



# Washington State PBDE Chemical Action Plan

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# Washington State PBDE Chemical Action Plan

by Cheri Peele

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## **Executive Summary**

PBDE (polybrominated diphenyl ether) flame retardants are chemical additives that have been found, in recent years, to be leaching from a wide variety of everyday products into the environment and food chain. PBDEs are building up in living organisms, including humans, at steadily increasing levels. This chemical action plan identifies actions the state may take to reduce threats posed by PBDEs.

Penta-BDE and Octa-BDE, two of the three commercial mixtures of PBDEs, have been found to cause health problems in lab animals at higher levels of PBDEs than have been seen in humans so far. The third commercial mixture, Deca-BDE, is considerably less toxic in its original state but has been shown in studies to break down into furans and harmful chemical forms similar to those of Penta-BDE and Octa-BDE.

Penta-BDE and Octa-BDE will be voluntarily phased out of production at the end of 2004. Penta-BDE is typically used in foams for sofas and chair seat pads; Octa-BDE is typically used in high-impact plastics, such as in telephones, kitchen appliances and computers.

Deca-BDE accounts for approximately 80 percent of the PBDE market, and its use is anticipated to increase at a rate of 2 percent annually. Additionally, a pending revision of federal regulations on flame retardants could substantially increase the market for Deca-BDE in the near future. Deca-BDE is typically used in housing for electronic products such as computers and stereos, coatings for wire and cable, and carpets and draperies; it is not used in clothing.

PBDEs have been measured in a variety of human tissues, such as blood, fat and breast milk in people around the world. The highest levels of PBDEs in human tissues have been found in Canada and in the U.S., which is the largest producer and consumer of PBDE products. Levels of PBDEs in Americans are 10 to 100 times higher than levels reported for Europe and Japan.

Although PBDEs have been detected in everything from food to house dust to indoor air, exactly how people are exposed to PBDEs is an area of ongoing study. Studies in Canada and the United Kingdom suggest that more than 90 percent of a person's total intake of PBDEs is through diet. PBDEs are believed to migrate from products into the air and dust that is then consumed by insects and moves up the food chain from there. PBDEs build up in the body at steadily increasing levels because they reside in fatty tissue and are not processed out of the system.

Given the long life of many PBDE products and the length of time PBDEs can remain in the environment, exposure can continue for years and even decades after the production or sale of a product.

The departments of Ecology and Health recommend a strategy that guides the handling and disposal of existing PBDE products and reduces the manufacture and sale of new PBDE products.

Even if no new PBDE products were produced or sold, merely dealing with existing products will require programs to limit human exposure and prevent the continued release of PBDEs into the environment for decades to come. The solution could mean changes to everything from recycling practices to landfills. Each additional year that PBDE products are produced and sold will extend that timetable – and any related costs – by a decade or more.

In the case of Penta-BDE and Octa-BDE, the production of new products will end soon with the exhaustion of existing stockpiles of chemicals, whose shelf life is less than a year. In the case of Deca-BDE – whose levels are steadily rising and could grow even faster if the chemical is used to meet new standards for reducing flammability in residential upholstery products – Ecology and Health recommend prohibiting its current use in consumer electronics products and its future application in residential textile products. Biological monitoring for PBDEs in blood and procedures for handling and disposal of PBDE-containing products should be explored to limit exposure to humans and to the environment.

## **Recommendations Summary**

The Washington State departments of Ecology and Health recommend that:

- The Department of Labor and Industries (L&I) develop and disseminate recommendations for minimizing occupational exposure to PBDE flame retardants.
- State agencies coordinate with federal agencies on national monitoring of PBDE levels and explore whether additional regional monitoring is needed.
- The Department of Health (DOH) and L&I implement a study of workplace exposure to PBDEs in collaboration with the Centers for Disease Control.
- Existing state monitoring programs be expanded to include testing for PBDEs.
- The Department of Ecology (Ecology) test sewage sludge (also known as biosolids) for PBDEs.
- Ecology examine and revise or add disposal and recycling practices for products that contain PBDEs in order to protect human health and the environment.
- DOH develop and communicate ways for the general population to minimize exposure to PBDEs.
- Other government agencies and research institutions conduct research on 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, people and other organisms, to establish a baseline for future studies; and product design and other solutions to chemical fire retardants.
- The Washington State Legislature prohibit the manufacture, distribution, or sale of new products containing Penta-BDE and Octa-BDE in Washington State as of July 2006.
- The Legislature prohibit the manufacture, distribution and sale of new consumer electronics products containing Deca-BDE as of July 2008 and prohibit the use of Deca-BDE in new upholstered fabric intended for the home or workplace that is manufactured, distributed or sold in Washington State as of July 2008. Defining the list of products that should be prohibited may require further study by Ecology and the Legislature.
- The Legislature restrict the state's purchase of PBDE products in appropriate contracts.

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# **Acronyms and Abbreviations**

ABS	acrylonitrile butadiene styrene
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
EIA	Electronic Industries Alliance
EICTA	European Industry Association for Information Systems, Communication Technologies and Consumer Electronics
EPDM	ethylene-propylene terpolymer
HIPS	high-impact polystyrene
IWGFM	Interagency Working Group on Fire and Materials
JGPSSI	Japanese Green Procurement Survey Standardization Initiative
L&I	Washington State Department of Labor and Industries
LDPE	low-density polyethene
PBDE	polybrominated diphenyl ether
PBDF	polybrominated dibenzofuran
PBT	persistent bioaccumulative toxin
POP	persistent organic pollutants
PSAMP	Puget Sound Ambient Monitoring Program
RFP	requests for proposal
RoHS	Restriction on Hazardous Substances
SNUR	Significant New Use Rule
TERT	Toxics Exposure Reporting and Tracking Review
THF	tetrahydrofuran
WEEL	Workplace Environmental Exposure Level

## I. Introduction

The Draft PBDE Chemical Action Plan is a joint document of the Washington State Department of Ecology (Ecology) and Department of Health (DOH). This is the second chemical action plan developed as part of Ecology's Persistent, Bioaccumulative Toxin (PBT) Initiative. The purpose of this document is to identify actions the state may take to reduce threats posed by the class of flame retardants known as polybrominated diphenyl ethers (PBDEs).

In January 2004, Governor Gary Locke issued Executive Order 04-01, directing the Department of Ecology, in consultation with the Department of Health, to move forward immediately in developing a chemical action plan for PBDEs, and recommend actions by December 1, 2004. Implementation of the plan is to begin no later than July 1, 2005.

In the 2004 supplemental budget (Engrossed Substitute House Bill 2459), the Washington Legislature provided \$83,000 solely for the development of a chemical action plan for the chemical compounds known as PBDE (polybrominated diphenyl ethers).

The development of the Draft PBDE CAP was managed by the PBT Steering Committee. The PBT Steering Committee is a joint standing committee of Ecology and the Department of Health (DOH). Members from Ecology include the Deputy Director, the Director of Governmental Relations, the Director of Communication and Education, and the managers of the Air Quality, Environmental Assessment, Hazardous Waste and Toxics Reduction, Solid Waste and Financial Assistance, Toxic Cleanup, and Water Quality programs. From DOH, the Director of the Office of Environmental Health Assessments is a member of the PBT Steering Committee.

In February 2004, Ecology hired a staff person to write the PBDE Chemical Action Plan (CAP), and research on the topic was begun. In March, Ecology and DOH formed a joint Technical Committee with members from DOH's Office of Environmental Health Assessments and the following programs within Ecology: Air Quality, Communication and Education, Environmental Assessment, Hazardous Waste and Toxic Reduction, Solid Waste and Financial Assistance, Toxic Cleanup, and Water Quality. During the summer and fall, the Technical Committee was informally expanded to include staff from the Safety & Health Assessment & Research for Prevention (SHARP) program at the Washington State Department of Labor and Industries.

The Technical Committee met weekly to develop a broad understanding of PBDEs, including their use, possible alternatives, potential environmental pathways, regulatory structure, and environmental and health impacts. Based on this understanding, the Technical Committee developed a list of policy options to minimize threats posed by PBDEs. These options were then evaluated to form a list of recommended actions. At each step in the process, the work of the Technical Committee was informed by advice from an external advisory committee, described below, and by direction from the PBT Steering Committee. At critical points in the Plan's development, the Technical Committee also received direction from Ecology's Senior Management Team, consisting of the Director and senior staff.

Ecology, with advice from DOH, formed an external advisory committee with broad representation from business, recycling, environmental and consumer advocacy, and local government interests. Where possible, individual members were chosen by the organization or association they represent. In addition to stakeholders, two science advisors and advisors from the Governor's office, the State Fire Marshal's office, and the SHARP program of the Department of Labor and Industries participated in committee meetings. Committee members, advisors, and their affiliations are listed on pages vi and vii. Cascadia Consulting was hired to facilitate advisory committee meetings.

The purpose of the advisory committee was to seek perspectives and knowledge of the members on the wide range of topics covered by the PBDE CAP. While Ecology and DOH were interested in identifying existing areas of consensus among members, working towards consensus-based understanding of the issues or solutions was not an objective of the committee.

The advisory committee met four times, once in June, once in July, and twice in August. Throughout the process, the committee rarely reached consensus. Committee members did all agree that Penta-BDE and Octa-BDE formulations should be banned from commerce. Around Deca-BDE, advisory committee members did not agree on the toxicity or potential breakdown of Deca-BDE, the interpretation of European Union's risk assessment for Deca-BDE, or proposed policy recommendations. A number of advisory committee members submitted written material to Ecology and DOH to support or clarify their positions on a range of topics.

The sections on human health and toxicity and photolytic degradation of PBDEs were reviewed in writing by A. Bergman (Stockholm University), L. Birnbaum (US 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).

Following a 30 day public comment period from October 11 to November 9, this draft will be revised in light of comments received. The external advisory committee will hold a final meeting on December 1, where Ecology and DOH will present revisions. The final PBDE CAP will be released December 31, 2004.

# **II. PBDEs: Intended Purpose and Applications**

## Identification

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

Over 175 flame retardant chemicals exist, classified in four major groups: halogenated organic (usually brominated or chlorinated), organophosphorous, nitrogen-based compounds and mixtures, and inorganic.<sup>1</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>2</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>3</sup>

Within the PBDE class, 209 different forms of the PBDE molecule, called congeners, theoretically exist. PBDEs do not exist naturally. To produce PBDEs, flame retardant manufacturers start with a diphenyl ether, which consists of two rings of six carbon atoms each, where one carbon on each ring is bound to an oxygen. The manufacturers then bind bromine atoms to the remaining carbons, up to five on each ring. 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 many 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>4</sup> A diagram of deca-BDE, the PBDE with the maximum number of bromine atoms, is shown in Figure 1.

<sup>&</sup>lt;sup>1</sup> M. Alaee and R. Wenning, "The significance of brominated flame retardants in the environment: current understanding, issues, and challenges," Chemosphere 46 (2002) 579 – 582.

<sup>&</sup>lt;sup>2</sup> OSPAR Commission, "Certain Brominated Flame Retardants: Polybrominated Diphenylethers, Polybrominated Biphenyls, and Hexabromo Cyclododecane," 2001, p. 8.

<sup>&</sup>lt;sup>3</sup> Andreas Sjodin, Donald G. Patterson, Åke Bergman, "A review on human exposure to brominated flame retardants- particularly polybrominated diphenyl ethers" Environment International 29 (2003) 829 – 839.

<sup>&</sup>lt;sup>4</sup> Birnbaum and Staskal, 2004. Brominated flame retardants: Cause for concern? Environmental Health Perspectives, 112(1)9 - 17.



Figure 1: deca-BDE Structure

Individual PBDE congeners are named BDE-1, BDE-2, BDE-3,....BDE-209, using the system developed by the International Union for Pure and Applied Chemistry 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 to the reader. Homologues are PBDEs with the same number of bromines.

Table 1. PBDE congeners of particular interest

Congener	Homologue	Major constituent 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.

\* BDE-209 not widely analyzed for in general population samples (see Hites, 2004).

The major commercial PBDE products consist mainly of penta-BDE's, octa-BDE's or deca-BDE, but contain other PBDEs. The general compositions of the commercial products are provided in Table 2.

		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

Table 2. General compositions of PBDE-based flame retardants given in percent of BDE congeners present<sup>5</sup>

For purposes of this report, the capitalized words "Deca-BDE," "Octa-BDE," and "Penta-BDE" refer to the commercial mixtures. Lower case mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and deca-BDE refer to homologues, groups of molecules with between one and ten bromine atoms.

The global demand for PBDEs has been estimated at 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. 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>6</sup>

Table 3. PBDE Volume Estimates: Total Market Demand by Region in 2001 in Metric Tons (and by Percent)

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%)

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

## How PBDEs work

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," when all combustible materials in a room ignite, allowing occupants extra time to escape.<sup>7</sup>

<sup>&</sup>lt;sup>5</sup> World Health Organization, "Environmental Health Criteria 162: Brominated Diphenyl Ethers", <u>www.inchem.org</u>, viewed 4 May 2004.

<sup>&</sup>lt;sup>6</sup> F. Gastrock, BRG Townsend, quoted by A. Tullo, "Resting Easier," Chemical and Engineering News, November 17, 2003, Vol. 81, Number 46, pp. 43 – 44.

<sup>&</sup>lt;sup>7</sup> Bromine Science and Environmental Forum, "An introduction to Brominated Flame Retardants," October 19, 2000, <u>http://www.ebfrip.org/download/weeeqa.pdf</u>, viewed on March 16, 2003, p. 5.

### **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>8</sup>

Fires are a leading cause of death among children in the U.S. Each year, more than 600 children ages 14 and under die, and nearly 47,000 are injured in fires (NSKC 2002). 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.

### **Manufacturing of PBDEs**

Four companies, listed in Table 4, are known to produce Deca-BDE. One of these, Great Lakes Chemical, is the only company known to still produce Penta-BDE and Octa-BDE. Great Lakes will voluntarily stop producing Penta and Octa-BDE by the end of 2004.

Company	Product Name	Country
Albemarle Corporation	SAYTEX 102E	Richmond, Virginia, US
Dead Sea Bromine	FR 1210	Israel
(subsidiary Israel Chemicals LTD)		
Great Lakes Chemical Corporation	DE-83R, DE-83	West Lafayette, Indiana, US
Tosoh Corporation	Flamecut 110R	Japan

Table 4. Companies that Produce Deca-BDE

### **PBDE Applications**

Penta-BDE is used in unsaturated polyester, rigid and flexible polyurethane foam, epoxies, laminates, adhesives and coatings.<sup>9,10,11</sup> Typical end products containing Penta-BDE include mattresses, seat cushions and other upholstered furniture, and rigid insulation.

Octa-BDE is used in acrylonitrile butadiene styrene (ABS), nylon, thermoplastic elastomers, and polyolefins.<sup>12</sup> Typical products containing Octa-BDE include housings for fax machines and computers, automobile trim, telephone handsets, and kitchen appliance casings.

<sup>9</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DE-71" www.e1.greatlakes.com/pdf/datasheet/DE-71%20ds.PDF, viewed 6 July 2004.

<sup>11</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DE-62" www.el.greatlakes.com/pdf/datasheet/DE-62%20Data%20Sheet.PDF, viewed 6 July 2004.

<sup>&</sup>lt;sup>8</sup> Bromine Science and Environmental Forum, "An introduction to Brominated Flame Retardants," October 19, 2000, <u>http://www.ebfrip.org/download/weeeqa.pdf</u>, viewed on March 16, 2003, p. 6.

<sup>&</sup>lt;sup>10</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DE-61"

www.el.greatlakes.com/pdf/datasheet/DD-61%20Data%20Sheet.PDF, viewed 6 July 2004.

Deca-BDE is used in thermoplastic, elastomeric and thermoset polymer systems, including highimpact polystyrene (HIPS), 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 backcoatings for fabrics.<sup>13,14</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 is not used in textiles used for clothing.<sup>15</sup>

In September 2004, the Safety & Health Assessment & Research for Prevention (SHARP) program at the Washington State Department of Labor and Industries conducted an informal telephone survey of Washington plastics and foam manufacturers to ascertain PBDE usage. Businesses were identified using a combination of the Owest-Dex Yellow Page heading "Plastics-Foam" and SIC code 3086 (Plastics-Foam).

It appeared that companies fabricating items from plastic or foam feedstock did not know which, if any, flame retardants were added to their materials. SHARP staff were generally referred to the manufacturers of the raw materials. A representative of the Polyurethane Foam Alliance suggested that newly manufactured foams and plastics are no longer formulated with Penta-BDE or Octa-BDE, reflecting concerns expressed in international markets. Similarly, two principal Washington plastics and foam manufacturers reported that they no longer use PBDEs for the same reason.

<sup>&</sup>lt;sup>12</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DE-79"

www.el.greatlakes.com/pdf/datasheet/DE-79%20Data%20Sheet.PDF, viewed 6 July 2004.

<sup>&</sup>lt;sup>13</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DE-83R"

www.el.greatlakes.com/pdf/datasheet/DE-83%20Data%20Sheet.PDF, viewed 6 July 2004. <sup>14</sup> Albemarle Corporation, <u>http://www.albemarle.com/saytexbrochf.htm</u>, viewed March 29, 2004.

