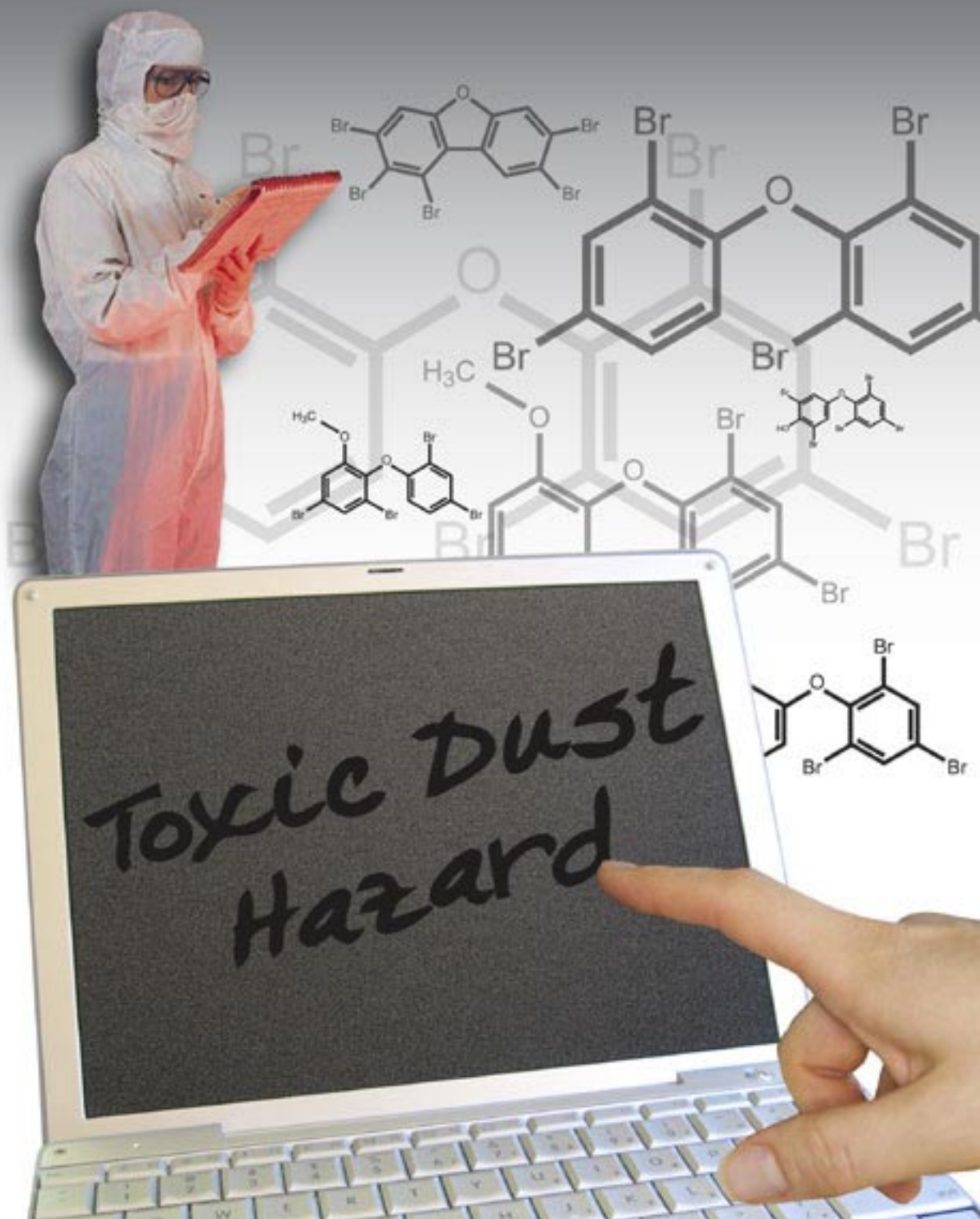
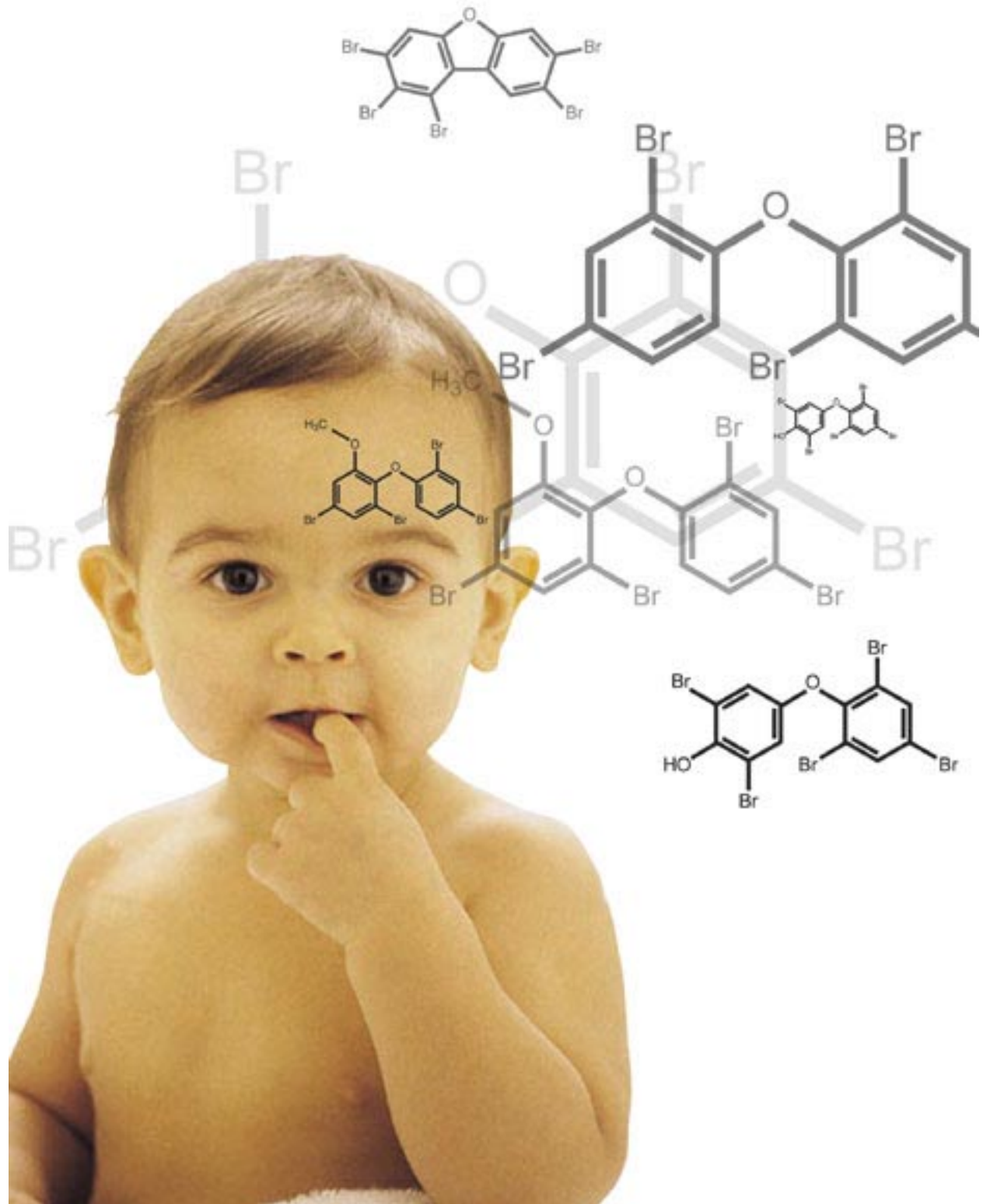


# Brominated Flame Retardants in Dust on Computers:

THE CASE FOR SAFER CHEMICALS AND BETTER COMPUTER DESIGN





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**June 2004**

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Additional information is available online at [computertakeback.org](http://computertakeback.org).

*This report was written by Alexandra McPherson, Beverley Thorpe, and Ann Blake, Ph.D.*

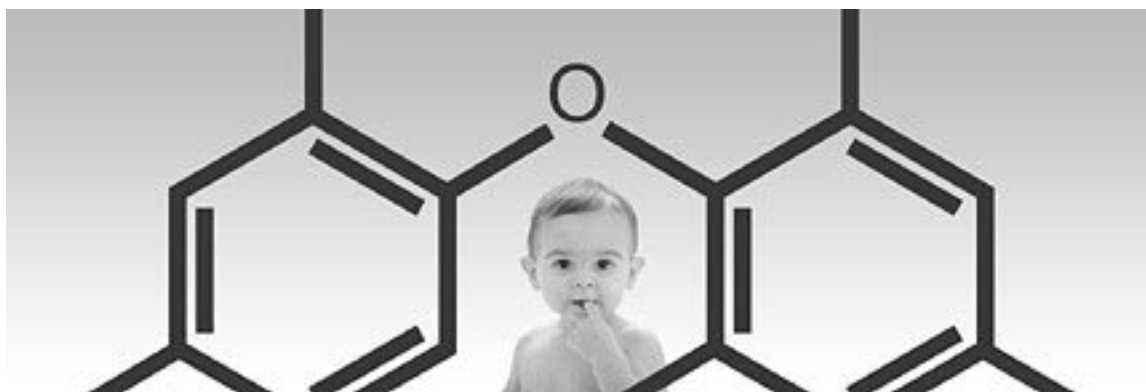


Clean Production Action (CPA) partners with environmental organizations, public health advocates, labor unions and community groups around the world to develop and build technical support for clean production policies. These policies and strategies promote the use of products that are safer and cleaner across their life cycle for consumers, workers, and communities.

