89.2 mg/kg (males and females) (1000 ppm in feed). Rat (14 day feeding study) NOAEL = 10% (Great Lakes Chemical Corp, 2002).	
Inhalation	Rat (inhalation, 4 hrs/day, 5 days/wk for 3 weeks), LOAEL = 5 mg/l (Great Lakes Chemical Corp, 2002).	
Dermal	Rabbit (dermal, 6 hrs/day, 5 days/week for 4 weeks), LOAEL > 5000 mg/kg bw (Great Lakes Chemical Corp, 2002).	
GENOTOXICITY AND CARCINOGENICITY		
Mutagenicity	Nonmutagenic in Ames Test and in yeast Saccharomyces cerevisiae tester strain DR. (HSDB).	
Gene mutation		
Chromosome abnormalities		
Other genotoxic effects		

Cancer review:

REPRODUCT	<b>REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY</b>	
Reproductive toxicity	Rat (90 feeding study): NOAEL (parental) = 8329 – 9364 mg/kg (males and females) (10%). Effects on reproductive organs. (Great Lakes Chemical Corp, 2002).	
Teratogenicity	Rat (gest. Day 6-15, by gavage): NOAEL (maternal) = 1000 mg/kg bw; NOAEL (fetal) = 10000 mg/kg bw. Rat (gest. Day 6-15, by gavage): NOAEL = 10000 mg/kg bw (both maternal and fetal) (Great Lakes Chemical Corp, 2002).	
Embryotoxicity		



Additional information

#### OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

Respiratory Tract	
Neurotoxicity	

Other toxicity information:

TOXICOKINETICS	
Absorption/Distribution	1,2-bis (2,4,6-tribromophenoxy)ethane was poorly absorbed from GI tract (rats fed 0.05, 0.5 and 5% of material for 1 day and 0.05% 10 days). (Great Lakes Chemical Corp., 2002).
Metabolic pathways/products	

Additional information:

# ECOTOXICITY DATA

Algae	Green algae EC50 = 33.66 mg/l for 96 hours (estimated by EPIWIN ECOSAR) (Great Lakes Chemical Corp., 2002).
Crustacean	Daphnia magna LC50 = 50.43 mg/l for 48 hours; Mysid shrimp LC50 = 5.573 mg/l for 96 hours (both LC50's estimated by EPIWIN ECOSAR) (Great Lakes Chemical Corp., 2002).
Fish	(Lepomis macrochirus) LC50 = 1531 mg/l for 96 hours; (rainbow trout) LC50 = 1410 mg/l for 96 hours; Oryzias latipes LC50 = 230 mg/l for 48 hours (Great Lakes Chemical Corp., 2002).
Bacteria	

Additional information

# ENVIRONMENTAL FATE

Bioaccumulative potential	
BCF or BAF	BCF: 8.6 – 27.1 (in Cyprinus carpio) (Great Lakes Chemical Corp., 2002).

Washington State Department of Health	Deca-BDE Alternatives Assessment

	BCF = 74 (estimated) (EPIWIN)
Half-life (include media)	Volatilization half-life for model river and model lake are 150 and 1700 days, respectively (HSDB)
Henry's Law Constant (atm- m <sup>3</sup> /mole)	Henry's Law constant: 4.3 x 10-7 atm-cu m/mole– not expected to volatilize from dry soil surfaces (HSDB). 7.32 10-9 atm-m3/mole @ 25 deg C (ChemIDplus).
Degradability	When incubated at 3 different concentrations (1%, 0.01% and 1 ppm) using an acclimated sewage and garden soil inoculum, 1.1, 0.53 and 1.41% of the total 14C-activity, respectively, was mineralized over a 26-30 week period. (HSDB). Not readily biodegradable (Great Lakes Chemical Corp., 2002).
Degradation products	
Aerobic biodegradation	
Anaerobic biodegradation	
Other	

Additional information:

Expected to have low mobility in soil and adsorb to suspended solids and sediment if release in water based on its of Koc = 72,000 (HSDB)

#### ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq$ 60 days.	T <sub>1/2</sub> in water 150-1700 days
2. Bioaccumulation/Bio-concentration factor: BCF or BAF > 1000; or log $K_{ow} > 5$	BCF +8.7-27.1; log $K_{OW}$ = 3.14 - 9.15 measured, 9.14 modeled
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Low acute toxicity in mammals (10 g/kg), low subchronic toxicity LOAEL 800-900 mg/kg; relatively low ecotoxicity. Not mutagenic (Ames), low reproductive, teratogenic potential
4. Is the chemical an Ecology PBT?	No, based on low toxicity; however it exceeds persistence and log $K_{ow}$ , but does not meet BCF criteria due to low toxicity.

Additional information



#### HEALTH AND ENVIRONMENT SUMMARY

#### NOTES

Reports/other sources that contributed information:

Danish reports: Yes German report: No UK report: No Lowell report: No CPSC/NAS reports: No EPA Penta report: No EPA FOIA request: Yes, and studies sent. EPA HPV: Yes EPA IRIS file: No Accelrys run: No EU Risk Assessment: No

#### SOURCES/REFERENCES

References:

- 1. HSDB datafile on 1,2-Bis(2,4,6-tribromophenosy)ethane. Available at: <u>http://toxnet.nlm.nih.gov/</u>
- 2. ChemIDplus datafile on 1,2-Bis(2,4,6-tribromophenosy)ethane. Available at: http://toxnet.nlm.nih.gov/
- 3. Great Lake Chemical Corp. Dossier and robust summaries for benzene, 1,1'-[1,2ethanediylbis(oxy)]bis[2,4,6-tribromo-, CAS No. 37853-59-1. December 11, 2002. Available at: www.epa.gov/chemrtk/benzethan/c14170rs.pdf .(accessed 09-21-05)
- 4. NTP (National Toxicology Program). Database Search Application for NTP Studies on Firemaster 680. Only in vitro (salmonella) study data available.
- 5. EPIWIN program. Available from <u>http://www.syrres.com/esc/epi.htm</u>.

# Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov



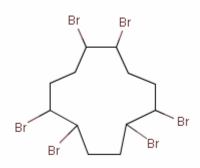
Name:	Hexabromocyclododecane (HBCD)	
Date Upo	dated:	11/21/05

#### **IDENTIFICATION**

CAS number:	3194-55-6 (1,2,5,6,9,10-HBCD); 25637-99-4 (mixed isomers of HBCD)
EINECS:	221-695-9 (1,2,5,6,9,10-HBCD); 247-148-4 (HBCD)
EINECS name:	1,2,5,6,9,10-Hexabromocyclododecane (1,2,5,6,9,10-HBCD); hexabromocyclododecane (HBCD)
Molecular formula:	C12-H18-Br6
Known uses:	Flame retardant in polystyrene (Danish EPA). Additive flame retardant for thermoplastic polymers, polystyrene foams, and other styrene resins. May also be used in latex binders, unsaturated polyesters, and polyvinyl chloride wire, cable and textile coatings (NAS, 2000)
Use (tonnage):	

Structural formula:

(1,2,5,6,9,10-HBCD)



(from ChemIDPlus)

EU classification annex:	
Synonyms	
Additive or Reactive FR	Additive (NAS, 2000)
Halogenated?	Yes

Additional Information:

Impurities: tetrabromocyclododecane and other brominated cyclododecanes (Dutch report). Technical HBCD is manufactured in two forms, high-melting and low-melting forms. It consists of three isomers ( $\alpha$ ,  $\beta$ , and  $\gamma$ ). The low-melting HBCD consists of 70-80%  $\gamma$ -isomer and 20-30% of  $\alpha$ - and  $\beta$ - isomers. The high-melting HBCD consists of >= 90% of the  $\gamma$ - isomer. (Danish EPA, 2000).



#### PHYSICO-CHEMICAL CHARACTERISTICS

Physical form	White to off-white odorless solid or crystalline powder (Danish EPA, 2000)
Molecular weight	641.7
Boiling point/range (deg C)	Decomposition occurs at 230 deg C (Danish EPA, 2000)
Melting point (deg C)	175 – 195, 178 – 183 (Danish EPA, 2000)
Decomposition temp. (deg C)	230 deg C
Vapor pressure (mg Hg)	1.6 x 10 <sup>-9</sup> (calculated), 1.7 x 10 <sup>-8</sup> , 1.3 x 10 <sup>-7</sup> , 3.8 x 10 <sup>-7</sup> (Danish EPA, 2000)
Relative density	2.38
Water Solubility (in water; g/L)	Water: 0.008 mg/l (no temp. provided); water: 0.12 mg/l (23 deg C) (Danish EPA, 2000). Water: 3.4 ug/L at 25 deg C; 2.08 – 48.8 ug/L at 20 deg C. (IUCLID data set, 2005).
Partition coefficient (log $K_{ow}$ )	5.81 (calculated), 7.59 (calculated) (Danish EPA, 2000). Log Kow = 7.74 (EPIWIN). Log Kow (measured) = 5.625 at 25 deg C (IUCLID data set, 2005).
РКа	
Flammability	
Explosivity	
Oxidizing properties	
Mobility	

Additional Information

#### HUMAN EPIDEMIOLOGICAL DATA

HUMAN	
Epidemiological studies	
Occupational studies	
Biomonitoring studies	

Additional information:

No dermal irritation reported among people who wore 1-inch squares of HBCD treated fabric for 6 days (NAS, 2000).

#### TOXICOLOGICAL DATA

ACUTE

Oral

Dermal

Deca-BDE Alternatives Assessment

Inhalation	
Other	
Skin irritation	Positive sensitization from intradermal injection in guinea pigs, however other studies report negative results (NAS, 2000).
Eye irritation	
Respiratory tract irritation	
Skin sensitization	
Inhalation sensitization	
	SUBCHRONIC
Oral	Rats (28 day feeding study) LOAEL = 900 mg/kg-day (increased liver weights). Rats (90 day feeding study) NOAEL = 450 mg/kg-day, LOAEL = 925 mg/kg-day (increased liver weights and other liver effects). Mice (18 month diet study) NOAEL = 100 ppm (13 mg/kg-day), LOAEL = 1000 ppm (130 mg/kg-day).
Inhalation	
Dermal	
	GENOTOXICITY AND CARCINOGENICITY
Mutagenicity	Negative in mutagencitiy assays in yeast and Salmonella (NAS, 2000).

Mutagenicity	Negative in mutagencitiy assays in yeast and Salmonella (NAS, 2000).
Gene mutation	
Chromosome abnormalities	Negative for chromosomal aberrations in human peripheral blood lymphocytes (NAS, 2000).
Other genotoxic effects	Not genotoxic (NAS, 2000).

Cancer review:

NAS reported that there was inadequate carcinogenicity data from any route of exposure to make any conclusions about the potential carcinogenicity of HBCD (NAS, 2000).

<b>REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY</b>	
Reproductive toxicity	
Teratogenicity	Rats (gestational day 0-20, diet) NOAEL ~ 500 mg/kg-day. Rats (gestational day 0-20, by gavage) NOAEL = ~ 1000 mg/kg-day (NAS, 2000).
Embryotoxicity	

Additional information

	Washington State Department of
	Health
47	1100111

#### OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

#### Respiratory Tract

Neurotoxicity

Other toxicity information:

RfD = 0.2 mg/kg/day based on increase liver weight (NAS, 2000).

#### TOXICOKINETICS

Absorption/Distribution	Rapid gastrointestinal absorption in rats (NAS, 2000). Rats eliminated 86% of an HBCD dose within 72 hours (NAS, 2000).
Metabolic pathways/products	

Additional information:

# ECOTOXICITY DATA

Algae	$ \begin{array}{l} EC50 > 500 \text{ mg/l} (96 \text{ h}, \text{Scenedesmus subspicatus}); > 2.5 \text{ ug/l} (4d, \text{Selenastrum capricornutum}); 9.3-12.0 \text{ ug/l} (72 \text{ h}, \text{Skeletonema costatum}); 50-370 \text{ ug/l} (72 \text{ h}, \text{Thalassiosira pseudonana}) \text{ and } > 1500 \text{ ug/l} (96 \text{ h}, \text{Chlorella sp.}) (\text{Danish EPA}) \end{array} $
Crustacean	EC50 > 3.2 ug/l (48h, Daphnia magna) and 146.34 mg/l (48h, Daphnia magna). Daphnia magna; NOEC = 0.003 mg/L. (KemI/EPA, 2002).
Fish	LC50 for fish: > 100 mg/l (96h, Lepomis macrochirus) and > 10000 mg/l (96h,
Bacteria	

Additional information

# ENVIRONMENTAL FATE

Bioaccumulative potential	
BCF or BAF	BCF > 100 (Danish EPA). BCF = 6210 (EPIWIN). BCF = 8974; BCF = 4.5 (IUCLID data set, 2005)
Half-life (include media)	Half-life = 60 days (in water), 120 days (in soil) and 540 days (in sediments) (EPA PBT Profiler).
Henry's Law Constant (atm- m <sup>3</sup> /mole)	
Degradability	

Deca-BDE Alternatives Assessment

Degradation products	
Aerobic biodegradation	
Anaerobic biodegradation	
Other	

Additional information

#### ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq$ 60 days.	60 day half-life in water (EPA PBT Profiler)
2. Bioaccumulation/Bio-concentration factor: BCF or BAF > 1000; or log $K_{ow} > 5$	BCF > 100 (Danish EPA) BCF = 6210 (EPIWIN) Log Kow = 5.81 (calculated), 7.59 (calculated) (Danish EPA, 2000). Log Kow = 7.74 (EPIWIN).
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	RfD = $0.2 \text{ mg/kg/day}$ based on increase liver weight (NAS, 2000). EPA RfD = $0.002 \text{ mg/kg/day}$ and ATSDR MRL = $0.0002 \text{ mg/kg/day}$ . HBCD is predicted to be toxic to aquatic organisms. (Ecology, 2005)
4. Is the chemical an Ecology PBT?	Yes. HBCD is currently on Ecology PBT list (draft PBT rule, 9/05).

Additional information

# HEALTH AND ENVIRONMENT SUMMARY

Deca-BDE Alternatives Assessment

#### NOTES

Reports/other sources that contributed information:

Danish reports: Yes German report: Yes UK report: No Lowell report: No CPSC/NAS reports: Yes EPA Penta report: No EPA FOIA request: Yes EPA HPV: Yes EPA IRIS file: No Accelrys run: No EU Risk Assessment: Yes (Sweden)

#### SOURCES/REFERENCES

- 1. Danish EPA, 2000. Brominated flame retardants; toxicity and ecotoxicity. Available at: http://www.mst.dk/udgiv/Publications/2000/87-7944-288-9/pdf/87-7944-289-7.PDF
- Environmental research plan of the German Federal Ministry for the Environment, Nature Conservancy and Nuclear Safety, 2000. Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals. Research report 297 44 542. Available at: <u>http://www.oekorecherche.de/english/berichte/volltext/Flame%20Retardants.pdf</u>
- 3. ChemIDplus through the National Library of Medicine. Available at: http://sis.nlm.nih.gov/chemical.html
- 4. NAS, 2000. Toxicological risks of selected flame-retardant chemicals. Available from: URL: <u>www.nap.edu/openbook/0309070473/html/78.html</u>
- 5. EPIWIN. From Syracuse Research Corporation. Available at <u>www.syrres.com/esc/epi.htm</u>.
- 6. IUCLID Data Set on HBCD, 2005. Available via EPA HPV website at:
- 7. HPV Data Summary and Test Plan for Hexabromocyclododecane (HBCD), CAS # 3194-55-6.
- 8. Great Lakes Chemical Corp. Technical Information for SP-75 and CD-75P.
- 9. Ecology, 2005. Draft PBT Rule (Chapter 173-333 WAC), dated Sept. 21, 2005.
- 10. Swedish National Chemicals Inspectorate/Swedish Environmental Protection Agency (KemI/EPA). 2002. Prioritisation of POP Candidates. Interim Report. November 29, 2002. Stockholm, Sweden.

Ecology, 2005. Technical Background Information for Proposed PBT List. October 2005. Available at: http://www.ecy.wa.gov/programs/eap/pbt/rule/docs/Summary-

TechnicalBackgroundInformationforProposedPBTList(October2005-Bradley).doc

# Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov HBCD Draft 11/21/05



Name:	Tetrabromobisphenol A	
Date Upo	lated:	11/22/05

#### **IDENTIFICATION**

CAS number:	79-94-7
EINECS:	201-236-9 (Danish EPA, 2000)
EINECS name:	Phenol, 4,4' (1-metholethylidene)bis[2,6-dibromo-]
Molecular formula:	C15H12Br4O2
Known uses:	Used as flame retardant in plastics (including HIPS), paper, textiles and used as a plasticizer. Its primary use is as a reactive intermediate in the manufacture of flame-retarded epoxy and polycarbonate resins (EU Risk Assessment, 2005)
Use (tonnage):	16,000 tonnes/year (1986; U.S.), 18,000 tonnes/year (1991; U.S.), 21,600 tonnes/year (1999; U.S.) (EU Risk Assessment, 2005)

Structural formula:

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	(from ChemIDPlus)
EU classification annex:	
Synonyms	TBBPA, 2,2-bis(3,5-bromo-4-hydroxyphenyl)propane; 4,4'- isopropylidenebis(2,6-dibromophenol); tetrabromodihydroxydiphenyl propane. Marketed as SAYTEX CP-2000 by Albemarle and BA-59P by Great Lakes Chemical. (Danish EPA, 2000)
Additive or Reactive FR	Additive and reactive depending on use. Reactive in HIPS. Used with antimony oxide as an additive flame retardants (EU Risk Assessment, 2005).
Halogenated?	Yes

Additional Information



Physical form	Off-white powder (Danish EPA, 2000)
Molecular weight	543.92
Boiling point/range (deg C)	Approx. 316 deg C (Danish EPA, 2000)
Melting point (deg C)	180-184, 181-182 (Danish EPA, 2000)
Decomposition temp. (deg C)	-
Vapor pressure (mg Hg)	<1 mmHg @ 20 deg C (Danish EPA, 2000)
Relative density	2.1 g/ml (Danish EPA, 2000)
Water Solubility (in water; g/L)	Water: 0.72 mg/l @ 15 deg C, 4.16 mg/l @ 25 deg C, 1.77 mg/l @ 35 deg C; methanol: 920 mg/l @ 25 deg C; acetone: 2400 mg/l @ 25 deg C. (Danish EPA, 2000)
Partition coefficient (log $K_{ow}$ )	4.5 – 5.3 (Danish EPA, 2000). Log Kow = 5.90 (measured) (EU Risk Assessment, 2005)
РКа	
Flammability	
Explosivity	
Oxidizing properties	
Mobility	

Additional Information

# HUMAN EPIDEMIOLOGICAL DATA

HUMAN	
Epidemiological studies	
Occupational studies	Inhalation exposures to TBBP-A have been identified in the production (loading and mixing) of plastics containing TBBP-A and at workplaces where computers were shredded or where laminates were manufactured (EU Risk Assessment, 2005)
Biomonitoring studies	

Additional information:

# TOXICOLOGICAL DATA

ACUTE	
Oral	Oral LD50, rats: > 5 g/kg body weight (b. w.); oral LD50, mice: 3.2 g/kg b.w.