<sup>&</sup>lt;sup>15</sup> OSPAR Commission, "Certain Brominated Flame Retardants: Polybrominated Diphenylethers, Polybrominated Biphenyls, and Hexabromo Cyclododecane," 2001, p. 8.

## **III. Unintended Consequences: PBDEs, Human** Health, and 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. Between 1972 and 1997, PBDE levels in human breast milk from Sweden were shown to exponentially increase, doubling every 5 years (Figure 1).<sup>16</sup> During this same time period, levels of PCBs and other organic pollutants in breast milk had decreased. Levels of PBDEs in Swedish breast milk are similar to these reported for many other European countries and Japan.<sup>17</sup> Levels of PBDEs in breast milk samples from Sweden have begun to decrease in the late 1990s.<sup>18</sup>



Figure 2. PBDEs in Swedish Breast Milk, 1972-2000.<sup>19,20</sup>

The highest levels of PBDEs in human tissues collected from the general public have been found in the U.S. and Canada (Figure 2).<sup>21,22,23,24,25,26</sup> Levels of PBDEs in human tissues in the U.S. are

<sup>&</sup>lt;sup>16</sup> Noren and Meironyte, 2000. Certain organochlorine and organobromine contaminants in Swedish human milk in perspective of past 20-30 years. Chemosphere 40:1111-1123. <sup>17</sup> Sjodin et al., 2003. A review on human exposure to brominated flame retardants – particularly polybrominated

diphenyl ethers. Environment International 29:829-839.

<sup>&</sup>lt;sup>18</sup> Meironyte, 2002. Organohalogen contaminants in humans with emphasis on polybrominated diphenyl ethers. PhD Thesis. Karolinska Instituted, Stockholm, Sweden. (data summarized in Sjodin et al., 2003)

<sup>&</sup>lt;sup>19</sup> Noren and Meironyte, 2000. Certain organochlorine and organobromine contaminants in Swedish human milk in perspective of past 20-30 years. Chemosphere 40:1111-1123.

<sup>&</sup>lt;sup>20</sup> Meironyte, 2002. Organohalogen contaminants in humans with emphasis on polybrominated diphenyl ethers. PhD Thesis. Karolinska Institute, Stockholm, Sweden. (data summarized in Sjodin et al., 2003)

<sup>&</sup>lt;sup>21</sup> Sjodin et al., 2003. A review on human exposure to brominated flame retardants – particularly polybrominated diphenyl ethers. Environment International 29:829-839.

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 uses about 98% of the world's supply of the Penta-BDE commercial product.<sup>27,28</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>29,30,31</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>32, 33</sup>





<sup>22</sup> Schecter et al., 2003. Polybrominated diphenyl ethers (PBDEs) in U.S. mother's milk. Environmental Health Perspectives 111(14): 1723-1729.

<sup>23</sup> Mazdai et al., 2003. Polybrominated diphenyl ethers in maternal and fetal blood samples. Environmental Health Perspectives 111(9): 1249-1252.

<sup>24</sup> She et al., 2002. PBDEs in the San Francisco Bay area: measurements in harbor seal blubber and human breast adipose tissue. Chemosphere 46:697-707.

<sup>25</sup> Environmental Working Group (EWG), 2003. Mothers' milk, record levels of toxic fire retardants found in American mothers' breast milk. Available at <u>www.ewg.org</u>.
 <sup>26</sup> Northwest Environment Watch, 2004. Flame retardants in Puget Sound residents. Available at:

<sup>26</sup> Northwest Environment Watch, 2004. Flame retardants in Puget Sound residents. Available at: <u>www.northwestwatch.org/pollution</u>

<sup>27</sup> Hale et al., 2003. Polybrominated diphenyl ether flame retardants in the North American environment. Environment International 29: 771-779.

<sup>28</sup> Sjodin et al., 2003. A review on human exposure to brominated flame retardants – particularly polybrominated diphenyl ethers. Environment International 29:829-839.

<sup>29</sup> Lind et al., 2003. Polybrominated diphenyl ethers in breast milk from Uppsala County, Sweden. Environmental Research 93:186-194.

<sup>30</sup> Akutsu et al., 2003. Time-trend (1973-2000) of polybrominated diphenyl ethers in Japanese mother's milk. Chemosphere 53:643-654.

<sup>31</sup> Sjodin et al., 2004. Retrospective time-trend study of polybrominated diphenyl ether and polybrominated and polychlorinated biphenyl levels in human serum from the United States. Environmental Health Perspectives 112(6): 654-658.

<sup>32</sup> Sjodin et al., 2004. Retrospective time-trend study of polybrominated diphenyl ether and polybrominated and polychlorinated biphenyl levels in human serum from the United States. Environmental Health Perspectives 112(6): 654-658.

<sup>33</sup> Schecter et al., 2004. PBDE contamination of U.S. food and human milk; and PBDE, PCDD/F, PCB, and levels in the U.S. human blood (1973-2003). Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

<sup>34</sup> Data from Noren and Meironyte, 2000; Meironyte, 2002; Sjodin et al., 2003; Mazdai et al., 2003 (\*median value; mean value not published); Schecter et al., 2003; She et al., 2002; EWG, 2004; and Northwest Environment Watch, 2004.

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>35</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>36</sup> This wide variability is seen in tissue samples from the U.S. and from other countries.<sup>37, 38</sup> The reasons for the large variability in tissue levels and why some people have high-end exposures to PBDEs are not known.

Studies indicate that there are differences in routes and timing of human exposures between PCBs and PBDEs. People are mainly exposed to PCBs through the diet and age has been shown to be a predictor of PCB levels in human tissues.<sup>39</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>40</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>41</sup> Studies in Sweden and Norway have also found that PBDE tissue levels were not correlated with age, except for infants.<sup>42, 43</sup> This suggests that exposures to PBDEs have occurred recently, i.e. PBDEs have not accumulated in older people over time.

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 congener). 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>44</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. A recent report from the Faroe Islands, found BDE-153, instead of BDE-47, as the most abundant PBDE congener in breast milk samples.<sup>45</sup>

<sup>&</sup>lt;sup>35</sup> McDonald, 2004. Distribution of PBDE levels among U.S. women: estimates of daily intake and risk of developmental effects. Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

<sup>&</sup>lt;sup>36</sup> Schecter et al., 2003. Polybrominated diphenyl ethers (PBDEs) in U.S. mother's milk. Environmental Health Perspectives 111(14): 1723-1729.

<sup>&</sup>lt;sup>37</sup> Petreas et al., 2003. High body burdens of 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) in California women. Environmental Health Perspectives 111(9):1175-1179.

<sup>&</sup>lt;sup>38</sup> Lind et al., 2003. Polybrominated diphenyl ethers in breast milk from Uppsala County, Sweden. Environmental Research 93:186-194.

<sup>&</sup>lt;sup>39</sup> Tee et al., 2003. A longitudinal examination of factors related to changes in serum polychlorinated biphenyl levels. Environmental Health Perspectives 111(5):702-707.

<sup>&</sup>lt;sup>40</sup> Meironyte Guvenius, et al., 2003. Human prenatal and postnatal exposure to polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorobiphenylols, and pentachlorophenol. Environmental Health Perspectives 111(9):1235-1241.

<sup>&</sup>lt;sup>41</sup> She et al., 2002. PBDEs in the San Francisco Bay area: measurements in harbor seal blubber and human breast adipose tissue. Chemosphere 46:697-707.

<sup>&</sup>lt;sup>42</sup> Sjodin et al., 2003. A review on human exposure to brominated flame retardants – particularly polybrominated diphenyl ethers. Environment International 29:829-839.

<sup>&</sup>lt;sup>43</sup> Thomsen et al., 2002. Brominated flame retardants in archived serum samples from Norway: a study on temporal trends and the role of age. Environmental Science & Technology 36:1414-1418.

<sup>&</sup>lt;sup>44</sup> Hakk et al., 2003. Metabolism in the toxicokinetics and fats of brominated flame retardants – a review. Environment International 29:801-828.

<sup>&</sup>lt;sup>45</sup> Fangstrom et al., 2004. A retrospective study of PBDEs in human milk from the Faroe Islands. Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

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>46,47</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>48</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>49</sup> BDE-209 has been found in fish and other food.<sup>50</sup>

#### Human Exposures to PBDEs - General Population

PBDEs have been detected in foods, house dust and indoor air.<sup>51, 52, 53, 54</sup> With the exception of nursing infants and some workers, how much these different sources of PBDEs contribute to a person's total exposure is currently an area of active research.<sup>55,56</sup> An 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>57</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

<sup>&</sup>lt;sup>46</sup> Schecter et al., 2003. Polybrominated diphenyl ethers (PBDEs) in U.S. mother's milk. Environmental Health Perspectives 111(14): 1723-1729.

<sup>&</sup>lt;sup>47</sup> Northwest Environment Watch, 2004. Flame retardants in the bodies of pacific northwest residents. Available at

www.northwestwatch.org. <sup>48</sup> Hites, 2004. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environmental Science & Technology 38(4): 945-956.

<sup>&</sup>lt;sup>49</sup> Butt et al., 2004. Spatial distribution of polybrominated diphenyl ethers in southern Ontario as measured in indoor and outdoor window organic films. Environmental Science & Technology 38(3):724-731.

<sup>&</sup>lt;sup>50</sup> Schecter et al., 2004. Polybrominated diphenyl ethers contamination of United States food. Environmental Science & Technology, web release September 1, 2004.

<sup>&</sup>lt;sup>51</sup> Schecter et al., 2004. Polybrominated diphenyl ethers contamination of United States food. Environmental Science & Technology, web release September 1, 2004. <sup>52</sup> Lukemburg et al., 2004. Levels of polybrominated Diphenyl ethers (PBDEs) in fish, beef, and fowl purchased in

food markets in northern California USA. Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

 $<sup>^{53}</sup>$  Sjodin et al., 2004. Concentration of polybrominated diphenyl ethers (PBDEs) in house hold dust – inhalation a potential route of human exposure. Abstract presented at BFR2004 Conference, Toronto Canada, June 2004.

<sup>&</sup>lt;sup>4</sup> Harrad et al., 2004. Preliminary assessment of U.K. human dietary and inhalation exposure to polybrominated diphenyl ethers. Environmental Science & Technology 38(8):2345-2350.

<sup>&</sup>lt;sup>55</sup> Darnerud et al., 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure and toxicology. Environmental Health Perspectives 109(Supplement 1): 49-68.

<sup>&</sup>lt;sup>56</sup> Sjodin et al., 2003. A review on human exposure to brominated flame retardants – particularly polybrominated diphenyl ethers. Environment International 29:829-839.

<sup>&</sup>lt;sup>57</sup> Health Canada, 2004. Screening assessment report – Polybrominated diphenyl ethers (PBDEs). Available at: http://www.hc-sc.gc.ca/hecs-sesc/exsd/screening\_assessment.htm (accessed Sept. 2004)

dust exposures.<sup>58</sup> A study in the U.K. that evaluated PBDEs in indoor air and the diet, estimated that 93% of a person's total daily intake of PBDEs came from the diet.<sup>59</sup>

Recent assessments have shown that nursing infants are mainly exposed to PBDEs through breast milk.<sup>60, 61</sup> In the analysis by Health Canada, breast fed 0-6 month old infants were identified as having the greatest exposures of all age groups, where 92% of their exposure came from breast milk.<sup>62</sup> Studies of PBDE levels in maternal and cord blood indicate that prenatal exposure to PBDEs occurs.<sup>63, 64</sup> While the levels of PBDEs in breast milk are a 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>65</sup> Breast milk contains factors to protect the infant from the effects of prenatal exposure, boost the immune system and develop brain tissue.

There are some recent data on levels of PBDEs in food in the U.S. 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>66, 67</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>68</sup> Studies in the U.S. and other countries report that fish contain the highest PBDE levels of different foods tested.<sup>69, 70, 71</sup> A study in Sweden reported that increasing blood plasma levels of PBDEs were associated with increasing intake of fatty fish

<sup>&</sup>lt;sup>58</sup> Jones-Otazo et al., 2004. A preliminary comparison of Canadian PBDE exposures from oral and inhalation routes. Poster presented at BFR 2004 Conference in Toronto Canada, June 2004.

<sup>&</sup>lt;sup>59</sup> Harrad et al., 2004. Preliminary assessment of U.K. human dietary and inhalation exposure to polybrominated diphenyl ethers. Environmental Science & Technology 38(8):2345-2350.

<sup>&</sup>lt;sup>60</sup> Jones-Otazo et al., 2004. A preliminary comparison of Canadian PBDE exposures from oral and inhalation routes. Poster presented at BFR 2004 Conference in Toronto Canada, June 2004.

<sup>&</sup>lt;sup>61</sup> Health Canada, 2004. Screening assessment report – Polybrominated diphenyl ethers (PBDEs). Available at: <u>http://www.hc-sc.gc.ca/hecs-sesc/exsd/screening\_assessment.htm</u> (accessed Sept. 2004)

<sup>&</sup>lt;sup>62</sup> Health Canada, 2004. Screening assessment report – Polybrominated diphenyl ethers (PBDEs). Available at: http://www.hc-sc.gc.ca/hecs-sesc/exsd/screening\_assessment.htm (accessed Sept. 2004)

<sup>&</sup>lt;sup>63</sup> Meironyte et al., 2003. Human prenatal and postnatal exposure to polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorobiphenylols, and pentachlorophenol. Environmental Health Perspectives 111(9): 1235-1241.

<sup>&</sup>lt;sup>64</sup> Mazdai et al., 2003. Polybrominated diphenyl ethers in maternal and fetal blood samples. Environmental Health Perspectives 111(9): 1249-1252.

<sup>&</sup>lt;sup>65</sup> Pronczuk et al., 2004. Breast milk: an optimal food. Environmental Health Perspectives 112(13): A722-723.

<sup>&</sup>lt;sup>66</sup> Schecter et al., 2004. Polybrominated diphenyl ethers contamination of United States food. Environmental Science & Technology, web release September 1, 2004.

<sup>&</sup>lt;sup>67</sup> Lukemburg et al., 2004. Levels of polybrominated diphenyl ethers (PBDEs) in fish, beef, and fowl purchased in food markets in northern California USA. Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

<sup>&</sup>lt;sup>68</sup> Huwe, 2004. Polybrominated diphenyl ethers in meat samples collected from supermarkets across the U.S. Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

<sup>&</sup>lt;sup>69</sup> Bocio et al., 2003. Polybrominated diphenyl ethers (PBDEs) in foodstuffs: human exposure through the diet. Journal of Agricultural and Food Chemistry 51:3191-3195.

<sup>&</sup>lt;sup>70</sup> Ohta et al., 2002. Comparison of polybrominated diphenyl ethers in fish, vegetables, and meats and levels in human milk of nursing women in Japan. Chemosphere 46:689-696.

<sup>&</sup>lt;sup>71</sup> Schecter et al., 2004. Polybrominated diphenyl ethers contamination of United States food. Environmental Science & Technology, web release September 1, 2004.

(mainly salmon and herring).<sup>72</sup> A study in Japan found higher PBDE levels in breast milk from women who had higher dietary intake of fish and shellfish.<sup>73</sup>

PBDEs have been detected in dust from homes and other buildings. Studies have identified mainly Penta-BDE associated congeners and BDE-209 in dust samples and some studies have reported higher levels in the U.S. compared to Europe. Household dust collected in Massachusetts had 5-10 times higher levels of PBDEs than levels reported for Germany and the U.K.<sup>74</sup> 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>75</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>76</sup> A study of dust in Parliament buildings from eight European countries identified BDE-209 as the predominant congener.<sup>77</sup> 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>78</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. Computer wipe samples collected from 16 offices around the U.S. detected PBDEs, with BDE-209 found as the predominant congener, although levels of PentaBDE congeners were not reported.<sup>79</sup>

Higher PBDE levels have been found in indoor air compared to outdoor air. A study in Canada used organic window films as a measure of ambient air levels of PBDEs both indoors and outdoors.<sup>80</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>81</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. A recent study in

 <sup>&</sup>lt;sup>72</sup> Sjodin et al., 2000. Influence of the consumption of fatty Baltic Sea fish on plasma levels of halogenated environmental contaminants in Latvian and Swedish men. Environmental Health Perspectives 108:1035-1041.
 <sup>73</sup> Ohta et al., 2002. Comparison of polybrominated diphenyl ethers in fish, vegetables, and meats and levels in human milk of nursing women in Japan. Chemosphere 46:689-696.

<sup>&</sup>lt;sup>74</sup> Rudel et al., 2003. Phthalates, alkylphenols, pesticides, polybrominated diphenyl ethers, and other endocrinedisrupting compounds in indoor air and dust. Environmental Science & Technology 37(20): 4543-4553.

<sup>&</sup>lt;sup>75</sup> Environmental Working Group, 2004. In the dust - levels of toxic fire retardants contaminate American homes. Available at www.ewg.org/reports/inthedust/summary.php.

<sup>&</sup>lt;sup>76</sup> Stapleton et al., 2004. Polybrominated diphenyl ether measurements in household dust. Abstract presented at BFR 2004 Conference, Toronto Canada, June 2004.