### [ **COMPUTER TAKE ← BACK CAMPAIGN** ]

The Computer Take Back Campaign is a national coalition of organizations promoting clean production and producer takeback in the computer and electronics industry. The Campaign seeks to protect the public health and the environment from the hazards of high-tech products by requiring brand owners to take financial responsibility for the life-cycle impacts of their products.

A special thanks to Ecology Center (Michigan), Clean Water Action (Massachusetts), Environmental Health Strategy Center (Maine), Basil Action Network (Washington), Washington Citizens for Resource Conservation, Washington Toxics Coalition, Silicon Valley Toxics Coalition (California), Texas Campaign for the Environment, Environmental Advocates (New York), Citizens Environmental Coalition (New York), and Grassroots Recycling Network (Wisconsin) for their participation in the computer dust study and review of this report.



## **CONTENTS**

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Executive Summary	<b>5</b>
Background on Brominated Flame Retardants and Their Use in Computers	<b>11</b>
Findings of National Computer Dust Sample Study	<b>13</b>
What Do the Levels Mean?	<b>15</b>
Multiple Low Level Exposures to BFRs Pose Unavoidable Risks to Human Health	<b>17</b>
Science on Deca-BDE	<b>18</b>
Other BFRs of Concern	<b>19</b>
Finding Safer Alternatives to BFRs: Industry Trends	<b>20</b>
Computer Company Policy on BFRs in the United States	<b>21</b>
Computer Casings: How Industry is Seeking Alternatives to BFRs	<b>24</b>
Printed Circuit Boards: How Industry is Seeking Alternatives to BFRs	<b>25</b>
Assessing Alternatives	<b>26</b>
Legislative Response to the Growing Threat of BFRs	<b>30</b>
Policy Recommendations for Flame Retardants in Electronic Products	<b>33</b>
Appendix: Collection Protocol	<b>37</b>
Endnotes	<b>41</b>

## EXECUTIVE SUMMARY

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In the first nationwide tests for brominated flame retardants in dust swiped from computers, the Computer Take-Back Campaign (CTBC) and Clean Production Action (CPA) found these neurotoxic chemicals on every computer sampled. The highest levels found were a form of polybrominated diphenyl ethers (PBDEs) called deca-BDE— one of the most widely used fire retardant chemicals in the electronics industry.

These results indicate that there is exposure to certain brominated flame retardants and that computers are likely to be a significant source of deca-BDE exposure in the dust of homes, offices, schools, and businesses. There is evidence that these chemicals could be hazardous to human health. All exposures, no matter how small, are of concern because deca-BDE is a bioaccumulative substance. This means that multiple exposures to low levels of deca-BDE add up over time and build up in the body. There is no safe dose associated with these chemicals. Fortunately, this report finds that computer manufacturers can prevent unnecessary risks by using safer alternatives that meet stringent fire standards in the United States and are less harmful to human health and the environment.

Brominated flame retardants (BFRs), especially PBDEs, are persistent in the environment and contaminate the food chain, animals, and people. The capacity of PBDEs to bioaccumulate in fatty tissue and biomagnify up the food chain, in combination with their persistence and toxicity make this class of chemicals of high concern to the environment and human health. PBDEs and related compounds are turning up just about everywhere scientists look for them, up and down the food chain, in sediments, beluga whales, seals, bird eggs, and human milk, serum and adipose tissue.

Of grave concern is the research showing that women in North America have the highest levels globally of these chemicals in their breast milk and evidence continues to mount about their effect on the neurological and endocrine systems. These levels are doubling every two to five years in the North American population.

Also of great concern is the alarming fact that the concentrations of deca-BDE found in peregrine falcons approach those concentrations reported to have caused neurological damage in mice. So, like penta- and octa-BDE before it, manufacturers' claims that the biological uptake of deca-BDE would not occur, certainly not in high concentrations, have not only proven to be false, but deca-BDE itself has been documented as having caused harm in lab research.

Since the 1970s, the electronics industry has been one of the largest consumers of PBDEs, relying on this class of chemicals (out of an identified 175 different types of fire retardants) to

meet fire safety standards. About 40% of PBDEs are used in the outer casings of computers, printers and televisions and by far the largest volume PBDE mixture used as a flame retardant has been deca-BDE. Two of the three forms of PBDEs —penta- and octa-BDE— will be taken off the market by the end of 2004, but deca-BDE and other brominated flame retardants will continue to be used in the United States, unless action is taken by state and federal governments.

To evaluate the potential for electronic equipment to be a source of exposure to certain brominated flame retardants, PBDEs in particular, the Computer Take Back Campaign and Clean Production Action gathered sixteen samples of dust from the central processing units (CPUs) and monitors of computers. These samples were taken in a variety of public locations in eight states across the United States including university computer labs, legislative offices and a children's museum to assess the presence of certain brominated flame retardants in our workplaces.

In our analyses of these “wipe samples” from computers, toxic PBDE residues were found in every sample (see Table 1). The highest levels found were deca-BDE. Other brominated flame retardants identified in the analyses were octa- and nona-BDE as well as tetrabromobisphenol A (TBBPA). Finding TBBPA even at very low levels was a surprise, given claims from the bromine and electronics industries that TBBPA is less likely to find its way into the environment than other brominated flame retardants. The samples were not analyzed for penta-BDE and hexabromocyclododecane (HBCD).



### **REPLACING BFRs WITH SAFER FLAME RETARDANTS**

Brominated organic chemicals are halogens, and many halogenated chemicals, such as PCBs, have proven to be persistent, bio-accumulative and/or toxic in the environment. For over two decades, halogenated chemicals have been the focus of concern for public health experts as evidence grows of their ability to persist and interfere with living processes. Research in Europe has detailed that a wide range of non-halogen alternatives in computer casings and printed circuit boards can be substituted for these brominated flame retardants and, indeed, progressive companies are already making the switch. Some of these alternatives themselves have hazardous characteristics while others are more environmentally benign. More information is needed from the chemical producers to allow ‘downstream’ users to make informed substitution decisions. But the generic move by industries to non-halogenated chemicals is a scientifically based precautionary action, which we endorse as an important first step in moving towards safer alternatives.

**TABLE 1: RESULTS OF COMPUTER WIPE SAMPLES FROM PUBLIC BUILDINGS IN EIGHT U.S. STATES, MARCH 2004**

<b>Sample Location</b>	<b>State</b>	<b>Make and Model</b>	<b>Deca-BDE Pg/cm<sup>2</sup></b>	<b>Octa-BDE pg/cm<sup>2</sup></b>	<b>Nona-BDE pg/cm<sup>2</sup></b>	<b>TBBPA pg/cm<sup>2</sup></b>
<b>University Office</b>	NY	Compaq	213.00	13.20	56.50	0.047
<b>State House Sample 2</b>	ME	Dell 2002	186.00	58.20	85.20	0.067
<b>Legislator's Office</b>	CA	Not reported	171.00	7.95	104.00	0.009
<b>University Computer Lab</b>	WI	Mitsubishi Diamond 2000	164.00	14.30	51.50	0.008
<b>School of Public Health</b>	NY	Dell	145.00	4.34	35.00	0.014
<b>Children's Museum</b>	ME	Proview 2002	72.50	1.91	15.00	0.107
<b>Legislator's Office</b>	MI	IBM 2001	67.40	2.29	20.50	0.015
<b>University</b>	MA	Sun Microsystem 2000	61.10	6.98	48.70	0.007
<b>Legislator's Office</b>	WI	Zenith 1995	49.60	4.10	17.50	0.089
<b>University Office</b>	TX	Not reported	39.10	1.26	13.00	0.006
<b>University</b>	WA	No brandname	33.30	6.19	17.00	0.013
<b>University Computer Lab</b>	WA	Gateway 700	13.70	0.55	3.40	1.760
<b>State House</b>	MA	Compaq 2002	11.80	0.98	11.50	2.420
<b>State House Sample 1</b>	ME	Dell 2000	11.30	4.58	12.10	0.022
<b>University Computer Lab</b>	MI	Dell 2002	6.87	0.87	4.40	<0.006
<b>University</b>	CA	Dell Optiplex	2.09	0.38	1.19	0.020
<b>Blank 1</b>			0.49	0.05	.25	0.006
<b>Blank 2</b>			0.53	0.03	<0.06	0.071
<b>Field Blank</b>			0.49	<0.05	<0.25	0.006

The highest single deca-BDE sample came from a new flat screen monitor in a university office with no other computers. Because these chemicals build up in the body, low levels of deca-BDE and other brominated chemicals found in the dust samples, no matter how small the amounts, are cause for concern as this study among others demonstrates that these chemicals are ubiquitous in our environment and immediately available for human ingestion.