Health		Washington State Department of Health
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	(Danish EPA, 2000)
Dermal	Dermal LD50, rabbits: > 2 g/kg b.w. (Danish EPA, 2000)
Inhalation	Inhalation LC50, rats: > 0.5 mg aerosols/kg b.w./ 8 hours (Danish EPA, 2000). Inhalation LC50, rats: > 2550 mg/m3 for a 2 hr. exposure (HPV Data Summary, 2004).
Other	
Skin irritation	Non-irritating (HPV Data Summary, 2004).
Eye irritation	Non-irritating (HPV Data Summary, 2004).
Respiratory tract irritation	
Skin sensitization	
Inhalation sensitization	
	SUBCHRONIC
Oral	Rat, 90-day oral toxicity study, NOAEL = 1000 mg/kg/day. Mice, 90-day diet study, NOAEL = 700 mg/kg bodyweight (HPV Data Summary, 2004).
Inhalation	
Dermal	

#### GENOTOXICITY AND CARCINOGENICITY

Mutagenicity	Negatives in Ames Salmonella test ) (HPV Data Summary, 2004).
Gene mutation	
Chromosome abnormalities	Negative in in vitro chromosome aberration test ) (HPV Data Summary, 2004).
Other genotoxic effects	

Cancer review:

<b>REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY</b>	
Reproductive toxicity	Rat two generational reproduction study, NOEL = 1000 mg/kg/day. (HPV Data Summary, 2004).
Teratogenicity	Rat developmental study, (dose $0 - 19$ days of gestation): NOAEL = 1000 mg/kg/day. ). (HPV Data Summary, 2004).
Embryotoxicity	

Additional information



#### OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

Respiratory Tract	
Neurotoxicity	Rat two generation reproduction study, NOEL = 100 mg/kg/day (delayed neurotoxicity/neuropathology). (HPV Data Summary, 2004).

Other toxicity information:

Thyroid function, rat 2-generation reproduction study, NOEL = 10 mg/kg/day. (HPV Data Summary, 2004).

# TOXICOKINETICS Absorption/Distribution In rats, TBBPA is readily absorbed, metabolized and eliminated within 72 hours after oral dosing (HPV Data Summary, 2004). In rats, half-life in the blood is reported as 20 hours, maximum half life in any tissue is < 3 days. (HPV Data Summary, 2004).</td> Metabolic pathways/products Studies indicate TBBPA has a short half life and is readily metabolized and excreted ) (HPV Data Summary, 2004).

Additional information:

# ECOTOXICITY DATA

Algae	(72 hr) EC50=0.09 mg/l (Danish EPA). EC50 > 5.6 mg/l (freshwater green algae). EC50 (96 hour) > 1.5 mg/l (Chlorella). EC50 (72 hour) = $0.09 - 1.14$ mg/l (Skeletonema costatum). EC50 (72 hour) = $0.13 - 1.0$ mg/l (Thalassiosira pseudonana). (HPV Data Summary, 2004).
Crustacean	Daphnia (48 hr) $LC50 = 0.96$ mg/l (Danish EPA). Eastern oyster, $LC50$ (96 hour) = 0.098 mg/l. Mysid shrimp LC50 (96 hour) = 0.86, 1.1, and 1.2 mg/l in <1 day, 5 day or 10 day old shrimp, respectively. (HPV Data Summary, 2004).
Fish	LC50 (96 hour, pH = $8.6-9.6$ ) = $0.51 \text{ mg/l}$ (bluegill sunfish), $0.40 \text{ mg/l}$ (rainbow trout), $0.54 \text{ mg/l}$ (fathead minnow). LC50 (48 hour) = $8.2 \text{ mg/l}$ . (HPV Data Summary, 2004).
Bacteria	

Additional information:

TBBPA is very toxic to aquatic organisms. EC/LC50 is below 1 mg/l. (Danish EPA).

#### ENVIRONMENTAL FATE

Bioaccumulative potential	
BCF or BAF	BCF is 20-3200 for invertebrates and vertebrates (Danish EPA). BCF for fish (fathead minnow) is 1200 (Danish EPA). BCF in fathead minnow = 307 (HPV

Deca-BDE Alternatives Assessment

	Data Summary, 2004). BCF 30-485 (carp) (IUCLID dataset, 2000).
Half-life (include media)	180 days (water), 320 days (soil), 1600 days (sediments) (EPA PBT Profiler)
Henry's Law Constant (atm- m <sup>3</sup> /mole)	< 0.1 Pa m3/mole; 0.014 – 0.054 Pa m3/mole (EU Risk Assessment, 2005).
Degradability	Biodegradation was 0% after 14 days (BOD) activated sludge. The biodegradation in soil (time not indicated) was $36 - 82\%$ and $44-91\%$ in anaerobic soil (highest in clay loam and lowest in sandy loam soil) (Danish EPA, 2000)
Degradation products	
Aerobic biodegradation	
Anaerobic biodegradation	
Other	

Additional information

# ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq$ 60 days.	180 days (water), 320 days (soil), 1600 days (sediments) (EPA PBT Profiler)
2. Bioaccumulation/Bio-concentration factor: BCF or BAF > 1000; or log $K_{ow} > 5$	Log Kow = 4.5 – 5.3 (Danish EPA, 2000). Log Kow = 5.90 (measured) (EU Risk Assessment, 2005)
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Toxicity to aquatic organisms (EPA used an acute toxicity values of 0.4 mg/L) (Ecology, 2005)
4. Is the chemical an Ecology PBT?	Yes (on Ecology's PBT list; draft PBT rule, Chapter 173-333, Sept. 21, 2005 ) (Ecology, 2005)

Additional information

# HEALTH AND ENVIRONMENT SUMMARY

Deca-BDE Alternatives Assessment

#### NOTES

Reports/other sources that contributed information:

Danish reports: Yes German report: Yes UK report: Yes Lowell report: No CPSC/NAS reports: No EPA Penta report: No EPA FOIA request: Yes, studies sent. EPA HPV: Yes (summary and test plan available) Accelrys run: No EU Risk Assessment: Yes (Draft 05/05, by UK)

#### SOURCES/REFERENCES

- 1. ChemIDplus through the National Library of Medicine. Available at: http://sis.nlm.nih.gov/chemical.html
- 2. Danish EPA, 2000. Brominated flame retardants; toxicity and ecotoxicity. Available at: http://www.mst.dk/udgiv/Publications/2000/87-7944-288-9/pdf/87-7944-289-7.PDF
- EU Risk Assessment for Tetrabromobisphenol A (CAS Number 79-94-7; EINECS Number 201-236-9), Draft May 2005. Available via ESIS (European chemical substances information): <u>http://ecb.jrc.it/esis/esis.php?PGM=ein</u>
- 4. IUCLID Dataset for Tetrabromobisphenol A. Available via ESIS (European chemical substances information): <u>http://ecb.jrc.it/esis/esis.php?PGM=ein</u>
- HPV Data Summary and Test Plan for Phenol, 4,4'-isopropylidenbis[2,6-dibromo (Tetrabromobisphenol A, TBBPA), 2004. Prepared by the American Chemistry Council's Brominated Flame Retardant Industry Panel. Originally submitted Dec. 20, 2001, revised Oct. 18, 2004. Available via EPA' HPV website.
- Ecology, 2005. Technical Background Information for Proposed PBT List. October 2005. Available at: <u>http://www.ecy.wa.gov/programs/eap/pbt/rule/docs/Summary-</u> <u>TechnicalBackgroundInformationforProposedPBTList(October2005-Bradley).doc</u>

# Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov



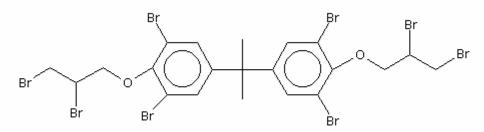
Name:	Tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPA-DBPE)	
Date Upo	dated:	10/11/05

# **IDENTIFICATION**

CAS number:	21850-44-2
EINECS:	244-617-5
EINECS name:	
Molecular formula:	$C_{21}H_{20}Br_8O_2$
Known uses:	Flame retardant for high-impact polystyrene. TBBPA-DBPE is a flame retardant for polyolefins and polymers, high-density polyethylene, and low- density polyethylene. Also used in fabricated plastic sheet materials for use in parts of electrical cabinets. The product is used in textiles, paints, and hot melts and it is used in polypropylene and HIPS applications including pipes, kitchen hoods, household and in TVs and electronics (NIEHS, 2002)
Una (tanna aa).	

Use (tonnage):

Structural formula:



# (from NIST Chemistry WebBook)

EU classification annex:	
Synonyms	Propane, 2,2-bis[3,5-dibromo-4-(2,3-dibromopropoxyl)phenyl-(8CI);bis(2,3- dibromopropoxy)tetrabromobisphenol A; tetrabromobisphenol A 2,3- dibromopropyl ether, tetrabromobisphenol A dibromopropylether, Bromkal 66-8, SAYTEX HP-800A
Additive or Reactive FR	Additive
Halogenated?	Yes

Additional Information

# PHYSICO-CHEMICAL CHARACTERISTICS

Physical form	Crystalline or powdered white/off-white solid (NIEHS, 2002).
Molecular weight	943.9
Boiling point/range (deg C)	
Melting point (deg C)	90-100
Decomposition temp. (deg C)	
Vapor pressure (mg Hg)	
Relative density	
Water Solubility (in water; g/L)	1 g/L @ 25 deg C
Partition coefficient (log Kow)	Log Kow = 11.52 (estimated, KowWin)
РКа	
Flammability	
Explosivity	
Oxidizing properties	
Mobility	
Additional Information	

HUMAN EPIDEMIOLOGICAL DATA

HUMAN	
Epidemiological studies	
Occupational studies	Three cases of workers developing skin and/or eye irritation have been reported by Great Lakes Chemical Corp. (NIEHS, 2002).
Biomonitoring studies	

Additional information:

# TOXICOLOGICAL DATA

ACUTE	
Oral	Mice, LD50 > 20 g/kg (NIEHS, 2002).
Dermal	Mice, LD50 > 20 g/kg (NIEHS, 2002).
Inhalation	
Other	
Skin irritation	

Eye irritation	
Respiratory tract irritation	
Skin sensitization	
Inhalation sensitization	

#### **SUBCHRONIC**

Oral	Mice (90 day feeding study), NOAEL = 200 mg/kg (NIEHS, 2002).
Inhalation	
Dermal	

#### GENOTOXICITY AND CARCINOGENICITY

Mutagenicity	Positive for mutagenic activity with and without metabolic activation in Salmonella typhimurium strains (NIEHS, 2002).
Gene mutation	
Chromosome abnormalities	
Other genotoxic effects	Negative in a rat unscheduled DNA synthesis assay. Did not induce sister chromatid exchanges in Chinese hamster ovary cells with or without metabolic activation (NIEHS, 2002).

Cancer review/comments:

"Tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPA-DBPE) was nominated for toxicological characterization by the National Institute of Environmental Health Sciences (NIEHS) based on studies of 2,3-dibromo-1-propanol (DBP) and the DBP-based flame retardant tris(2,3-dibromopropyl)phosphate (TBP) that showed clear evidence of carcinogenicity in all sex-species combinations in two-year dermal and feed studies, respectively, conducted by the National Toxicology Program (NTP). Out of 32 compounds identified with the DBP substructure, only TBBPA-DBPE was found to be currently in production and use." (NIEHS, 2002).

# REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY

Reproductive toxicity	
Teratogenicity	
Embryotoxicity	

Additional information

# OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

Respiratory Tract

Neurotoxicity



Other toxicity information:

TOXICOKINETICS

Absorption/Distribution	
Metabolic pathways/products	

Additional information:

#### ECOTOXICITY DATA

Algae	
Crustacean	
Fish	
Bacteria	

Additional information

# ENVIRONMENTAL FATE

Bioaccumulative potential	"Only small amounts of TBBPA-DBPE were found to bioaccumulate in carp." (NIEHS, 2002).
BCF or BAF	
Half-life (include media)	
Henry's Law Constant (atm- m <sup>3</sup> /mole)	
Degradability	TBBPA-DBPE was negative in biodegradation tests (NIEHS, 2002).
Degradation products	
Aerobic biodegradation	
Anaerobic biodegradation	
Other	

Additional information

# ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq 60$ days.	Insufficient data; low degradability
2. Bioaccumulation/Bio-concentration factor: BCF or BAF > 1000; or log $K_{ow} > 5$	Log Kow = 11.52 (estimated, KowWin)
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Low acute toxicity ( $LD_{50} = 20g/kg$ , oral); relatively low sub-chronic NOAEL = 200 mg/kg; mutagenic NTP thinks it has carcinogenic potential
4. Is the chemical an Ecology PBT?	unknown

Additional information:

Carcinogenic potential troublesome; few data

#### HEALTH AND ENVIRONMENT SUMMARY

	Washington State Department of
	Health
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#### NOTES

Some information on its use is mentioned in the IPCS (International Programme on Chemical Safety), 1995 report titled Tetrabromobisphenol A and derivatives, available at <a href="http://www.inchem.org/documents/ehc/ehc/ehc172.htm">http://www.inchem.org/documents/ehc/ehc172.htm</a>) Also mentioned in the IPCS, 1997 report titled Flame retardants: A general introduction, available at: <a href="http://www.inchem.org/documents/ehc/ehc/ehc192.htm">http://www.inchem.org/documents/ehc/ehc172.htm</a>) Also mentioned in the IPCS, 1997 report titled Flame retardants: A general introduction, available at: <a href="http://www.inchem.org/documents/ehc/ehc/ehc192.htm">http://www.inchem.org/documents/ehc/ehc172.htm</a>) Also mentioned in the IPCS, 1997 report titled Flame retardants: A general introduction, available at: <a href="http://www.inchem.org/documents/ehc/ehc/ehc192.htm">http://www.inchem.org/documents/ehc/ehc192.htm</a>).

Reports/other sources that contributed information:

Danish reports: 1999 report only, Substance Flow Analysis and Assessment of Alternatives. German report: No UK report: No Lowell report: No CPSC/NAS reports: No EPA Penta report: No EPA FOIA request: Yes, and studies available EPA HPV: No EPA IRIS file: No Accelrys run: No EU Risk Assessment: Yes, part of tetrabromobisphenol A risk assessment (draft May 2005)

#### SOURCES/REFERENCES

- National Institute of Environmental Health Science, Tetrabromobisphenol A bis(2,3-dibromopropyl ether) [21850-44-2]. Review of the Toxicological Literature. November 2002. Available at <u>http://ntp-server.niehs.nih.gov/ntp/htdocs/Chem\_Background/ExSumPdf/TBBPA-BDPE.pdf</u> (accessed 09/21/05)
- 2. Albemarle Corp. SAYTEX PH-800A Flame Retardant product information sheet. Available at: http://www.albemarle.com/acrofiles/bc1054f.pdf (accessed 09/21/05)
- 3. NIST Chemistry WebBook. Available at: http://webbook.nist.gov/chemistry/
- 4. Log Kow/KowWin program. Available at www.syrres.com/esc/est\_kowdemo.htm

# Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov

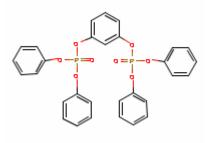


Name:	Resorcinol bis(diphenylphosphate) (RDP)	
Date Upo	dated:	12/14/05

# **IDENTIFICATION**

CAS number:	57583-54-7 (alternate CAS# 125997-21-9; see EPA HPV submissions, 2002)
EINECS:	260-830-6
EINECS name:	
Molecular formula:	C30H24O8P2
Known uses:	Engineering thermoplastics
Use (tonnage):	8000-9000 tonnes of all organic phosphorus compounds including RDP (in Germany, 1997) (Danish, EPA, 2000); 17,150 metric tons/year in TV housings (U.S.) (Lowell Center, 2005).

Structural formula:



	(from ChemIDPlus)
EU classification annex:	
Synonyms	Tetraphenyl resorcinol bis(diphenylphosphate) Tetraphenyl resorcinol diphopshpate Fyrolflex RDP REOFOS RDP (Great Lakes Chemical Company) CR-733S (HPV submission, 2002)
Additive or Reactive FR	Additive
Halogenated?	No

Additional Information: Contains 3-5% TPP (CAS No. 115-86-6) (Great Lakes Chemical Corp., 2003).

Physical form	Pale Yellow Liquid (Great Lakes Chemical Corp., 2003).
Molecular weight	
Boiling point/range (deg C)	>300 deg C (Great Lakes Chemical Corp., 2003).
Melting point (deg C)	
Decomposition temp. (deg C)	>300 deg C (Great Lakes Chemical Corp., 2003).
Vapor pressure (mg Hg)	< 0.1 hPa at 38 deg C (HPV submission IUCLID Data Set, 2001).
Relative density	
Water Solubility (in water; g/L)	< 10 mg/l at 25 deg C (HPV submission IUCLID Data Set, 2001).
Partition coefficient (log $K_{ow}$ )	Log Kow = 7.41 (estimated using KowWin). (Measured) Log Kow = $3.9 - 4.8$ (personal communication $10/31/05$ Andy Wang, Supresta LLC; Akzo Nobel, 2003)
РКа	
Flammability	Not flammable but combustible if exposed to external flame. (Great Lakes Chemical Corp., 2003).
Explosivity	No explosion hazard (Great Lakes Chemical Corp., 2003).
Oxidizing properties	
Mobility	
Additional Information	

Additional Information

### HUMAN EPIDEMIOLOGICAL DATA

HUMAN	
Epidemiological studies	
Occupational studies	Occupational exposure standard 3 mg/m <sup>3</sup> . (Great Lakes Chemical Corp., 2003).
Biomonitoring studies	

Additional information:

### TOXICOLOGICAL DATA

ACUTE	
Oral	>5000 mg/kg (oral rat) (Great Lakes Chemical Corp., 2003)
Dermal	LD50 (rat, 24 hour exposure) > 2 g/kg (HPV submission IUCLID Data Set, 2001).

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Inhalation	>4860 mg/m3 (NTI). LC50 (rats, 4 hour exposure) >4.14 mg/L (HPV submission IUCLID Data Set, 2001).
Other	
Skin irritation	Non-irritant. (Great Lakes Chemical Corp., 2003)

	LD50 2000mg/kg (rat) (NTI). Non-irritating in rabbits (4 hour exposure, observation period 45 min. – 96 hours; 0.5 ml applied to gauze patch) (HPV submission IUCLID Data Set, 2001).
Eye irritation	Irritant (Great Lakes Chemical Corp., 2003). Minimally irritating in rabbits at 0.1 ml (HPV submission IUCLID Data Set, 2001).

Respiratory tract irritation	
Skin sensitization	Non-sensitizing. (Great Lakes Chemical Corp., 2003)
Inhalation sensitization	

### **SUBCHRONIC**

Oral	Rat (28 day oral gavage); doses 0.1, 0.3 and 1.0 g/kg bw. $LOAEL = 0.1$ g/kg bw for increase in liver weight only (A. Little Inc., for GE Corp., 1989).	
Inhalation	Rat (28 day inhalation study; 6 hr/day, 5 days/week; 60 day recovery period); Air concentrations tested: 0.1, 0.5 and 2.0 mg/l. NOEL = 0.1 mg/l. (Henrich et al., 2000). From same study, LOAEL (rat, inhalation, 28 day daily (repeated) exposure with 60 day recovery) = 0.5 mg/l (exposure related changes in lung) (HPV submission IUCLID Data Set, 2001).	
Dermal		
GENOTOXICITY AND CARCINOGENICITY		
Mutagenicity	Negative in Ames Test (with salmonella typimurium and Escherichia coli) (HPV submission IUCLID Data Set, 2001).	
Gene mutation		
Chromosome abnormalities	Negative in chromosomal aberration test (cultured human lymphocytes) with and without metabolic activation (HPV submission IUCLID Data Set, 2001).	
Other genotoxic effects	Negative in mouse micronucleus assay (HPV submission IUCLID Data Set, 2001).	