<sup>&</sup>lt;sup>77</sup> Greenpeace Research Laboratories, 2001. The presence of brominated flame retardants and organotin compounds in dusts collected from Parliament buildings from eight countries. Available at <a href="http://archive.greenpeace.org/toxics/reports/eudust.pdf">http://archive.greenpeace.org/toxics/reports/eudust.pdf</a>.

<sup>&</sup>lt;sup>78</sup> Sjodin et al., 2004. Concentration of polybrominated diphenyl ethers (PBDEs) in house hold dust – inhalation a potential route of human exposure. Abstract presented at BFR2004 Conference, Toronto Canada, June 2004.

<sup>&</sup>lt;sup>79</sup> Computer Take-Back Campaign and Clean Product Action, 2004. Brominated flame retardants in dust on computers. Available at: <u>www.computertakeback.com/the\_problem/bfr.cfm</u>.

<sup>&</sup>lt;sup>80</sup> Butt et al., 2004. Spatial distribution of polybrominated diphenyl ethers in southern Ontario as measured in indoor and outdoor window organic films. Environmental Science & Technology 38(3): 724-731.

<sup>&</sup>lt;sup>81</sup> Harrad et al., 2004. Preliminary assessment of U.K. human dietary and inhalation exposure to polybrominated diphenyl ethers. Environmental Science & Technology 38(8):2345-2350.

Ottawa Canada of 74 homes 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>82</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>83</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.

#### Human Exposures to PBDEs - Workers

Occupational studies of PBDE exposures are mainly limited to studies conducted in Sweden. PBDEs have been detected in air samples taken from a variety of workplaces (electronics recycling plant, a factory assembling printed circuit boards, a computer repair facility, and offices equipped with computers).<sup>84</sup> The highest PBDE concentrations in air were found at an 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 detected in the particles in air samples. The measured levels of BDE-209 at the electronics recycling plant were more than 25,000 times below the Workplace Environmental Exposure Level (WEEL) of 5 mg/m<sup>3</sup> set by the American Industrial Hygiene Association.<sup>85</sup> For comparison, the Washington State occupational limits for PCBs are 1 mg/m<sup>3</sup> as an 8 hour time weighted average. There are currently no occupational limits for PBDEs in Washington State.<sup>86</sup>

Studies of workers at the Swedish electronics recycling facility found that blood levels of PBDEs in workers who dismantle electronics were higher than levels found in hospital cleaners and computer clerks (control groups).<sup>87</sup> This same study also reported a difference in the types of PBDE congeners found in the three occupational groups. BDE-47 was the congener detected at

<sup>&</sup>lt;sup>82</sup> Wilford et al., 2004. Passive sampling survey of polybrominated diphenyl ether flame retardant in indoor and outdoor air in Ottawa, Canada; implications for sources and exposure. Environmental Science and & Technology, web release September 14, 2004.

<sup>&</sup>lt;sup>83</sup> Wilford et al., 2004. Passive sampling survey of polybrominated diphenyl ether flame retardant in indoor and outdoor air in Ottawa, Canada; implications for sources and exposure. Environmental Science and & Technology, web release September 14, 2004.

<sup>&</sup>lt;sup>84</sup> Sjodin et al., 2001. Flame retardants in indoor air at the an electronics recycling plant and at other work environments. Environmental Science & Technology 35(3):448-454.

<sup>&</sup>lt;sup>85</sup> American Chemistry Council, 2002. Voluntary children's chemical evaluation program (VCCEP), data summary, decabromodiphenyl ether.

<sup>&</sup>lt;sup>86</sup> Available at: http://www.lni.wa.gov/WISHA/Rules/respiratoryhazards/default.htm

<sup>&</sup>lt;sup>87</sup> Sjodin et al., 1999. Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers. Environmental Health Perspectives 107: 643-648.

the highest levels in the blood of the two control groups, however, BDE-183 and BDE-209 were detected in high levels in the blood of the electronics dismantlers (Figure 3). Computer technicians were also found to have higher levels of PBDE in their blood compared to hospital cleaners and computer clerks, but not as high as in electronics dismantlers.<sup>88</sup> BDE-153, BDE-183 and BDE-209 contributed more to the total PBDEs measured in blood of the computer technicians compared to the two control groups. A recent follow-up study reported a reduction in blood levels of BDE-183 and BDE-209 among electronics dismantlers following workplace changes such as upgrading the ventilation system and moving some equipment outside.<sup>8</sup> However, PBDE blood levels of electronics dismantlers remained higher than hospital cleaners.



Figure 3. Serum PBDE Levels in Four Occupational Groups (Sweden)

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

<sup>&</sup>lt;sup>88</sup> Jakobsson et al., 2002. Exposure to polybrominated diphenyl ethers and tetrabromobisphenol A among computer technicians. Chemosphere 46:709-716.

<sup>&</sup>lt;sup>89</sup> Thuresson et al., 2004. Polybrominated diphenyl ethers in blood from Swedish workers – a follow up study in an electronics recycling industry. Abstract presented at BFR2004 Conference, Toronto Canada, June 2004.

#### Estimates of human daily intake of PBDEs

Several studies have estimated the daily intake of PBDEs for people in different countries (Table 1). While many of these estimates have primarily focused on the 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>90 91</sup>

		/			
Daily PBDE intake	Country	Age	Sources of	PBDE congeners	Ref.
(mg/kg bodyweight)			exposure		
0.0000007	Sweden	adult	food	47, 99, 100, 153, 154	92
0.00001 <sup>a</sup>	Sweden	infant (0-6 mo.)	breast milk	47, 99, 100, 153, 154	93
.00000062 <sup>b</sup>	Canada	adult	food	28, 47, 99, 100, 153,	94
(0.044 µg/day)				154	
0.00000019 -	The	adult	food	28, 47, 99, 100, 153,	95
0.000003 <sup>b</sup>	Netherlands			154	
(0.013-0.213 µg/day)					
0.00000140000011 <sup>b</sup>	Spain	adult	food	Sum of tetra- to	96
(0.097-0.082 µg/day)	-			octa-BDEs	
.00000059 <sup>b</sup>	Sweden	adult	food	47, 99, 100, 153, 154	97
(0.041 µg/day)					
0.0000013 <sup>b</sup>	U.K.	adult	diet, air,	47, 99, 100, 153, 154	98
(0.091 µg/day)			occupational		
0.00000073 <sup>b</sup>	Canada	infant	breast milk	Sum of tri-BDEs to	99
(0.051 µg/day)				hepta-BDEs	
0.00000043 <sup>b</sup>	Canada	adult	diet, air,	Sum of tri- to	100
(0.030 µg/day)			occupational	hepta-BDEs	
0.00020026	Canada	0-6 mo., 0.5-4,	air, water, food,	Sum of (tetra- to	101
		5-11, 12-19,	breast milk, and	deca-BDEs)	
		20-59, 60+ yrs.	dust		

Table 5. Estimates of PBDE daily human intake for different countries.

Notes: mg/kg, milligram per kilogram bodyweight per day;  $\mu$ g/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>&</sup>lt;sup>c</sup> Calculated from value in cited reference using an assumed 60 kg bodyweight for adult woman.

<sup>&</sup>lt;sup>90</sup> Health Canada, 2004. Screening assessment report – Polybrominated diphenyl ethers (PBDEs). Available at: http://www.hc-sc.gc.ca/hecs-sesc/exsd/screening\_assessment.htm (accessed Sept. 2004).

 <sup>&</sup>lt;sup>91</sup> Schecter et al., 2004. PBDE contamination of U.S. food and human milk; and PBDE, PCDD/F, PCB, and levels in the U.S. human blood (1973-2003). Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.
 <sup>92</sup> Darnerud et al., 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure and toxicology.

Environmental Health Perspectives 109(Supplement 1): 49-68.

<sup>&</sup>lt;sup>93</sup> ibid.

<sup>&</sup>lt;sup>94</sup> Ryan and Patry, 2001. Organohalogen Compounds 51:226-229, as cited in Harrad et al., 2004.

<sup>&</sup>lt;sup>95</sup> De Winter-Sorkina et al. Dietary intake of brominated flame retardants by the Dutch population; RIVM Report 310305001/2003. As cited in Harrad et al., 2004.

<sup>&</sup>lt;sup>96</sup> Bocio et al., 2003. Polybrominated diphenyl ethers (PBDEs) in foodstuffs: human exposure through the diet. Journal of Agricultural and Food Chemistry 51:3191-3195.

<sup>&</sup>lt;sup>97</sup> Lind et al., 2002. Organohalogen Compounds 58:181-184. As cited in Harrad et al., 2004.

<sup>&</sup>lt;sup>98</sup> Harrad et al., 2004. Preliminary assessment of U.K. human dietary and inhalation exposure to polybrominated diphenyl ethers. Environmental Science & Technology 38(8):2345-2350.

 <sup>&</sup>lt;sup>99</sup> Jones-Otazo et al., 2004. A preliminary comparison of Canadian PBDE exposures from oral and inhalation routes. Poster presented at BFR 2004 Conference in Toronto Canada, June 2004.
 <sup>100</sup> ibid

<sup>&</sup>lt;sup>101</sup> Health Canada, 2004. Screening assessment report – Polybrominated diphenyl ethers (PBDEs). Available at: <u>http://www.hc-sc.gc.ca/hecs-sesc/exsd/screening\_assessment.htm</u> (accessed Sept. 2004).

#### Table 5 continued

Daily PBDE intake	Country	Age	Sources of	PBDE congeners	Ref.
(mg/kg bodyweight)			exposure		
0.000355 (U.S)	U.S. and	nursing infants	breast milk	17, 28, 47, 66, 77,	102
0.000011 (Germany)	Germany			85, 99, 100, 138,	
	-			153, 154, 183, 209	
max 0.000004 (child);	U.S. (CA)	children (<18	food (fish, meat,	Sum of (mono- to	103
max 0.000003 (adult)		yrs) and adults	fowl)	deca-BDEs)	
0.00004-0.0009	U.S.	<1 yr, 1-2 yrs,	multiple pathways	Penta-BDE	104,
		3-5 yrs.		congeners	105
$0.000014 - 0.00004^{b}$	U.S.	adult women	back-calculated	Total; mostly 47,	106
(0.86-2.4 µg/day)			from tissue levels	99, 100, 153, 154	

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 60 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 2). Doses (milligrams PBDE per kilogram bodyweight per day; mg/kg) at which health effects were observed in animal studies are provided to allow comparisons between PBDE products. An overview of health effects associated with each of the three flame retardant commercial products (Penta-BDE, Octa-BDE and Deca-BDE) is provided below. Two recent articles reviewed PBDE toxicity studies and are recommended as sources of additional background information.<sup>107,108</sup>

#### **Penta-BDE**

Animal toxicity studies have been used to evaluate commercial Penta-BDE products (consisting of a mixture of PBDE congeners) or the predominant congeners in the commercial product (BDE-47 and BDE-99). The most sensitive toxic effect (i.e. effect that occurs at the lowest dose)

<sup>&</sup>lt;sup>102</sup> Schecter et al., 2004. PBDE contamination of U.S. food and human milk: and PBDE, PCDD/F, PCB, and levels in the U.S. human blood (1973-2003). Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

<sup>&</sup>lt;sup>103</sup> Lukemburg et al., 2004. Levels of polybrominated diphenyl ethers (PBDEs) in fish, beef, and fowl purchased in food markets in northern California USA. Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

<sup>&</sup>lt;sup>104</sup> Serex et al., 2004. Children's health risk assessment of the commercial pentabromodiphenyl ether product. The Toxicologist. Abstract presented at the Society of Toxicology annual meeting, 2004.

<sup>&</sup>lt;sup>105</sup> Great Lakes Chemical Corporation, 2003. Tier 1 assessment of the potential health risks to children associated with exposure to the commercial pentabromodiphenyl ether product, voluntary children's chemical evaluation program pilot. <sup>106</sup> McDonald, 2004. Distribution of PBDE levels among U.S. women: estimates of daily intake and risk of

developmental effects. Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

<sup>&</sup>lt;sup>107</sup> Birnbaum et al., 2004. Brominated flame retardants: cause for concern? Environmental Health Perspectives 112(1): 9-17.

<sup>&</sup>lt;sup>108</sup> Darnerud, 2003. Toxic effects of brominated flame retardants in man and wildlife. Environment International 29:841-853.

associated with Penta-BDE congeners appears to be developmental neurotoxicity. Rodents exposed to Penta-BDE products either in the womb (*in utero*) or soon after birth (post-natally) showed impacts on brain function including changes in behavior, learning and memory. 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>109, 110, 11</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>112</sup> Adequate thyroid hormone levels are necessary for normal brain development *in utero* and post-natally.<sup>113</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>114</sup> Penta-BDE may also impact other hormone systems, having estrogen-like activity being one possible mechanism.<sup>115</sup> Recent animal studies report impacts on both male and female reproduction, occurring at doses as low at 0.06 mg/kg.<sup>116, 117, 118</sup>

#### **Octa-BDE**

Fetal toxicity has been identified as a sensitive toxic endpoint in rat and rabbit studies involving Octa-BDE.<sup>119</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>120, 121</sup>

<sup>&</sup>lt;sup>109</sup> Eriksson et al., 2001. Brominated flame retardants: a novel class of developmental neurotoxicants in our environment? Environmental Health Perspectives 109(9):903-908.

<sup>&</sup>lt;sup>110</sup> Eriksson et al., 2002. A brominated flame retardant, 2,2',4,4',5-pentabromodiphenyl ether: uptake, retention, and induction of neurobehavioral alterations in mice during a critical phase of neonatal brain development. Toxicological Sciences 67:98-103.

<sup>&</sup>lt;sup>111</sup> Birnbaum et al., 2004. Brominated flame retardants: cause for concern? Environmental Health Perspectives

<sup>112(1): 9-17.</sup> <sup>112</sup> Zhou et al., 2002. Developmental exposure to brominated diphenyl ethers results in thyroid hormone disruption. Toxicological Sciences 66:105-116.

<sup>&</sup>lt;sup>113</sup> Zoeller et al., 2002. Thyroid Hormone, Brain Development, and the Environment. Environmental Health Perspectives 110(Supp. 3): 355-361.

<sup>&</sup>lt;sup>114</sup> Meironyte Guvenius, 2003. Human prenatal and postnatal exposure to polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorobiphenylols, and pentachlorophenol. Environmental Health Perspectives 111(9): 1235-1241.

<sup>&</sup>lt;sup>115</sup> Birnbaum et al., 2004. Brominated flame retardants: cause for concern? Environmental Health Perspectives 112(1): 9-17.

<sup>&</sup>lt;sup>116</sup> McDonald, 2004. Distribution of PBDE levels among U.S. women: estimates of daily intake and risk of developmental effects. Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

<sup>&</sup>lt;sup>117</sup> Talsness et al., 2003. Ultrastructural changes in the ovaries of adult offspring following single maternal exposure to low dose 2,2',4,4',5-pentabromodiphenyl ether. Organohalogen Compounds 61: 88-91.

<sup>&</sup>lt;sup>118</sup> Kuriyama et al., 2003. Maternal exposure to low dose 2,2',4,4',5-pentabromodiphenyl ether (PBDE 99) impairs male reproductive performance in adult rat offspring. Organohalogen Compounds 61: 92-95.

<sup>&</sup>lt;sup>119</sup> Darnerud, 2003. Toxic effects of brominated flame retardants in man and wildlife. Environment International 29:841-853.

<sup>&</sup>lt;sup>120</sup> Health Canada, 2004. Screening assessment report – Polybrominated diphenyl ethers (PBDEs). Available at: http://www.hc-sc.gc.ca/hecs-sesc/exsd/screening\_assessment.htm (accessed Sept. 2004).

<sup>&</sup>lt;sup>121</sup> Darnerud et al., 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure and toxicology. Environmental Health Perspectives 109(Supplement 1): 49-68.

#### **Deca-BDE**

Deca-BDE is the only PBDE product that has been evaluated in rodent cancer studies.<sup>122</sup> These studies indicate that dietary intake of Deca-BDE is associated with liver, pancreas and thyroid tumors, but at very high doses (2500 - 5000 mg/kg).<sup>123</sup> In addition, thyroid changes, liver and kidney effects and fetal death have been observed in rodent studies of Deca-BDE at a dose of 80 mg/kg. A recent study reported developmental neurotoxic effects of Deca-BDE at 20.1 mg/kg, however the methodology of this study has been criticized.<sup>124, 125</sup> BDE-209 is a large molecule and it had been thought that its size would prevent it from being absorbed into the body.<sup>126</sup> 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>127</sup>

<sup>&</sup>lt;sup>122</sup> NTP, 1986. Toxicology and carcinogenesis studies of decabromodiphenyl oxide (CAS. No. 1163-19-5) in F344/N rats and B6C3F1 mice (feed studies).

<sup>&</sup>lt;sup>123</sup> NAS, 2000. Toxicological risks of selected flame-retardant chemicals. National Research Council. Available at www.nap.edu/openbook/0309070473/html/78.html.

<sup>&</sup>lt;sup>124</sup> Viberg et al., 2003. Neurobehavioral derangements in adult mice receiving decabrominated diphenyl ether (PBDE 209) during a defined period of neonatal brain development. Tox. Sciences 76: 112-120.

<sup>&</sup>lt;sup>125</sup> Vijverberg et al., 2004. Letter to the Editor. Toxicological Sciences 79:205-206.