These findings strongly indicate that consumer products, such as computers that use brominated flame retardants, are likely to be a source of exposure and add to the growing body of evidence showing that deca-BDE is quickly becoming one of the most abundant congeners found in samples of indoor dust.

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*“Deca-BDE is more of a problem than perhaps realized and we do have a number of arguments now to ban it. We know it is accumulating in birds of prey and seeing it in mother’s milk is a bad observation.”*

— Ake Bergman, Stockholm University environmental chemist who conducted the first studies on BFR uptake in the human body, quoted in the Los Angeles Times August 24, 2003.

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The Bromine Science and Environmental Forum (BSEF), a trade association representing the largest three bromine manufacturers (Great Lakes Chemical, Albemarle and Dead Sea Bromine Company) plus one other manufacturer, continues to dismiss concerns that bromine chemicals present exposure risks to the general public and the environment or that these chemicals could have an effect on human health. Our dust findings contradict their assurances that there is little risk of exposure to deca-BDE and thus the chemical should be assumed safe for use in products.

The use of BFRs in consumer products poses further exposure risks along the life cycle of a product – particularly when the products are disposed of. For example these chemicals can turn into brominated dioxins when electronic waste, or other products containing these chemicals, are incinerated or combusted. A review by the World Health Organization’s International Program on Chemical Safety has concluded that brominated flame retardants are significant sources of polybrominated dioxins and furans. The report’s conclusion is clear: they “should not be used where suitable replacements are available and future efforts should encourage the development of further substitutes.”<sup>1</sup>



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*“It’s easy to raise questions in the media and speculate on what might happen. Those raising questions aren’t required to have any particular expertise or to have demonstrated knowledge about the existing database. To date, no human health or environmental effects have been associated with the BFRs detected.”*

— Bromine Science and Environmental Forum website

*“Brominated flame retardants should not be used where suitable replacements are available, and future efforts should encourage the development of further substitutes.”*

— World Health Organization’s International Program on Chemical Safety, Environmental Health Criteria 205: Polybrominated dibenzo-p-dioxins and dibenzofurans

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Due to the similarities between many brominated flame retardants and other chemical compounds that have been proven to be harmful to human health, such as polychlorinated biphenyls (PCBs), many governments have determined that the health risks are too high to allow continued and in many cases increased exposure to these chemicals. Twelve years ago, the international Oslo Paris Convention (OSPAR)<sup>2</sup> for European countries in the North East Atlantic placed the entire class of brominated flame retardants on their list of hazardous materials targeted for phase out. Individual European countries, such as Norway, Germany and Sweden started to require companies to replace BFRs with safer alternatives. To harmonize efforts in Europe, the European Union recently banned the use of all PBDEs and polybrominated biphenyls (PBBs) in electronic products starting in 2006.

In the United States, the state of Maine passed a bill to ban penta- and octa-BDE by January 1, 2006, and deca-BDE by January 1, 2008, becoming the first state in the nation to ban deca-BDE assuming safer alternatives exist. In the state of Washington, the Governor signed an Executive Order in January of 2004 instructing the Department of Ecology to develop a phase out plan by December of 2004 for all PBDEs including deca-BDE. California also passed legislation in 2003 calling for a ban and phase-out of penta- and octa-BDE. Variations of these bills are being developed in other states, including New York, Massachusetts and Wisconsin.

Despite action to ban PBDEs in a handful of states, the United States lags behind Europe in working to reduce human exposure to these chemicals. The continued use of brominated flame retardants in consumer products, such as personal computers, is symptomatic of a larger problem in the United States – the lack of a sustainable chemical policy. Chemicals that persist in the environment and in our breast milk, blood, livers and thyroids should not be allowed in commerce.

The evidence of widespread BFR contamination supports an aggressive call for enactment of the substitution principle at the federal level. This means that brominated flame retardants should be replaced with less hazardous alternatives when they are available. It is technically and economically feasible to produce electronic products that meet the top level flame resistance standards regulated by the Underwriters Laboratories (UL 94 5V and UL94V-O) while using safer flame retardants.

We have enough evidence to act now and indeed progressive industries are moving to safer alternatives. This report evaluates the latest advancements in product redesign within the electronics sector whereby companies have been able to replace flammable materials with nontoxic flame resistant materials. Apple, for example, is replacing the plastic exterior casings on its new laptops with metal to negate the need for flame retardants. Toshiba now uses an inherently flame resistant plastic, polyphenylene sulphide, for casings of electronics. NEC has a new biobased plastic that negates the need for brominated or phosphorus based flame retardants.

There is universal agreement that preventing fires and reducing burn time is critical in buildings, transportation vehicles and consumer products. However, in the face of new evidence and increasing chemical contamination of the general public, the United States can no longer ignore the evidence that deca-BDE and other toxic fire retardants pose a high risk to public health and the environment. The United States government must focus its chemical policy on safer chemicals and materials and be more proactive in pushing green chemistry solutions and sustainable product design.

The following policy recommendations will help spur the rapid adoption of currently available safer materials and catalyze the on-going development of more environmentally compatible fire retardants:

- State and federal governments should make the phase out of deca-BDE and all other PBDEs a priority.
- Governments should require that all brominated flame retardants are replaced with safer non-halogenated alternatives.
- States should require electronic manufacturers to take back products for reuse and recycling to encourage better product design.
- State and federal governments should implement recycling guidelines for electronic products to ensure that brominated flame retardants are not continually put into new products.
- Government purchasing guidelines should include criteria for electronic products that do not contain PBDEs and phases out other brominated flame retardants.
- Federal and state governments need to implement new chemical policies. Such policies would require safer substitutes, the phase-out of persistent, bioaccumulative, or highly toxic chemicals; full access to chemical information in the workplace and in products, reaction to early warnings, and comprehensive toxicity data from the chemical industry for all their chemicals in commerce.

# BACKGROUND ON BROMINATED FLAME RETARDANTS AND THEIR USE IN COMPUTERS

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Over 175 different types of flame retardant chemicals are currently on the market. These fall into several classes, including the halogenated organics (brominated and chlorinated), phosphorus-containing, nitrogen-containing, and inorganic flame retardants. Flame retardant chemicals have been increasingly added to consumer products such as consumer electronics, upholstered furniture and cars and buses since the 1970s.

Printed circuit boards and casings represent the largest uses of brominated flame retardants in electronics. BFRs are added to high-impact plastics used in televisions and computer monitors at concentrations of 5%-30% by weight.

The electronics industry has used a wide range of BFRs in their products including polybrominated diphenyl ethers (PBDEs), and tetrabromobisphenol A (TBBPA). TBBPA is the most widely used brominated flame retardant.

There are 209 PBDE congeners, or different types of molecules, of PBDEs. Only some of these are in use and present in three commercial mixtures, called the 'penta-BDE', the 'octa-BDE', and the 'deca-BDE', because the molecules in each mixtures have on average about 5, 8 or 10 bromines. The 'deca-BDE' is the major commercial PBDE mixture (about 80%) and is most commonly used in electronic products.

<b>Brominated Flame Retardant</b>	<b>Use</b>
<b>Tetrabromobisphenol A (TBBPA)</b>	Epoxy resins (printed circuit boards and printed wire boards of computers and other electronic products), and acrylonitrile butadiene styrene (ABS) (housings of computers, PC monitors, televisions and other electronic products).
<b>Decabromodiphenyl Oxide (Deca-BDE)</b>	High impact polystyrene (HIPS) (electronic equipment), polyethylenes (wire and cables of electronic equipment), upholstery textiles, building and construction applications.
<b>Octabromodiphenyl Oxide (Octa-BDE)</b>	ABS plastics (PC monitors, housings for televisions, mobile phones, and copy machine parts).
<b>Pentabromodiphenyl Oxide (Penta-BDE)</b>	Polyurethane foam, mattresses, seat cushions, upholstered furniture, carpet underlay, and bedding.
<b>Hexabromocyclododecane (HBCD)</b>	Polystyrene foam (building materials, i.e. insulation) and textiles (upholstered textiles).

Source: Bromine Science and Environmental Forum Website: [www.bsef.com](http://www.bsef.com)

**KEY PLAYERS:  
COUNTRIES WITH BFR PRODUCTION SITES**

Albemarle Corporation (Baton Rouge, Louisiana), Great Lakes Chemical (West Lafayette, Indiana), and the Dead Sea Bromine Company (Israel) are the three largest global producers of brominated flame retardants.