Cancer review:

No rodent chronic bioassay.

<b>REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY</b>	
Reproductive toxicity	Rat (2-generational diet study); concentration in food administered: 1000, 10000, and 20000 ppm. NOAEL of F1 and F2 offspring > 20,000 ppm. Study reported no adverse effects on reproductive performance or fertility parameters (Henrich et al., 2000; HPV submission IUCLID Data Set, 2001).
Teratogenicity	Rabbit (exposure period gestational days 6-28, by gavage). NOAEL (maternal

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and developmental toxicity) > 1000 mg/kg bodyweight (HPV submission IUCLID Data Set, 2001).

Embryotoxicity

Additional information:

Immunotoxicity: Mice (28 day gavage study; 1 day or 60 day recovery period) with doses of 500, 1500, and 5000 mg/kg-day bodyweight. NOAEL = 5000 mg/kg. (Sherwood et al., 2000).

#### OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

Respiratory Tract	
Neurotoxicity	

Other toxicity information:

TOXICOKINETICS		
Absorption/Distribution	Comparative metabolic/toxicokinetic study with rats, mice and monkeys (intravenous, inhalation, oral and dermal routes). Rats and monkeys received a single target does of 100 mg/kg. Absorption from inhalation, oral and dermal exposures in rats reported as 42%, 10% and 1%, respectively. Study reported 20% absorption of applied dermal dose in rats, 10% absorption of applied dermal dose in primates. Minimal tissue accumulation and retention indicating complete clearance of administered dose (Freudenthal et al., 2000; HPV submission IUCLID Data Set, 2001).	
Metabolic pathways/products	Comparative metabolic/toxicokinetic study with rats, mice and monkeys (intravenous, inhalation, oral and dermal routes). Similar metabolic pathways and products reported between rats, mice and primates (Freudenthal et al., 2000). Major fecal metabolites were resorcinol diphenylphosphate (the half ester), hydroxyl-resorcinol diphenylphosphate, dihydroxy-resorcinol diphenyl phosphate and hydroxyleated parent compound.	

Additional information:

### ECOTOXICITY DATA

Algae	LOEC (96 hours) = 48.64 mg/l (HPV submission IUCLID Data Set, 2001).
Crustacean	EC50 (Daphnia magna, 48 hours) = 0.76 mg/l (HPV submission IUCLID Data Set, 2001).
Fish	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment. (Great Lakes Chemical Corp., 2003) LC50 (96 hours) 12.4 mg/l (Great Lakes Chemical Corp., 2003)

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Bacteria

Robra-test EC10> 121.6 mg/l (Great Lakes Chemical Corp., 2003)

Additional information

### ENVIRONMENTAL FATE

Bioaccumulative potential	
BCF or BAF	BCF = 3000 (from EPA's PBT Profiler). Calculated BCF = 316 (from measured Kow of 3.9-4.8) (personal communication 10/31/05 Andy Wang, Supresta LLC; Akzo Nobel, 2003)
Half-life (include media)	In water (at 20 deg C; pH 7) = 7-17 days (EFRA). In water, 11 days at 20 deg C at pH 4; 17 days at 20 deg C at pH 7; 21 days at 20 deg C at pH 9 (HPV submission IUCLID Data Set, 2001).
Henry's Law Constant (atm- m <sup>3</sup> /mole)	
Degradability	Fire or high temperatures create toxic gases/vapors/fumes of: Carbon dioxide (CO2), carbon monoxide (CO), and oxides of nitrogen
Degradation products	
Aerobic biodegradation	Hydrolysis in water produces phenols (Great Lakes Chemical Corp., 2003). Aerobic degradation with activated sludge: 66% degradation after 56 days (at 2.7 mg/l) (HPV submission IUCLID Data Set, 2001).
Anaerobic biodegradation	
Other	

Additional information:

RDP was submitted to Accelrys Software Inc. for a Toxicity Assessment run (09/05). RDP fell outside the optimal predictive space (OPS) for the TOPKAT model used for this run. A representative from Accelrys explained that phosphorous is not covered in the TOPKAT models when it appears in sp3 or sp3d hybridization (Accelrys report, 2005).

### ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq$ 60 days.	In water (at 20 deg C; pH 7) = 7-17 days (EFRA). In water, 11 days at 20 deg C at pH 4; 17 days at 20 deg C at pH 7; 21 days at 20 deg C at pH 9 (HPV submission IUCLID Data Set, 2001).
2. Bioaccumulation/Bio-concentration factor: BCF or BAF $> 1000$ ; or log K <sub>ow</sub> $> 5$	Log Kow (estimated) = 7.41; BCF (estimated) = 3000 (EPA PBT Profiler). BCF = 316 (calculated) based on measured Kow = 3.9-4.8 (personal communication Andy Wang, Supresta)

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3. Toxicity: Is a carcinogen, a developmental or reproductive a neurotoxicant; has an RfD or equivalent of $< 0$ day; or has a chronic NOEC or equivalent of $< 0$ an acute NOEC or equivalent of $< 1.0$ mg/L.	03 mg/kg- studies.

4. Is the chemical an Ecology PBT?

No

Additional information

### HEALTH AND ENVIRONMENT SUMMARY

### NOTES

Reports/other sources that contributed information:

Danish reports: Yes German report: Yes UK report: No Lowell report: Yes CPSC/NAS reports: No EPA Penta report: No EPA FOIA request: Yes, studies available. EPA HPV: Yes (includes IUCLID Data Set, 2001; under CAS# 125997-21-9) EPA IRIS file: No Accelrys run: Yes EU Risk Assessment: No

#### SOURCES/REFERENCES

Environmental research plan of the German Federal Ministry for the Environment, Nature Conservancy and Nuclear Safety, 2000. Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals. Research report 297 44 542. Available at: <u>http://www.oekorecherche.de/english/berichte/volltext/Flame%20Retardants.pdf</u>

Danish EPA, 2000. Alternatives to brominated flame retardants – screening for environmental and health data. Available at: <u>http://www.mst.dk/udgiv/Publications/2000/87-7944-218-8/pdf/87-7944-219-6.PDF</u>

Lowell Center, 2005. An investigation of non-halogen substitutes in electronic enclosure and textile applications. Available at: <u>http://www.sustainableproduction.org/proj.clea.publ.shtml</u>

Great Lakes Chemical Corporation, 2003. Safety Data Sheet REOFOS RDP.

NTI. National Technical Information Service Vol. OTS0516678. (date?)

A Little, Inc., 1989. Evaluation of CR-7335 in a repeated dose 28 day oral gavage study in rats. Final Report to General Electric Corp. Received as part of FOIA request to EPA under TSCA.

Henrich RT, et al., 2000. Twenty-eight day nose-only inhalation toxicity study of resorcinol bis-diphenylphosphate (Fyrolflex RDP) in rats. International Journal of Toxicology 19(4): 223-231.

Henrich R, et al., 2000. Two-generation oral (diet) reproductive toxicity study of resorcinol bis-diphenylphosphate (Fyrolflex RDP) in rats. International Journal of Toxicology 19(4): 243-255.

Sherwood RL, et al., 2000. Immunotoxicity evaluation of resorcinol bis-diphenylphosphate (Fyrolflex RDP) in B6C3F1 Mice. International Journal of Toxicology 19(4): 265-275.

Freudenthal RI, et al., 2000. Comparative metabolism and toxicokinetics of 14C-Resorcinol bis-diphenylphosphate (RDP) in the rat, mouse and monkey. International Journal of Toxicology 19(4): 233-242.

Ryan BM, et al., 2000. Developmental toxicity study of orally administered resorcinol bis-diphenyl phosphate (RDP) in rabbits. International Journal of Toxicology 19(4): 257-264.

EPA PBT Profiler. Available at www.pbtprofiler.net/

Log Kow/KowWin program. Available at www.syrres.com/esc/est kowdemo.htm

Accelrys Software Inc., 2005. Report on run of RDP. Prepared for Washington State Department of Ecology.

EFRA (European Flame Retardants Association), undated. Flame retardant fact sheet, Bisarylphosphates.

Personal communication with Andy Wang, Supresta LLP (10/31/05). Supresta LLC Ardsley, NY.

Akzo Nobel, 2003. Determination of the n-octanol/water partition coefficient of Fyrolflex RDP by the shake flask method. Conducted for Akzo Nobel by Wildlife International, LTD. Project number 497-127. (provided by Andy Wang, Supresta)

EPA HPV Robust Summary and Test Plan for Phosphoryl chloride, polymer with resorcinol, phenyl ester (CAS# 125997-21-9). Various submissions including an IUCLID Data Set (2001) available at: http://www.epa.gov/chemrtk/phoschlr/c13275tc.htm .



### Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov



### Name: Phosphoric trichloride, reaction products with Bisphenol A and Phenol [Tradenames: Reofos BAPP (Great Lakes Chemical); NcendX P-30 (Albemarle); Fyrolflex BDP (Akzo Nobel)]

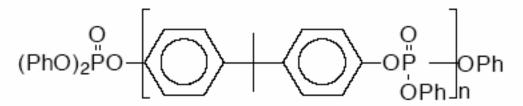
Date Updated: 12/30/05

### **IDENTIFICATION**

CAS number:	181028-79-5 (includes components with CAS numbers: 5945-33-5 (BDP), 83029-72-5, and 115-86-6 (triphenyl phosphate))
EINECS:	
EINECS name:	
Molecular formula:	C39 H34 O8 P2 (ChemIDPlus)
Known uses:	Flame retardant for polycarbonate/acrylonitrile-butadiene-styrene blend (PC/ABS) and polystyrene/polyphenylene oxide blend (PS/PPO) resin systems. The PC/ABS and PS/PPO resin systems are used to make electronic enclosures, such as monitors, televisions and computers. Bisphenol A diphosphate is expected to be present in these products in the range of 10-20% (Australian DHA, 2005). Flame retardant plasticizer in engineering resin applications including polyphenylene oxide and polycarbonate (Akzo Nobel, Product Information for Fyrolflex BDP)

Use (tonnage):

Structural formula:



EU classification annex:	
Synonyms	BAPP, Phosphoric trichloride reaction product with bisphenol A and phenol, Reofos® BAPP (Great Lakes Chemical Corp. MSDS). Product names Reofos BAPP, CN-1985, DVP 506 (IUCLID Data Set, 2004). Phosphoric acid, (1- methylethylidene) di-4,1-phenylene tetraphenyl ester (BDP), Fyrolflex BDP, BPA-BDPP, 4,4'-(Isopropylidenediphenyl) bis (diphenyl phosphate), Tetraphenyl bisphenol A biphosphate, BDP (Australian National Industrial Chemicals Notification and Assessment Scheme, 2000)
Additive or Reactive FR	Additive
Halogenated?	No



Additional Information:

Contains triphenyl phosphate and phenol as an impurities at 0.5 - 5.0% and < 0.05% by weight, respectively (Australian DHA, 2005).

### PHYSICO-CHEMICAL CHARACTERISTICS

Physical form	Pale Yellow odorless liquid (Great Lakes Chemical Corp. MSDS)	
Molecular weight	693.25 (Australian Gov., 2000)	
Boiling point/range (deg C)	<ul> <li>&gt;300 deg C @ 760 mmHg (Great Lakes Chemical Corp. MSDS). Approx. 41</li> <li>- 69 deg C (Australian Gov., 2000)</li> </ul>	
Melting point (deg C)		
Decomposition temp. (deg C)	201 deg C (Australian Gov., 2000)	
Vapor pressure (mg Hg)	3.1 x 10 <sup>-19</sup> kPa at 25 deg C (Australian DHA, 2005).	
Relative density	1.2576 at 20 deg C (Australian DHA, 2005).	
Water Solubility (in water; g/L)	0.19-0.49mg/L at 20 deg C (Great Lakes Chemical Corp. MSDS). $<2 \times 10^{-5}$ g/L at pH 4.0, 7.0 and 9.0 at 20 deg C (flask method) (Australian DHA, 2005). 0.415 mg/L at 20 deg C (Australian Gov., 2000)	
Partition coefficient (log K <sub>ow</sub> )	Octanol/water partition coefficient >5.7 at 20 deg C (Great Lakes Chemical Corp. MSDS). Log Pow = $4.0 - 5.2$ (HPLC method) (Australian DHA, 2005). Log Kow (Pow) > $4.9$ at 20 deg C (IUCLID Data Set, 2004). Log Pow => 6 at 25 deg C (measured) (Australian Gov., 2000). Experimentally measured Log Kow = $4.5$ (Akzo Nobel, 2002).	
РКа		
Flammability	Non-combustible (Great Lakes Chemical Corp. MSDS)	
Explosivity		
Oxidizing properties		
Mobility		

Additional Information: Impurities include triphenyl phosphate, phenol,, bisphenol A (Australian Gov., 2000).

### HUMAN EPIDEMIOLOGICAL DATA

HUMAN	
Epidemiological studies	
Occupational studies	"Not expected to be a hazard in normal industrial use" (Great Lakes Chemical Corp. MSDS)
Biomonitoring studies	

Additional information:

### TOXICOLOGICAL DATA

ACUTE	
Oral	Rat LD50 or LC50 > 5000mg/kg (Great Lakes Chemical Corp. MSDS). Rat (oral gavage; 14 day observation) LD50 > 2000 mg/kg (Australian DHA, 2005). LD50 (rats) > 2000 mg/kg (Australian Gov., 2000)
Dermal	Rat LD50 or LC50 > 2000mg/kg (Great Lakes Chemical Corp. MSDS). Rat LD50 (applied via occlusive dressing for 24 hours; 14 day observation) LD50 > 2000 mg/kg (Australian DHA, 2005). LD50 (rats) > 2000 mg/kg (Australian Gov., 2000)
Inhalation	
Other	
Skin irritation	Not irritating (Great Lakes Chemical Corp. MSDS). Slightly irritating in rabbits (applied via semi-occlusive dressing for 4 hours; 7 day observation) (Australian DHA, 2005). Non-irritant (in rabbits) (Australian Gov., 2000)
Eye irritation	Minimally irritating (Great Lakes Chemical Corp. MSDS). Slightly irritating in rabbits (Australian DHA, 2005). Non-irritant (in rabbits) (Australian Gov., 2000)
Respiratory tract irritation	
Skin sensitization	Not found to be a skin sensitizer in guinea pigs (Great Lakes Chemical Corp. MSDS; Australian DHA, 2005). Non-sensitising (guinea pig) (Australian Gov., 2000)
Inhalation sensitization	
	SUBCHRONIC
Oral	28 day study in rats, NOAEL = 1000 mg/kg/day (Australian Gov., 2000). No treatment effect in 28 day feeding study (rats). NOAEL > 20,000 ppm (1862 and 1968 mg/kg/day for males and females respectively) (Great Lakes Chemical Corp. MSDS). Rats (28 day oral gavage study), NOEL = 1000 mg/kg/day (Australian DHA, 2005).
Inhalation	
Dermal	
	GENOTOXICITY AND CARCINOGENICITY
Mutagenicity	Not mutagenic in bacteria (Australian Gov., 2000). Not mutagenic in Ames test (Great Lakes Chemical Corp. MSDS). Non-mutagenic in reverse mutation assay (Salmonella typhimurium TA1535, TA1537, TA98 and TA100, and Escherichia coli WP2uvrA; +/- metabolic activation). (Australian DHA, 2005).
Gene mutation	

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Chromosome abnormalities	lung o hamst clasto	ot increase incidence of chromosomal aberrations in Chinese hamster vells (Australian Gov., 2000). Non-clastogenic in in vitro Chinese er ovary (CHO) cell assay with and without metabolic activation. Non- genic in mice bone marrow cells (at 2000 mg/kg at 0 and 24 hours by avage) (Australian DHA, 2005).
Other genotoxic effects		

Cancer review:

### REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY

Reproductive toxicity	
Teratogenicity	Rat (exposed gestational days 6-19; by gavage): NOAEL (for maternal and developmental toxicity) = 1000 mg/kg bodyweight (highest dose tested). Test material was product CN-1985 listed as having 98.5% purity. Rat (exposed gestational days 8-19, by gavage): NOAEL (for maternal and developmental toxicity) = 1000 mg/kg bodyweight (IUCLID data set, 2004).
Embryotoxicity	

Additional information

### OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

Respiratory Tract	
Neurotoxicity	

Other toxicity information:

TOXICOKINETICS	
Absorption/Distribution	Study in rats using radio-labelled technical product DVP 506 (unknown purity) indicated low GI absorption (<= 3.5 % of administered dose; gastric gavage; 5 g/kg dosw) (IUCLID Data Set, 2004).
Metabolic pathways/products	

Additional information:

Following gastric gavage, primary route of excretion is by feces (45-88%) in rats (IUCLID Data Set, 2004).

ECOTOXICITY DATA

Algae	EbC50 (72 hours; inhibition of algal growth) Selanstrum subspicatus, > 1 mg/L, NOEC > 1 mg/L (Australian Gov., 2000). EC50 (96H) > 100ppm; NOEC= 100ppm (Great Lakes Chemical Corp. MSDS). EbC50 (Selanastrum subspicatus, inhibition of algal growth, 72 hour) > 0.02 mg/L (NOEC) (Australian DHA, 2005).
Crustacean	EC50 (48 hours), Daphnia magna, > 1 mg/l, NOEC > 1 mg/L (Australian Gov., 2000). EC50 (Daphnia magna, acute immobilization, 48 hour): > 0.034 mg/L (NOEC). EC50 (Daphnia magna, reproduction test, 21 days) > 0.02 mg/L (NOEC) (Australian DHA, 2005). Technical product DVP 506, (Daphnia magna; 48 hour exposure period) NOEC . 100 mg/l. Technical product DVP 506 (Daphnia magna; 21 day exposure period) EC50 > 5 mg/l (IUCLID Data Set, 2004).
Fish	LC50 (96 hours), Rainbow trout, > 1 mg/L, NOEC > 1 mg/L (Australian Gov., 2000). LC50 in rainbow trout (96H) >100 mg/L; NOEL = 100 mg/L. LC50 in orange kill fish (48H) >500 mg/L (Great Lakes Chemical Corp. MSDS). LC50 (Rainbow trout; 96 hour) > 0.025 mg/L (NOEC) (Australian DHA, 2005). Technical product DVP 506: Pimephales promelas (fish, fresh water) (21 day exposure period) NOEC = 5 mg/l (IUCLID Data Set, 2004).
Bacteria	Bacterial Inhibition Test: EC50>1000 mg/L (Great Lakes Chemical Corp. MSDS).

Additional information:

BAPP was submitted to Accelrys Software Inc. for a Toxicity Assessment run using TOPKAT model (09/05). BAPP fell outside the optimal predictive space (OPS) for most parameters under the TOPKAT model used for this run. (Accelrys report, 2005).