<sup>&</sup>lt;sup>126</sup> Birnbaum et al., 2004. Brominated flame retardants: cause for concern? Environmental Health Perspectives 112(1): 9-17.

<sup>&</sup>lt;sup>127</sup> Sjodin et al., 2003. A review on human exposure to brominated flame retardants – particularly polybrominated diphenyl ethers. Environment International 29:829-839.

Associated PBDE product	Endpoint	Duration/time of exposure	Lowest Observed Effects Level (mg/kg bodyweight)	Ref.*
Penta-BDE	Davalonmental	1 day/past notal	0.8	128
Репа-БДЕ	Developmental	1 day/post-natal	0.8	
	neurotoxicity	day 10		129
	Decreased thyroid	15 days/	1.0	129
	hormone (exposure	gestational days		
	during development)	6-20		
	Reproductive effects	1 day/	0.06	130
	-	gestational day 6		
Octa-BDE	Fetotoxicity	13 days/	2-5	131
		gestational days		
		7-19		
	Liver changes	28 days and 13	10	132;133
		weeks		
Deca-BDE	Developmental	1 day/post-natal	20.1	134
	neurotoxicity	day 3		
	Thyroid changes, liver	30 days	80	135
	and kidney effects and	-		
	fetal death			
	Cancer	103 weeks	1120 - 3200	136

Table 6	Lowest observed	offorte	lovale in	DDDE	animal	tovicity	ctudiac
		UTICUS		IDDL	ammai	ισλισιτή	studies.

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

### Build Up of PBDEs in the Body

PBDEs, like PCBs, can build up in the body and remain stored there for years. The term biological half-life, refers to how long it takes the body to excrete half of an accumulated amount.<sup>137</sup> Different PBDEs have different half-lives.<sup>138</sup> For BDE-47 and BDE-153, human

<sup>&</sup>lt;sup>128</sup> Eriksson et al., 2001. Brominated flame retardants: a novel class of developmental neurotoxicants in our environment? Environmental Health Perspectives 109(9):903-908.

<sup>&</sup>lt;sup>129</sup> Zhou et al., 2002. Developmental exposure to brominated diphenyl ethers results in thyroid hormone disruption. Toxicological Sciences 66:105-116.

<sup>&</sup>lt;sup>130</sup> McDonald, 2004. Distribution of PBDE levels among U.S. women: estimates of daily intake and risk of developmental effects. Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

<sup>&</sup>lt;sup>131</sup> Darnerud et al., 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure and toxicology. Environmental Health Perspectives 109(Supplement 1): 49-68.

<sup>&</sup>lt;sup>132</sup> Health Canada, 2004. Screening assessment report – Polybrominated diphenyl ethers (PBDEs). Available at: http://www.hc-sc.gc.ca/hecs-sesc/exsd/screening\_assessment.htm (accessed Sept. 2004). <sup>133</sup> Darnerud et al., 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure and toxicology.

Environmental Health Perspectives 109(Supplement 1): 49-68.

<sup>&</sup>lt;sup>134</sup> Viberg et al., 2003. Neurobehavioral derangements in adult mice receiving decabrominated diphenyl ether (PBDE 209) during a defined period of neonatal brain development. Tox. Sciences 76: 112-120.

<sup>&</sup>lt;sup>135</sup> Darnerud et al., 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure and toxicology. Environmental Health Perspectives 109(Supplement 1): 49-68.

<sup>&</sup>lt;sup>136</sup> Darnerud et al., 2001. Polybrominated diphenyl ethers: occurrence, dietary exposure and toxicology. Environmental Health Perspectives 109(Supplement 1): 49-68.

<sup>&</sup>lt;sup>137</sup> Casarett & Doull's Toxicology, 1996. C.D. Klaassen editor. McGraw-Hill Publishers, New York.

<sup>&</sup>lt;sup>138</sup> Hakk et al., 2003. Metabolism in the toxicokinetics and fate of brominated flame retardants – a review. Environment International 29:801-828.

half-lives of 2 to 26 years have been predicted, respectively<sup>139</sup> BDE-209 has a much shorter half-life estimated to be about 2 days to a week in people, while the half-life estimated for BDE-183 is 3 months.<sup>140 141</sup> Half-lives of tetra-, penta- and hexa-BDEs in rats are much shorter than for people and range from about 19 to 119 days.<sup>142</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 2 are not directly comparable to most of the human exposure estimates presented in Table 1 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 associated congeners.<sup>143</sup>

<sup>&</sup>lt;sup>139</sup> Geyer et al., 2004. Terminal elimination half-lives of the brominated flame retardants TBBPA, HBCD, and lower brominated PBDEs in humans. Organohalogen Compounds 66:3867-3872.

<sup>&</sup>lt;sup>140</sup> Watanabe et al., 2003. Environmental release and behavior of brominated flame retardants. Environment International 29:665-682.

<sup>&</sup>lt;sup>141</sup> Sjodin et al., 2003. A review on human exposure to brominated flame retardants – particularly polybrominated diphenyl ethers. Environment International 29:829-839.

 $<sup>^{142}</sup>$  Hakk et al., 2003. Metabolism in the toxicokinetics and fate of brominated flame retardants – a review. Environment International 29:801-828.

<sup>&</sup>lt;sup>143</sup> McDonald, 2004. Distribution of PBDE levels among U.S. women: estimates of daily intake and risk of developmental effects. Abstract presented at BFR 2004 Conference in Toronto Canada, June 2004.

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

While pathways for PBDEs from products to the environment is unknown, it is thought that much 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 disposed.

Waste composition information available for the state of Washington indicates that as much as 6.5%, or 360,000 tons annually, of the disposed municipal solid waste stream could be products containing PBDEs.

Table 7. Waste composition analysis for the state of Washington, 2003

	Percent of total
Waste category	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%

### **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>144</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>145</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. The fate of PBDEs in the landfill environment is unknown.

"Auto fluff" is waste left over after metals have been separated from shredded scrap cars. A large percentage of auto fluff is made up of plastic and foam, which may or may not be flame retarded with PBDEs. Auto fluff is used at the LRI landfill in Tacoma for daily cover and the construction of internal berms in the active cell. The environmental impact of this practice is unknown; it is possible that using auto fluff as daily cover is the best waste management practice with regard to PBDEs.

### Formation of Polybrominated Dioxins and Furans

Aside from the direct release of PBDEs into the environment, disposal of PBDE-containing substances also 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.

Halogenated dioxins and furans (including brominated ones) are thought to 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 act to catalyze the reactions.

Dioxins and furans can from de novo 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

<sup>&</sup>lt;sup>144</sup> Craig M. Butt, Miriam L. Diamond, Jennifer Truong, Michael Ikonomou, and Arnout F. H. Ter Schure, "Spatial Distribution of Polybrominated Diphenyl Ethers in Southern Ontario as Measured in Indoor and Outdoor Window Organic Films," Environmental Science and Technology, Vol. 38, No. 3, 2004, pp. 724 – 731.

<sup>&</sup>lt;sup>145</sup> Andreas Sjödin, Lars Hagmar, Eva Klasson-Wehler, Kerstin Kronholm-Diab, Eva Jakobsson, and Åke Bergman, "Flame Retardant Exposure: Polybrominated Diphenyl Ether Exposure in Swedish Workers," Environmental Health Perspectives, Vol. 107, No.8, 1999, pp. 643 – 648.
phenols). Photochemical reactions involving UV light and some biological processes may also form dioxins and furans.

For all industrial and natural processes creating 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 (has been confirmed for both brominated dioxins /IPCS 1998/ and chlorinated dioxins /Carroll et al 1999 quoted by Greenpeace 2000/). On the other hand glass and metals containing virtually no organic matter should not be expected to contain dioxins.<sup>146</sup>

### **Municipal Waste Combustors**

Washington State has one operating municipal waste combustor, in Spokane. The minimum temperature for the Spokane incinerator is given in WAC 173-434-160, not below 982 C (1800 F) for a fifteen minute average nor below 871 C (1600 F) for any reading.

## **Biosolids and Sewage Sludge**

Biosolids are sewage sludge processed for land application. PBDEs have been detected in biosolids and sewage sludge in the US 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  $1,100 - 2,290 \mu g/kg dry$  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 constituents of Penta were fairly consistent across samples, concentrations of deca-BDE, or BDE-209, varied widely among US biosolids analyzed.<sup>147</sup> Washington State does not monitor PBDEs in biosolids.

Washington State has five sewage sludge incinerators, in Anacortes, Bellingham, Edmonds, Lynnwood, and Vancouver. A few smaller communities also send their biosolids to these cities to be incinerated. In Washington, US EPA has the authority to permit sludge incinerators for their emissions. The criteria for sewage sludge incinerators are located in 40 CFR 503. 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 do burn some plastics (mostly polyethylene and some PVC). Boiler temperature is not subject to legal regulation, but would typically be in the 1200° to 1800°F range.

<sup>&</sup>lt;sup>146</sup> Substance Flow Analysis for dioxins in Denmark http://www.mst.dk/udgiv/Publications/2000/87-7944-295-1/html/kap01\_eng.htm

<sup>&</sup>lt;sup>147</sup> Robert C. Hale, Mark J. LaGuardia, Ellen P. Harvey, Michael O. Gaylor, Matteson Mainor, William H. Duff, "Flame Retardants: Persistent Pollutants in Land-Applied Sludges," Nature, Vol. 412, July 12, 2001.

## **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.

## 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>148,149</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 United States tend to be much higher than those detected in similar media in Europe or Japan. While PBDEs are the subject of increasing study, knowledge regarding environmental behavior, exposure, and toxicity remains limited. Specific data on the presence of PBDEs in Washington State is also currently 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>150</sup>

Many sources of PBDEs are found indoors, resulting in elevated levels of PBDEs in indoor air. Indoor contaminants are less prone to degradation and atmospheric dilution, increasing their persistence. Butt et al. found 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>151</sup>

<sup>&</sup>lt;sup>148</sup> Siodin, Patterson, and Bergman, 2003. "A review on human exposure to brominated flame retardantsparticularly polybrominated diphenyl ethers," Environment International (29) 829 – 839. <sup>149</sup> Maria Cone, "Cause for Alarm Over Chemicals," Los Angeles Times, April 20, 2003, pp. A1 and A30.

<sup>&</sup>lt;sup>150</sup> Bo Strandberg, Nathan Dodder, Ilora Basu, and Ronald Hites, "Concentrations and Spatial variations of Polybrominated Diphneyl Ethers and Other Organohalogen Compounds in Great Lakes Air" Environmental Science and Technology, 2001, vol. 35, pp. 1078-1083.

<sup>&</sup>lt;sup>151</sup> Craig M. Butt, Miriam L. Diamond, Jennifer Truong, Michael Ikonomou, and Arnout F. H. Ter Schure, "Spatial Distribution of Polybrominated Diphenyl Ethers in Southern Ontario as Measured in Indoor and Outdoor Window Organic Films," Environmental Science and Technology, Vol. 38, No. 3, 2004, pp. 724 – 731.

Three studies were identified that examined PBDEs in household dust in the United States. All three used small sample sizes, and two have not been peer-reviewed.

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  $0.7 - 4.1 \mu g/g \text{ dust.}^{152}$ 

In 2004, Sharp and Lunder measured concentrations of 13 BDE congeners in dust samples from 10 houses across the United States. Results varied widely between houses, from 614 to 16,366 ppb 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 ninety percent of the PBDEs by weight. BDE-47 and -99, major components of Penta-BDE; each accounted for 24 percent on average. BDE-209, the major component of Deca-BDE, 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>153</sup>

Stapleton et al. measured 14 congeners in 16 household dust samples from the Washington, DC area. Total BDE concentrations ranged from 310 ng/g dry mass to 30,140 ng/g dry mass.

### **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. Total PBDEs showed a significant increase in recent years. Excluding BDE-209, concentration of total PBDEs ranged from 0.5 to 3  $\mu$ g/kg. 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>154</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>155</sup>

### **Biota**

Animal species appear to vary widely in their ability to metabolize or accumulate specific PBDE congeners. Wolker et al examined congener-specific accumulation and transfer of PBDEs in two arctic food chains. In the first, consisting of polar cod, ringed seal and polar bears, the pattern in the ringed seal was somewhat simpler than that of polar cod, while only one congener was

<sup>&</sup>lt;sup>152</sup> Ruthann Rudell, David Camann, John Spengler, Leo Korn, and Julia Brody, "Phthalates, Alkyphenols, Pesticides, Polybrominated Diphenyl Ethers, and Other Endocrine Disrupting Hormones in Indoor Air and Dust" Environmental Science and Technology,

<sup>&</sup>lt;sup>153</sup> Renee Sharp and Sonya Lunder, "In the Dust: Toxic Fire Retardants in American Homes" Environmental Working Group, 2004

<sup>&</sup>lt;sup>154</sup> Song et al., 2004. Polybrominated diphenyl ethers in the Sediments of the Great Lakes. 1. Lake Superior. Environmental Science and Technology 38(12)3286 – 3293.

<sup>&</sup>lt;sup>155</sup> Rayne et al. 2003. Rapidly increasing polybrominated diphenyl ether concentrations in the Columbia River system from 1992 to 2000. Environmental Science and Technology, 37(13) 2847 – 2854.

detected in polar bears. In the second, polar cod and beluga whale, the beluga whale, with similar diet to ringed seal, showed higher and more complex PBDE levels than ringed seal.<sup>156</sup>

Buck measured total PBDEs in bald eagle eggs collected along the Lower Columbia River at 446  $-1,206 \mu g/kg$  wet weight.<sup>157</sup>

In 2000, the Washington State Department of 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) compared to 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. 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.<sup>158</sup>

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 - 10 times greater than those reported for sperm whales from the north Atlantic near industrialized regions of Europe and the range of total PBDE concentrations in pilot whales in the North Sea. 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 - 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 contaminants in aquatic biota.<sup>159</sup>

Temporal trends indicate increasing levels of PBDEs in animals. Ikonomou et al. measured the blubber of Arctic male ringed seals over the period 1981 - 2000. Mean total PBDE concentrations increased exponentially from approximately 0.6 µg/kg lipid in 1981 to 6.0 µg/kg lipid in 2000.<sup>160</sup> Between 1989 and 1998, PBDE concentrations in tissue from harbor seals in

<sup>&</sup>lt;sup>156</sup> Hans Wolkers, Bert van Bavel, Øystein Wiig, Kit M. Kovacs, Christian Lydersen, and Gunilla Lindstrom, "Congener-Specific Accumulation and Food Chain Transfer of Polybrominated Diphenyl Ethers n Two Arctic Food Chains," Environmental Science and Technology, Vol. 38, No. 6, 2004, pp. 1667 – 1674.

<sup>&</sup>lt;sup>157</sup> Buck, 1999. Changes in productivity and environmental contaminants in bald eagles nesting along the lower Columbia River, US Fish and Wildlife Service, Portland, Oregon.

<sup>&</sup>lt;sup>158</sup> A. Johnson, N. Olsen, "Analysis and Occurrence of Polybrominated Diphenyl Ethers in Washington State Freshwater Fish," Archives of Environmental Contamination and Toxicology, 2001, 41, pp. 339 – 344,

<sup>&</sup>lt;sup>159</sup> Rayne et al., 2004. PBDEs, PBBs, and PCNs in three communities of free-ranging killer whales (Orcinus orca) from the Northeastern Pacific Ocean. Environmental Science and Technology, (38)4293 - 4299.

<sup>&</sup>lt;sup>160</sup> Ikonomou et al., 2000. Congener patterns, spatial and temporal trends of polybrominated diphenyl ethers in biota samples from the Canadian West Coast and the Northwest Territories. Organohalogen Compounds 47: 77 - 80.

San Francisco Bay doubled every 1.8 years.<sup>161</sup> Lebeuf et al. measured PBDEs in blubber from beluga whales in the St. Lawrence Estuary in Canada for the period 1988 – 1999. Total PBDEs measured exponentially increased over the period, with a doubling period of no longer than three years.<sup>162</sup>

Table 7 summarizes PBDEs measured in North American biota.

 $<sup>^{161}</sup>$  She W. et al, 2002. PBDEs in the San Francisco Bay Area: Measurements in harbor seal blubber and human breast adipose tissue. Chemosphere (46)697 – 707.

<sup>&</sup>lt;sup>162</sup> Lebeuf et al. 2004. Levels and Temporal Trends (1988 – 1999) of polybrominated diphenyl ethers in beluga whales (Delphinapterus leucas) from the St. Lawrence Estuary, Canada. Environmental Science and Technology, 39(11)2971 - 2977.