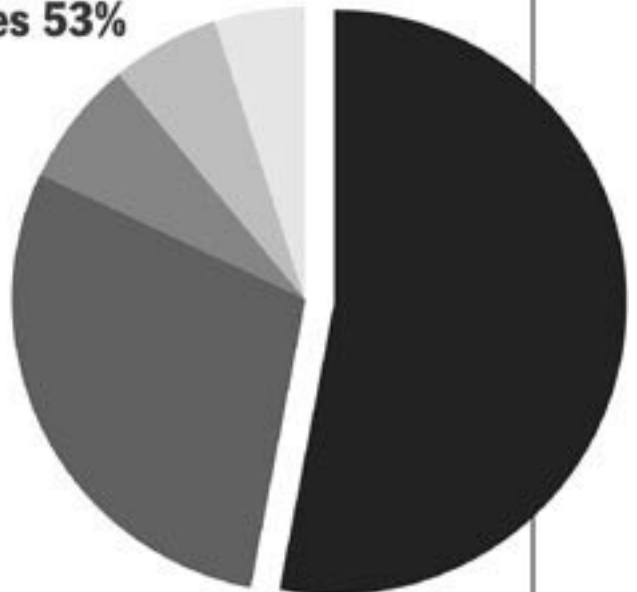
<b>BSEF companies</b>	<b>Albemarle</b>	<b>Great Lakes Chemical Corporation</b>	<b>Dead Sea Bromine Group</b>
<b>Countries with BFR production sites</b>	USA France Belgium United Kingdom Germany Austria Jordan Japan	USA United Kingdom	Israel USA The Netherlands China

Source: Bromine Science and Environmental Forum website: [www.bsef.com](http://www.bsef.com)

**International Distribution of Bromine Production for 1997**



- **United States 53%**
- **Israel 29%**
- **China 7%**
- **UK 6%**
- **Others 5%**



Source: "Bromine,"  
Phyllis A. Lyday, 1997

# FINDINGS OF NATIONAL COMPUTER DUST SAMPLE STUDY

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To investigate the levels of some brominated flame retardants in dust on computer equipment, the Computer Take-Back Campaign and Clean Production Action initiated a collection and analysis of dust samples from public facilities, including university computer labs, legislative offices and a children's museum. A total of sixteen wipe samples were taken from the central processing units (CPUs) and monitors of individual computers in various locations in eight states: Michigan, Wisconsin, New York, Texas, Massachusetts, California, Maine, and Washington.

The methodology is outlined in the Appendix. Sampled computers came from a range of manufacturers, included both old and new models, and were located in various places, ranging from offices with single computers to computer labs with multiple computers in one room. The study evaluates the presence of deca-, nona-, and octa-brominated diphenyl ethers (BDE) and TBBPA in dust. Due to extraction difficulties, HBCD was not tested for despite concerns that it could be persistent and bioaccumulative. Penta-BDE was also not included in this study. The results are shown in Table 1 (see next page).

The results indicate that deca-, nona-, and octa-brominated diphenyl ethers (BDE) were found in all locations, in concentrations ranging 2.09 to 213.00 pg/cm<sup>2</sup> for deca, 1.19 to 104.00 pg/cm<sup>2</sup> for nona-, and 0.38 to 58.20 pg/cm<sup>2</sup> for octa-BDE. Tetrabromobisphenol A (TBBPA) concentrations ranged from less than 0.006 to 2.420 pg/cm<sup>2</sup>.

There was no apparent geographic regional variation in the levels of chemicals detected, nor were there any apparent differences in chemical concentration associated with the type of facility (e.g., academic institution, legislative office, or public facility such as a museum).

There was similarly no apparent effect on chemical concentration associated with the location of the sample computer in an isolated office versus a computer lab. This supports our hypothesis that the computers were the primary source of BFRs found in these dust samples. An analysis of the data demonstrated a fairly high correlation between the deca-BDE concentrations and the concentrations of the nona- and octa-PBDEs; in other words if the deca-BDE concentration was high in a sample, the concentrations of the other chemicals were high as well. The highest single deca-BDE concentration, taken from an isolated computer in a university office, was a sample obtained from a new flat screen model.

**TABLE 1: RESULTS OF COMPUTER WIPE SAMPLES FROM PUBLIC BUILDINGS IN EIGHT U.S. STATES, MARCH 2004**

<b>Sample Location</b>	<b>State</b>	<b>Make and Model</b>	<b>Deca-BDE Pg/cm2</b>	<b>Octa-BDE pg/cm2</b>	<b>Nona-BDE pg/cm2</b>	<b>TBBPA pg/cm2</b>
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## WHAT DO THE LEVELS MEAN?

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The study contains a few samples from a wide geographic area. However, even this limited data set demonstrates the pervasiveness of hazardous chemicals in our homes, workplaces, and public buildings. These findings complement other studies, which found detectable levels of BFRs in dust, but used different testing methodologies. A 2003 Silent Spring Institute study of indoor air and dust in 120 homes on Cape Cod, Massachusetts<sup>3</sup> showed levels of tetra- and penta-brominated BDEs ranging from 0.7 to 4.1 µg/g of dust. The Silent Spring Institute did not test for deca-BDE. A 2003 Greenpeace study of dust from 100 households across the United Kingdom, with a small additional sample of households from Finland, Denmark, Sweden, France and Spain<sup>4</sup>, showed deca-BDE to be the most abundant BDE in house dust, ranging from 3.8 to 19.9 ppm. Penta-BDE was present at levels ranging from 0.018 to 2.1 ppm, and TBBPA at up to 0.34 ppm.

Because these chemicals build up in the body, low levels of deca-BDE and other brominated chemicals found in the dust samples, no matter how small the amounts, are cause for concern as this study among others demonstrates that these chemicals are ubiquitous in our environment and immediately available for human ingestion. PBDEs and related compounds are turning up just about everywhere scientists look for them, up and down the food chain, in sediments, beluga whales, seals, bird eggs, and human milk, serum and adipose tissue<sup>5</sup>. As such, the levels found in this study cannot be evaluated in isolation, since we are vulnerable to multiple low level exposures in our homes and workplaces, through the food we eat, the dust we touch and the air we breathe.

The bromine industry still maintains that ongoing exposures are too low to cause injury to humans. The scientific findings however show otherwise. This is evident in the fact that the breast milk of American women contains some of the highest levels of PBDEs in the world. Of great concern is the fact that these levels of PBDEs in North Americans appear to be doubling every two to five years<sup>6</sup>. Studies of several hundred people show that women in Indianapolis, Texas and the San Francisco Bay Area have 10 to 100 times more PBDEs in their breast milk and blood than European women.

Also of great concern is the alarming fact that the concentrations of deca-BDE found in peregrine falcons approach those concentrations reported to have caused neurological damage in mice<sup>7</sup>. So, like penta- and octa-BDE before it, manufacturers' claims that biological uptake of deca-BDE would not occur, certainly not in high concentrations, have not only proven to be false, but deca-BDE itself has been documented as having caused harm in lab research.

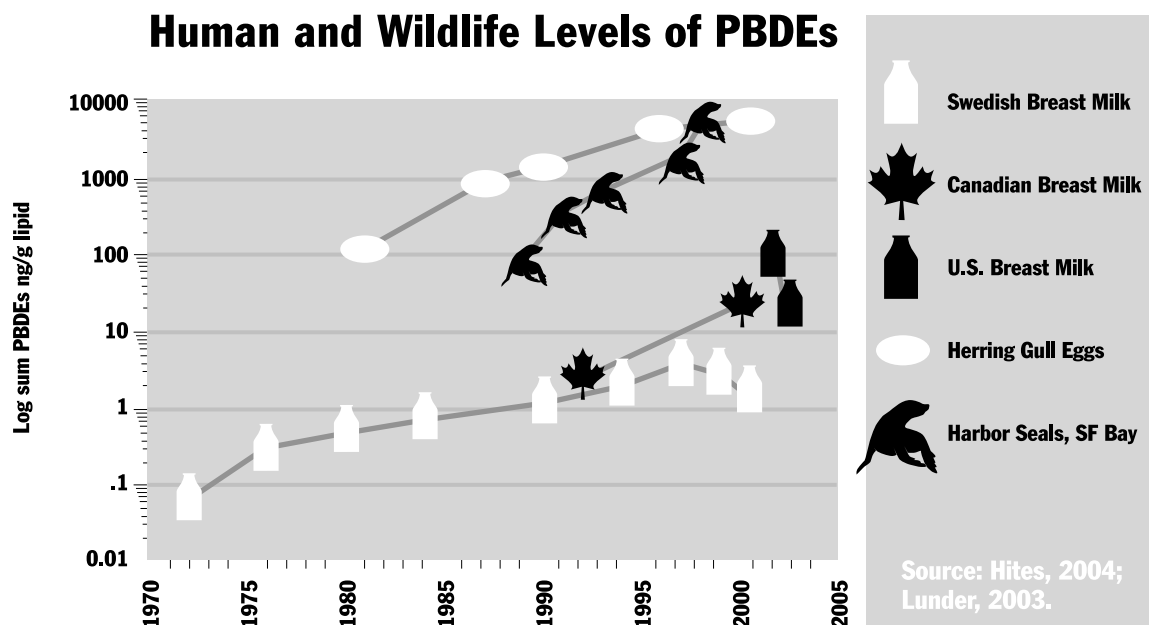
The use of BFRs in consumer products poses further exposure risks along the life cycle of a product – particularly when the products are disposed of. These chemicals can turn into brominated dioxins and furans when electronic waste, or other products containing BFRs, are incinerated or combusted. A review by the World Health Organization’s International Program on Chemical Safety has concluded that BFRs are significant sources of polybrominated dioxins and furans. The report’s conclusion on BFRs is clear: they “should not be used where suitable replacements are available and future efforts should encourage the development of further substitutes.”<sup>8</sup>