ENVIRONMENT	AL FATE
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Bioaccumulative potential	"This material does not bioaccumulate" (Great Lakes Chemical Corp. MSDS). "The high value for log Pow (4.0-5.2), relatively low molecular weight (692.7- 1425.4) and low water solubility (<2 x 10-5 g/L) indicate large potential for bioaccumulation. However, since the compound is expected to slowly biodegrade, and is in any case unlikely to enter the water compartment in significant volumes, the potential for bioaccumulation is expected to be low." (Australian DHA, 2005).
BCF or BAF	Calculated BCF = 3.16 (Supresta LLC, 2002)
Half-life (include media)	Half –life (T <sub>1/2</sub> ) at pH 4.0 > 1 year @ 25 deg C, T <sub>1/2</sub> at pH 7.0 > 1 year @ 25 deg C, T <sub>1/2</sub> at pH 9.0 > 1 year at 25 deg C (Australian Gov., 2000). Hydrolysis of product CN-1985 reported as between 1 day and 1 year. Hydrolysis had occurred after 2.4 hours and greater than 10% hydrolysis had occurred after 5 days at pH 4, 7, and 9 @ 50 deg C (IUCLID Data Set, 2004)
Henry's Law Constant (atm- m <sup>3</sup> /mole)	
Degradability	This material is not readily biodegradable at concentrations of 10 and 20 mg carbon/L. (Great Lakes Chemical Corp. MSDS).
Degradation products	Under fire conditions, toxic and irritating fumes may be emitted, including

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Washington State Department of Health	Deca-BDE Alternatives Assessment

	oxides of phosphorous and phosphine, carbon monoxide and carbon dioxide (Great Lakes Chemical Corp. MSDS)
Aerobic biodegradation	
Anaerobic biodegradation	
Other	
	•

Additional information

### ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq$ 60 days.	Half –life (T <sub>1/2</sub> ) at pH 4.0 > 1 year @ 25 deg C, T <sub>1/2</sub> at at pH 7.0 > 1 year @ 25 deg C, T <sub>1/2</sub> at pH 9.0 > 1 year at 25 deg C. T <sub>1/2</sub> also reported to be between 1 day and 1 year.
2. Bioaccumulation/Bio-concentration factor: BCF or BAF $> 1000$ ; or log K <sub>ow</sub> $> 5$	Log Pow => 6 at 25 deg C (measured). Experimentally derived log Kow = 4.5 with a calculated BCF = 3.16 (Supresta LLC, 2002; Akzo Nobel, 2002). Ecology criterion > 5
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Low acute toxicity (>2000 mg/kg rat). Low subchronic toxicity NOAEL ~2000 mg/kg ; not mutagenic Ames test. No chronic bioassays.
4. Is the chemical an Ecology PBT?	No

Additional information: No human data, but occupational hazard considered low

### HEALTH AND ENVIRONMENT SUMMARY

Deca-BDE Alternatives Assessment

### NOTES

Reports/other sources that contributed information:

Danish reports: No German report: No UK report: No Lowell report: Yes CPSC/NAS reports: No EPA Penta report: No EPA FOIA request: Yes, but no studies available EPA HPV: No EPA IRIS file: No Accelrys run: Yes, very limited information available from modeling. EU Risk Assessment: No

### SOURCES/REFERENCES

- 1. Material Safety Data Sheet: Reofos BAPP: Great Lakes Chemical Corporation.
- The Lowell Center for Sustainable Production, University of Massachusetts Lowell, 2005. Decabromodiphenylether; an investigation of non-halogen substitutes in electronic enclosure and textile applications (63 pages). Available at: <u>http://www.sustainableproduction.org/proj.clea.publ.shtml</u>
- Accelrys, Inc., 2005. TOPKAT Toxicity Assessment report for Department of Ecology on BAPP (CAS # 181028-79-5)
- 4. Australian Department of Health and Ageing (DHA), 2005. National Industrial Chemicals Notification and Assessment Scheme (NICNAS) Full Public Report for Phosphoric trichloride, reaction products with bisphenol A and phenol. File No: EX/69 (NA/869). May 23, 2005.
- 5. IUCLID Data Set, 2004. Great Lakes Chemical Corporation (provided by Richard Henrich, Great Lakes Chemical Corp., 11/02/05)
- 6. Supresta LLC, 2002. Akzo Nobel memo to A.G.M. Kroon from M.G.J. Geurts, dated April 18, 2002; Subject: BCF phosphorus chemical (8 pages). Provided by Andy Wang, Supresta LLC.
- Akzo Nobel Functional Chemicals LLC, 2002. Determination of the n-octanol/water partition coefficient of Fyrolflex BDP by the shake flask method. Test conducted for Akzo Nobel by Wildlife International, LTD. Project number: 497C-122. Provided by Andy Wang, Supresta LLC.
- Australian Government, Department of Health and Aging, 2000. National industrial chemicals notification and assessment scheme, full public report on Fyrolflex BDP. Available at: http://www.nicnas.gov.au/PUBLICATIONS/CAR/NEW/NA/NASUMMR/NA0700SR/na773.asp
- 9. ChemIDplus. Available through the National Library of Medicine at: http://sis.nlm.nih.gov/chemical.html
- 10. Akzo Nobel. Product information for Fyrolflex BDP. Available at: <u>http://phosphorus.akzonobelusa.com/business/phosphorus/TDS/TDS\_FyrolFlex.html</u>

### Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov

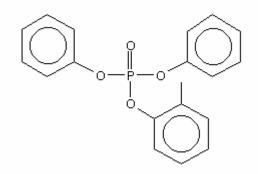


Name:	Diphenyl cresyl phosphate		
Date Up	dated:	10/11/05	

### **IDENTIFICATION**

CAS number:	26444-49-5
EINECS:	
EINECS name:	
Molecular formula:	С19-Н17-О4-Р
Known uses:	Plasticizer, gasoline additive, food packaging, flame retardant,
Use (tonnage):	The production volume in Japan was estimated to be 1,700 tonnes (1990 - 1993) and more than 1,000 tonnes/year with a highest production volume of 5,000 tonnes/year in Germany. The chemical is not produced but imported into Sweden, Denmark and Canada in volumes of 350 kg/year, 3 tonnes/year and 10 - 100 tonnes/year respectively. The chemical is also produced in the United States, however precise production data were not available. This chemical is used as the consumer product at 7 % in a filling foam for insulating air spaces. (UNEP, IPCS, 1997)

### Structural formula:



(from NIST Chemistry WebBook)

EU classification annex:	
Synonyms	Cresol diphenyl phosphate, cresyldiphenyl phosphate, diphenyl cresol phosphate, diphenyl tolyl phosphate, disflamol DPK, Kronitex CDP, methylphenyldiphenyl phosphate, monocresyl diphenyl phosphate, phosflex 112, phosphoric acid cresyl diphenyl ester, phosphoric acid diphenyl tolyl ester, phosphoric acid methylphenyl diphenyl ester, santicizer 140, tolyl diphenyl phosphate

Final PBDE CAP January 19, 2006		
Washington State Department of Health		Deca-BDE Alternatives Assessment
Additive or Reactive FR	Addit	tive (IUCLID Dataset, 2000)
Halogenated?	No	

Additional Information

### PHYSICO-CHEMICAL CHARACTERISTICS

Physical form	Clear transparent liquid
Molecular weight	340.33
Boiling point/range (deg C)	390 deg C @ 760 mmHg (Lefaux, 1968) 235-255 deg C @ 4mmHg (Sax, 1987).
Melting point (deg C)	-38 deg C (Sax, 1987).
Decomposition temp. (deg C)	
Vapor pressure (mg Hg)	<1.2x10(-4) Pa @ 25C (UNEP, IPCS, 1997)
Relative density	1.2 g/cm3 at 20 deg C
Water Solubility (in water; g/L)	Insoluble in water and glycerol. (Sax, 1987). Soluble in most organic solvents, except glycerol. (Sax, 1987). 2.4 mg/l. (UNEP, IPCS, 1997); < 0.1 g/l at 20 deg C; 0.0026 g/l at 25 deg C (IUCLID dataset, 2000)
Partition coefficient (log K <sub>ow</sub> )	Log Pow = 3.7 (UNEP, IPCS, 1997); log Pow = 4.5; log Pow = 5.1 (IUCLID dataset, 2000). Log Kow (estimated) = 4.77 (KowWin). Log Kow = 5.25 (EPIWIN).
РКа	
Flammability	
Explosivity	
Oxidizing properties	
Mobility	
Additional Information	

Additional Information

### HUMAN EPIDEMIOLOGICAL DATA

HUMAN		
Epidemiological studies		
Occupational studies		

Deca-BDE Alternatives Assessment

Biomonitoring studies

Additional information:

Foods sometimes become contaminated with aryl/alkyl phosphates by diffusion from phosphate treated packaging materials. Food samples also become contaminated during analysis through laboratory reagents that contain these esters, eg, bulk alcohols & organic solvents. (Daft, 1982)

### TOXICOLOGICAL DATA

ACUTE		
Oral	4g/kg (rat) tolerated, but autopsy demonstrated general capillary paralysis, edema and cerebral hemorrhage. (Lefaux, 1968)	
	LD50(rat)=6,400mg/kg (UNEP, IPCS, 1997). LD50 (rat) > 5000 mg/kg bw. LD50 (mouse) 6400 – 12800 mg/kg bw. LD 50 (rabbit) 1028 mg/kg bw. LD 50 guinea pig 1600 – 3200 mg/kg bw. (IUCLID Dataset, 2000)	
Dermal	LD50(rabbit)> 5,000 - > 10000 mg/kg bw. (IUCLID Dataset, 2000).	
Inhalation	LC50(sheep)>0.37 mg/m3/1hr (UNEP, IPCS, 1997)	
Other	Intraperitoneal LD50 1g/kg (rat). (Lefaux, 1968)	
Skin irritation	Non irritating to slightly irritating in rabbits, guinea pigs and rats; moderately irritating to humans. (IUCLID Dataset, 2000)	
Eye irritation		
Respiratory tract irritation		
Skin sensitization		
Inhalation sensitization		
	SUBCHRONIC	
Oral	2.5mg/kg/d decreased Hen brain and spinal cord neurotoxic esterase by 40%- 55%. (Lotti et al., 1980). NOEL(rat)=12mg/kg/d (UNEP, IPCS, 1997).	
Inhalation		
Dermal		
	GENOTOXICITY AND CARCINOGENICITY	
Autagenicity Evaluated for mutagenicity in the Salmonella/microsome preincubation using a standard protocol approved by National Toxicology Program. D 0, 100, 333, 1000, 3333, and 10000 ug/plate were tested in four Salmon typhimurium strains (TA98, TA100, TA1535, and TA1537) in the press and absence of Aroclor-induced rat or hamster liver S9. These tests wer negative and the highest ineffective dose level tested without formation precipitate in any Salmonella tester strain was 1000 ug/plate. (Zeiger et 1987). Negative in Ames test (IUCLID Dataset, 2000)		
Gene mutation		
Chromosome abnormalities		
D'al and an and all and a state	D 015	

Deca-BDE Alternatives Assessment

Other genotoxic effects

Cancer review:

### REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY

Reproductive toxicity	NOEL(rat) reproductive toxicity Parental: 60mg/kg (UNEP, IPCS, 1997) NOEL(rat) reproductive toxicity F1 generation: 300mg/kg (UNEP, IPCS, 1997)
Teratogenicity	
Embryotoxicity	

Additional information

OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)		
Respiratory Tract		
Neurotoxicity	Neurotoxicity: (hen, single oral dose, 6 week observation period) acute toxicity at $\geq$ 2500 mg/kg bw; (hen, single i.p.) LOAEL = 5000 mg/kg bw; (hen, single oral dose of 50 mg/kg bw, 0-isomer) signs of neurotoxicity; (hen, single oral dose) NOAEL 30 mg/kg bw (ataxia endpoint); Monkey, i.p. 1000 mg/kg bw - 89% reduction in plasma cholinesterase activity. (IUCLID Dataset, 2000).	

Other toxicity information:

A commercial cresyl diphenyl phosphate preparation containing approximately 35% of triphenyl phosphate, 45% of cresyl diphenyl phosphates, 18% of dicresyl phenyl phosphates and 2% of tricresyl phosphates was given in a single intraperitoneal injection (150 or 300 mg/kg) causing an induction of microsomal cytochrome P-450 in the liver of Wistar rats with a concomitant increase in the activities of mixed function monooxygenases and proliferation of smooth endoplasmic reticulum 24 h after the treatment. The morphological changes in hepatocytes included the enlargement of nuclei and mitochondria with increased cristae. The hepatic morphology returned to normal 2 weeks after the treatment. The activity of pseudocholine esterase in blood was inhibited 4 h and 24 h after the injection but the effect levelled off. The concentration of the organophosphates in blood and liver decreased rapidly with only traces detected in blood after 24 h. No effects on the activities of cerebral and muscle acetylcholine esterase were observed. The treatment (300 mg/kg) inhibited the brain--2',3'-cyclic nucleotide 3'-phosphohydrolase through the 2-week observation period associated with demyelination in peripheral nerves. (Vainiotalo et al., 1987).

### TOXICOKINETICS

Absorption/Distribution	
Metabolic pathways/products	



Additional information:

### ECOTOXICITY DATA

Algae	Ankistrodesmus falcatus, endpoint of primary productivity, 4 hour exposure period: EC50 0.7 mgl. Scenedesum quadricauda, endpoint of primary productivity, 4 hour exposure period: EC50 1 mg/l. Lake Ontario phytoplankton, endpoint of primary productivity, 4 hour exposure period: EC50 0.5 mg/l. (IUCLID Dataset, 2000)
Crustacean	
Fish	Oryzias latipes: LC50(24hr)= 2.7mg/L, LC50(48hr)=1.7mg/L LC50(72hr)=1.3mg/L, LC50(96hr)=1.3mg/L <sup>1</sup> . Brachydanio rerio: LC50 = 8.1 mg/l, LC90 = 11.5 mg/l (IUCLID Dataset, 2000)
Bacteria	Activated sludge, test for inhibition of oxygen consumption, 3 hour exposure period: EC50 > 10000 mg/l. (IUCLID Dataset, 2000)

Additional information

### ENVIRONMENTAL FATE

Bioaccumulative potential	
BCF or BAF	BCF 360 or 980 (UNEP, IPCS, 1997); BCF = 360 (BCF calculated with Pow = 32000) ; BCF = 980 (BCF calculated with log Pow = 4.5) (IUCLID Dataset, 2000)
Half-life (include media)	Half-life at pH 7 is about 47 days. (IUCLID Dataset, 2000). Half-life in water = 38 days (PBT Profiler)
Henry's Law Constant (atm-m <sup>3</sup> /mole)	
Degradability	Photodegradation, sunlight: In water T1/2= 4.86 years (UNEP, IPCS, 1997);
Degradation products	
Aerobic biodegradation	Predominantly domestic sewage at a concentration of 100 mg/l: 75% degradation after 28 days. Acclimated composite seed at a concentration of 23.1 mg/l: 84% degradation after 28 days. Mississippi river water at a concentration of 1 mg/l: 100% degradation after 4 days. Activated sludge at a concentration of 3 mg/l: 82% degradation after 154 days. (IUCLID Dataset, 2000)
Anaerobic biodegradation	
Other	



### ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq 60$ days.	$T_{1/2} = 4.86$ years in water
2. Bioaccumulation/Bio-concentration factor: BCF or BAF $> 1000$ ; or log K <sub>ow</sub> $> 5$	BCF 980 (calculated with $P_{OW} = 4.5$ )
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Low acute oral toxicity in multiple species; inhalation toxicity relatively high (sheep); not mutagenic; has reproductive and developmental toxicity, moderate aquatic toxicity.
4. Is the chemical an Ecology PBT?	Borderline

Additional information

### HEALTH AND ENVIRONMENT SUMMARY

### Environment

The chemical is toxic to aquatic organisms and considered not readily biodegradable. However the predicted environmental concentration is lower than the predicted no effect concentration. Therefore, it is considered of low potential risk and low priority for further work. (UNEP, IPCS, 1997).

### Health

The chemical is moderately toxic in a repeated dose toxicity study (i.e. liver, kidney, adrenal). This chemical is considered to be non-genotoxic. As margin of safety is very large, it is currently considered of low potential risk and low priority for further work (UNEP, IPCS, 1997). For human health, a margin of safety was estimated to be 2400, based on occupational exposure. However, the frequency of exposure is very limited and the very few workers involved wear personal protective equipment. The human health risks for the public from indirect exposure via the environment and consumer use are also low. (UNEP, IPCS, 1997).

Deca-BDE Alternatives Assessment

### NOTES

Reports/other sources that contributed information:

Danish reports: No German report: No UK report: No Lowell report: Yes CPSC/NAS reports: No EPA Penta report: No EPA FOIA request: Yes, but no studies available EPA HPV: No EPA IRIS file: Accelrys run: No EU Risk Assessment: No

### SOURCES/REFERENCES

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- 6. Lotti M, Johnson MK. Repeated small doses of a neurotoxic organophosphate. Monitoring of neurotoxic esterase in brain and spinal cord. *Arch Toxicol* 1980;**45**(4):263-71.
- Zeiger E, Anderson B, Haworth S, Lawlor T, Mortelmans K, Speck W. Salmonella mutagenicity tests: III. Results from the testing of 255 chemicals. *Environ Mutagen* 1987;9 Suppl 9:1-109.
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- 10. Syracuse Research Corp., EPIWIN program. Available at: <u>http://www.syrres.com/esc/epi.htm</u>
- 11. EPA PBT Profiler. Available at http://www.pbtprofiler.net/

### Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov

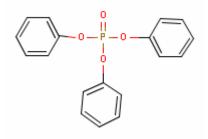


Name:	Triphenyl Phosphate	
Date Upo	lated:	10/12/05

### **IDENTIFICATION**

CAS number:	115-86-6
EINECS:	204-112-2
EINECS name:	
Molecular formula:	C18H15O4P
Known uses:	Flame retardant in electronic enclosures (Lowell Center, 2005). Used in PPO- HIPS with RDP (German alternatives report, 2000).
Use (tonnage):	

Structural formula:



c)	Plu	ID	Chem	(from	(
S	PIU	ID	Cnem	Irom	(

EU classification annex:	
Synonyms	Triaryl Phosphate Phosphoric Acid Triphenyl Ester Celluflex tpp TPP
Additive or Reactive FR	Additive (EPA, 2005)
Halogenated?	No

Additional Information



### PHYSICO-CHEMICAL CHARACTERISTICS

Physical form	White/off white flake/crystal (HSDB, 2005)	
Molecular weight	326.28 (HSDB, 2005)	
Boiling point/range (deg C)	245 deg C at 11mm Hg (HSDB, 2005)	
Melting point (deg C)	49-50 deg C (HSDB, 2005)	
Decomposition temp. (deg C)		
Vapor pressure (mg Hg)	6.3 x 10(-6) (EPA, 2005)	
Relative density		
Water Solubility (in water; g/L)	0.002% solubility in water; 1.9 mg/l @ 25 deg . Soluble in alcohol, benzene, ether, chloroform, carbon tetrachloride and acetone (HSDB, 2005); 1.9x 10(-3) (EPA, 2005).)	
Partition coefficient (log K <sub>ow</sub> )	4.61-4.76 (WHO, 1991). Estimated log Kow = 4.70 (EPIWIN). Log Kow = 4.59 (EPA, 2005)	
РКа		
Flammability		
Explosivity	Non-explosive (WHO, 1991)	
Oxidizing properties		
Mobility		

Additional Information

### HUMAN EPIDEMIOLOGICAL DATA

HUMAN		
Epidemiological studies		
Occupational studies		
Biomonitoring studies		

Additional information:

### TOXICOLOGICAL DATA

ACUTE		
Oral	LD50 > 20,000 mg/kg (rat, oral). LD50 = 10,800 mg/kg (rat, oral). LD50> 5000 mg/kg (mouse, oral). LD>5000 mg/ (rabbit, oral) (EPA, 2005)	
Dermal	Negative acute dermal irritation study in rabbits at 500 mg. (EPA, 2005).	