Organism	Location; year	Total PBDEs	Reference
Dungeness crab hepatopancreas	West coast, Canada; 1993 - 1995	4.2 – 480 μg/kg lipid	163
Bald eagle egg	Lower Columbia River, Washington and Oregon, 1994 - 1995	446 – 1,206 μg/kg ww	164
Heron egg	British Columbia; 1983 - 2000	1.308 – 288 μg/kg ww	165
Murre egg	Northern Canada; 1975 - 1998	0.442 – 2.93 μg/kg ww	
Fulmar egg	Northern Canada; 1975 - 1998	0.212 – 2.37 μg/kg ww	
Herring gull egg	Great Lakes; 1981 - 2000	9.4 – 1544 μg/kg ww	166
Beluga whale blubber	Canadian Arctic	81.2 – 160 μg/kg lipid	167
Beluga whale blubber	St. Lawrence Estuary, Canada, 1988 - 1999	17.2 – 935 µg/kg lipid	168
Orca blubber	Northeastern Pacific Ocean; 1993 - 1996	87 – 1,620 μg/kg lipid	169
Mountain whitefish (muscle)	Columbia River, British Columbia; 1992 - 2000	0.726 – 131 µg/kg ww	170
Lake trout	Lake Ontario; 1997	95 μg/kg ww	171
	Lake Erie; 1997	27 μg/kg ww	
	Lake Superior; 1997	56 μg/kg ww	
	Lake Huron; 1997	50 μg/kg ww	
Rainbow trout	Spokane River, Washington;	297 µg/kg ww	172
Mountain whitefish	1999	1250 µg/kg ww	
Largescale sucker		105 µg/kg ww	
Carp	Virginia; 1998 - 1999	1140 µg/kg ww	173

Table 7	Magurad	aanaantrations	of DDDE	in North	American biota
	Measureu	concentrations	01 F DDES	III INOLUI	American biota

<sup>&</sup>lt;sup>163</sup> Ikonomou et al., 2002. Occurrence and congener profiles of polybrominated diphenyl ethers (PBDEs) in environmental samples from coastal British Columbia, Canada. Chemosphere (46) 649 - 663. <sup>164</sup> Buck, 1999. Changes in productivity and environmental contaminants in bald eagles nesting along the lower

Columbia River, US Fish and Wildlife Service, Portland, Oregon.

<sup>&</sup>lt;sup>165</sup> Wakeford et al. 2002. Analysis of polybrominated diphenyl ethers (BDEs) in wildlife tissues – Canadian Wildlife Service contributions. Abstracts of the 4<sup>th</sup> Annual Workshop on Brominated Flame Retardants in the Environment, June 17 – 18, Canada Center for Inland Waters, Burlington, Ontario.

<sup>&</sup>lt;sup>166</sup> Norstrom et al. 2002. Geographical distribution (2000) and temporal trends (1981 – 2000) of brominated diphenyl ethers in Great Lakes herring gull eggs. Environmental Science and Technology, 36(22)4783 - 4789

<sup>&</sup>lt;sup>167</sup> Alaee et al. 1999. Distribution of polybrominated diphenyl ethers in the Canadian environment. Organohalogen Compounds (40) 347 - 350.

<sup>&</sup>lt;sup>168</sup> Lebeuf et al. 2004. Levels and Temporal Trends (1988 – 1999) of polybrominated diphenyl ethers in beluga whales (Delphinapterus leucas) from the St. Lawrence Estuary, Canada. Environmental Science and Technology, 39(11)2971 - 2977.

<sup>&</sup>lt;sup>169</sup> Rayne et al., 2004. PBDEs, PBBs, and PCNs in three communities of free-ranging killer whales (Orcinus orca) from the Northeastern Pacific Ocean. Environmental Science and Technology, (38)4293 - 4299.

<sup>&</sup>lt;sup>170</sup> Ravne et al. 2003. Rapidly increasing polybrominated diphenyl ether concentrations in the Columbia River system from 1992 to 2000. Environmental Science and Technology, 37(13) 2847 – 2854. <sup>171</sup> Luross et al. 2002. Spatial distribution of polybrominated diphenyl ethers and polybrominated biphenyls in lake

trout from the Laurentian Great Lakes. Chemosphere, 46: 665 - 672.

<sup>&</sup>lt;sup>172</sup> Johnson and Olson, 2001. Analysis and occurrence of polybrominated diphenyl ethers in Washington State freshwater fish. Bulletin of Environmental Contamination and Toxicology, 41: 339 – 344.

<sup>&</sup>lt;sup>173</sup> Hale et al. 2001. Polybrominated diphenyl ether flame retardants in Virginia freshwater fishes (USA). Environmental Science and Technology 35(23):4585 – 4591.

## **Environmental Fate and Pathways**

#### 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.

By far the largest percentage of PBDEs detected were of the decabrominated BDE-209 congener, a marker for the environmental distribution of the commercial deca-BDE formulation. This was followed by the tetrabrominated BDE-47 and the pentabrominated BDE-99 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 from 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-209 still has primary sources. The difference in PBDE congeners therefore reflects the change in usage of commercial PBDE formulations.

BDE-17, a tribrominated congener, was also detected in the air on the Baltic Sea island. It has not been detected in the air at source areas, such as electronics recycling facilities and highly urbanized environments. The researchers believe it is likely BDE-17 is a breakdown product from atmospheric debromination processes, possibly from BDE-209.<sup>174</sup>

PBDEs have been identified in polar cod, ringed seal, polar bear and beluga whale.<sup>175</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 POP in arctic habitats.<sup>176</sup>

### **Environmental breakdown of PBDEs**

A number of studies, summarized in Appendix A, suggest that PBDEs may break down in the environment, both as a result of exposure to light, known as photolytic degradation, and as a

<sup>&</sup>lt;sup>174</sup> Ter Schure, Larsson, Agrell, and Boon, 2004. Atmospheric Transport of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls to the Baltic Sea. Environmental Science and Technology, 38(5)1282 – 1286.

<sup>&</sup>lt;sup>175</sup> Wolkers, van Bavel, Wiig, Kovacs, Lydersen, and Lindstrom, 2004. Congener-Specific Accumulation and Food Chain Transfer of Polybrominated Diphenyl Ethers n Two Arctic Food Chains. Environmental Science and Technology, 38(6)1667 – 1674.

<sup>&</sup>lt;sup>176</sup> National Marine Fisheries Service, 2004. Alaska Essential Fish Habitat Environmental Impact Statement: Appendix G: Non-fishing Impacts to Essential Fish Habitat and Recommended Conservation Measures. p. G-61, <u>http://www.fakr.noaa.gov</u>, viewed 17 May 2004.

result of biological processes. Environmental degradation would be important because PBDEs become more water soluble and bioavailable the fewer the bromines attached to the molecule.

Photochemical reaction rates for PBDEs as a class appear to vary as a result of a number of conditions.

Photolytic reaction rates become slower as the number of bromine atoms attached to the PBDE molecule decrease. Deca-BDE breaks down more quickly than nona-BDE, which breaks down more quickly than octa-BDE, and so on.

Molecules with the maximum of five bromine atoms attached to one of the carbon rings appear to degrade more quickly. The effect of bromine position on photolytic reaction rate for molecules with less than five bromine atoms on one of the carbon rings is unclear. Bezares-Cruz et al. found greatest reactivity for congeners with bromine atoms in all of the ortho positions, while Ericksson et al. found inconclusive results for congeners with less than five bromine atoms attached to one of the carbon rings.

In experiments with BDE-209, or deca-BDE, where the molecule is in or on a substance that maximizes exposure to UV light, for example, a smooth, hard, surface or in a clear solution, photolytic reaction rates increase. Conversely, it appears that when the BDE-209 molecule is in or on a substance that minimizes exposure to UV light, such as sediment or soil, photolytic reaction rates decrease.

Reaction rates are fastest in or on substances with readily available hydrogen donors, such as organic solvents. Photolytic reaction rates appear slower when PBDEs are in or on substances with lower concentrations of hydrogen donors or less favorable hydrogen donors, such as humic acids in water. Photolytic reaction rates are also expected to be slower where organic carbon may bind to the PBDE molecule.

Degradation products and rate both appear to vary with the intensity of UV light. As the number of bromine atoms on the PBDE molecule decreases, the molecule's ability to absorb solar radiation decreases. This is because the upper limit on the range of light wavelengths that the molecule can absorb decreases as the number of bromine atoms decreases. The overlap in the range of solar wavelengths at ground level and the range of wavelengths absorbed by PBDE molecules thus decreases as the number of bromine atoms decreases.

The chemical properties of the matrix may also affect breakdown products. The first step in the photolysis reaction is the cleavage of the carbon-bromine bond. In laboratory experiments using organic solvents, water with dissolved humic substances, sand, soil, and sediment, the nonabrominated aryl radical formed can then abstract a hydrogen atom from the solvent or from humic substances dissolved in water or on the sand, soil or sediment. The debrominated product is thus formed through reductive debromination. As reductive debromination has been observed in experiments using water with dissolved humic substances, it must be assumed that this may also occur in the environment. Other factors, not yet explored, may also influence both photolytic degradation rate and products.

Globally, Deca-BDE has become the most used commercial PBDE product; after December 2004, it will be the only PBDE product still in production. There is a weight of evidence suggesting that highly brominated PBDEs are precursors of the more bioaccumulative and persistent lower brominated PBDEs, as well as PBDFs. While the degree to which this phenomenon adds to the overall risk presented to organisms from formation of the more toxic and persistent tetra- to hexa-BDE congeners or from the formation of PBDFs is not known, there is sufficient evidence to warrant concern.

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

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 this criteria, many products containing PBDEs would probably be considered dangerous waste at end-of-life.

A web search was conducted to identify regulations and legislation pertaining to PBDEs at the state, federal, and international levels. Activities other than those identified below may also exist.

## **Federal Overview**

Deca-BDE is the only one of the commercial PBDE formulations for which reporting is required for the US Environmental Protection Agency's (EPA's) Toxic Release Inventory. The Toxics Release Inventory (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 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 dispose. 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, including Deca-BDE, by March 2005.

EPA is in the process of developing a Significant New Use Rule (SNUR) for Penta- and Octa-BDE. The rule would require notification to EPA prior to manufacture or import of Penta- or Octa-BDE for any use after January 1, 2005.<sup>177</sup> EPA's authority to issue SNUR's comes from The Toxic Substances Control Act section 5(a).

EPA is developing a rule 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>178</sup>

TSCA contains an "unreasonable risk" regulatory standard, which is the basis, for control of new flame retardants introduced into commerce through EPA's New Chemicals Program. It is also

<sup>&</sup>lt;sup>177</sup> Kenneth Moss, "BFR Regulatory Update" The Third International Workshop on Brominated Flame Retardants: BFR 2004 abstracts, p. 7.

<sup>&</sup>lt;sup>178</sup> Kenneth Moss, "BFR Regulatory Update" The Third International Workshop on Brominated Flame Retardants: BFR 2004 abstracts, p. 7.

the basis for certain brominated flame retardants to determine dioxin and furan contamination under EPA's 1987 TSCA Section 4 Dioxin/Furan Test Rule (CFR 766). Since 1979, approximately 150 Premanufacture Notices submitted for new flame retardant chemicals have been reviewed by EPA.

Directly or through grant mechanisms, EPA research managed by the Office of Research and Development 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.

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.

EPA is conducting an Integrated Risk Information System assessment of PBDEs to be completed by the end of 2004.

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. 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<sup>179</sup>

## **Other States: Overview**

## California

<sup>&</sup>lt;sup>179</sup> US Navy. Interagency Workgroup on Fire and Materials. Available at: <u>http://www.dt.navy.mil/sur-str-mat/fun-mat/fir-pro-sea/int-wor-gro/</u>, viewed 1 October 2004.

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>180</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 DecaBDE 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 decaBDE and the known human exposures to this chemical, it does not appear that human exposure to decaBDE 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>181</sup>

The report went on to state that, because of the 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>182</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>183</sup>

### Hawaii

In June 2004, Hawaii enacted HB2013/SD2/CD1, which prohibits the manufacturing, 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>184</sup>

## New York

In August 2004, New York enacted A 10050/S 7621, which prohibits the manufacture, process, or distribution of BFRs. It does not prohibit the use or sale of products containing BFRs. 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>185</sup>

<sup>&</sup>lt;sup>180</sup> State of California Legislative Counsel, <u>http://www.leginfo.ca.gov/</u>, viewed 15 September 2004.

<sup>&</sup>lt;sup>181</sup> Wiley and McCarthy, 2004. Polybrominated Diphenyl Ethers (PBDEs): Potential Hazards from DecaBDE and Unresolved Issues from AB 302. California Senate Office of Research.

<sup>&</sup>lt;sup>182</sup> Wiley and McCarthy, 2004. Polybrominated Diphenyl Ethers (PBDEs): Potential Hazards from DecaBDE and Unresolved Issues from AB 302. California Senate Office of Research.

<sup>&</sup>lt;sup>183</sup> Wiley and McCarthy, 2004. Polybrominated Diphenyl Ethers (PBDEs): Potential Hazards from DecaBDE and Unresolved Issues from AB 302. California Senate Office of Research.

<sup>&</sup>lt;sup>184</sup> Hawaii State Legislature, <u>http://www.capitol.hawaii.gov/</u>, viewed 1 September 2004.

<sup>&</sup>lt;sup>185</sup> New York State Assembly, <u>http://assembly.state.ny.us/leg</u>, viewed 8 October 2004.

### Maine

In April 2004, Maine enacted LD1790, which prohibits, effective January 1, 2006, the sale or distribution for promotional purposes of products that contain more than 1% of the penta or octa mixtures of PBDEs. The Maine Department of Environmental Protection will report annually to the Joint Natural Resource Committee on whether a safer alternative to the Deca-BDE mixture of PBDEs is nationally available. If the Committee determines that this is the case, it may recommend that the Legislature enact legislation to implement risk management measures or enact a prohibition on the sale and distribution of products containing Deca-BDE.<sup>186</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>187</sup>

### Michigan

### Proposed Legislation:

<u>HB 4406</u> regulates release of PBDEs and was referred to the House Committee on Land Use and Environment in March 2003.

<u>HB 4407</u> provides sentencing guidelines for the crime of releasing polybrominated diphenyl ethers (PBDEs) into the environment and was referred to the House Committee on Criminal Justice in March 2003.

### **New Jersey**

Deca-BDE is subject to the New Jersey Right to Know Hazardous Substance List (1 percent reporting limit)<sup>188</sup>

### Pennsylvania

Deca-BDE is subject to the Pennsylvania Environmental Hazard List.<sup>189</sup>

<sup>&</sup>lt;sup>186</sup> Maine State Legislature, <u>http://janus.state.me.us/</u>, viewed 29 April 2004.

<sup>&</sup>lt;sup>187</sup> Great Lakes Chemical Corporation, Material Safety Data Sheet for Great Lakes DE-83R and DE83, viewed at <u>http://www.greatlakes.com/common/msdspdf/00001.pdf</u> on March 29, 2004.

<sup>&</sup>lt;sup>188</sup> Great Lakes Chemical Corporation, Material Safety Data Sheet for Great Lakes DE-83R and DE83, viewed at <u>http://www.greatlakes.com/common/msdspdf/00001.pdf</u> on March 29, 2004.

<sup>&</sup>lt;sup>189</sup> Great Lakes Chemical Corporation, Material Safety Data Sheet for Great Lakes DE-83R and DE83, viewed at <u>http://www.greatlakes.com/common/msdspdf/00001.pdf</u> on March 29, 2004.

## International Overview

### **European Union**

Directive 2003/11/EC of February 6, 2003, bans the marketing and use of Penta-BDE, including the marketing of articles containing Penta-BDE, as of August 15, 2004.

In January 2003, the European Parliament and the Council of the European Union passed Directive 2002/95/EC, restricting the use of certain hazardous substances in electrical and electronic equipment (RoHS). Article 4(1) lists the substances which are to be phased out of electrical and electronic equipment by July 1, 2006, including all forms of PBDE. The Directive also states that the European Commission Joint Research Center should evaluate 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 February 2004, France completed the Human Health Draft of the Draft Update Risk Assessment of Bis(Pentabromophenyl) Ether (Decabromodiphenyl Ether), within the framework of the Existing Substances Regulation (793/93 EEC). 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>190</sup>

In May 2004, the United Kingdom completed the Final Environmental Draft of the Draft Update Risk Assessment of Bis(Pentabromophenyl) Ether (Decabromodiphenyl Ether). This portion of the Draft Update made two conclusions about Deca-BDE.

First, it first concluded that there is a need for further information and/or testing with regard to the PBT assessment for Deca-BDE. The Draft Update stated that, using criteria presented in the Technical Guidance document used for the risk assessment, Deca-BDE is likely to be very persistent, but not bioaccumulative or toxic in the marine environment. However, the PBT assessment is complicated by data available on the:

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

The risk assessment states that this means the available assessment methodology might not be applicable to Deca-BDE. Further, it states that at a minimum there is a continued need to monitor environmental contamination for a suitable time period for both Deca-BDE and, if possible, its more toxic and bioaccumulative degradation products. At a minimum, estuarine

<sup>&</sup>lt;sup>190</sup> European Commission Joint Research Center, 2004. Update of the risk assessment of Bis(Pentabromophenyl) Ether (Decabromodiphenyl Ether): Human Health Draft of February 2004.

sediment, bird of prey tissues and sewage sludge samples should be sampled. Any programme should be reviewed at a suitable point to decide if further action is necessary.

The risk assessment points out that this additional work will take some years to deliver results. It states that the evidence presented in the updated assessment should be examined further at the policy level to review whether precautionary risk management is still considered necessary.

The second conclusion stated 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 with regard to the assessment of surface water and sediment (freshwater and marine), waste water treatment plants, the terrestrial compartment, the air compartment and secondary poisoning for all life cycle stages.<sup>191</sup>

Some confusion has resulted over the meaning of these conclusions. In an effort to clarify matters, Ecology staff wrote to EU staff working on the risk assessment and asked: "The Risk Assessment is being circulated here as proof that Deca is a safe product, with no further regulation required. Would you agree with this conclusion?"