*“It’s easy to raise questions in the media and speculate on what might happen. Those raising questions aren’t required to have any particular expertise or to have demonstrated knowledge about the existing database. To date, no human health or environmental effects have been associated with the BFRs detected.”*

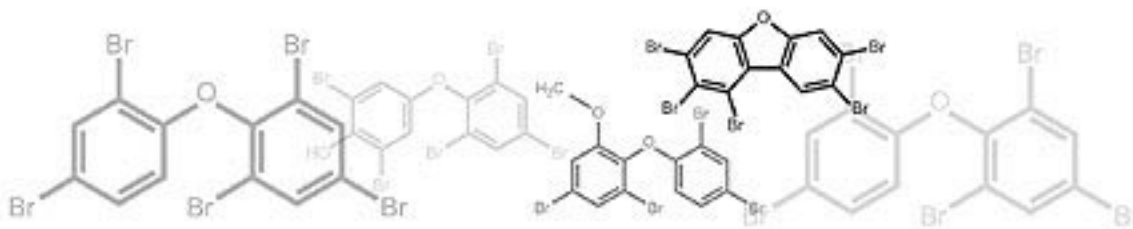
— Bromine Science and Environmental Forum website

*“Brominated flame retardants should not be used where suitable replacements are available, and future efforts should encourage the development of further substitutes.”*

— World Health Organization’s International Programme on Chemical Safety, Environmental Health Criteria 205: Polybrominated dibenzo-p-dioxins and dibenzofurans







Within the BFRs, the PBDEs are of the highest concern due to their bioaccumulative properties. The similarity in chemical structure and biological mechanism of polychlorinated biphenyls (PCBs) and PBDEs have raised concerns that exposure to PBDEs might worsen the impacts of PCBs and similar chemicals to which we are all already exposed<sup>9</sup>. Children, who are at a delicate stage of development, are most vulnerable to adverse health effects. Recent studies have shown that long-term exposure to even low levels of PCBs can affect the intelligence and learning ability of human children<sup>10</sup>.

Animal studies emphasize the dangers of fetal exposure to PBDEs. Laboratory studies in rodents show adverse effects in adulthood from pre-natal exposure. A mouse given a dose of 0.8 milligrams of PBDEs per kilogram of weight on the tenth day of life will show developmental damage which grows more severe as time passes, including abnormal behavior and impaired learning skills.<sup>11</sup> A no observable effect level for neurological toxicity has yet to be found for PBDEs.

## **MULTIPLE LOW LEVEL EXPOSURES TO BFRs POSE UNAVOIDABLE RISKS TO HUMAN HEALTH**

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*At the very least, we recommend that where synthetic chemicals are found in elevated concentrations in biological fluids such as breast milk and tissues of humans, marine mammals or top predators, regulatory steps be taken to remove them from the market immediately.*

— Royal Commission on Environmental Pollution, UK - Chemicals in Products, 2003

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The health concerns of exposure to PBDEs and other BFRs include evidence from animal studies that they are endocrine disruptors that affect the function of the thyroid hormone

and are neurological and developmental reproductive toxicants. The thyroid hormone regulates growth and development in the newborn child. The PBDEs block the thyroid hormone transport protein and PBDE exposure in rodents results in decreased thyroid hormone levels (hypothyroidism). It has long been known that hypothyroidism, as determined by small decreases in thyroid hormone levels, produces cognitive impairment in children including lowered IQ scores<sup>12</sup>. Neurobehavioral changes have been identified in neonatal rodents exposed to PBDEs and HBCD<sup>13</sup>.

Within the PBDEs, penta-BDE is the most bioavailable, lipophilic, and bioaccumulative. The bioaccumulative properties of the PBDEs decrease with the increasing number of bromines--deca- and octa-BDE are less bioavailable than penta-BDE. Recent evidence demonstrates that the higher bromine-containing PBDEs such as deca-BDE can break down in the body and in the environment to the lower, more bioavailable PBDEs -- such as penta-BDE.

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*“We were thinking that [Deca-BDE] will not enter the biological system and it will not be bioavailable, but this has been proven wrong.”*

— Mehran Alaee, research scientist with Canada’s National Water Research Institute, 2003

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There has been considerable effort both in the United States and Europe over the last two years to assess the potential public health and environmental impacts of the PBDEs. Available data was sufficient for the European Union to take action to phase-out penta- and octa-BDE by mid-2004 in all uses and all PBDEs in consumer electronics starting in 2006. However, deca-BDE, the most used PBDE in commerce, has been fiercely defended by the bromine industry.

## **SCIENCE ON DECA-BDE**

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The bromine manufacturing industry has claimed that deca-BDE does not escape into the environment, and even if it did, it is such a large and chemically stable molecule, it would not be taken up by humans or wildlife, nor would it break down into the more toxic forms of PBDEs such as penta-BDE<sup>14</sup>. This was the state of the science when the initial PBDE bans described above went into effect. However, recent data from ongoing studies contradict these claims, and show that deca-BDE has toxicity concerns on all these counts.

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*“Deca-BDE is more of a problem than perhaps realized and we do have a number of arguments now to ban it. We know it is accumulating in birds of prey and seeing it in mother’s milk is a bad observation.”*

— Ake Bergman, Stockholm University environmental chemist who conducted the first studies on BFR uptake in the human body, quoted in the Los Angeles Times August 24, 2003

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First, deca-BDE can be absorbed by humans, animals, and fish, and at higher rates than were previously known. Recent studies have found significant amounts of deca-BDE in fish and peregrine falcons<sup>15</sup>. Deca-BDE has been found in the blood of Swedish electronics recycling workers<sup>16</sup> and in human breast milk across the United States<sup>17</sup>. More significantly, deca-BDE is breaking down in the environment and in animals to the smaller, more toxic compounds that are more readily available in the environment. Deca-BDE is absorbed and degraded to lower BDEs in carp<sup>18</sup> and other metabolites in Baltic salmon<sup>19</sup>.

The European Union risk assessment of deca-BDE in May 2004 decided not to take immediate legislative action against the chemical but confirmed concerns about deca-BDE and appealed for companies to stop producing it. Sweden, Netherlands and Denmark are understood to have pushed for further controls and Sweden, which has announced plans for a national ban on deca-BDE, is to propose alternatives to the substance when experts meet again in October, 2004. According to EU officials, an extra study on neurotoxicological effects is likely to be commissioned, for completion by the end of 2006. This separate biomonitoring programme will track deca-BDE levels in the environment and humans and if either of these raises concerns the risk assessment could be reopened<sup>20</sup>.

## **OTHER BFRs OF CONCERN**

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Other members of the BFR class of chemicals, such as HBCD and TBBPA, have their own toxicological concerns. HBCD is persistent, bioaccumulative and a developmental neurotoxicant, while TBBPA is immunotoxic, hepatotoxic, neurotoxic, and an endocrine disruptor<sup>21</sup>. TBBPA, like the PBDEs similarly blocks the thyroid hormone receptor, but no effects on rodent hormone levels have yet been seen.

Both TBBPA and HBCD alter levels of two neurotransmitters, glutamate and dopamine, and, as with the PBDEs, HBCD exposure causes changes in memory and learning in rats<sup>22</sup>. HBCD and deca-BDE are associated with liver tumors, and deca-BDE with thyroid tumors<sup>23</sup>. Finally,

both the PBDEs and TBBPA have general immuno-suppressing effects<sup>24</sup>. TBBPA has been found in river sediments in Japan and Sweden, and HBCD has also been identified in river sediments and fish; neither has yet been reported in food<sup>25</sup>.

While the main toxicological concern from current research focuses on the neurodevelopmental and endocrine disrupting effects of the BFRs, there may be other toxicological endpoints, such as cancer, for which they have not yet even been tested<sup>26</sup>.