Deca-BDE Alternatives Assessment

<b>.</b>	
Inhalation	
Other	
Skin irritation	Low concern, negative in guinea pigs, low incidence in humans (EPA, 2005).
Eye irritation	Moderate, mild in rabbits (EPA, 2005).
Respiratory tract irritation	
Skin sensitization	
Inhalation sensitization	
	SUBCHRONIC
Oral	
Inhalation	
Dermal	LOAEL = 345 mg/kg/day (1%); 21-d repeated dose study (inadequate), rabbits, dermal, systemic effects (EPA, 2004)
6	ENOTOXICITY AND CARCINOGENICITY
Mutagenicity	Low concern, negative Ames assay mouse lymphoma cells. (EPA, 2005)
Gene mutation	Negative in mitotic gene conversion assay (EPA, 2005)
Chromosome abnormalities	
Other genotoxic effects	

Cancer review: Overall carcinogenic concern LOW, based on modeling results (EPA, 2005) A4; Not classifiable as a human carcinogen (ACGIH, 2005)

REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY		
Reproductive toxicity Low concern, 91-112d repro/developmental study (incomplete) rate reproductive effects, NOAEL= 690 mg/kg/d (EPA, 2005).		
Teratogenicity	Low concern, 91-112d repro/developmental study (incomplete) rats, diet, no reproductive effects, NOAEL= 690 mg/kg/d (EPA, 2005).	
Embryotoxicity		

Additional information

<b>OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)</b>	
Respiratory Tract	
Neurotoxicity	Neurotoxicity: Low concern, negative studies in hens up to 10,000 mg/kg/day

1	Washington State Department of Health
	<u>Health</u>

(oral 6d), neg studies in cat subcutaneous 700mg/kg/day. NOAEL=711 mg/kg/day (EPA, 2005) Neurotoxicity screening study, rats, diet, decreased body weight gain without decreased food consumption, NOAEL = 161 mg/kg/day (0.25%) (EPA, 2005)

Other toxicity information:

Immune system effects: Low; 120-d repeated-dose study, rats, diet, no immune system effects, NOAEL = 700 mg/kg/day (1%)

Systemic effects: Moderate; 35-d repeated-dose study (inadequate), rats, diet, increased relative liver weight at 0.5%, NOAEL = 0.1%; 120-d repeated dose (EPA, 2005)

### TOXICOKINETICS

Absorption/Distribution	Absorption. Poor through skin as neat solid, moderate through skin in solution; moderate through lungs and GI tract based on closely related analogs (EPA, 2005)
Metabolic pathways/products	

Additional information:

### ECOTOXICITY DATA

Algae	Green Algae Acute : 96-h EC50, 2.0 mg/L (EPA, 2005) Green Algae Chronic: ChV (chronic): 0.140 mg/L (EPA, 2005)	
Crustacean	Daphnid LC50 = 48-h LC50, 1.2 mg/L; 48-h LC50, 1.1 mg/L. Daphnic ChV = 0.1 mg/l (EPA, 2005).	
Fish	LC50: 96-h, 0.870 mg/L. Fish ChV = 0.14 mg/l (EPA, 2005)	
Bacteria		

Additional information:

Overall hazard concern for aquatic toxicity is high (EPA, 2005)

### ENVIRONMENTAL FATE

Bioaccumulative potential	
BCF or BAF	BCF= 113 – 264 (Rainbow trout), BCF = 218 – 1743 (Fathead minnow) (EPA, 2005)
Half-life (include media)	12 hours (atmospheric half life). @ 20 deg C: 366 days @ pH3, 406 days @ pH 7, <5 days @ pH 9 (EPA, 2005)
Henry's Law Constant (atm- m <sup>3</sup> /mole)	1.2 x 10 <sup>-5</sup> (EPA, 2005)
Degradability	Not readily biodegradable (EPA, 2005)

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Washington State Department of Health			Deca-BDE Alternatives Assessment
Degradation products	Diph	enyl phosphate, phenol (EPA, 2005)	
Aerobic biodegradation			
Anaerobic biodegradation			
Other			
Additional information			

### ECOLOGY PBT CRITERIA

1. Persistence:	$T_{1/2}$ =12 hours atmospheric; $T_{1/2}$ hydrolysis <5 days
Half life in water, soil or sediments $\geq 60$ days.	- 366 days (pH 9 – pH 3); criterion is > 60 days.
2. Bioaccumulation/Bio-concentration factor:	BCF= $113 - 1743$ ; criterion is >1000; K <sub>OW</sub> < 4.77;
BCF or BAF > 1000; or log $K_{ow} > 5$	Criterion = >5.
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Low oral rat 3500-20000mg/kg; HOWEVER aquatic toxicity is high, not mutagenic Ames test; low repro, low teratogenic toxicity, low neurotoxicity.
4. Is the chemical an Ecology PBT?	No

Additional information: No human data

### HEALTH AND ENVIRONMENT SUMMARY

Reports/other sources that contributed information:

Danish reports: Yes German report: No UK report: No Lowell report: Yes CPSC/NAS reports: No EPA Penta report: Yes (full toxicity profile available) EPA FOIA request: Yes, studies available. EPA HPV: Yes EPA IRIS file: No Accelrys run: No EU Risk Assessment: No

### SOURCES/REFERENCES

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- 10. EPIWIN program from Syracuse Research Corp. Available at: <u>http://www.syrres.com/esc/epi.htm</u>

### Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov



Name:	Zinc Borate	
Date Updated:		10/12/05

### **IDENTIFICATION**

CAS number:	1332-07-6
EINECS:	215-566-6
EINECS name:	Boric acid, zinc salt
Molecular formula:	$ZnO(B_2O_3)_2$
Known uses:	Flame retardant/smoke suppressant in polyamides, PVC, polyethylene, polypropylene, epoxy, polyesters, elastomers and rubber. (Great Lakes, Technical Information). Antimicrobial in cosmetics (Danish EPA, 1999)
Use (tonnage):	

Structural formula:

EU classification annex:	
Synonyms	Borax-2335-, Boric-acid, zinc-salt-, ZB112-, ZB237-, ZN-100- (HSDB)
Additive or Reactive FR	
Halogenated?	No

Additional Information



### PHYSICO-CHEMICAL CHARACTERISTICS

Physical form	White powder (HSDB)
Molecular weight	383.41 (Danish EPA, 1999)
Boiling point/range (deg C)	
Melting point (deg C)	980 deg C (HSDB)
Decomposition temp. (deg C)	
Vapor pressure (mg Hg)	
Relative density	3.64 g/cm3 (HSDB)
Water Solubility (in water; g/L)	0.3% (3g/l) in water at 20 deg C (HSDB)
Partition coefficient (log Kow)	
РКа	
Flammability	Non-flammable (HSDB)
Explosivity	
Oxidizing properties	
Mobility	
Additional Information	

Additional Information

### HUMAN EPIDEMIOLOGICAL DATA

HUMAN		
Epidemiological studies	LOAEL = $0.91 \text{ mg/kg/day}$ based on intake of zinc dietary supplements. Critical effect is a decrease in erythrocyte Cu, Zn-superoxide dismutase (ESOD) activity in health adult male and female volunteers. Used to develop a reference dose = $0.3 \text{ mg/kg-day}$ (EPA, 2005)	
Occupational studies		
Biomonitoring studies		

Additional information: Human ingestion of 12 g of elemental zinc over a 2-day period did not result in hematological, hepatic or renal toxicity (Danish EPA, 1999). Contact with skin and eyes causes irritation (HSDB) Zinc is an essential element (EPA, 2005)

### TOXICOLOGICAL DATA

ACUTE	
Oral	LD50 for boric acid reported to be between 2000 and 3500 mg/kg (Danish EPA, 1999). LD50 (rats) > 10 g/kg (NAS, 2000). Zinc borate may cause effects on the central nervous system.
Zinc borate	Page 227

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Dermal	
Inhalation	
Other	
Skin irritation	Negative in guinea pig sensitization test. Produced mild conjunctivitis in albino rabbits (NAS, 2000).
Eye irritation	
Respiratory tract irritation	
Skin sensitization	
Inhalation sensitization	
	SUBCHRONIC
Oral	
Inhalation	
Dermal	
G	ENOTOXICITY AND CARCINOGENICITY
Mutagenicity	
Gene mutation	
Chromosome abnormalities	
Other genotoxic effects	
Cancer review:	

### REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY

Reproductive toxicity	
Teratogenicity	
Embryotoxicity	

Additional information

### OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

 Respiratory Tract

 Neurotoxicity



### Other toxicity information:

### TOXICOKINETICS

Absorption/Distribution	
Metabolic pathways/products	

Additional information:

### ECOTOXICITY DATA

Algae	For zinc: Selenastrum capricornutum: EC50 (24 hour) = 0.015-0.178 mg/l. Zinc ion is very toxic in aquatic standard test (acute effects, 1 mg/l) (Danish EPA, 1999).
Crustacean	For disodium tetraborate: Daphnia magna: LC50 (48 hour) = 141.0 mg/l. For zinc: Daphnia magna LC50 (48 hour) = 1.59 mg/l and 0.068 mg/l. Ceriodaphnia dubia: LC50 = $0.07 - 0.153$ mg/l. Ceriodaphnia reticulate LC50 (48 hour) = $0.076 - 0.264$ mg/l (Danish EPA, 1999).
Fish	For disodium tetraborate: Ganbusia affinis: LC50 (24 hour) = 3460 mg/l, (48 hour) = 2360 mg/l, (96 hour) = 1040 mg/l, (6 day) = 547 mg/l. Lepomis macrochirus: LC50 (24 hour) = 15 mg/l. For zinc: Oncorhynchus mykiis: LC50 (48 hour) = $0.79-5.9$ mg/l and $0.59-5.3$ mg/l. LC50 (14 day) = $0.410$ mg/l. Pimephales promelas: LC50(14 day) = $2.154 - 2.540$ mg/l. (Danish EPA, 1999)
Bacteria	

Additional information:

For disodium tetraborate: Chironomus decorus: LC50 (48 hour) = 1376 mg/l. For zinc: Thalassiosira guillardii: LC50 (48 hour) = 0.5 - 20 mg/l (Danish EPA, 1999).

### ENVIRONMENTAL FATE

Bioaccumulative potential	
BCF or BAF	
Half-life (include media)	
Henry's Law Constant (atm- m <sup>3</sup> /mole)	
Degradability	
Degradation products	

Deca-BDE Alternatives Assessment

Aerobic biodegradation	
Anaerobic biodegradation	
Other	

Additional information

### ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq 60$ days.	unknown
2. Bioaccumulation/Bio-concentration factor: BCF or BAF $> 1000$ ; or log K <sub>ow</sub> $> 5$	Unknown; fairly soluble in water, but $K_{ow}$ , BCF not listed
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Not to toxic to Gambusia fish, but fairly toxic to salmonids
4. Is the chemical an Ecology PBT?	unknown

Additional information

### HEALTH AND ENVIRONMENT SUMMARY



Health:

- There is not sufficient data to make a health screening of zinc borate.
- Boric acid can be formed, if zinc borate gets in contact with water such as body fluids.
- The solubility of zinc borate is < 10% of the solubility of disodium tetraborate, which is used to predict toxicity of zinc borate.
- There is a risk of formation of boric acid upon skin contact which can irritate skin and eyes.
- Boric acid is a suspected teratogen.
- Inhalation of zinc borate dust may cause respiratory tract irritation.

Environment:

- No data was found on the compound ZnO(B2O3)2. Disodium tetraborate (CAS # 1330-43-4) is not harmful to crustaceans or fish based on a limited data set. The zinc ion is toxic in a standard test with crustaceans and fish (acute effects 10 < 1 mg/l).
- This approach is based on the assumption that the total toxicity of zinc borate originate from the boric acid and zinc ion formed upon dissolution.

(Summary from Danish EPA, 1999)

Zinc is an essential element (EPA, 2005)

Deca-BDE Alternatives Assessment

### NOTES

Reports/other sources that contributed information:

Danish reports: Yes German report: No UK report: No Lowell report: No CPSC/NAS reports: Yes EPA Penta report: No EPA FOIA request: Yes, but no studies available EPA HPV: No EPA IRIS file: Yes (zinc and compounds) Accelrys run: No EU Risk Assessment: No (although there are EU risk assessments on zinc oxide and boric acid).

### SOURCES/REFERENCES

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- 2. (HSDB) Hazardous Substance DataBank. File on zinc borate (CAS# 1332-17-6). Available at <u>http://toxnet.nlm.nih.gov/</u>
- 3. NAS, 2000. Toxicological risks of selected flame-retardant chemicals. Available from: URL: <u>www.nap.edu/openbook/0309070473/html/78.html</u>
- 4. Danish EPA, 2000. Alternatives to brominated flame retardants, screening for environmental and health data. Available at: <u>http://www.mst.dk/homepage/</u>
- 5. EPA, 2005. IRIS file for Zinc and Compounds. Available at: http://www.epa.gov/iris/subst/index.html .

### Additional information should be submitted to:

Denise Laflamme Washington State Dept. of Health telephone: 360/236-3174 fax: 360/236-2251 email: denise.laflamme@doh.wa.gov



Name:	Polytetrafluoroethylene (Teflon)	
Date Upo	lated:	10/12/05

### **IDENTIFICATION**

CAS number:	9002-84-0 (HSDB, 2005)
EINECS:	204-126-9 (Oxford Univ., 2005)
EINECS name:	
Molecular formula:	(C2-F4)n-, where n≥20000 (Merck,1989)
Known uses:	<ul> <li>Tubing and sheets for chemical lab work, lining reaction vessels, gaskets, pump packings, electrical insulator, filtration fabrics, protective clothing, prosthetic aid (Merck, 1989).</li> <li>Inert ingredient in pesticides (FANPP, 2005).</li> <li>In mechanical tapes &amp; glass fibers; in cable connectors, circuit breakers, &amp; stand-off insulators; polymer for parts used in handling liquids, seals, piston rings, &amp; bearings; polymer for rods, sheets, tubes, wire &amp; cable insulation, anti-stick coatings in consumer applications; in lubricant powders, fibers, &amp; impregnated fabrics (HSDB, 2005).</li> </ul>
Use (tonnage):	1.29E10 g in 1984 (=1.29E4 metric tons) (HSDB, 2005)

Structural formula:

EU classification annex:	
Synonyms	Tetrafluoroethene homopolymer, tetrafluoroethylene polymer, polytetrafluoroethylene resin, polytef, PTFE, Fluon, Fluoroflex, Teflon (Merck, 1989)
Additive or Reactive FR	
Halogenated?	Yes (Fluorinated)

#### Additional Information

### PHYSICO-CHEMICAL CHARACTERISTICS

Physical form	White translucent to opaque solid (Merck, 1989)
Molecular weight	Not Applicable (polymer), MW for tetrafluoroethylene (monomer)=100.2 (HSDB, 2005)
Boiling point/range (deg C)	>400°C (Merck, 1989)
Melting point (deg C)	327°C (Oxford Univ., 2005)
Decomposition temp. (deg C)	Decomposition temperature=500-550°C (BSEF, 2005)
	Melts to extremely viscous gel at 327°C and reverts to gaseous monomer above 400°C (Merck, 1989)
Vapor pressure (mg Hg)	
Relative density	2.2 (Merck, 1989)
Water Solubility (in water; g/L)	Insoluble (Oxford Univ., 2005)
Partition coefficient (log Kow)	
РКа	
Flammability	Flash ignition temperature=560°C, Self ignition temperature=580°C (BSEF, 2005).
	Nonflammable (Merck, 1989)
Explosivity	
Oxidizing properties	
Mobility	

Additional Information:

Useful temp range -75 deg C to +250 deg C; @ 400 deg C reverts to gaseous monomer; shore hardness 55-56; tensile strength 3500-4500 psi; flexural strength 2000 psi; brittle point below -80 deg C; dielectric constant: 2.0-2.05 @ 60 to 3x10+9 cycles; cannot be molded, but can be extruded & pressed into shapes @ around 205 deg C (HSDB, 2005).

### HUMAN EPIDEMIOLOGICAL DATA

HUMAN
-------

Epidemiological studies	
Occupational studies	The finished compound is inert under ordinary conditions. There have been reports of polymer fume fever in humans exposed to unfinished product. Pyrolysis products are irritating to mucous membrane (HSDB, 2005).

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Three occupational studies on Teflon polymer fume fever are described in FANPP (2005).

Biomonitoring studies

Additional information:

### TOXICOLOGICAL DATA

ACUTE Oral Dermal Inhalation Although polytetrafluoroethylene (Teflon) is inert under ordinary circumstances, when the polymer is heated under conditions of inadequate ventilation, polymer fume fever may result. Pulmonary edema has been reported in some cases, with symptoms of chest discomfort and shortness of breath. Pulmonary edema is more likely to be noted with exposure to fumes evolved from **Teflon** at temperatures up to 500 degrees C or greater (HSDB, 2005). Other Skin irritation Eye irritation Although **polytetrafluoroethylene** (**Teflon**) is inert under ordinary Respiratory tract irritation circumstances, when the polymer is heated under conditions of inadequate ventilation, polymer fume fever may result (HSDB, 2005). Skin sensitization Inhalation sensitization **SUBCHRONIC** Oral No toxicity was observed in male & female rats fed **polytetrafluoroethylene** for 90 days, even with a level of 25% in the diet. The polymer has not been found to produce skin irritation or to act as an allergenic agent (HSDB, 2005). Inhalation Biochemical changes and a decrease in body weight were observed in rats exposed to Teflon pyrolysis products over a five day period (FANPP, 2005). Polytetrafluoroethylene heated to 300 deg C in air was lethal to rats... Gases identified during pyrolysis include tetrafluorethylene, hexafluorethylene, hexafluoropropylene, octafluorocyclobutane & octafluoroisobutylene (HSDB, 2005). Eleven animal studies are cited in HSDB (2005) on the toxicity of inhalation of pyrolysis products of Teflon. Dermal

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### GENOTOXICITY AND CARCINOGENICITY

Mutagenicity	
Gene mutation	
Chromosome abnormalities	
Other genotoxic effects	

#### Cancer review:

No data are available in humans. Inadequate evidence of carcinogenicity in animals. Overall evaluation: Group 3: The agent is not classifiable as to its carcinogenicity to humans (HSDB, 2005).

Type of Test	Route of Exposure	Species Observed	Dose Data	Toxic Effects	Reference
TDLo - Lowest published toxic dose	Implant	Rodent - rat		Tumorigenic - equivocal tumorigenic agent by RTECS criteria Tumorigenic - tumors at site of application	CNREA8 Cancer Research. (Public Ledger Building, Suit 816, 6th & Chestnut Sts., Philadelphia, PA 19106) V.1- 1941- Volume(issue)/page/year: 15,333,1955
TDLo - Lowest published toxic dose	Implant	Rodent - mouse	1140 mg/kg	Tumorigenic - equivocal tumorigenic agent by RTECS criteria Tumorigenic - tumors at site of application	TUMOAB Tumori. (Casa Editrice Ambrosiana, Via G. Frua 6, 20146 Milan, Italy) V.1- 1911- Volume(issue)/page/year: 62,565,1976

Above table from RTECS (2005).

A case of a fibrosarcoma /reported/ in 31-yr old man, which was diagnosed 10.5 yr after implantation of a 5 cm woven **PTFE**-dacron arterial prosthesis. The tumor (9x8x4 cm) constricted & encircled more than half of length of femoral artery, including the implant, but did not invade the vessel--no evidence of metastasis (HSDB, 2005).