EU staff responded: "The Conclusion is that further information and testing are required in an attempt to demonstrate whether the substance is or is not a safe product. So the current risk assessment does not support the above statement."<sup>192</sup>

In a letter dated August 24, 2004, Margot Wallström, the European Union's Commissioner for the Environment, stated that she sees "...outstanding safety concerns related to DecaBDE and ... that proportionate precautionary measures are necessary to reduce DecaBDE's emissions in the environment. (She) therefore will not propose to the (European) Commission that it lift the ban on DecaBDE currently existing under the RoHS Directive."<sup>193</sup>

Deca-BDE is currently being evaluated by the European Commission for exemption from the ban under the RoHS Directive. Through July 5, 2004, the Commission solicited written stakeholder comments in response to the following questions with regard to Deca-BDE:

- Do feasible substitutes currently exist in an industrial and/or commercial scale?
- Do any restrictions apply to such substitutes?
- What are the costs and benefits and advantages and disadvantages of such substitutes?

Responses are posted on the Commission's website at <u>http://europa.eu.int/comm/environment/waste/weee\_index.htm</u>.

## Australia

Australia published an assessment of PBDEs in June 2001, conducted under its National Industrial Chemicals Notification and Assessment Scheme. The assessment recommended that,

<sup>192</sup> pers. comm., S. Munn to C. Peele, August 26, 2004 by e-mail.

<sup>&</sup>lt;sup>191</sup> European Commission Joint Research Center, 2004. Update of the risk assessment of Bis(Pentabromophenyl) Ether (Decabromodiphenyl Ether): Final Environmental Draft of May 2004.

<sup>&</sup>lt;sup>193</sup> M. Wallström in letter to J. Hontelez, M. Taylor, J. Riss, and M. Warhurst, August 24, 2004.

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>194</sup>

### Canada

Deca-BDE is listed on the Domestic Substances List, <sup>195</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>196</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>197</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>198</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.<sup>199</sup>

In February 2004, Health Canada released a "Screening Assessment Report- Health: Polybrominated Diphenyl Ethers (PBDEs) [Tetra-, Penta-, Hexa-, Hepta-, Octa-, Nona- and

<sup>198</sup> Environment Canada, "CEPA Environmental Registry Substances Lists: Virtual Elimination List" <u>http://www.ec.gc.ca/CEPARegistry/subs\_list/VirtualEliminationList.cfm</u>, viewed 12 July 2004.

<sup>199</sup> Environment Canada, "Management of Toxic Substances: Track 1",

 <sup>&</sup>lt;sup>194</sup> "Polybrominated Flame Retardants (PBFRs): Priority Existing Chemical Assessment Report No. 20" National Industrial Chemicals Notification and Assessment Scheme, June 2001.
 <sup>195</sup> Great Lakes Chemical Corporation, Material Safety Data Sheet for Great Lakes DE-83R and DE83, viewed at

<sup>&</sup>lt;sup>195</sup> Great Lakes Chemical Corporation, Material Safety Data Sheet for Great Lakes DE-83R and DE83, viewed at <u>http://www.greatlakes.com/common/msdspdf/00001.pdf</u> on March 29, 2004.

<sup>&</sup>lt;sup>196</sup> Environment Canada, "Existing Substances Evaluation: Domestic Substances List Categorization and Screening Program," <u>www.ec.gc.ca</u>, viewed 26 May 2005.

 <sup>&</sup>lt;sup>197</sup> Environment Canada, "Draft for Public Comments: Canadian Environmental Protection Act 1999 Environmental Screening Assessment Report on Polybrominated Diphenyl Ethers (PBDEs)" February 2004, p. 14.
 <sup>198</sup> Environment Canada, "CEPA Environmental Registry Substances Lists: Virtual Elimination List"

http://www.ec.gc.ca/toxics/TSMP/en/track1.cfm, viewed 12 July 2004.

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>200</sup>

## China

China's Ministry of Information draft regulation entitled the "Management Methods for the Prevention and Control of Pollution from Electronics Information Products" (Methods) is expected to be finalized by mid-2004. 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>201</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>202</sup>

## Germany

Deca-BDE is not used on a voluntary basis in Germany by association-bound companies in the plastics and textile industry.<sup>203</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>204</sup>

## Sweden

In May 2004, Sweden commissioned the national chemicals inspectorate, KemI, to draft plans for banning Deca-BDE, in advance of an EU ban. KemI is considering a national ban on all brominated flame retardants and is examining risks associated with a number of other substances.<sup>205</sup>

<sup>&</sup>lt;sup>200</sup> Health Canada, "Screening Assessment Report- Health: Polybrominated Diphenyl Ethers (PBDEs) [Tetra-, Penta-, Hexa-, Hepta-, Octa-, Nona- and Deca- Congeners]", February 2004, p. 6.

 <sup>&</sup>lt;sup>201</sup> American Electronics Association, "AeA Update: International Environmental Regulations affecting High-Tech Companies," <u>www.aeanet.org</u>, viewed 4 May 2004.
 <sup>202</sup> "Action Plan for Brominated Flame Retardants" Danish Environmental Protection Agency, March 2001, p. 7.

 <sup>&</sup>lt;sup>202</sup> "Action Plan for Brominated Flame Retardants" Danish Environmental Protection Agency, March 2001, p. 7.
 <sup>203</sup> A. Leisewitz, H. Kruse, and E. Schramm, "Substituting Environmentally-Relevant Flame Retardants: Assessment Fundamentals" Environmental Research of the Federal Ministry of the Environment, Nature Conservation and Nuclear Safety, June 2001, p. 74.

<sup>&</sup>lt;sup>204</sup> Carsten Lassen, Søren Løkke, Lina Ivar Andersen, Brominated Flame Retardants: Substance Flow Analysis and Assessment of Alternatives, Danish Environmental Protection Agency, 1999, p. 122.

<sup>&</sup>lt;sup>205</sup> Environment Daily 1662, 06/05/04

## OECD

The Organization for Economic Cooperation and Development (OECD) is made up of 30 member countries, including the US, and has active relationships with about 70 other countries.<sup>206</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>207</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>208</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>209</sup>

### **POPS Treaty**

The Stockholm Convention on Persistent Organic Pollutants is a global treaty to protect human health and the environment from persistent organic pollutants (POPs). The Convention outlines measures to reduce or eliminate releases from 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>210</sup>

The US has signed the Stockholm Convention, but has not yet ratified it. A bill to implement the Convention in the US, 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 United States will not automatically adopt the change.

<sup>&</sup>lt;sup>206</sup> "About OECD" Organization for Economic Development and Cooperation, http://www.oecd.org/about/0,2337,en\_2649\_201185\_1\_1\_1\_1\_00.html, viewed 13 July 2004.

<sup>&</sup>lt;sup>207</sup> "Action Plan for Brominated Flame Retardants," Ministry of Environment and Energy Danish Environmental Protection Agency, English Translation, March 2001, p. 22.

<sup>&</sup>lt;sup>208</sup> OSPAR Commission, "Certain Brominated Flame Retardants- Polybrominated Diphenylethers, Polybrominated Biphenyls, Hexabromo Cyclododecane" 2001

<sup>&</sup>lt;sup>209</sup> OECD, "Brominated Flame Retardants (BFRs): Hazard/Risk Information Sheets" February 2004, http://www.oecd.org/dataoecd/53/60/32021808.pdf, viewed 12 July 2004.

<sup>&</sup>lt;sup>210</sup> United Nations Environment Programme, "Stockholm Convention on Persistent Organic Pollutants (POPs), <u>www.pops.int</u>, viewed May 17, 2004.

Instead, the EPA administrator will follow an independent process to determine whether and how the chemical substance will be restricted in the United States. On April 29, 2004, the bill was placed on the Senate Legislative Calendar under General Orders.<sup>211</sup>

Jim Willis, the head of the United Nations Environment Programme chemicals division, told other chemicals.<sup>212</sup> The Nordic countries are working together to nominate Penta-BDE as a POP candidate.<sup>213</sup> Reuters that "brominated flame retardants are a possibility (for addition to the list) as are many

<sup>&</sup>lt;sup>211</sup> US Senate, "S. 1486" 108<sup>th</sup> Congress, Second Session, Calendar No. 481, thomas.loc.gov, viewed 17 May 2004.
<sup>212</sup> Alistar Doyle, "Dirty dozen' toxins are banned by UN pact," The Guardian, 17 May 2004.
<sup>213</sup> OECD, "Brominated Flame Retardants (BFRs): Hazard/Risk Information Sheets" February 2004,

# V. Alternatives and Market Changes

## **Alternatives to PBDEs**

Four documents have been identified that evaluate flame retardants. Three focus 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.

The Danish Environmental Protection Agency issued "Brominated Flame Retardants: Substance Flow Analysis and Assessment of Alternatives" in June 1999. The report assesses 11 non-brominated flame retardants.

Leisewitz, Kruse, and Schramm produced "Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals: Results and Summary Overview" for the German Environmental Research of the Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety in June 2001. The report examines the properties of 13 major flame retardants and six product categories that typically use brominated flame retardants.

Fisk, Girling and Wildey produced "Prioritization of Flame Retardants for Environmental Risk Assessment," for the United Kingdom Environment Agency in August 2003. The report presents an overview of flame retardants in use in the United Kingdom and identifies substances that might require detailed consideration based on their impact to the environment. The report does not consider human health benefits or risks. It summarizes the uses, mechanisms of action and environmental regulation of flame retardants and considers routes by which they may enter the environment.

The fourth document was produced in 2000, by the National Academy of Sciences (NAS). NAS reviewed the toxicological and exposure data of 16 flame retardants, including Deca-BDE, to assess potential health risk to consumers and the general population resulting from potential exposure from the chemicals in residential furniture.

Despite the lack of a complete database, the report concluded that Deca-BDE, along with a number of other flame retardants listed in Table 8, could be used on furniture with minimal risk, even under worst-case assumptions. It should be noted that Ecology's and DOH's concerns about Deca-BDE stem mainly from its potential to break down in the environment, supported by studies conducted primarily since 2000.<sup>214</sup>

Conclusions from the four reports are summarized in Table 8.

<sup>&</sup>lt;sup>214</sup> National Research Council, 2000. Toxicological risks of selected flame retardant chemicals. Available at http://www.nap.edu/catalog/9841.html.

	Perceived availability of data on substitutes for BFR's (UK and Denmark, 2003)				
Substance	Physico- chemical data	Health data	Environmental data	German recommendation (2001)	NAS recommendation (2000)
Ammonium polyphosphates	medium	medium	medium	Application unproblematic	Could be used on residential furniture with minimal risk
Aluminum trioxide	not addressed	not addressed	not addressed	Application unproblematic	not addressed
Alumina trihydrate	not addressed	not addressed	not addressed	not addressed	Could be used on residential furniture with minimal risk
Antimony pentoxide	not addressed	not addressed	not addressed	not addressed	Recommend exposure studies
Antimony trioxide	good	good	good	Problematic properties, reduction sensible	Recommend exposure studies
Aromatic phosphate plasticizers	not addressed	not addressed	not addressed	not addressed	Recommend exposure studies
Calcium and zinc molybdates	not addressed	not addressed	not addressed	not addressed	Recommend exposure studies
Chlorinated parafins	not addressed	not addressed	not addressed	not addressed	Recommend exposure studies
Hexabromocyclodo decane	not addressed	not addressed	not addressed	Problematic properties, reduction sensible	Could be used on residential furniture with minimal risk
Magnesium hydroxide	medium	good	medium	not addressed	Could be used on residential furniture with minimal risk
Melamine	good	good	good	not addressed	not addressed
Melamine cyanurate	not addressed	not addressed	not addressed	Recommendation impossible due to data deficit	not addressed
Organic phosphonates	not addressed	not addressed	not addressed	not addressed	Recommend exposure studies
Phosphonic acid (dimethyl ester)	poor	poor	poor	not addressed	Could be used on residential furniture with minimal risk
Pyrovatex CP new	not addressed	not addressed	not addressed	Recommendation impossible due to data deficit	not addressed
Red phosphorus	medium	medium	medium	Application unproblematic	not addressed

## Table 8. Summary of evaluation of alternative flame retardants

	Perceived availability of data on substitutes for BFR's (UK and Denmark, 2003)				
Substance	Physico- chemical data	Health data	Environmental data	German recommendation (2001)	NAS recommendation (2000)
Resorcinol bis(diphenyl phosphate)	medium	medium	medium	Recommendation impossible due to data deficit	not addressed
Sodium antimonate	not addressed	not addressed	not addressed	not addressed	Recommend exposure studies
Sodium borate decahydrate	not addressed	not addressed	not addressed	Problematic properties, reduction sensible	not addressed
Tetrabromobisphen ol A, additive	not addressed	not addressed	not addressed	Application rejected	not addressed
Tetrabromobisphen ol A, reactive	not addressed	not addressed	not addressed	Reduction sensible, substitution desired	not addressed
Tetrakis (hydroxymethyl) phosphonium salts (chloride salt)	not addressed	not addressed	not addressed	not addressed	Could be used on residential furniture with minimal risk
Tricresyl phosphate	good	good	good	not addressed	not addressed
Triphenyl phosphate	good	good	good	not addressed	not addressed
Tris(1-chloro-2- propyl) phosphate	not addressed	not addressed	not addressed	Reduction sensible, substitution desired	Recommend exposure studies
Tris (1,3- dichloropropyl-2) phosphate	not addressed	not addressed	not addressed	not addressed	Recommend exposure studies
Zinc borate	medium	medium	medium	not addressed	Could be used on residential furniture with minimal risk

Replacing PBDE's can take place in three ways.

1. PBDEs could be replaced by another flame retardant without changing the base polymer, or substrate.

2. The plastic material, i.e. the base polymer with flame retardants and other additives, could be replaced by another plastic material.

3. The product could be replaced by another product, or the function of the PBDE's could be fulfilled by a totally different solution.

For the selection of alternative flame retardants for a specific application the following subjects must be considered:

- Physical/chemical properties of alternatives during manufacturing.
- Physical/chemical properties of alternatives during use.
- Environmental and health risk of alternatives during manufacturing, use and disposal.
- Price of alternatives.
- Expenses of changes in tools and machinery.

In principle alternatives to PBDEs will exist for almost all applications, though cost and technical disadvantages may prove prohibitive.<sup>215</sup>

<sup>&</sup>lt;sup>215</sup> Danish Environmental Protection Agency, 1999. Brominated flame retardants: substance flow analysis and assessment of alternatives.

## Alternatives to Penta-BDE

Alternative flame retardants for Penta-BDE are listed by substrate in Table 8. Ecology and DOH have not examined the human health or environmental impacts of these alternatives. However, US EPA, working with textile manufacturers, flame retardant manufacturers, foam manufacturers, and furniture manufacturers, is in the process of writing and alternatives assessment for Penta-BDE, scheduled to be released in early December 2004.<sup>216</sup>

Table 9. 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, UK Environment Agency, 2003)

Substrate	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
Epoxy	<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>217</sup></li> <li>Tetrabromophthalic Anhydride Based Diol<sup>218</sup></li> <li>Tetrabromophthalic Anhydride<sup>219</sup></li> <li>Bis (Tribromophenoxy) ethane<sup>220</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>221</sup></li> <li>Tetrabromophthalic Anhydride Based Diol<sup>222</sup></li> <li>Bisphosphate <sup>223</sup></li> </ul>	• Some applications: mineral wool or other technical solutions

<sup>&</sup>lt;sup>216</sup> Pers. comm., K. Rindfusz to J. Shepard by e-mail, September 29, 2004.