## **FINDING SAFER ALTERNATIVES TO BFRs: INDUSTRY TRENDS**

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*“It’s encouraging that there is a general trend from the use of halogenated flame retardants in products to replacing them with less problematic flame retardants or to redesign flame retardant systems, e.g. by creating greater distances to potential heat sources”*

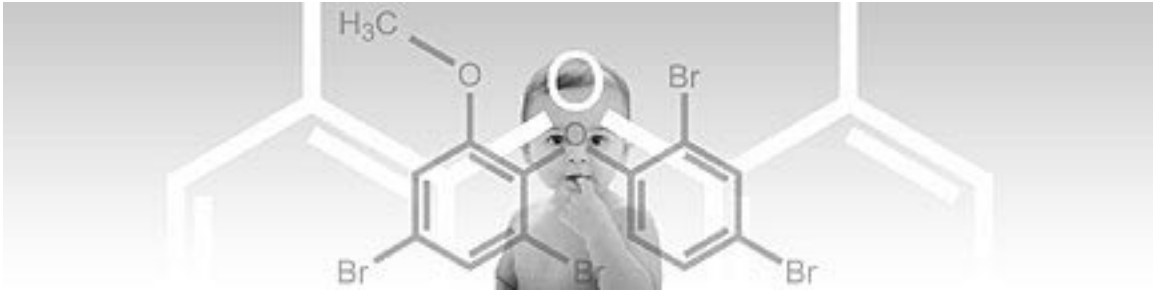
— German Federal Ministry of the Environment

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Fire safety standards for electronic products are established by the National Electronic Manufacturers Association and developed by the Underwriters Laboratory, based in the United States. The standards range from UL94 HB (the lowest standard) to UL94 VO (the highest standard). This standard is accepted globally. There is a wide range of halogen free flame retardants that meet UL94 VO.

The high tech sector has made progress in redesigning products to eliminate the need for brominated chemical additives. Much of the stimulus for better design and less hazardous material use was catalyzed by the EU’s Directive on Waste from Electrical and Electronic Equipment (WEEE) and the EU’s Directive on Restriction of Hazardous Substances (RoHS) with their emphasis on recycling and chemical bans<sup>27</sup>. The RoHS Directive mandates the phase out of all polybrominated biphenyls (PBBs) and PBDEs in new electrical and electronic equipment sold in the European Union starting in 2006.

Ecolabeling requirements such as TCO95 and TCO99<sup>28</sup>, which stipulate that plastic components (with the exception of those used in printed circuit boards) weighing more than 25 grams must not contain flame retardants with organically bound bromine or chlorine, has also encouraged design changes.



As it became more recognized that BFR use in printed circuit boards and computer casings are contributing to toxic contamination in the environment during production, use and disposal, manufacturers started evaluating alternative chemicals and material streams. The electronics industry has been reluctant to disclose specific information on the alternatives they are using, which makes it difficult for concerned consumers to know whether or not the alternatives are safer.

To better understand the direction industry is moving in, we compiled the best information available through web based searches to track both industry trends in material and chemical choices for computer casings and printed circuit boards as well as company positions on the use of brominated flame retardants and other halogenated chemicals. Our alternatives research reveals that halogen free flame retardants that meet the top level flame resistance standards regulated by the Underwriter Laboratories (UL94 VO) are commercially available.

## **COMPUTER COMPANY POLICY ON THE USE OF BFRs IN THE UNITED STATES**

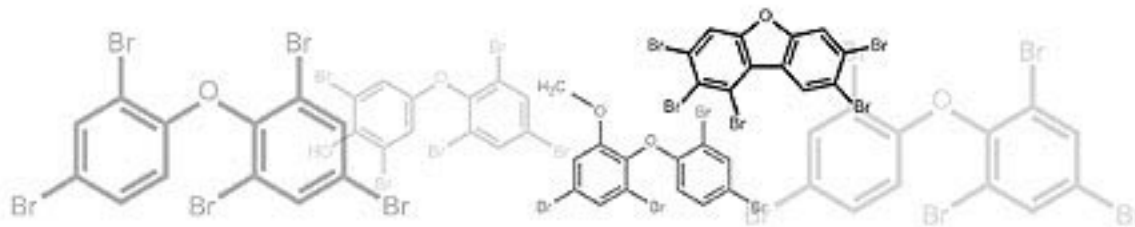
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Many companies have moved forward to achieve safer flame retardant features in their products through design changes and/or by finding safer chemical substitutes for BFRs. However the changeover is far from complete. The following information provides a sampling of company efforts to eliminate bromine and/or all halogen based flame retardant chemicals. The information was compiled from reports and by on-line research and is by no means complete since many companies do not give information on their web sites about their chemical policy or specifically their use of flame retardants. There are information gaps that make it difficult to know which products contain BFRs and which ones contain safer alternatives. What is clear however from the table below is that the technology for safer flame retardants is available and in the marketplace today.

Note that the following information reflects current efforts, therefore equipment produced at an earlier time may contain different flame retardants.

## COMPUTER MANUFACTURERS POLICIES ON BROMINATED FLAME RETARDANTS

Company	Policy on BFRs	Use of BFRs	Technology Development	Performance Benefits
<b>NEC</b>	Plans to phase out all BFR use by 2011.		Flame resistant bio-based plastic (polylactic acid) that does not require the use of toxic additives.	New material passes top level flame resistance standards (UL 94 5V and UL94V-0); product's fire resistance, moldability and strength make it a viable alternative to polycarbonate plastics
<b>Hewlett Packard</b>	Monitor housings now typically contain phosphorus based flame retardants.	No information about its use of TBBPA in circuit boards.		
<b>Apple</b>	The base material of printed wire boards must not contain any PBBs, PBDEs or chlorinated paraffins. Plastic components that weigh >25 g shall not contain flame retardants that contain organically bound chlorine or bromine. <sup>29</sup>	TBBPA used in printed circuit boards.	Replacing polycarbonate housings in some of its laptops with metal housings using aluminum alloy.	Exploring alternative substances, but has not yet identified flame retardants, which meet all of Apple's qualifying criteria.
<b>Dell</b>	Evaluating the technical and environmental aspects of halogen-free printed circuit board materials such as white phosphorus. <sup>30</sup>	TBBPA is used in circuit boards.	Triarylphosphate esters (halogen-free) are used in mechanical plastic parts.	
<b>IBM</b>	Mandates its suppliers not to use PBB or PBDEs. <sup>31</sup>			
<b>Toshiba</b>			Uses an inherently flame resistant plastic, polyphenylene sulphide, for casings of electronics and has developed a phosphorous based flame retardant as an alternative to TBBPA in printed circuit boards.	
<b>Gateway</b>	No information on their website, although they profile some monitors with TCO labels.			
<b>Fujitsu Siemens</b>			Eliminated TBBPA from their memory cards and has developed halogen free housings for some of the product lines.	
<b>Sun Microsystems</b>	No information on their website.			



## OTHER ELECTRONIC MANUFACTURERS

Company	Action on BFRs	Use of BFRs	Technology Developments	Impact on Product Performance
<b>Motorola</b> <sup>32</sup>	New products use a safer halogen free flame retardant that is a nitrogen/phosphorus combination.		Some halogen free printed wire boards (PWBs) have demonstrated compatibility with lead free assembly. Cost curve is very acceptable and is projected to meet current costs for best in class flame standards.	Eliminating BFRs from PWBs reduces risks associated with dioxin formation in fires, enhances ISO 14000 performance, possess better electrical and mechanical properties.
<b>Intel</b>	Does not use PBB/PBDE in its products.	Phased out the use of TBBPA and other halogenated flame retardants in select server products.	Continues to work with its suppliers to evaluate alternative flame retardants. <sup>33</sup>	
<b>Sony</b>	As of 2005, Sony aims to globally have all of its product lines free of halogenated flame retardants if substitutes are found to be safer.		Developed bromine free circuit boards for European television sets, VCRs and DVD players.	
<b>Philips Semiconductors</b>	The company plans to phase out tetrabromobisphenol A (TBBPA) from printed wiring boards by January 2006.		Manufactured a 'green plastic', which is achieved by eliminating materials such as brominated flame-retardants and antimony, which are not only harmful to the environment, but also corrosive and shorten the life of products when exposed to high temperatures." <sup>34</sup>	Green plastic "offers considerable improvements over conventional packaging by significantly increasing the product lifetimes at high temperatures."
<b>Hitachi</b>	Plans to remove all brominated flame retardants by March 2005.		Developed phosphorous based flame retardants for printed circuit boards.	
<b>Panasonic/Matsushita</b>	In the United States, the company is targeting the elimination of PBBs and PBDEs by the end of 2005, or March 31, 2006.		Developed halogen-free compounds for low voltage internal wires, in the cabinet, the back cover, and from a number of printed wiring boards. <sup>35</sup>	

## **COMPUTER CASINGS: HOW INDUSTRY IS SEEKING ALTERNATIVES TO BFRs**

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Plastic outer casings for monitors, computers, printers and televisions represent 40% of flame retarded plastics used in electrical and electronic devices.

Thermoplastics, predominantly used in casings, rely largely on additive flame retardants. These chemicals are not firmly bound into the matrix of the plastic, making them more vulnerable to off gassing harmful toxins into the environment<sup>36</sup>, which is evident by the findings of this dust study and others.