A group of 89 random-bred female Swiss mice, 7-9 wk old, received sc implant in left flank of a square sheet of **polytetrafluoroethylene (PTFE)** measuring 12x12x1.2 mm. The first local tumor developed 25 wk after implantation; a total of 11 (12.5%) fibrosarcomas were found after an average latent period of 54.5 weeks (HSDB, 2005).

### REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY

Reproductive toxicity	
Teratogenicity	
Embryotoxicity	

Additional information

### OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)

Respiratory Tract Neurotoxicity



Other toxicity information:

### TOXICOKINETICS

Absorption/Distribution	
Metabolic pathways/products	(products) Urinary fluoride (HSDB, 2005)

Additional information:

Fluoride levels in urine are greater than normal in workers exposed to fumes of **polytetrafluoroethylene**. **Teflon** paste material can be transported by lymphatics (HSDB, 2005).

### ECOTOXICITY DATA

Algae	
Crustacean	
Fish	
Bacteria	

Additional information:

Birds are susceptible to a respiratory condition called "Teflon toxicity" or "PTFE poisoning/toxicosis" (Wells, 1983). Deaths can result from this condition, which is due to the noxious fumes emitted from overheated cookware coated with polytetrafluoroethylene (PTFE). This chemical is found on most non-stick cookware and appliances, some stain repellant products, and other household items.

Eight other studies on Teflon toxicity to birds are cited in FANPP (2005).

### ENVIRONMENTAL FATE

Bioaccumulative potential	
BCF or BAF	
Half-life (include media)	
Henry's Law Constant (atm- m <sup>3</sup> /mole)	
Degradability	
Degradation products	Specific dose-response relationships for human exposures are difficult to determine due to the differences in <b>Teflon</b> decomposition products generated under various workplace conditions. Different <b>Teflon</b> decomposition products vary widely in toxicity in experimental animals (HSDB, 2005). Pyrolysis products are irritating to mucous membrane (HSDB, 2005). Above 400 deg C the quantity of pyrolysis products increases rapidly & so

Washington State Department of Health	Deca-BDE Alternatives Assessment
	<ul> <li>does their toxic nature. Small amounts of hydrogen fluoride have been identified, as well as octafluoroisobutylene (HSDB, 2005).</li> <li>At temp above 500 deg C, other toxic thermodegradation products are produced. When heated in temp range of 500-650 deg C, the predominant product is carbonyl fluoride. If the temp is increased above 650 deg C, the products formed are carbon tetrafluoride &amp; carbon dioxide (HSDB, 2005).</li> <li>When heated to above 750 deg F, decomposes to yield highly toxic fumes of fluorides (HSDB, 2005).</li> <li>Perfluoroisobutene, oxygen difluoride, and carbonyl fluoride are thermal decomposition products with respiratory toxicity (FANPP, 2005).</li> </ul>
Aerobic biodegradation	
Anaerobic biodegradation	
Other	

Additional information

### ECOLOGY PBT CRITERIA

<ol> <li>Persistence: Half life in water, soil or sediments ≥ 60 days.</li> </ol>	
2. Bioaccumulation/Bio-concentration factor: BCF or BAF $> 1000$ ; or log K <sub>ow</sub> $> 5$	
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	Mammalian and avian toxicity, primarily due to inhalation of heated Teflon.
4. Is the chemical an Ecology PBT?	

Additional information

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### HEALTH AND ENVIRONMENT SUMMARY

- Polymer fume fever may result upon inhalation of heated Teflon. Many pyrolysis products (e.g., perfluoroisobutene, oxygen difluoride, carbonyl fluoride) have associated toxicity. This has been observed in humans, other mammals, and birds. Avian species appear particularly sensitive to this exposure pathway.
- 2) In terms of carcinogenicity, no reliable data are available in humans, and there is inadequate evidence of carcinogenicity in animals. The overall evaluation by the International Agency for Research on Cancer (IARC) is Group 3 (i.e., agent is not classifiable as to its carcinogenicity to humans). Note that tumors have been noted with Teflon implants in rats, although results appear equivocal.
- 3) Based on toxic pyrolysis products associated with Teflon, Teflon should not be recommended as an alternative to deca-BDE.

#### NOTES

Reports/other sources that contributed information:

Danish reports: No German report: No UK report: No Lowell report: Yes CPSC/NAS reports: No EPA Penta report: No EPA FOIA request: No EPA HPV: No EPA IRIS file: No Accelrys run: No EU Risk Assessment: No

### Washington State Department of Health

### SOURCES/REFERENCES

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- 2. FANPP. 2005. Fluoride Action Network Pesticide Project. Online at <u>http://www.fluoridealert.org/pesticides/epage.Teflon.htm</u>.
- 3. HSDB. 2005. Hazardous Substance Data Bank. Online at <u>http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?./temp/~BAxqaT:1</u>.
- 4. Merck. 1989. The Merck Index, 11<sup>th</sup> ed., Merck and Co., Inc., Rahway, NJ.
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- 6. RTECS. 2005. Registry for Toxic Effects of Chemical Substances. Online at <u>http://ccinfoweb2.ccohs.ca/rtecs/Action.lasso?-database=rtecs&-layout=Display&-response=detail.html&-op=eq&RTECS+NUMBER=KX4025000&-search</u>.
- 7. Wells, RE. 1983. Fatal toxicosis in pet birds caused by an overheated cooking pan lined with polytetrafluoroethylene. J Amer Veter Med Assoc 182:1248-1250.

### Additional information should be submitted to:

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# **Deca-BDE** Alternatives Assessment

Name: Anti	nony trioxide
Date Updated:	12/30/05

#### **IDENTIFICATION**

CAS number:	1309-64-4
EINECS:	215-175-0
EINECS name:	
Molecular formula:	Sb2O3
Known uses:	Flame retardant synergist used with organohalogen flame retardants or halogen containing resins such as PVC and other polymers. Other applications include paint and coatings, textile treatments, glass, ceramics, inorganic pigments, chemical manufacturing, petroleum refining, electronics and solid lubricants. (GLCC Laurel LLC, Technical Information on Thermoguard S (Antimony trioxide). Used in combination with some brominated flame retardant as a synergist and may also be used with zinc borate. (NAS, 2000). Used in combination with halogenated flame retardants in ratio 2:1 to 3:1 (halogenated flame retardant: antimony trioxide). (German report, 2000)
Use (tonnage):	

Structural formula:

<sup>0</sup>≈<sub>Sb</sub>∽<sup>0</sup>∼<sub>Sb</sub>≠<sup>0</sup>

(from NIST Chemistry Web Book)

EU classification annex:	
Synonyms	Diantimony trioxide
Additive or Reactive FR	
Halogenated?	No

Washington State Department of Health

### Additional Information

### PHYSICO-CHEMICAL CHARACTERISTICS

Physical form	Crystal (NAS, 2000). Colorless, crystalline compound (German report, 2000).
Molecular weight	291.5 g/mol
Boiling point/range (deg C)	1550 deg C
Melting point (deg C)	656 deg C
Decomposition temp. (deg C)	
Vapor pressure (mg Hg)	1 x 10 <sup>-10</sup> mm Hg
Relative density	5.2 g/cm3 (senarmontite), 5.7 g/cm3 (valentinite) (NAS, 2000). Relative density: 5.5 kg/m3 (IUCLID Dataset, 2000).
Water Solubility (in water; g/L)	0.066 mg/L @ 25 deg C (EPIWIN). Very slightly soluble in cold water; slightly soluble in hot water; soluble in KOH, HCl, tartaric acid and acetic acid (NAS, 2000). < 0.0287 g/l at 20 deg C (IUCLID Dataset for diantimony trioxide, 2000).
Partition coefficient (log Kow)	$Log K_{ow} = 6.23$ (modeled using EPIWIN).
РКа	
Flammability	
Explosivity	
Oxidizing properties	
Mobility	

Additional Information

### HUMAN EPIDEMIOLOGICAL DATA

HUMAN		
Epidemiological studies	The potential carcinogenicity of antimony trioxide has been evaluated in 3 occupational epidemiological studies. One study suggests a correlation between antimony trioxide exposure and lung cancer. However limitations of this study include lack of a control group and failure to control for confounding factors (NAS, 2000).	
Occupational studies	Primary concern in occupational setting is inhalation of antimony trioxide dust. ACGIH TLV for antimony trioxide of 0.5 mg antimony/m3 (ACGIH, 2004).	

Washington State Department of Health	Deca-BDE Alternatives Assessment
	es of antimony smelter workers showed that workers developed noconiosis, chronic cough, and upper airway inflammation associated

pneumoconiosis, chronic cough, and upper airway inflammation associated with chronic exposure to antimony trioxide. However, these studies lacked individual exposure data and appropriate control for other exposures that precluded implicating antimony trioxide as the causative agent (NAS, 2000). Dermatitis reported in workers related to antimony trioxide present in the workplace, although quantitative data on dermal exposure was lacking (NAS, 2000). Blood and urine antimony levels have been monitored in workers (NAS, 2000).

Biomonitoring studies

Additional information: Antimony trioxide did not appear to be a skin irritant or sensitizer in a controlled human study (NAS, 2000).

### TOXICOLOGICAL DATA

ACUTE		
Oral	LD50 (rats) > 20 g/kg bodyweight. LD50 (rats) > 34.6 g/kg. Diarrhea was reported in rats administered 16.7 g/kg bw antimony trioxide in oil by gavage.	
Dermal		
Inhalation	Rat (100-125 mg/m3; 100 hr/mo; 14.5 mo) LOAEL = 13.9 mg/m3. Rabbit (89 mg/m3; 100 hr/mo for 10 mo) LOAEL = 12.4 mg/m3. Guinea pig (45.4 mg/m3 (avg); 2-3 hr/day, 7day/wk for 6 mo) LOAEL = 3.8 mg/m3. Rat (45.5 mg/m3; 7 hr/day; 5 day/wk for 52 wk; 20 wk observation) LOAEL = 9.4 mg/m3. Rat (0.25, 1.08, 4.92, or 23.46 mg/m3; 6 hr/day, 5 day/wk for 13 wk; 27 wk observation) NOAEL (human equiv. Conc.) = 0.006 mg/m3; LOAEL (human equiv. Conc.) = 0.006 mg/m3; 6 hr/day, 5 day/wk for 1 yr) LOAEL = 0.01 mg/m3; LOAEL (human equiv. Conc.) = 0.004 mg/m3. Rat (1.9, 5.0 mg/m3; 6 hr/day, 5 day/wk for 1 yr) LOAEL = 0.3 mg/m3. Rat (0.027, 0.082, 0.27 mg/m3 for 24 hr/day for 21 day of gestation) NOAEL = 0.027 mg/m3; LOAEL = 0.082 mg/m3. (NAS, 2000; Table 10-2)	
Other		
Skin irritation		
Eye irritation		
Respiratory tract irritation		
Skin sensitization		
Inhalation sensitization		
	SUBCHRONIC	

Oral	Rats (500 and 1000 mg/kg-day for 24 weeks) LOAEL = 500 mg/kg-day. Rats (90 day feeding study) NOAEL = 494 mg/kg-day; LOAEL = 1879 mg/kg-day. (NAS, 2000). Based on this last study, an oral RfD of 0.2 mg antimony trioxide/kg-day was determined by NAS (NAS, 2000). Critical effects used for the basis of the RfD are increases in serum enzymes and increased liver weight.
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Washington State Department of Health	Deca-BDE Alternatives Assessment	
Inhalation	Guinea pigs exposed to antimony trioxide for 2-3 hr/day for 6 months developed pneumonitis, liver and spleen effects and decreased white blood cell counts (NAS, 2000). Rats and rabbits developed pneumonia following exposure for 100 hr/month for 14.5 months and 10 months, respectively (NAS, 2000).	
Dermal		
	GENOTOXICITY AND CARCINOGENICITY	
Mutagenicity	Not mutagenic in Salmonella typhimurium or E. coli strains. (NAS, 2000)	
Gene mutation		
Chromosome abnormalities	Mice: Chromosomal aberrations in bone marrow cells were observed following repeated doses of antimony trioxide. Repeated oral doses of antimony trioxide	

caused unscheduled DNA synthesis in rat liver cells or an increase in micronucleated polychromatic erythrocytes in mouse bone marrow micronulceus assey. (NAS, 2000). Sister chromatid exchange has been observed in V79 Chinese hamster cells. DNA damage observed in Bacillus

#### Cancer review:

Other genotoxic effects

Antimony trioxide was associated with cancers in two rat studies. However, conflicting results were obtained in a different rat study and in a pig study. (NAS, 2000). Studies that reported positive findings: Rat (45.5 mg/m3; 7 hr/day; 5 day/wk for 52 wk; 20 wk observation) LOAEL (duration adjusted exposure) = 9.4 mg/m3 (lung tumors); Rat (1.9, 5.0 mg/m3; 6 hr/day, 5 day/wk for 1 yr) LOAEL = 0.3 mg/m3 (lung tumors) (NAS, 2000).

subtilis in Rec assays (NAS, 2000).

Antimony trioxide is designated as a "possibly carcinogenic to humans" by IARC. (IARC, 2005).

### **REPRODUCTIVE TOXICITY, EMBRYOTOXICITY, AND TERATOGENICITY**

Reproductive toxicity	
Teratogenicity	Rats (0.027, 0.082, and 0.27 mg/m3 for 24 hr/day throughout 21 days of gestation) LOAEL = 0.082 mg/m3; NOAEL = 0.027 mg/m3. However, study lacked information on purity and particle size of antimony trioxide used and observation of maternal toxicity (NAS, 2000).
Embryotoxicity	

Additional information

OTHER TOXIC ENDPOINTS (NEUROTOXICITY, RESPIRATORY TRACT)		
Respiratory Tract	EPA RfC = $2 \times 10^{-4}$ mg/m3 (pulmonary toxicity, chronic interstitial inflammation, based on rat 1-year inhalation toxicity study) (EPA IRIS file)	
Neurotoxicity		



Deca-BDE Alternatives Assessment

Other toxicity information:

### TOXICOKINETICS

Absorption/Distribution	Studies indicate that antimony trioxide is absorbed dermally in rabbits (NAS, 2000). Elevated antimony levels have been measured in blood and urine of workers occupationally exposed to antimony. This suggests that antimony trioxide is absorbed following inhalation exposure. (NAS, 2000).
Metabolic pathways/products	
Metabolic pathways/products	

Additional information:

### ECOTOXICITY DATA

Algae	EC50 = 67 mg/l (72 hours) (Selenastrum capricornutum) (IUCLID Dataset, 2000).
Crustacean	EC50 > 1000 mg/l (48 hours) (Daphnia magna) (IUCLID Dataset, 2000).
Fish	LC50 > 1000 mg/l (96 hours) (Brachydanio rerio) (IUCLID Dataset, 2000).
Bacteria	EC10 and EC50 > 3.5 mg/l (7 hours) (Pseudomonas putida) (IUCLID Dataset, 2000).

Additional information

### ENVIRONMENTAL FATE

Bioaccumulative potential	
BCF or BAF	BCF = 12500 (modeled using EPIWIN). BAF = 100 (L/kg) (Oak Ridge National Laboratory, RAIS database, 10/05). However, estimating BCF and BAF may not be appropriate for metals (McGeer et al., 2003).
Half-life (include media)	
Henry's Law Constant (atm- m <sup>3</sup> /mole)	
Degradability	
Degradation products	

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Aerobic biodegradation		
Anaerobic biodegradation		
Other		

Additional information

### ECOLOGY PBT CRITERIA

1. Persistence: Half life in water, soil or sediments $\geq 60$ days.	Not readily degrade by heat; not very soluble; no persistence data given
2. Bioaccumulation/Bio-concentration factor: BCF or BAF $> 1000$ ; or log K <sub>ow</sub> $> 5$	Log $K_{ow} = 6.23$ (modeled); BCF = 12500 (modeled); BAF = 100 (L/kg). Conflicting BAF/BCF, possibly related to inappropriate application of BAF/BCF for a metal compound.
3. Toxicity: Is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant; has an RfD or equivalent of $< 0.003$ mg/kg- day; or has a chronic NOEC or equivalent of $< 0.1$ mg/L or an acute NOEC or equivalent of $< 1.0$ mg/L.	RfC = 2E-4
4. Is the chemical an Ecology PBT?	Probably, depending on persistence determination which is likely to be >60 days based on its heat stability and low solubility. Need experimental information on bioaccumulation potential to validate modeled Kow and BCFs.

Additional information

### HEALTH AND ENVIRONMENT SUMMARY



Deca-BDE Alternatives Assessment

### NOTES

Reports/other sources that contributed information:

Danish reports: Yes German report: Yes UK report: Yes Lowell report: No CPSC/NAS reports: Yes EPA Penta report: No EPA FOIA request: Yes, with available studies EPA HPV: No EPA IRIS file: Yes (has an RfC) Accelrys run: No EU Risk Assessment: Yes (by Sweden) Washington State Department of Health Deca-BDE Alternatives Assessment

### SOURCES/REFERENCES

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- GLCC Laurel LLC, Technical Information on Thermoguard S (antimony trioxide), FireShield H (antimony trioxide) and TMS/Timonex Red Star (antimony trioxide). Available at: <u>http://www.el.greatlakes.com/corp/common/jsp/index.jsp</u>
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- Environmental research plan of the German Federal Ministry for the Environment, Nature Conservancy and Nuclear Safety, 2000. Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals. Research report 297 44 542.
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- McGeer et al., 2003. Inverse relationship between bioconcentration factor and exposure concentration for metals: implication for hazard assessment of metals in the aquatic environment. Environmental Toxicology and Chemistry, 22(5): 1017-1037.

### Additional information should be submitted to:

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# Appendix G: Definitions of terms and ranking criteria for Table 12

### Table 12 appears in Chapter V, Alternatives.

### Definitions/Technical Notes for Columns in Table 12

### Use:

This parameter describes the use of chemical in either HIPS or HIPS/PPO. Use in other materials or products are not listed in table, but may occur.

### Reactive or Additive:

This parameter describes whether the chemical is a reactive or additive flame retardant in HIPS or HIPS/PPO. Some chemicals can be both reactive and additive depending on the material in which they are used.

### Human Health Effects:

The system of low, medium and high concern for health effects is based on the ranking system developed by EPA for the analysis of alternatives to Penta-BDE in low-density furniture foam.<sup>469</sup> The concern levels are defined as:

Concern Level	Human health criteria
Low	No concern identified
Medium	Suggestive animal studies, analog data, or chemical class known to produce toxicity
High	Evidence of adverse effects in human populations or conclusive evidence of severe effects in animal studies

- 1. Cancer hazard: Degree of concern for chemical as a cancer causing agent is ranked as low, medium, or high depending on available information from human epidemiological studies, animal toxicity studies, or in vitro bioassays.
- Non-cancer effects: Degree of concern for non-cancer effects is ranked as low, medium, or high depending on available information from human epidemiological studies, animal toxicity studies, or in vitro bioassays. Non-cancer effects include developmental and reproductive effects, neurotoxic effects, or effects on specific organs/organ systems such as the liver, kidney or respiratory tract.
- 3. Mutagenicity: Degree of concern for mutagenic activity of chemical ranked as low, medium, or high depending on available information from the Ames test or other mutagenicity or chromosomal aberration tests.