<sup>217</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DBS"

- www.el.greatlakes.com/pdf/datasheet/PHT4%20ds.PDF, viewed 7 July 2004.

http://www.el.greatlakes.com/pdf/datasheet/FF-680 ds.PDF viewed 15 July, 2004

Great Lakes Chemical Corp., "Technical Information: Great Lakes PHT4-DIOL"

www.el.greatlakes.com/pdf/datasheet/PHT4%20Diol%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>222</sup> Great Lakes Chemical Corp., "Technical Information: Firemaster® 520"

www.el.greatlakes.com/pdf/datasheet/DBS%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>218</sup> Great Lakes Chemical Corp., "Technical Information: Firemaster® 520" www.el.greatlakes.com/pdf/datasheet/firemaster\_520 tech\_data\_sheet\_finalfinal.PDF, viewed 7 July 2004. <sup>219</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes PHT4"

Great Lakes Chemical Corp., "Technical Information: Great Lakes FF 680"

www.el.greatlakes.com/pdf/datasheet/firemaster 520 tech data sheet finalfinal.PDF, viewed 7 July 2004. <sup>223</sup> Great Lakes Chemical Corp.; "Technical Information: Great Lakes Reofos RDP"

http://www.el.greatlakes.com/pdf/datasheet/Technical Data Sheet - Reofos RDP.pdf

	Products in which the substrate is used in flame	Alternative flame retardants in	Alternative materials: Non-flammable or containing halogen-free
Substrate	retardant quantity	commercial materials	flame retardants
Flexible polyurethane	• Furniture	Ammonium polyphosphate	None identified
foam	• Components in	• Melamine	
	transportation	Reactive phosphorus polyols	
		• Tetrabromophthalic anhydride derivative <sup>224</sup>	
		• Phosphorous-Bromine <sup>225</sup>	
		• Reofos NHP (halogen-free	
		phosphorus flame retardant) <sup>226</sup>	
		• Bisphosphate <sup>227</sup>	
Laminates		Triaryl phosphate	None identified
		isopropylated <sup>228</sup>	
Adhesives		• Tetrabromophthalate diol <sup>229</sup>	None identified
		• Tetrabromophthalic anhydride	
		based diol <sup>230</sup>	
		• Hexabromocyclododecane <sup>231</sup>	
		• Reomol® TOP <sup>232</sup>	
		• Bis (Tribromophenoxy)	
		ethane <sup>233</sup>	
Coatings		• Tetrabromophthalate Diol <sup>234</sup>	None identified
		• Tetrabromophthalic anhydride	
		based diol <sup>235</sup>	
		• Hexabromocyclododecane <sup>236</sup>	
		• Triaryl phosphate <sup>237</sup>	
		• Bis (Tribromophenoxy)	
		ethane <sup>238</sup>	

<sup>&</sup>lt;sup>224</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes Firemaster® BZ-54" www.el.greatlakes.com/pdf/datasheet/BZ-54%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>225</sup> Great Lakes Chemical Corp., "Technical Information: Firemaster® 550"

www.el.greatlakes.com/pdf/datasheet/Firemaster 550P ds.PDF, viewed 7 July 2004.

<sup>&</sup>lt;sup>226</sup> Great Lakes Chemical Corp.; "Technical Information: Great Lakes Reofos NHP"

http://www.el.greatlakes.com/pdf/datasheet/Reofos NHP Data Sheet -Revised 09.02.pdf Great Lakes Chemical Corp.; "Technical Information: Great Lakes Reofos RDP"

http://www.el.greatlakes.com/pdf/datasheet/Technical Data Sheet - Reofos RDP.pdf

<sup>&</sup>lt;sup>228</sup> Great Lakes Chemical Corp.; "Technical Information: Great Lakes Refos35"

http://www.e1.greatlakes.com/pdf/datasheet/Reofos 35 Data Sheet.PDF

<sup>&</sup>lt;sup>229</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes PHT4-DIOL"

www.e1.greatlakes.com/pdf/datasheet/PHT4%20Diol%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>230</sup> Great Lakes Chemical Corp., "Technical Information: Firemaster® 520"

www.el.greatlakes.com/pdf/datasheet/firemaster\_520\_tech\_data\_sheet\_finalfinal.PDF, viewed 7 July 2004. <sup>231</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes CD-75P"

www.el.greatlakes.com/pdf/datasheet/CD-75P%20Data%20Sheet.PDF, viewed 7 July 2004.

<sup>&</sup>lt;sup>232</sup> Great Lakes Chemical Corp.; "Technical Information: Great Lakes Remol TOP"

http://www.e1.greatlakes.com/pdf/datasheet/Reomol TOP.pdf

Great Lakes Chemical Corp., "Technical Information: Great Lakes FF 680" http://www.el.greatlakes.com/pdf/datasheet/FF-680 ds.PDF viewed 15 July, 2004

<sup>&</sup>lt;sup>4</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes PHT4-DIOL"

www.e1.greatlakes.com/pdf/datasheet/PHT4%20Diol%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>235</sup> Great Lakes Chemical Corp., "Technical Information: Firemaster® 520"

www.el.greatlakes.com/pdf/datasheet/firemaster 520 tech data sheet finalfinal.PDF, viewed 7 July 2004.

<sup>&</sup>lt;sup>236</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes CD-75P"

www.el.greatlakes.com/pdf/datasheet/CD-75P%20Data%20Sheet.PDF, viewed 7 July 2004.

## Alternatives to Octa-BDE

Alternative flame retardants for Octa-BDE are listed by substrate in Table 9. Ecology and DOH have not evaluated the human health or environmental impacts of these alternatives.

Table 10. 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	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>239, 240</sup></li> <li>Triaryl phosphate<sup>241</sup></li> <li>Triaryl phosphates butylated<sup>242</sup></li> <li>Bisphosphate<sup>243</sup></li> <li>Bis (Tribromophenoxy) ethane<sup>244</sup></li> <li>Phenoxy-terminated carbonate oligomer of tetrabromobisphenol A<sup>245</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	<ul> <li>Furniture, textiles</li> <li>Components in transportation</li> <li>Protective clothing</li> </ul>	<ul> <li>Reactive phosphorus constituents</li> <li>Hexabromocyclododecane<sup>246</sup></li> </ul>	None identified
Thermoplastic elastomers		<ul> <li>Bis (Tribromophenoxy) ethane<sup>247</sup></li> <li>Tribromophenyl allyl ether<sup>248</sup></li> </ul>	None identified

<sup>237</sup> Great Lakes Chemical Corp.; "Technical Information: Great Lakes Kronitex TCP" http://www.el.greatlakes.com/pdf/datasheet/kronitex TCP data sheet.pdf <sup>238</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes FF 680" http://www.el.greatlakes.com/pdf/datasheet/FF-680 ds.PDF viewed 15 July, 2004 <sup>9</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes BC-52" www.e1.greatlakes.com/pdf/datasheet/BC-52%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>240</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes BA-59P" www.el.greatlakes.com/pdf/datasheet/BA-59%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>241</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes Reofos TPP" http://www.e1.greatlakes.com/pdf/datasheet/Reofos TPP Data Sheet.PDF 242 Great Lakes Chemical Corp., "Technical Information: Great Lakes Refos 507" http://www.el.greatlakes.com/pdf/datasheet/Reofos 507 Data Sheet.PDF <sup>243</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes Reofos RDP" http://www.el.greatlakes.com/pdf/datasheet/Technical Data Sheet - Reofos RDP.pdf <sup>244</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes FF 680" http://www.el.greatlakes.com/pdf/datasheet/FF-680 ds.PDF 245 Great Lakes Chemical Corp., "Technical Information: Great Lakes BC52-HP" http://www.el.greatlakes.com/pdf/datasheet/BC-52HP Data Sheet.PDF viewed 15 July, 2004 246 Great Lakes Chemical Corp., "Technical Information: Great Lakes CD-75P" www.el.greatlakes.com/pdf/datasheet/CD-75P%20Data%20Sheet.PDF, viewed 7 July 2004. Great Lakes Chemical Corp., "Technical Information: Great Lakes FF 680"

	Products in which the		Alternative materials: Non-flammable or
	substrate is used in flame	Alternative flame retardants in	containing halogen-free
Substrate	retardant quantity	commercial materials	flame retardants
Polyolefins		Polypropylene-	None identified
		dibromostyrene <sup>249,250</sup>	
		• Dibromostyrene <sup>251</sup>	
		• Tetrabromobisphenol A bis <sup>252</sup>	
		<ul> <li>No non-halogenated alternatives</li> </ul>	
		identified in commercial use	

<sup>248</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes PHE 65" <u>http://www.el.greatlakes.com/pdf/datasheet/PHE-65 Data Sheet.PDF</u> viewed 15 July, 2004 <sup>249</sup> Great Lakes Chemical Corp., "The height Corp." <sup>249</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes GPP-39" <u>www.e1.greatlakes.com/pdf/datasheet/GPP-39%20Data%20Sheet.PDF</u>, viewed 7 July 2004. <sup>250</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes GPP-36" www.el.greatlakes.com/pdf/datasheet/GPP-36%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>251</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DBS"

www.e1.greatlakes.com/pdf/datasheet/DBS%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>252</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes PE-68"

www.el.greatlakes.com/pdf/datasheet/datasheet/Pe-68.PDF, viewed 7 July 2004.

http://www.el.greatlakes.com/pdf/datasheet/FF-680 ds.PDF

## Alternatives to Deca-BDE

Alternative flame retardants for Deca-BDE are listed by substrate in Table 10. Ecology and DOH have not evaluated the human health or environmental impact of these alternatives.

Table 11. Alternative Flame Retardants for Deca-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 Epoxy	Products in which the substrate is used in flame retardant quantity • Printed circuit boards • Electronic component encapsulation • Technical laminates	Alternative flame retardants in commercial materials • Reactive nitrogen and phosphorus constituents • Ammonium polyphosphate • Aluminium trihydroxide	Alternative materials: Non-flammable or containing halogen-free flame retardants • 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>253</sup></li> <li>Hexabromocyclododecane<sup>254</sup></li> <li>Bis (Tribromophenoxy) ethane<sup>255</sup></li> </ul>	None identified
Polystyrene	<ul> <li>Housings for electronic products</li> <li>Wiring parts.</li> </ul>	<ul> <li>Organic phosphorus compounds</li> <li>Magnesium hydroxide</li> <li>Hexabromocyclododecane<sup>256</sup></li> <li>Tetrabromobisphenol A<sup>257</sup></li> </ul>	None identified
PBT/PET	<ul> <li>Switches</li> <li>Sockets</li> <li>Parts of electrical machines</li> </ul>	<ul> <li>Poly(dibromostyrene)<sup>258,259,260</sup></li> <li>Firemaster® CP-44HF (no generic name indicated)<sup>261</sup></li> <li>Tetrabromobisphenol A (oligomer)<sup>262</sup></li> <li>No non-halogenated alternatives identified in commercial use</li> </ul>	Some applications: • Polyamide • Polyketone • Ceramics • Self-extinguishing plastics

<sup>&</sup>lt;sup>253</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DBS" www.el.greatlakes.com/pdf/datasheet/DBS%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>254</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes CD-75P"

www.el.greatlakes.com/pdf/datasheet/PBDS%2080%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>259</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes PBS-64"

www.el.greatlakes.com/pdf/datasheet/CD-75P%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>255</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes FF 680"

http://www.el.greatlakes.com/pdf/datasheet/FF-680 ds.PDF viewed 15 July, 2004 <sup>256</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes CD-75P"

www.el.greatlakes.com/pdf/datasheet/CD-75P%20Data%20Sheet.PDF, viewed 7 July 2004.

<sup>&</sup>lt;sup>257</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes BA-59P"

www.el.greatlakes.com/pdf/datasheet/BA-59%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>258</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes PBDS-80"

www.el.greatlakes.com/pdf/datasheet/PBS-64%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>260</sup> Great Lakes Chemical Corp., "Technical Information: Firemaster®CP-44B" www.el.greatlakes.com/pdf/datasheet/Firemaster%20CP-44B%20ds.PDF, viewed 7 July 2004.

Substrate Polypropylene and polyethylene	Products in which the substrate is used in flame retardant quantity • Roofing foils • Injection molded parts	Alternative flame retardants in commercial materials • Ammonium polyphosphate • Magnesium hydroxide	Alternative materials: Non-flammable or containing halogen-free flame retardants None identified
	(electronic equipment)	• Reogard® 1000 (proprietary composition) <sup>263</sup>	
Cotton textiles	Furniture, textiles     Components in     transportation	<ul> <li>Ammonium polyphosphate</li> <li>Diammonium phosphate</li> <li>Tetrabromophthalate ester<sup>264</sup></li> <li>Hexabromocyclododecane<sup>265</sup></li> </ul>	None identified
Synthetic textiles	<ul> <li>Furniture, textiles</li> <li>Components in transportation</li> <li>Protective clothing</li> </ul>	<ul> <li>Reactive phosphorus constituents</li> <li>Tetrabromophthalate ester<sup>266</sup></li> <li>Hexabromocyclododecane<sup>267</sup></li> </ul>	None identified
PVC	• Wire and cable insulation	<ul> <li>Tetrabromophthalate ester<sup>268</sup></li> <li>Triaryl phosphates isopropylated<sup>269</sup></li> <li>No non-halogenated alternatives identified in commercial use</li> </ul>	None identified

Evaluating human health and environmental data generated since 2000 for the other products covered by the NAS report is beyond the scope of this document. However, it appears that a number of alternative flame retardants exist for Deca-BDE used on upholstery fabric.

EPA, working with textile manufacturers, furniture manufacturers, foam manufacturers, and flame retardant manufacturers, plans to evaluate alternatives to Deca-BDE for use in textiles as the second phase of its Design for the Environment alternatives analysis currently being conducted for Penta-BDE.270

In 2000, representatives from the electronics industry wrote to US EPA, requesting that the agency's Design for the Environment Program investigate the environmental and public health

www.e1.greatlakes.com/pdf/datasheet/DP-45%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>269</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes Reofos 65"

http://www.el.greatlakes.com/pdf/datasheet/Reofos 65 Data Sheet.pdf <sup>270</sup> pers. comm, K. Rindfusz to C. Peele, October 11, 2004.

<sup>&</sup>lt;sup>261</sup> Great Lakes Chemical Corp., "Technical Information: Firemaster® CP-44HF"

www.el.greatlakes.com/pdf/datasheet/Firemaster\_CP-44HF.PDF, viewed 7 July 2004. <sup>262</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes BC-52" www.el.greatlakes.com/pdf/datasheet/BC-52%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>263</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes Reogard 1000" http://www.el.greatlakes.com/pdf/datasheet/Reogard\_1000\_ds.PDF <sup>264</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DP-45" <sup>264</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DP-45"

www.e1.greatlakes.com/pdf/datasheet/DP-45%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>265</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes CD-75P"

www.el.greatlakes.com/pdf/datasheet/CD-75P%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>266</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DP-45" www.el.greatlakes.com/pdf/datasheet/DP-45%20Data%20Sheet.PDF, viewed 7 July 2004. <sup>267</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes CD-75P"

www.el.greatlakes.com/pdf/datasheet/CD-75P%20Data%20Sheet.PDF, viewed 7 July 2004.

<sup>&</sup>lt;sup>268</sup> Great Lakes Chemical Corp., "Technical Information: Great Lakes DP-45"

implications of both brominated flame retardants and their alternatives.<sup>271</sup> EPA has not started such a project.

## Market Changes

## Consumer Electronics Manufacturers and Deca-BDE Alternatives

In anticipation of the phase-out of Penta-BDE and Octa-BDE, it is expected that manufacturers are moving away from these products and identifying alternatives. In addition, a number of electronics manufacturers have been identified that are phasing out of all PBDEs, including Deca-BDE. Specific policies are listed in Appendix C. Electronics manufacturers phasing out of PBDEs in some or all of their products include: Apple, Brother, Daikin, Dell, Ericsson, Hewlett Packard, Matsushita, Mitsubishi, NEC, Samsung, Sharp, Sony, ViewSonic, and Xerox. IKEA has also phased out all PBDEs.<sup>272</sup>

## **Environmentally Preferable Purchasing**

According to Dell Corporation, many governments and large corporations have also developed green procurement guidelines that prohibit the use of PBDEs in electronic products.<sup>273</sup> Three government requests for proposal (RFPs) for computers with restrictions on PBDEs were identified.

### **Commonwealth of Massachusetts**

Massachusetts' RFP for computers specifies that no brominated flame retardants be used. <u>http://www.state.ma.us/osd/enviro/info/factsheets2/Computer\_EPP\_Language.pdf</u>

### Denver, CO

Denver's RFP for computers specifies that the vendor must offer equipment that has been certified by third-party certification organizations such as TCO, Blue Angel, or others.

### Seattle, WA

Seattle's RFP for laptops specifies that vendors must disclose use of halogenated flame retardants. <u>http://www.seattle.gov/environment/Documents/Laptops.pdf</u>

<sup>&</sup>lt;sup>271</sup> Letter to K. Hart, US EPA, from J. Lott, IPC ("Association Connecting Electronics Industries"); H. Evans, Electronic Industries Alliance; and D. Bendz, Institute of Electrical and Electronics Engineers, Inc.; May 11, 2000, viewed at <u>www.halogenfree.org</u>, 5 May 2004.

<sup>&</sup>lt;sup>272</sup> M. Bjork, 2004. Banning brominated flame retardants, BFR2004.

<sup>&</sup>lt;sup>273</sup> Dell Corporation, "Industry Use of Brominated Flame Retardants," <u>www.dell.com</u>, viewed 27 April 2004.

# **VI. Policy Recommendations**

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

### **Key Findings**

PBDEs are found in a vast number of consumer products, with vast potential for continued human exposure. Under WAC 173-303, 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. 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.
- Establish a separate process to 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 a "special waste" designation that is consistent in hazardous waste, solid waste, water quality, and toxic cleanup regulations to isolate PBDEs and remove them from the waste stream. This could include chronic, sublethal 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 PBDE's, and workers are adequately protected.
- Require separation of electronics containing brominated flame retardants during separation.
- 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 PBDE's 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 landfilling 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 PBDE's 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

To examine current disposal and recycling practices and determine reasonable end-of-life procedures that are protective of human health and the environment, Ecology should establish a process to be completed by July 2007 that would:

- 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 with waste management issues, and service industries such as carpet cleaners and upholsterers.
- 2. Through a literature search and limited product testing, characterize PBDE content of products along high-priority exposure pathways.
- 3. Evaluate and recommend most effective and practical methods for managing products containing PBDEs at end-of-life that protect human health and the environment. Ecology anticipates that this will require a rule revision of WAC 173-303, outlining recommended methods for disposal. As part of the rule revision process Ecology will consider the following:
  - Creating 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.
  - Impacts of disposal practices for products containing polyurethane foam, including degradation of foam in upholstered furniture and foam recycling.
  - Coordinating with ongoing e-waste efforts to determine best practices for handling electronic material containing Deca-BDE.
  - Allowing the disposal of products containing PBDEs in waste disposal facilities where they will be safely contained.
  - Recommending an alternate disposal system, including financing options, if it is determined that PBDEs are not safely handled in the solid-waste system.