Historically, acrylonitrile butadiene styrene (ABS) plastics, flame retarded with TBBPA or octa-BDE, were predominantly used in the casings. Since, ABS plastics are currently not compatible with halogen free flame retardants<sup>37</sup>, manufacturers started combining ABS plastics with polycarbonate (PC) plastics—a polymer mixture more compatible with halogen free options. However other manufacturers have increased the use of high impact polystyrene(HIPS), one of the main application areas for deca-BDE.

The use of deca-BDE has declined in Japanese and European electronic products due to concerns about the chemical's ability to bioaccumulate in the environment and generate brominated dioxins in incinerators and fires. Manufacturers are increasing the use of organic phosphorus compounds, which do not generate dioxins and are good smoke inhibitors. Some of the phosphate alternatives for ABS/PC plastics include diphenylphosphate (DPK), triphenyl phosphate (TPP), resorcinol-bis-diphenylphosphate (RDP), and bisphenol A diphenyl phosphate (BADP). Currently, Bayer AG and GE Plastics have patented protection on PC/ABS plastic flame retarded with RDP<sup>38</sup>. Dow and BASF are developing organic phosphorus flame retardants without halogen compounds.

Some of the organic phosphorus substitutes are problematic while others are considered acceptable from a human health and environmental standpoint (for more information on the hazards of the alternatives, please see the next section). For example, the organic phosphorus alternatives have a higher volatility than brominated compounds and significant levels of both TCEP and TCPP have been found in the environment. It is important to avoid replacing BFRs with alternatives that could be equally harmful to human health and the environment. For this reason, RDP is often used as a substitute for TCEP and TCPP as it is less volatile.



Unfortunately some of the more benign mineral based and nitrogen based flame retardants are incompatible with some of the thermoplastics used in casings.

In the search for safer materials some manufacturers have been working to replace plastics with less flammable materials or redesigning their products to isolate the potential source of combustion. Apple, for example, is replacing the plastic exterior casings on its new laptops with metal to negate the need for flame retardants. Toshiba now uses an inherently flame resistant plastic, polyphenylene sulphide, for casings of electronics.

## **PRINTED CIRCUIT BOARDS: HOW INDUSTRY IS SEEKING ALTERNATIVES TO BFRs**

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The use of halogenated compounds in thermoplastics is declining, making the printed circuit board one of the main application areas for halogenated flame retardants.

Phenolic and epoxy resins are the most commonly used materials in printed circuit boards. Unfortunately, epoxy resins, which burn quickly, are replacing the more fire resistant phenolic resins. Due to their flammability, many manufacturers use TBBPA in epoxy resins, contributing to TBBPA being the most widely used brominated flame retardant.

However, there are halogen-free flame retardants for printed circuit boards. Reactive phosphoric acid compounds, sometimes combined with nitrogen compounds as well as aluminum trihydroxide (ATH), can replace TBBPA. Mineral based flame retardants are also being evaluated. Manufacturers using phenolic resin as a base, are more likely to depend on a combination of phosphorus and nitrogen additives. Unfortunately red phosphorus, one of the least problematic flame retardants from an environmental and public health perspective, has not been successful.

There are some known advantages to phosphorus compounds. In the event of a fire, organic phosphorus based compounds form a carbon layer, which reduces fire and emissions, thereby making the toxicity of fire gases from ATH and phosphorus based compounds far lower than the toxic by-products created by brominated compounds<sup>39</sup>. Some phosphate compounds increase the recyclability of printed circuit boards, as it is more feasible and cost effective to recover copper from halogen free circuit boards.

Although there is the technical capacity to use non-brominated flame retardants, the issue of costs still drives many companies to replace harmful BFRs with less studied BFRs.

According to German research, manufacturers of the base material for halogen free printed circuit boards pay an estimated 30% more than those who continue to use BFRs, although the price per unit is declining<sup>40</sup>. There is also a debate among the many producers involved in the manufacturing of printed circuit boards about who should bear the additional costs currently associated with halogen free options.

It should be noted, however, that chemical substitution is only one option. Product redesign can often lead to the use of materials that do not require high levels of flame retardants. The German Research Ministry has a Green TV research project, which is evaluating alternative materials for the duroplastics commonly used in printed circuit boards. Some of the alternatives include polysiloxan foil and various injection molded thermoplastics, which can be soldered without lead and the base material does not require additional flame retardants.

## **ASSESSING ALTERNATIVES**

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Working with the limited studies available, both the Danish and German governments issued reports that evaluated the human health and toxicity data for a wide range of flame retardants, including those BFRs targeted for phase out. Both reports conclude that the use of halogen free flame retardants is a good first step forward in making the product safer. However, the potential environmental and human health impacts of halogen free alternatives cannot be overlooked.

The German Environmental Protection Agency used the substitution principle to assess and rank thirteen flame retardants based on toxicity to humans and the environment and their suitability to work within closed loop material systems. The study assumes that penta-BDE and octa-BDE are already phased out due to European wide regulations banning the use of both flame retardants.

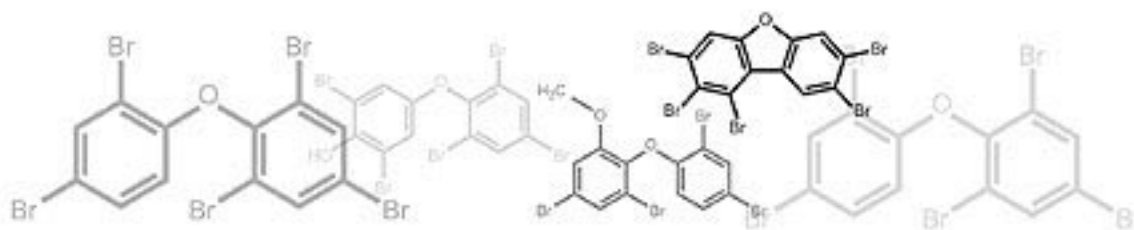
The German report, *Substituting Environmentally Relevant Flame Retardants: Assessment Fundamentals*, ranks the flame retardants based on evaluation criteria:

- Accumulation potential in environmental media (occurrences in humans and environment)
- Persistence
- Chronic toxicity—carcinogenicity is a top priority
- Acute toxicity—in contact with skin and the post application process during disposal and recycling
- Recycling impediment
- Emissions tendency (production, use and waste disposal)
- By-products of fire (smoke density, smoke gas toxicity, and corrosiveness and fire extinguishing water loads, etc)

## RANKING OF FLAME RETARDANTS <sup>41</sup>

Recommendation	Flame Retardant Type/Summary of Data	Trade Name
<b>Phase-out recommended</b>	Deca-BDE: Neurotoxicity possible, carcinogenic, bioaccumulation probable, persistent, high concentrations found in sediment.	Saytex 120E (Albemarle, 1999), DE-83 and DE-83 R (Great Lakes Chemical 1997)
<b>Phase-out recommended</b>	Tetrabromobisphenol A (TBBPA) Additive: Bioaccumulation probable, accumulation in liver, detected in mother's milk and sewage sludge. No studies available on its carcinogenic effects.	Saytex CP-2000, Saytex RB-100 (Albemarle 1999 and 1997), BA-59P and BA-59PC (Great Lakes Chemical 1998) and FR-1524 (Bromine Compounds 1998)
<b>Reduce use immediately and replace with safer alternatives</b>	Tetrabromobisphenol A, Reactive	
<b>Reduce use immediately and replace with safer alternatives</b>	Tris(chloropropyl) Phosphate (TCPP): Bio-accumulation cannot be excluded, accumulation in liver and kidney, mutagenic (mutates cells), detection in water, sediment and house dust, high risk of carcinogenic effects.	Fyrol PCF (Akzo Nobel, 1995), Antiblaze TMCP (Albright and Wilson 1998), Levagard: (Bayer, 1999) , TCPP (Clariant, 1999)
<b>Problematic Properties, reduction expedient</b>	Hexabromocyclo-decane (HBCD): Bioaccumulation probable, evidence of accumulation in fat tissue, significant levels found in sediment surrounding textile manufacturers, persistent and neurotoxicant.	FR-1206 (Dead Sea Bromine Compounds 1995), Saytex HBCD (Albemarle, 1995), and Micronized CD-75P (Great Lakes Chemical, 1998)
<b>Problematic Properties, reduction expedient</b>	Sodium Borate Decahydrate: Mineral flame retardant, unlikely to bioaccumulate, data indicates it can have teratogenic effects (linked to birth defects), high doses lead to stomach problems with the risk of subsequent anorexia after a few months, the reproductive toxic effect of borax is very important —exposure can lead to infertility, background levels in food is already so high that the daily tolerable intake is probably already reached.	Sodium Borate Decahydrate (Sigma-Aldrich, 1999)
<b>Problematic Properties, reduction expedient</b>	Antimony Trioxide (ATO): Synergist for bromo- and chloro-containing flame retardants, accumulation in the thyroid glands, liver, spleen, kidneys, heart and bones, suspected carcinogen and mutagen, ubiquitous in the environment. Exposure to ATO from rub off of domestic consumer goods or through direct object to mouth contact for children can be assumed. Concerning carcinogenicity, there are strong indications that high pollution (antimony workers) increases lung cancer mortality significantly. During fires, increases the ability for bromo and chloro FR to release dioxins.	Timonox (Great Lakes Chemical, 1993) and White, Blue Star (Campine N.V.)
<b>Use is not problematic</b>	Red Phosphorus (RP): Does not dissolve easily in water, risks of the environment being contaminated with phosphorus as a result of the use of red phosphorus is unlikely, accumulation unlikely; effects on organs unlikely, skin irritation.	Exploit RP 614 (Clariant, 2000), and RP (Sigma Aldrich, 1999)