### *Ecotoxicity (aquatic and microbial):*

This parameter provides the degree of concern for chemicals to cause toxicity in aquatic and microbial organisms including acute or chronic effects. The acute effect values consist of a  $LC_{50}$ 

for fish and daphnid, and an  $EC_{50}$  for algae. The system of low, medium and high concern for ecotoxic effects is based on the ranking system used by EPA for the analysis of alternatives to Penta-BDE in low-density furniture foam.<sup>470</sup> The concern levels are defined as:

Concern Level	Ecotoxicity (aquatic) criteria
Low	Acute value is $> 100 \text{ mg/L}$ (chronic value $> 10 \text{ mg/L}$ ).*
Medium	Acute value is between 1 and 100 mg/L (chronic value >0.1 and <10 mg/L)
High	Acute value is $< 1 \text{ mg/L}$ (or chronic value is $< 0.1 \text{ mg/L}$ )

\* It is noted in the EPA Penta-BDE alternatives report, that "if the water solubility is estimated, the chemical will not be considered to have no effects at saturation if the estimated value is within a factor of 10 percent of the cutoff value. The concern level will be considered low if no effects at saturation (below the solubility limit)."

The toxicity criteria in the Ecology PBT rule (Chapter 173-333 WAC) are:

The chemical or chemical group has the potential to be toxic to humans or plants and wildlife based on credible scientific information that:

- *i. The chemical (or chemical group) is a carcinogen, a developmental or reproductive toxicant or a neurotoxicant;*
- *ii.* The chemical (or chemical group) has a reference dose or equivalent toxicity measure that is less than 0.003 mg/kg/day; or
- iii. The chemical (or chemical group) has a chronic no-observed effect concentration (NOEC) or equivalent toxicity measure that is less than 0.1 mg/L or an acute non-observed effect concentration (NOEC) or equivalent toxicity measure that is less than 1.0 mg/L. (Note: This is equivalent to the "High" concern level listed in the table above take. These chronic criteria are also the chronic criteria listed in EPA's PBT Profiler (Fish chronic value = geometric mean of LOEC and NOEC; available at <u>http://www.pbtprofiler.net/criteria.asp</u>)

The assessment of ecotoxicity omits terrestrial (soil) ecotoxicity criteria (e.g., birds, mammals, reptiles). This omission is due to the complexity and lack of data on chemical bioavailability and bioaccumulation in soil matrices, relative to aquatic systems. Considerable effort would be needed to develop defensible PBT criteria for soil ecotoxicity.

### Amount of toxicity information:

This parameter provides a summary of the amount of toxicity information available with which to make an assessment of human health effects or ecotoxicity (aquatic and microbial toxicity).

Amount of toxicity information	Number, types and sources of studies and other information
Low	Studies/information lacking for more than one endpoint (human health or ecotoxicity). Existing studies consist mainly of unpublished literature.
Medium	Studies/information is available for most endpoints. Studies include peer-reviewed published (e.g. MEDLINE) and unpublished literature.
High	Available studies/information for each endpoint of interest. Studies consisting of mainly published literature.

### Potential routes of exposure:

This parameter indicates whether there is information on potential routes of human exposure. This information could be in the form of biomonitoring data, occupational studies, environmental monitoring data, or predicted/modeled exposure estimates.

### Persistence:

Environmental persistence was evaluated using the persistence criteria in Ecology's PBT rule:

"The chemical or chemical group can persist in the environment based on credible scientific information that:

- i. The half-life of the chemical in water is greater than or equal to 60 days; or
- ii. The half-life of the chemical in soil is greater than or equal to 60 days; or
- iii. The half-life of the chemical in sediments is greater than or equal to 60 days;"

### Bioaccumulation:

Bioaccumulation potential was evaluated using the bioaccumulation criteria in Ecology's PBT rule:

"The chemical or chemical group has a high potential to bioaccumulate based on credible scientific information that the bioconcentration factor or bioaccumulation factor in aquatic species for the chemical is greater than 1000 or, in the absence of such data, that the log-octanol water partition coefficient (log Kow) is greater than 5...."

### PBT:

This parameter refers to whether the chemical qualifies as a PBT under Ecology PBT criteria (the PBT rule can be viewed at: <u>http://www.ecy.wa.gov/programs/eap/pbt/pbtfaq.html</u>). The criteria for persistence, bioaccumulation, and toxicity are outlined above. In order for a chemical to be categorized as a PBT, it must meet Ecology's criteria for persistence, bioaccumulation and toxicity.

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# Appendix H: Cost Benefit Analysis Tables

### Table H-1

### Assumptions Underlying the Choice of Electronic Housings as Focus

- Large percentage of Deca-BDE use is in consumer electronics as part of electronic housings. (See below for data sources and range)
- European Union (EU) had already listed consumer electronics in the context of PBDE removal.
- Business community had reported removal of Deca-BDE in response to the EU's actions. This would reduce the cost of a Washington action. (See Table H-3)

http://www.bsef-site.com/bromine/our\_industry/index.php Total Market Demand by Region in 1999 in Metric Tons (MT)

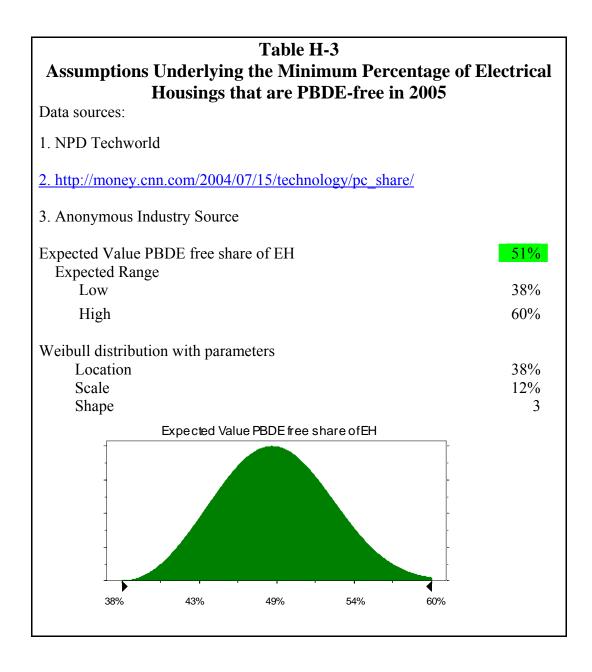
Business Communications Co. Inc. C-004A Flame Retardant Chemicals Marcanne Green, Project Analyst

Lowell Center for Sustainable Development, Decabromodiphenylether: An Investigation of Non-Halogen Substitutes in Electronic Enclosure and Textile Applications 2005

Estimated average percent of total deca use in electronic housings (for Monte Carlo) 58% Range Low 44% High 72% Insufficient data for distribution

## Assumptions about Affected Sectors in Washington

- Washington manufacturers have many customers outside of the state and therefore would be likely to pass costs imposed by a ban on to their wholesalers.
- Washington wholesalers would incur some additional costs, depending on what share of their retailers sell in Washington.
- Washington retailers would incur significant costs in so far as they sell to Washington buyers.
- Washington consumers probably expect that the trend of lower and lower prices for electronics will continue. Thus they would react negatively to increased prices. They may choose not to face additional costs since they can function in a world market. A general buying trend is for purchases to be made via the internet with 18% of computers and 10% of other electronics being done as e-purchases. (Census 2000) (Shipping costs are rarely higher than the Washington sales tax.) If prices rose or failed to drop as expected the continued shift to online purchasing may be exacerbated. We assumed therefore a limited ability of retailers to shift costs to consumers and that consumers will continue to shop out-of-state to buy at cheaper prices (driving to Oregon, using the internet, etc.), rather than pay higher prices for deca-free products. A lower share of the monitors offered for sale on the internet are CRTs (6%) than in stores (15%) [Data collected Nov. 2005].



# Table H-4Business Cost Model

Business Cost Model							
NAICS data							
The Department of Revenue has gross business income data based on NAICS codes. This data was to be used in conjunction with survey data in order to estimate the impact of a ban on businesses by sector. NAICS codes were converted to SIC codes in order to obtain data on names and addresses of companies from Work Force Explorer. From the 10 firm listings businesses were selected at random based on numbers drawn from a random number table. The following SIC codes were selected: 5045 5064 5065 5311 5331 5399 5731 5961							
The set of random numbers used was structured to attempt to get approximately 30 companies in each SIC code. An exception to this was code 5045, which initially seemed to have a larger number of yes responses to question 1 on the survey. The sample size in this SIC was doubled. Sources							
http://dor.wa.gov/content/statistics/TID/ResultsGBISet.aspx?Results=GBI&Year=2003, &Code1=313210&Code2=812332&Format=HTML&Sumby=n6&SicNaics=2 download 7/29/05							
http://www.census.gov/epcd/naics02/N02TOS87.HTM http://www.workforceexplorer.com/cgi/databrowsing/industryexplorerselection.asp menuChoice=indExplorer							
Calculations							
The NAICS data was used to establish the initial cut offs for income and employment for the survey.							
I. Average Gross Business Income = Gross Business Income/Number of Firms							
This yielded the average figure \$2.5 million in sales as the cut off for small vs. large firms for the survey. Once the survey was completed and several sectors were eliminated as having no possible impact, the average figure changed to \$4.5 million. This tends to indicate that impacts will be more prevalent in somewhat larger firms than Ecology initially expected.							
Sources: NAICS DOR data.							
Center point for employment ranges							
Companies in workforce explorer are divided by employment classes. The following center point was selected for each of the following classes:							
Emp. Range $1-4 = 2$ Emp. Range $5-9 = 7$							
Emp. Range 10-19 = 15							
Emp. Range 20-49 = 35 Emp. Range 50-99 = 75							
Emp. Range $30-99 = 75$ Emp. Range $100-249 = 175$							
Emp. Range 250-499 = 350							
Emp. Range 1,000-4,999 = 3000							

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			Tab	ole H-4					
Business Cost Model –cont.									
Survey data									
Emp	all small	small - r	ne small - m	e range	small - me	all small	small - 1 lg	small	
			als: all Sicc				Ĭ		
	5045					5399			Row totals
No tv or comp 1-4	2		16 13			17			
No tv or comp 5-9	7		2 7				4		29
No tv or comp 10-19	3		5 4			1			22
No tv or comp 20-49	4		2 1				1		16
No tv or comp 50-99 No tv or comp 100-249				1 2					1
No tv or comp 250-499	2			1					3
No tv or comp 1,000-4,999				1					1
Never got through	27		2	5		7	/ 15	7	
Refusal								1	1
Phone disconnected	11		3	3 1		4	9		
Bankruptcy					1			2	
Duplicates				2					2
Surveys sent	13			4			9		28
Surveys received	3						3		0.07
Column totals	69		27 30		29	29	51		
sell:	Ye			Yes1				Yes	
% of sales TVs:		0%		709					90
% from list companies:		0%		1009					95
% of sales electronic not tv	r.	100%		309	%				10
% from list companies:		0%		1009	%				50
employees > 50:	5 to	o 9		1 to 4				Yes	4
dollars > 2.5M:	Ye	s5		Yes5				Yes	
B1:		bmit		Submit				Sub	-
51.	00	Junit		Cubinit				Out	
Affected		100%							
		100 %			0				
% br					0				
sell:	Ye							No1	
% of sales TVs:		0							
% from list companies:									
% of sales electronic not tv	r.	100%							0
% from list companies:		100%							0
	<b>F</b> .							1 to 19	4 or 10 ·
employees > 50:	5 to								-
dollars > 2.5M:	noŝ							Yes	
B1:	Su	bmit						Sub	mit
		0							
sell:	Ye	s1						Yes	1
% of sales TVs:		0							5
% from list companies:		0							
% of sales electronic not tv	r.	100							95
% from list companies:		20							70
employees > 50:	1 to							5 to	
dollars > 2.5M:	not	o bmit						no5	
B1:		trong						Sub	tion

### Business Cost Model – cont.

Data calculations

Ecology had intended to use the survey data to do the following calculation but was unable to do so because of problems with the survey.

II. SIC Weighted Average of Affected Sales = 
$$\sum_{i} SiEiNi / \sum_{i} NiEi$$

Where for each SIC:

Si = percent share of sales affected in employment group i

Ei = number of employees in group i

Ni = number of firms in employment group i

This would constitute a weighted average for an SIC percentage share of affected sales.

### NAICS conversion

The SIC to NAICS conversion is not perfect. Some codes have one for one correspondence. Some codes have more than one SIC. Some SICs must be divided across NAICS codes. This is the conversion Ecology intended to use.

III. NAICS % Affected Sales = Average of SIC weighted averages

```
423430 5045
423690 5065
424610 5162 & 5199
425110 many + 5045, 5064
443112 5064 & 5731
443120 5045
452111 5311
452112 5311
452910 5399, 5411
452990 5331, 5399, 5513
454111 5961
454112 5961
```

For NAICS with multiple SICs the average impact would have been used. For SICs with multiple NAICS (ex. 5045) the impact for both NAICS would have been the same.

### Affected sales

Affected sales would have been summed over all sectors based on the percent of affected sales multiplied by the NAICS total sales for each sector.

IV. Total affected sales = 
$$\sum_{j} GBIjNAICS\% j$$

Where:

GBIj = Gross Business Income for NAICS sector j NAICS%j = The percent of sales affected for NAICS sector j

Total costs

The total costs were expected to be based on the price increase that would have been necessary for the retail sector to recover their expected costs. Thus the share of affected sales would have been multiplied by a percentage increase in the cost of the product offered to consumers.

V. Total Cost = Total Affected Sales x % Price Increase

The % price increase would have been based on a survey of manufacturers.

This survey is incomplete because of the failure of the initial survey and because of the difficulty in providing manufacturers with confidentiality.

# Table H-5Individual Cost Model

The individual's expenditures are estimated based on the estimated price of products, the estimated lifespan of products and the rate at which the products are turned over in the home.

I. 
$$C = \sum_{i=0}^{n} \sum_{x=1}^{z} P_{ix} x N_{ix} S_x / (1+r)^i$$
  
Where:  $P_{ix} = the price of product x in time period i
 $N_{ix} = the number of products x purchased in time period i
 $x = the product type$   
 $S_x = affected share of the product$$$ 

### **Basis for Assumption that Cost of Illness Values Used are Conservative**

### **Underestimation Bias**

- Cost of illness does not measure the consumer surplus provided to the patient by good health.
- Cost of illness and the outcomes of treatment are likely to be affected by comorbidity in a patient. Given this, the simple use of illnesses that present as linked to a pollutant may understate the effect. The depressive effect of a pollutant on health may exacerbate the effect of other disease and conditions.
- Some models predict that under specific sets of insurance circumstances the level of treatment for conditions may be suboptimal. Further, chronic illness reduces the likelihood of adequate coverage by 10 percent.
- For insured employees who are affected by either their own or by a family member's chronic illness, job lock reduces job mobility by 40% and has statistically significant effects on income in spite of HIPPA.
- The unemployed are less likely to be insured and therefore less likely to have adequate care. About 10% of the unemployed are unemployed due to chronic illness.
- Willingness to sell differs from willingness to pay. A patient affected by a pollutant probably has the legal right to say no to a contaminant being introduced into their home. The willingness to sell value is not constrained by ability to pay.
- Unequal information can create a situation where a patient might have avoided a risk, had it been known. Inadequate warning labels can lead to excessive introduction of risk due to unequal availability of information.
- Parents are willing to pay more to avoid impacts to their child than to avoid impacts to themselves.

### **Overestimation Bias**

Moral hazard creates excessive use of medical services. With insurance and government subsidies, the direct payment for a specific medical service is not fully carried by the patient, and thus may not equal willingness to pay. Therefore the societal cost of the illness is not necessarily equal to the societal willingness to pay.

### Key Assumptions Underlying Benefits Estimates for Thyroid-Related Development Effects

### Hazard Assessment

- Pregnant women and the developing fetus are sensitive to thyroid hormone disruption and small changes in maternal thyroid hormone levels can adversely impact on the intelligence and psychomotor skills of children.
- People are exposed to a mixture of congeners because Deca-BDE can break down into lower-brominated congeners in the environment. The nature and extent of Deca-BDE degradation is uncertain.
- Results from rodent bioassays are a predictor of risks to human health. Deca-BDE and its' potential breakdown products have been found to disrupt thyroid function (e.g. reduced thyroid hormone levels, thyroid follicular cell hyperplasia, etc.) in rodent bioassays (Zhou et al. 2001, 2002; NTP, 1986).

### **Dose Response Relationship**

- Maternal levels of thyroxine ( $T_4$ ) are a measure of thyroid hormone homeostasis. A 20% reduction in  $T_4$  levels is an indicator of hypothyroidism in rodent bioassays.
- Dose-response information for Penta-BDE and Octa-BDE mixtures provides a reasonable basis for evaluating the health risks associated with Deca-BDE/breakdown products.
- Linear extrapolation from the lower 95<sup>th</sup> percent confidence limit on the benchmark dose (BMDL) provides a reasonable method for extrapolating from high to low exposures.
- Probability of adverse effects in the developing fetus/pregnant mother can be estimated based on relationships between maternal hypothyroidism and specific health endpoints (e.g. reduction in IQ scores, low birth weight, hypertension, fetal death/miscarriage).

### **Exposure Assessment**

- Daily intakes (ug/kg/day) can be estimated using information on lipid normalized concentrations (expressed in terms of ug/g<sub>lipid</sub>) of Deca-BDE in serum and breast milk, fraction body fat, body weights, half-life of Deca-BDE in the human body and the fraction of ingested Deca-BDE absorbed into the body.
- Monte Carlo simulation can be used to factor in the variability in exposure parameters. The median, mean, and 95<sup>th</sup> percentile values from the calculated distribution provide low, mid-range and high exposure estimates.
- Information on lipid normalized blood and breast milk concentrations from other parts of the United States can be used to estimate concentrations in WA.
- The EPA Exposure Assessment Guidelines (EPA, 1997, 2002) provide point estimates and distributions for key exposure parameters (e.g. body weight) that are applicable to the WA population.
- Exposure reductions will occur over a 1-18 year period as existing TVs and computers are replaced with products that do not contain Deca-BDE.

### **Potentially Exposed Populations**

- All WA residents may be exposed to Deca-BDE because it is used as a flame retardant in TVs and computers.
- There will continue to be @80,000 births/year in WA (WDOH, 2005).

### **Uncertainty and Variability**

- Sources of uncertainty include: (1) nature and extent of Deca-BDE degradation; (2) use of dose-response information from lower-brominated PBDE mixtures to evaluate Deca-BDE risks; (3) significance of reductions in T<sub>4</sub> levels observed in rodent studies in terms of predicting human health risks; (4) shape of the dose-response curve at low levels of exposure (including the presence/absence of a threshold for adverse effects in a heterogeneous population); (5) current and projected changes in Deca-BDE uses and environmental levels.
- Sources of variability include: (1) Variability in environmental concentrations of Deca-BDE and its potential degradation products; (2) intra-individual variability in exposure and factors that influence exposure; and (3) intra-individual variability in thyroid hormone levels and sensitivity to predicted reductions.

### Key Assumptions Underlying Benefits Estimates for Thyroid-Related Systemic Effects

### Hazard Assessment

- Children and adults are sensitive to thyroid hormone disruption and reductions in thyroid hormone levels can adversely impact human health (e.g. memory loss).
- Females and males are both sensitive to thyroid hormone disruption.
- People are exposed to a mixture of congeners because Deca-BDE can break down into lower-brominated congeners in the environment. The nature and extent of Deca-BDE degradation is uncertain.
- Results from rodent bioassays are a predictor of risks to human health. Deca-BDE and its potential breakdown products have been found to disrupt thyroid function (e.g. reduced thyroid hormone levels, thyroid follicular cell hyperplasia, etc.) in rodent bioassays (Zhou et al. 2001, 2002; NTP, 1986).