### Rationale

Currently, not enough is known about the environmental and relative cost impacts of disposal practices for products containing PBDEs. Additional study is required before well-founded recommendations can be made.

## **Source Control**

### Penta-BDE and Octa-BDE

### **Key Findings**

The only current manufacturer of Penta-BDE and Octa-BDE, Great Lakes Chemical Corp., will phase out production of both products at the end of December 2004. 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.

U.S. EPA is writing a Significant New Use Rule (SNUR) that will prohibit the import of Penta-BDE and Octa-BDE, but will not prohibit the import of products containing Penta-BDE or Octa-BDE (e.g., mattresses, upholstered furniture).

#### **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, or sale of new products containing Penta-BDE and Octa-BDE in Washington State by July 2006.

### 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, 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 arranging alternatives for these chemicals in order to comply with the EU ban and the discontinuation of supplies to the U.S.

## **Deca-BDE**

### **Key Findings**

Consumer electronics currently account for approximately 80% of Deca-BDE use. In preparation for the European Union's Restriction on Hazardous Substances (RoHS) ban on Deca-BDE, currently in effect for July 2006, most major consumer electronics manufacturers have announced that they have phased out or plan to phase out the use of Deca-BDE. These manufacturers include: Apple, Brother, Daikin, Dell, Hewlett Packard, IBM, Matsushita, Samsung, Sharp, Sony, and Xerox. A ban on Deca-BDE in these products would therefore have little or no effect on these manufacturers.

At the same time, the market for Deca-BDE is expected to shift and grow in response to a national flammability standard for residential upholstered furniture under consideration by the Consumer Product Safety Commission (CPSC). 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 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. If Deca-BDE were banned for these fabrics 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 on..

### **Policy Options**

- Ban 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.
- 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 Legislature should pass a ban on the manufacture, distribution, and sale of new electronics and electrical equipment containing Deca-BDE, in Washington State effective July 2008. The list of products to be banned needs further review by Ecology, DOH and the Legislature. One possible list is that adopted by the EU, which covers 10 categories of products: large and small appliances; IT and telecommunications equipment; lighting equipment; electronic and electrical tools; toys, leisure and sports equipment; medical devices; monitoring equipment; and automatic dispensers. The scope of products covered by the European Union's Directive 2002/96/EC is outlined in Appendix B.

The Legislature also should pass a ban on the manufacture, distribution, and sale of new upholstered fabric intended for the home, office, or workplace, in Washington State effective July 2008.

### Rationale

Globally, Deca-BDE has become the most used PBDE product; after December 2004, it will be the only PBDE product in production. There is a weight of evidence suggesting that Deca-BDE breaks down into more bioaccumulative compounds. The amount of Deca-BDE in use, its expected continual increase and its expected breakdown in the environment argue that Deca-BDE use should be decreased, not allowed to increase.

Banning consumer electronics products containing Deca-BDE would be consistent with regulations and market practices that are already occurring in the EU and elsewhere internationally. The proposal to ban Deca-BDE recognizes the need for additional study to better define which consumer electronics products should be banned. It should be noted that Deca-BDE is already being phased out of use in consumer electronics by a number of major manufacturers, an indication that some industries are starting to move away from using Deca-BDE.

The proposal to ban Deca-BDE in residential upholstery products addresses the need to avoid increasing the use of the chemical before manufacturers have invested in it. By banning Deca-BDE now, before manufacturers have selected it as a means to meet pending standards for

flammability, it would stem the expanded use of Deca-BDE without requiring manufacturers to redesign or retool later.

## **Minimizing Human Exposure**

### **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**

- Specify that goods purchased on state contracts should not contain PBDEs.
- Specify that bidders on state contracts should disclose which PBDE formulations, if any, are used in products.
- Within constraints of best available knowledge, develop health messages for the general population to minimize exposure to PBDEs.
- 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. Although there are no specific workplace exposure limits for PBDEs, make employers and employees aware of the resources available from the Department of Labor and Industries to address exposure to dusts.
- 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.

#### Recommendations

#### State Purchasing

Restrict the state's purchase of PBDEs in appropriate contracts.

- General Administration should require bidders to disclose Deca-BDE in products. If the product is one that commonly uses Deca-BDE but has adopted an alternative, require disclosure of the alternative method for meeting fire safety standards.
- General Administration should specify that goods purchased on state contracts should not contain Penta-BDE and Octa-BDE.

#### General Population (residential exposure, plus at-risk groups that may be identified)
• The Department of Health should develop and communicate ways for the general population to minimize exposure to PBDEs. Develop methods and materials for health education about PBDEs. Include information about what is known and not known about sources of exposure and provide an appropriate range of options for exposure reduction.

#### Occupational Exposure

• The Department of Labor and Industries should develop and disseminate recommendations for minimizing occupational exposure to PBDEs. Recommend that exposure to PBDE-containing dusts should be controlled using standard industrial hygiene controls. Although there are no specific workplace exposure limits for PBDEs, make employers and employees aware of the resources available to them from L&I to address exposure to dusts. This process should be informed by the proposed biological monitoring of high-risk workers.

## **Monitoring and Research**

## **Key Findings**

Current regulations do not require any 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 is necessary to inform decision-making and protect human and environmental health.

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 biomonitoring program that includes examination of PBDE's in blood and breast milk to monitor trends and identify at risk populations should be undertaken for PBDEs.
- 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 a 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, then proceed to Phase 2.
- Phase 2 Biomonitoring of workers for PBDEs Measure blood levels of PBDEs in potentially exposed workers with comparison to a matched control group.
- Test biosolids, leachate and incinerator emissions for PBDE's. Top priorities may include biosolids used for food production and leachate from the LRI landfill, which uses auto fluff for daily cover.
- Require the bromine industry or manufacturers of products containing PBDE's to finance monitoring and research through direct financing or a tax on products containing PBDE's.
- In collaboration with other government agencies and research institutions, conduct research on the following issues:
  - The fate of PBDE's 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, nonbrominated 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 retardancy.

#### Recommendations

#### Human Health Monitoring

- DOH should coordinate with federal agencies on existing national biomonitoring.
- DOH should explore whether additional regional biomonitoring is needed.
- 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, then proceed to Phase 2.
- Phase 2 Biomonitoring of workers for PBDEs Measure blood levels of PBDEs in potentially exposed workers with comparison to a matched control group.

#### Environmental Monitoring

• To maximize efficient use of limited funds, use existing systems for multi-agency coordination, for example the Puget Sound Ambient Monitoring Program (PSAMP), to develop a multi-media monitoring program for PBDEs. Environmental monitoring will include monitoring of fish for PBDEs. Fish consumption has been identified as an important route of human exposure to PBDEs.

### Environmental Sampling

• Ecology should test biosolids for PBDEs.

### 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 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.

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## **Appendix A: Degradation of PBDEs**

A number of studies have shown that PBDEs are subject to some degree of degradation under a variety of laboratory conditions. The section below on photolytic degradation, along with the conclusions on photolytic degradation presented in the body of the report were reviewed in writing by A. Bergman (Stockholm University), L. Birnbaum (US 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 was discussed at length by phone with C. Jafvert (Purdue University). The following section, on biological degradation, was not reviewed.

#### **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.<sup>274</sup>

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>275</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

 $<sup>^{274}</sup>$  Norris et al., 1973. Toxicological and environmental factors involved in the selection of decabromodiphenyl oxide as a fire retardant chemical. Applied Polymer Symposium 22:195 – 219.

 $<sup>^{275}</sup>$  Watanabe and Tatsukawa, 1987. Formation of brominated dibenzofurans from the photolysis of flame retardant decabromobiphenyl ether in hexane solution by UV and sunlight. Bulletin of Environmental Contamination and Toxicology 39: 953 – 959.

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>276</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>277</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>278</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,

<sup>&</sup>lt;sup>276</sup> Jafvert and Hua, 2001. Photochemical reactions of decabromodiphenyl oxide and 2,2'4,4'-tetrabromodiphenyl oxide. Submitted to American Chemistry Council Brominated Flame Retardant Industry Panel.

 <sup>&</sup>lt;sup>277</sup> Ohta et al. Characterization of the Photolysis of Decabromodiphenyl ether and the levels of PBDEs as its photoproducts in atmospheric air of Japan
<sup>278</sup> European Chemicals Bureau. Update of the Risk Assessment of Bis(pentabromophenyl) ether

<sup>&</sup>lt;sup>278</sup> European Chemicals Bureau. Update of the Risk Assessment of Bis(pentabromophenyl) ether (decabromodiphenyl ether). Final draft of May 2004.

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>279</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 sediment was 53 hours. The half-life for BDE-209 exposed to UV light on soil was between 150 and 200 hours. BDE-

<sup>&</sup>lt;sup>279</sup> European Chemicals Bureau. Update of the Risk Assessment of Bis(pentabromophenyl) ether (decabromodiphenyl ether). Final draft of May 2004.

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>280</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 noncovalently 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 hexaBDEs, one unknown heptaPBDE, and four unknown octaBDEs 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>281</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 decaBDE in all other media measured resulted in an almost identical set of products, though in water containing humic substances a higher proportion of pentaBDFs was observed. Each of the three nonaBDEs were formed and produced a number of octaBDEs. although the major products were different for each nonaBDE congener. Hepta- and hexaBDEs and mono- to pentaBDFs were also formed. The UV degradation products of two heptaBDEs. BDE-190 and BDE-183, and three hexaBDEs, 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 tetraBDEs 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>282</sup>

<sup>&</sup>lt;sup>280</sup> Söderstrom et al., 2004. Photolytic debromination of decabromodiphenyl ether (BDE 209). Environmental Science and Technology 38(1):127-132.

 <sup>&</sup>lt;sup>281</sup> Söderstrom et al., 2004. Photolytic debromination of decabromodiphenyl ether (BDE 209). Environmental Science and Technology 38(1):127-132.

<sup>&</sup>lt;sup>282</sup> Eriksson, et al., 2004. Photochemical decomposition of 15 polybrominated diphenyl ether congeners in methanol/water. Environmental Science and Technology 38:3119 - 3125.

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>283</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>284</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

<sup>&</sup>lt;sup>283</sup> Eriksson, et al., 2004. Photochemical decomposition of 15 polybrominated diphenyl ether congeners in methanol/water. Environmental Science and Technology 38:3119 – 3125.

<sup>&</sup>lt;sup>284</sup> Bezares-Cruz, et al., 2004. Solar Photodecomposition of Decabromodiphenyl ether: products and quantum yield. Environmental Science and Technology 38:4149 – 4156.

period, BDE-209 concentrations declined significantly, but concentrations of some of the lower brominated congeners were unaffected.<sup>285</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>286</sup>

 <sup>&</sup>lt;sup>285</sup> Kierkegaard et al., 1999. Dietary uptake and biological effects of decabromodiphenyl ether in rainbow trout (*Oncorhynchus mykiss*). Environmental Science and Technology (33)1612 – 1617.
<sup>286</sup> Stapleton et al., 2004. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (*Cyprius*)

<sup>&</sup>lt;sup>286</sup> Stapleton et al., 2004. Debromination of the flame retardant decabromodiphenyl ether by juvenile carp (*Cyprius carpio*) following dietary exposure. Environmental Science and Technology, (38)112 - 119.

## Appendix B: Scope of Products Covered by Recommended Ban on Deca-BDE in Electronics and Electrical Equipment

The Draft PBDE Chemical Action Plan recommends that Deca-BDE be banned in electronics and electrical equipment as of July 2008. The specific list of products to be banned will require further review by the departments of Ecology, Health and the Legislature, but a possible model for the list could be Directive 2002/96/EC of the European Parliament and of the European Council on waste electrical and electronic equipment, which outlines a variety of measures for electrical and electronic equipment. Most notably, Directive 2002/95/EC, restricting the use of certain hazardous substances in electrical and electronic equipment, bans Deca-BDE in electrical and electronic equipment as defined in Directive 2002/96/EC.

Annex 1B of Directive 2002/96/EC outlines the scope of products covered by the Directive.

## Annex 1B of Directive 2002/96/EC

List of products which shall be taken into account for the purpose of this Directive and which fall under the categories of Annex 1A

#### 1. Large household appliances

Large cooling appliances Refrigerators Freezers Other large appliances used for refrigeration, conservation and storage of food Washing machines Clothes dryers Dish washing machines Cooking Electric stoves Electric hot plates Microwaves Other large appliances used for cooking and other processing of food Electric heating appliances Electric radiators Other large appliances for heating rooms, beds, heating furniture Electric fans Air conditioner appliances Other fanning, exhaust ventilation and conditioning equipment

#### 2. Small household appliances

Vacuum cleaners Carpet sweepers Other appliances for cleaning Appliances used for knitting, weaving, and other processing for textiles Irons and other appliances for ironing, mangling and other care of clothing Toasters Fryers Grinder, coffee machines and equipment for opening or sealing containers or packages Electric knives Appliances for hair-cutting, hair drying, tooth brushing, shaving, massage and other body care appliances Clocks, watches and equipment for the purpose of measuring, indicating or registering time Scales

#### 3. IT and telecommunications equipment

Centralized data processing: Mainframes Minicomputers Printer units Personal computing: Personal computers (CPU, mouse, screen and keyboard included) Laptop computers (CPU, mouse, screen and keyboard included) Notebook computers Notepad computers Printers Copying equipment Electrical and electronic typewriters Pocket and desk calculators And other products and equipment for the collection, storage, processing, presentation, or communication of information by electronic means User terminals and systems Facsimile Telex Pay telephones Cordless telephones Cellular telephones Answering systems And other products or equipment for transmitting sound, images or other information by telecommunications

#### 4. Consumer equipment

Radio sets Television sets Video cameras Video recorders Hi-fi recorders Audio amplifiers Musical instruments And other products or equipment for the purpose of recording or reproducing sound or images, including signals or other technologies for the distribution of sound and image than by telecommunications

#### 5. Lighting equipment

Luminaries for fluorescent lamps with the exception of luminaries in households

Straight fluorescent lamps

Compact fluorescent lamps

High intensity discharge lamps, including pressure sodium lamps and metal halide lamps

Low pressure sodium lamps

Other lighting equipment for the purpose of spreading or controlling light with the exception of filament bulbs

#### 6. Electrical and electronic tools (with the exception of large-scale stationary industrial tools)

Drills

Saws

Sewing machines

Equipment for turning, milling, sanding, grinding, sawing, cutting, shearing, drilling, making holes, punching, folding, bending or similar processing of wood, metal or other materials

Tools for riveting, nailing or screwing or removing rivets, nails or screws or similar uses

Tools for welding, soldering or similar use

Equipment for spraying, spreading, dispersing or other treatment of liquid or gaseous substances by other means

Tools for mowing or other gardening activities

#### 7. Toys, leisure and sports equipment

Electric trains or car racing sets Hand-held video game consoles Video games Computers for biking, diving, running, rowing, etc. Sports equipment with electric or electronic components Coin slot machines

#### 8. Medical devices (with the exception of all implanted and infected products)

Radiotherapy equipment Cardiology Dialysis Pulmonary ventilators Nuclear medicine Laboratory equipment for *in-vitro* diagnosis Analyzers Freezers Freezers Fertilization tests Other appliances for detecting, preventing, monitoring, treating, alleviating illness, injury or disability

#### 9. Monitoring and control instruments

Smoke detector Heating regulators Thermostats Measuring, weighing, or adjusting appliances for household or laboratory equipment Other monitoring and control instruments used in industrial installations (e.g. in control panels)

#### **10.** Automatic dispensers

Automatic dispensers for hot drinks Automatic dispensers for hot or cold bottles or cans Automatic dispensers for solid products Automatic dispensers for money All appliances which deliver automatically all kinds of products

# **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> , "Environmental Assessment	5/14/2004
Daikin Industries	Plans to phase out PBDEs by the end of March 2006	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
<u>Eizo Nanao</u> <u>Corporation</u>	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" "RoHS" Position Statement,	4/27/2004
Hewlett Packard	Prohibits use of PBDEs.	http://www.hp.com/hpinfo/ globalcitizenship/environm ent/pdf/leadposition.pdf Matsushita Electronic Components Group Chemical Substances	10/1/2004
<u>Matsushita</u>	Intends to phase out all PBDEs by March 2005.	Management Guidelines, http://panasonic.co.jp/maco/ en/environment/pdf/kagaku <u>kanri.pdf;</u> pers. comm., D. Swanson	6/3/2004
<u>Mitsubishi Electric</u>	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, http://www.nec- lcd.com/english/profile/envi ronment_energy.html	10/1/2004

Company	Policy	Source	Date viewed
<u>Philips Electronics</u> Ind. (Taiwan) Ltd., <u>CED</u>	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 US	"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
TOTOKU Electric Co., Ltd.	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
<u>ViewSonic</u> <u>Corporation</u>	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
Xerox	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