### **Dose Response Relationship**

- Levels of thyroxine (T<sub>4</sub>) are a measure of thyroid hormone homeostasis. A 20% reduction in T<sub>4</sub> levels is an indicator of hypothyroidism in rodent bioassays.
- Dose-response information for Penta-BDE and Octa-BDE mixtures provides a reasonable basis for evaluating the health risks associated with Deca-BDE/breakdown products.
- Linear extrapolation from the lower 95<sup>th</sup> percent confidence limit on the benchmark dose (BMDL) provides a reasonable method for extrapolating from high to low exposures.
- Probability of adverse effects can be estimated using information on the relationships between hypothyroidism and particular health endpoints (e.g. memory loss).

### **Exposure Assessment**

- See exposure assumptions in Table H-7.
- Estimated daily intakes for females (expressed in terms of ug/kg/day) can be extrapolated to males.

### **Potentially Exposed Populations**

- All WA residents may be exposed to Deca-BDE because it is used as a fire retardant in TVs and computers.
- Washington's estimated 2005 population is 6,256,000 people (OFM Intercensal Population Estimates) and will continue to increase in size by @1-2 percent per year.

### **Uncertainty and Variability**

- Sources of uncertainty include: (1) nature and extent of Deca-BDE degradation; (2) use of dose-response information from lower-brominated PBDE mixtures to evaluate Deca-BDE risks; (3) significance of reductions in T<sub>4</sub> levels observed in rodent studies in terms of predicting human health risks (e.g. relative sensitivity, adaptation/compensation, etc.); (4) shape of the dose-response curve at low levels of exposure (including the presence/absence of a threshold for adverse effects in a heterogeneous population); (5) current and projected changes in Deca-BDE uses and environmental levels.
- Sources of variability include: (1) variability in environmental concentrations of Deca-BDE and its potential degradation products; (2) intra-individual variability in exposure and factors that influence exposure; and (3) intra-individual variability in thyroid hormone levels and sensitivity to predicted reductions.

# Key Assumptions Underlying Benefits Estimates for Neurobehavioral Effects

### Hazard Assessment

- Pregnant women may be exposed to a mixture of congeners because Deca-BDE can break down into lowerbrominated congeners in the environment. The nature and extent of Deca-BDE degradation is uncertain.
- The developing fetus may be exposed to Deca-BDE and its breakdown products as a result of maternal exposure to these substances. The developing brain is particularly sensitive to environmental pollutants.
- Results from rodent bioassays are a predictor of risks to human health. Studies by Swedish researchers (Viberg et al. 2002, 2003a,b; Eriksson et al. 1996, 2002, 2003, 2004) have shown that several PBDEs (including Deca-BDE) adversely affect the ability of mice to habituate to new surroundings following exposure during early post-natal development. The ability to habituate is considered a simple test of learning and failure to habituate is considered evidence of cognitive impairment.

### **Dose Response Relationship**

- Dose-response information for PCBs provides a reasonable basis for evaluating the health risks associated with Deca-BDE/breakdown products.
- Scores on Intelligence Quotient (IQ) tests provide a measure of cognitive development.
- Dose-response information from Jacobson et al. (2002) provides a reasonable basis for estimating the relationship between PCB exposure and IQ scores.

### **Exposure Assessment**

- Estimated breast milk levels can be used as a measure of daily exposure (expressed in terms of ug/glipid).
- Information on lipid normalized breast milk levels from other parts of the United States can be used to estimate levels in WA.
- Adjustments for differences in the absorption of PCBs and Deca-BDE are not necessary because exposure is expressed in terms of internal exposure (e.g. breast milk levels) that already factors in such differences.
- Exposure reductions will occur over a 1-18 year period as existing TVs and computers are replaced with products that do not contain Deca-BDE.

### **Potentially Exposed Populations**

• See assumptions for potentially exposed populations in Table H-8.

### Sources of Uncertainty and Variability

- Sources of uncertainty include: (1) nature and extent of Deca-BDE degradation; (2) use of dose-response information for PCBs to evaluate risks associated with Deca-BDE/breakdown products; (3) significance of reductions in rodent's ability to habituate in terms of predicting human health risks; (4) shape of the dose-response curve at low levels of exposure (including the presence/absence of a threshold for adverse effects in a heterogeneous population); (5) current and future changes in Deca-BDE uses and environmental levels; (6) mechanisms of action and whether neurobehavioral effects are the result of thyroid hormone disruption or other mechanisms. (Results based on this calculation will need to be integrated with results based on thyroid-related development effects in order to avoid double-counting.)
- Sources of variability include: (1) variability in environmental concentrations of Deca-BDE and its potential degradation products; (2) intra-individual variability in exposure and factors that influence exposure; and (3) intra-individual variability in sensitivity to Deca-BDE.

# Table H-10Key Assumptions Underlying Benefits Estimates for Liver Cancer

### Hazard Assessment

- People are exposed to a mixture of congeners because Deca-BDE can break down into lower-brominated congeners in the environment. The nature and extent of Deca-BDE degradation is uncertain.
- Results from rodent bioassays are a predictor of risks to human health. Dose-related increases in the incidence of liver neoplastic nodules (current nomenclature = hepatoproliferative lesions) were observed in rats exposed to high levels of Deca-BDE (NTP, 1986).
- EPA (1990) has classified Deca-BDE as a possible human carcinogen. [NOTE: IARC and the NTP do not classify Deca-BDE as a carcinogen. Deca-BDE has not been found to be genotoxic in a variety of test systems.]

### **Dose Response Relationship**

- Dose-response information for PCBs provides a reasonable basis for evaluating the health risks associated with Deca-BDE/breakdown products.
- Slope of the line resulting from a linear extrapolation from the TD50 (dose estimated to induce tumors in 50% of experimental animals) to zero provides a reasonable estimate of a cancer potency factor for Deca-BDE. A TD50 can be calculated from the NTP (1986) study results.
- Eighty percent of people developing liver cancer in a given year will die of the disease in that year.

### **Exposure Assessment**

- See assumptions for exposure assessment in Tables H-7 and H-8.
- Adjustments for differences in the absorption of PCBs and Deca-BDE/breakdown products are needed because exposure is expressed in terms of estimated daily intakes (ug/kg/day).

### **Potentially Exposed Populations**

• See assumptions for potentially exposed populations in Table H-8.

### **Uncertainty and Variability**

- Sources of uncertainty include: (1) nature and extent of Deca-BDE degradation; (2) significance of the NTP (1986) bioassay results in terms of evaluating human cancer risks; (3) use of dose-response information from PCBs to evaluate Deca-BDE risks; (4) shape of the dose-response curve at low levels of exposure (including the presence/absence of a threshold for adverse effects in a heterogeneous population); (5) current and future changes in Deca-BDE uses and environmental levels; and (6) length of time between exposure and cancer development (latency period).
- Sources of variability include: (1) variability in environmental concentrations of Deca-BDE and its potential degradation products; (2) intra-individual variability in exposure and factors that influence exposure; and (3) intra-individual variability in sensitivity to Deca-BDE.

# Table H-11Description of the Methods Used and Theoretical Basis<br/>for Valuation of Health Impacts

### **Estimation Methods**

Medical costs of diagnosis and treatment:

Medical costs include the cost of diagnostic testing, in-patient or out-patient visits, and treatment of the illness or condition.

Direct care costs:

Direct care is the cost of non-medical care required. This can include care giver home visits, family lost hours of work, or institutional care.

The value of foregone wages:

Foregone wages is the most common measure of production losses due to illness. This would be an appropriate measure of loss unless there is more than frictional unemployment in the economy.

The value of lost productivity in the workplace:

Foregone wages are at least as high as the value of the marginal productivity of the worker. The value of lost wages may not constitute the total value of foregone production from absenteeism due to illness. Additional losses may take place if substitutes for the employee are imperfect, if the employee occupies a place in a team, or if there is a penalty associated with a product shortfall or a missed deadline. In cases involving a team approach, there will be losses beyond the wages that will come from higher wages, additional effort, additional overtime, and foregone leisure for a team. For substitutable workers, there may be overstaffing costs or overtime costs.

### Quality of Life Year (QUALY)

This technique compares diseases and disorders and their treatment against foregone time of life in order to create a comparative value for disease. The value of a QUALY for insurance and standard of care decisions is generally held to range between \$50,000 and \$80,000.

Willingness to pay:

Willingness to pay is based on the costs listed above plus some amount that people are willing to pay on behalf of them selves or on behalf of another to avoid feeling ill or experiencing damages to the body. Willingness to pay is constrained by income.

# Key Assumptions Regarding Health Values Selected

### Hypothyroid

- Individuals expend money to overcome disorders. The annual cost per case of thyroid conditions is \$7,940 based on 2004 direct billings to the Health Care Authority. Billings do not reflect all losses due to illness.
- The implicit assumption here is that this does not overstate the cost of hypothyroid and is therefore a conservative assumption.

### **IQ Losses**

- Individuals use their minds to obtain income for survival and quality of life. IQ losses are valued at \$14,500 per IQ point based on foregone earnings in 2000 dollars, with a range from \$12,700 to \$17,200. This value has been assigned a Weibull distribution with values ranging from \$12,700 to \$17,000 for the Monte Carlo and then indexed to 2004 values.
- The implicit assumptions here are that foregone income is a reasonable minimum value for IQ and that no major additional values are foregone.

### **Liver Cancer**

- Individuals expend money to overcome disorders and or to save their own lives. The cost of a single year of liver cancer per case was estimated at \$26,976 based on 2004 direct billings to the Health Care Authority. Billings do not reflect all losses due to illness. This cancer and its treatment are debilitating and for most there would also be foregone wages and/or a loss of quality of life. This value assumes recovery or mortality within one year and no value is added for a second year of treatment.
- The implicit assumption here is that the cost of treating cancer is, at a minimum, some part of actual willingness to pay.

#### Life

- Individuals understand risk and income or risk and expenditure trade offs. The values are based on cost of illness, wage and risk studies, and reported willingness to pay. The latter method assumes they do not lie on surveys. The value of a statistical life is large and values range from \$1 to \$16 million. Ecology chose \$4 million dollars as the value of life. This value has been assigned a Weibull distribution with a range from \$3 million to \$7 million in value for the Monte Carlo.
- The implicit assumption here is that the value of a life can be determined by one of several methods: Derived demand such as Wage/risk tradeoffs, and Expenditure/risk tradeoffs, or Stated Preference.

# Table H-13Benefits Model

Individual benefits are calculated based on:

The benefit for Washington = Reduced liver cancer x the cost of treating liver cancer +

Reduced mortality x the value of a statistical life +

Reduced subclinical hypothyroid x the cost of treating hypothyroid +

Reduced IQ loss x the value of IQ

Present Value (PV): The benefits are reduced to a present value by dividing each year's benefit by the principal plus interest accrued on a single dollar for that year. The benefits are calculated based on a lifetime of 82 years. The interest rate used is called "the social rate of time preference."

The value to the individual is calculated as:

The present value of lifetime benefits for all Washington citizens from banning all PBDE (formula I)

÷ The population of Washington (formula II)

x The share of PBDE in electronic enclosures

- x The multiplier for a reduction due to any delay in replacing electronic equipment
- x The multiplier for a reduction due to any delay between exposure and a health impact (formula III)

I. PV (B)= 
$$\sum_{i=0}^{n} Bi/(1+r)^{i}$$
  
Where: B = annual benefits  
i = the year which ranges from year 0 to year 82,  
r = the social rate of time preference

This present value will be reduced by the population to obtain the average value per person. Formula I would be calculated for both models.

II. 
$$b = PV(B) / P$$

Where:b=PV of individual benefits from immediate removal of all Deca-BDEP=the population of Washington

Formula II is done only for the individual model.

This individual value must be reduced because Deca-BDE removal does not occur immediately because product replacement takes place over time, the deca reduction is incomplete unless all product is deca free, and there is a waiting period between exposure and the beginning of the disorder.

III. 
$$bj = b \times \prod_{k} p_{k}$$

Where: bj  $= p_k$  = PV of individual benefits given the reduction and postponement of gain multiplier basis for postponement or reduction

Formula III would be done for both models.

Note: these values will be for current exposure levels and no allowance is made for a ramping up of the contaminants in the environment.

# Table H-14Cost Benefit Model

Lifetime Health Impacts	Number	Unit value	Index	Valu	es
Annual Cancer	5	\$ 26,97	6	S	134,879
Annual Cancer Mortality	4			\$	16,000,000
Annual Hypothyroid Cases Entering Treatment	2,400	\$ 7.94	1	S	19,056,000
Memory QUALYs foregone		NC		Ť	10,000,000
Annual Subclinical Hypothyroid Pregnancies	30		0	S	238,200
Annual Eclampsia/High blood pressure		NC	-	-	,
Annual Low Birth Weight	0	NC			
Annual Fetal Death	0.7	NC			
Annual Preterm					
Annual C Section	0.9	NC			
Annual IQ impacts	210	\$ 14,50	1.067	\$	3,250,327
				_	4 457 005 000
PV Health Impacts 82 years	P 1 2 2			\$	1,457,865,068
Share based on reducers below: EH, replacement,	disorder timing.			\$	500,214,838
Population	6,250,000				
Unparsed: Value per person				\$	233
DecaPBDE electronic housing share reduction	44%			\$	102
Delay to replace electronics	87%			\$	88
Delay to disorder timing	91%			\$	80
Per person value				\$	80
Electronics Expenditures					
Assumptions					
TV life span = purchase frequency	14.0				
# TVs in lifespan	5.9				
Computer lifespan = purchase frequency	10.0				
Computers in lifespan	8.2				
CRT Share	0.14				
Share of TV Product Affected			43%		
Maximum Share of Computer Product Affected*			5%		
Index			1.051		
Average current price of TV	\$ 465				
Average current price of Computer	\$ 1,120				
Monitor share of computer price	0.22				
PV lifetime TV expenditure				\$	579
PV lifetime computer expenditure				\$	52
PV Lifetime Expenditure				\$	630
Price increase for current PBDE laden product re	quired to break ev	ven.			12.70%

# Appendix I: Consumer Product Safety Commission Proposed Rules

# **Consumer Product Safety Commission (CPSC) Draft for Upholstered Furniture Flammability**

The Consumer Product Safety Commission is undergoing a rulemaking process and currently no flammability standards for residential upholstered furniture exist. Federally speaking, all flame retardant efforts undertaken by industry are completely voluntary. In 2000 it was estimated that less than 0.2% of all U.S. residential upholstery fabric was treated with flame retardant chemicals.<sup>471</sup> Individual states however, may have their own laws that drive the industry to develop flame retardant materials. California's flammability standard for upholstered furniture (TB 117)<sup>472</sup> currently leads the way, and some manufacturers make all upholstered furniture sold in the U.S. compliant to TB 117.<sup>473</sup> Manufacturers generally comply with TB 117 by using flame retardant-treated polyurethane foam or other foam filling materials, as cover fabrics need not be treated with flame retardant chemicals to comply with TB 117.<sup>474</sup> The new CPSC standards would include flammability requirements for cover fabrics, and when the rule on upholstery fabrics goes into effect it is estimated that flame retardants would be applied to approximately 600 million square yards of upholstery fabric each year.<sup>475</sup>

The CPSC is currently developing flammability standards for upholstered furniture, and has released a draft standard for the purpose of discussion.<sup>476</sup> The draft standard sets out four methods of compliance: Type 1, Type 2, Type 3, and Type 4, with each representing a type of upholstered furniture. The four Types are based on the kind of materials used in the makeup of upholstered furniture, including cover fabrics, filling materials, interior fire barrier materials, or end product materials. Each Type has its own flame test standard. The standard conducts two main flame tests: smoldering resistance, and an open flame test. For all Types of upholstered furniture, the smoldering resistance test requires that the various materials outlined in the standard withstand smoldering for 30 minutes with a maximum of 10% mass loss of the substrate material or loose resilient filling [depending on Type]. The second test requires an open flame resistance for 45 minutes, where the Types outlined in the standard lose no more than 20% of their mass. To give the industry greater flexibility in meeting compliance, the draft standard includes an optional seating barrier test that would allow the use of fire retardant barriers, or interliners, instead of retardant cover fabrics<sup>477</sup>. The draft standard requires that manufacturers and importers label their finished product with the method of compliance and the name of manufacturer or importer.

The CPSC is in the Advance Notice for Proposed Rulemaking Stage, with no date set for when the rule would be published in the Federal Register. A rule goes into effect 12 months after its publish date. The consumption of bromine-based flame retardants is expected to grow an average of 13.9% annually in response to upholstered furniture regulations in the U.S.<sup>478</sup> Currently, CPSC staff are conducting technical research to support the development of a draft flammability performance standard and released in July 2005 a series of technical documents available for public review at http://www.cpsc.gov/library/foia/foia05/brief/uphols1.pdf.

# Consumer Product Safety Commission (CPSC) Proposed Requirements for Mattresses and Mattress Pads.

The CPSC is proposing new flammability standards for mattresses and mattress pads, which would update previous federal regulations already in effect (16 C.F.R. Part 1632). The new standard will address open flame ignition of mattresses and mattress pads, and either replace or amend the previous standard, which focuses on preventing ignition from cigarettes. Included in the updated definition of mattresses and mattress pads are foundations, futons, multi-purpose items, and mattresses in upholstered furniture as well as renovated and imported products. The objectives for the new standards are:

- To keep fire size below 1,000 kW;
- To reduce the likelihood of involving other items in the fire; and
- To provide time for discovery and escape of fire by preventing or delaying flashover (the point at which ignition breaks out all surfaces and objects in a space)<sup>479</sup>

The regulation includes two performance measures to ensure the objectives for the proposed standards are met. Mattresses and mattress pads undergo a full-scale 30-minute flame test with gas burners and three replicate tests. The regulations dictate that total heat release from the test cannot exceed 15 MJ, and the peak rate of heat release cannot exceed 200 kW. The standards are designed to relate to escape time, to account for the contribution of bedclothes to the fire, and to minimize the early involvement of a mattress in a fire.<sup>480</sup> The CPSC estimates that the proposed standards would prevent an estimated 310-333 deaths and 1,780 injuries from fire each year.<sup>481</sup> To demonstrate compliance, mattresses and mattress pads will be required to have a permanent label with the manufacturer's name, the date and location of manufacture, model type, prototype identification number, and certification of compliance with the standard.

Throughout the rulemaking process concerns have been raised over the use of flame retardant chemicals in the mattresses. The CPSC has noted that of the 543 comments received on the proposed rule, the major concern revolves around flame retardant chemicals.<sup>482</sup> The CPSC's Directorate for Health Sciences (HS) conducted a toxicity review and environmental assessment, but due to a lack of exposure data on flame retardant chemicals from mattresses, the HS was unable to make a quantitative assessment of the potential health effects. Instead the HS staff completed a qualitative assessment of the potential risk from the use of selected flame retardant chemicals, including Deca-BDE, in mattresses, but concluded that exposure data for Deca-BDE was necessary before the staff could make a definitive conclusion about its potential health risks to consumers.<sup>483</sup>

Despite concerns, the CPSC is moving forward and issued draft regulations in a Notice for Proposed Rulemaking, published January 13, 2005 in the Federal Register.<sup>484</sup> The law will go into effect 12 months after the final rule is published in the Federal Register; no publish dates have been given.

# Appendix J: Bibliography

Note: This is a complete alphabetical listing of all the references used to create this CAP. Refer to the Endnotes section that follows to identify specific references noted within the text.

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# Appendix K: Endnotes

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