CONTINUED ON NEXT PAGE



## RANKING OF FLAME RETARDANTS <sup>41</sup>

CONTINUED FROM PREVIOUS PAGE

Recommendation	Flame Retardant Type/ Summary of Data	Trade Name
<b>Use is not problematic</b>	Ammonium Polyphosphate (AP): Used in plastics, from a toxicological point of view APP is unproblematic.	Antiblaze CL/TR ( Albright and Wilson, 1998), Exolit AP 422 (Hoechst, 1982), and FR CROS 484 (Budenheim Iberica 1996) and Melapur (DSM, 1999)
<b>Use is not problematic</b>	Aluminum Trihydroxide (ATH): Mineral flame retardant either used with a plastic covering on a wide range of duro and thermoplastics, lattices, not hazardous to humans and the environment.	Aluisse Martinswek (GmbH, 1998) and Alcan (Chemicals Europe, 1998)
<b>No recommendation possible due to gaps in knowledge</b>	Bis(pentabromophenyl)ethane: Bioaccumulation possible, no detection however found in food chains, low potential for dioxin formation. Toxicology has not been sufficiently analyzed.	Saytex 8010 (Albemarle 1999)
<b>No recommendation possible due to gaps in knowledge</b>	Resorcinol-bis-diphenyl-phosphate (RDP): Bioaccumulation unlikely, very little health and environmental toxicity data available.	Fyrolflex (Akzo Nobel, 1999), CR-733-S (NRC, 1997), and Reofos (Great Lakes Chemical, 2000)
<b>No recommendation possible due to gaps in knowledge</b>	N-Hydroxymethyl-3-dimethylphosphonpropionamide; Halogen-free dimethylester of phosphonopropionic acidamide: Bioaccumulation unlikely, no evidence of mutagenicity, insufficient human health and environmental toxicity data.	Pyrovatex CP new (Ciba 2000)
<b>No recommendation possible due to gaps in knowledge</b>	Melamine Cyanurate (MC): Mainly used for polyamide, hazards in the workplace (MC found in dust), low accumulation, biodegradable in principle, insufficient data on human toxicity.	Fyrol MC (Akzo Nobel, 1994), Budit 315 (Budenheim Iberica 1997), Melapur: (DSM, 1999)

*“In order to promote the development of cleaner products that do not contain brominated flame retardants, the Programme for Cleaner Products will continue to support the development, testing and assessment of alternatives, as well as the dissemination of knowledge to manufacturers about the possibilities for using the alternatives.”*

— Danish EPA, Action Plan for Brominated Flame Retardants, 2001

The Danish Environmental Protection Agency's report, Alternatives to Brominated Flame Retardants: Screening for Environmental and Health Data, evaluates non-brominated flame retardants and does not provide specific recommendations, but supports the findings of the German study.

## SUMMARY OF TOXICITY DATA <sup>42</sup>

Type	Toxicity Data
<b>Red Phosphorus (RP)</b>	Low ecological and human health impact as long as it is not mixed with white and yellow phosphorus.
<b>Triphenyl phosphates (TPP)</b>	Low impact on human health, very toxic to aquatic ecosystems, high bioaccumulation (BCF>100).
<b>Tricresyl Phosphate</b>	Possible reproductive toxin; high bioaccumulation (BCF>100).
<b>Resorcinol bis(diphenylphosphate) (RDP)</b>	Minimal effects on human health, little data available on bioaccumulation.
<b>Phosphonic acids (dimethyl ester)</b>	Insufficient human health data. Very toxic to fish.
<b>Aluminum Trihydroxide (ATH)</b>	Low impact on fish and wildlife.
<b>Magnesium Hydroxide</b>	Insufficient human health data.
<b>Ammonium Sulfate (Polyphosphate)</b>	Very low ecological and human health impact. <sup>43</sup>
<b>Zinc Borate</b>	Can be harmful to unborn child, little is known about other health effects.
<b>Melamine</b>	Low health effects, no evidence of irritation, cancer induction or mutagenicity, low bioaccumulation.
<b>Antimony Trioxide (ATO)</b>	Teratogenic, bioaccumulative, reproductive toxin, and carcinogenic. <sup>44</sup>
<b>Quinidine Carbonate</b>	Insufficient human health and ecological data.

The bromine industry has repetitively argued that TBBPA and deca-BDE are safe for use in consumer products, but based on the toxicity data available, it is clear that this is not the case. The German study makes a strong recommendation that both deca-BDE and TBBPA be replaced immediately with safer alternatives.

Both studies conclude that a move away from halogenated compounds is an important first step in reducing the environmental and human health impacts of consumer products. It is clear however that the human and environmental impacts of the phosphate and other compounds cannot be ignored. The German study concludes that red phosphorus, aluminum trihydroxide, and ammonium polyphosphate are the least problematic flame retardants to use based on the best available information.

Unfortunately, the electronic manufacturers have not had success with red phosphorus. Triphenyl phosphates (TPP), a substance likely to bioaccumulate, is compatible with plastics used in electronic casings. Resorcinol-bis-diphenyl-phosphate (RDP), less volatile than some of the other phosphate compounds, is technically compatible with plastics used in electronics, but more information is needed on its human health effects.

These studies show the limitations of solely focusing on chemical substitution versus redesigning a product by using safer materials, physically separating heat generating components from highly flammable components or lowering the operating temperature of heat-generating components<sup>45</sup>. As shown in the previous section, many electronic companies are showing the technical possibilities of redesigning products—this needs to be more widespread throughout the industry sector to ensure that all products are designed with the safest materials possible for both flame retardancy and human health and the environment.

## **LEGISLATIVE RESPONSE TO THE GROWING THREAT OF BFRs**

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*Sweden has commissioned the national chemicals inspectorate KemI to draft plans for banning the brominated flame retardant deca-BDE, the government announced on May 6, 2004. Although Sweden would have preferred an EU-wide ban, for which it had pressed for some years, deliberations in Brussels were taking so long that “we must now address the issue ourselves”.*

— Swedish Environment minister, Lena Sommestad,  
quoted in Environment Daily, May 6, 2004.

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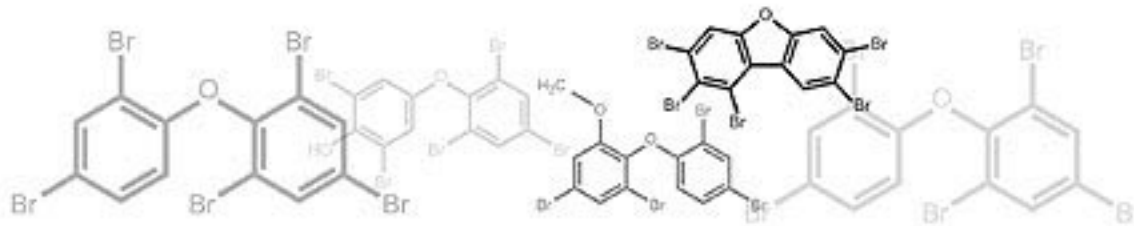
Environmentally advanced companies and some governments have promoted the phase out of brominated chemicals over the years. Fifteen years ago, industrial users in Germany agreed voluntarily to phase out the production and use of PBBs and PBDEs. Twelve years ago the international OSPAR Convention for countries in the North East Atlantic placed BFRs as a class on their list of hazardous materials. It is highly likely that some BFRs will be considered by the Review Committee of the Stockholm Convention on Persistent Organic Pollutants (POPs), which seeks to ban or severely restrict the production and use of some of the world’s most toxic chemicals, including PCBs and DDT. Unfortunately, nationally,

neither the US nor Canadian governments have put legislative controls on brominated chemicals even though North Americans have the highest levels of these chemicals in their bodies.

In the United States, the state of Maine passed a bill to ban penta- and octa- BDE by January 1, 2006, and deca-BDE by January 1, 2008, becoming the first state in the nation to ban deca-BDE assuming safer alternatives exist. In the state of Washington, the Governor signed an Executive Order in January of 2004 instructing the Department of Ecology to develop a phase out plan by December of 2004 for all PBDEs including deca-BDE. California also passed legislation in 2003 calling for a ban and phase-out of penta- and octa-BDE. Variations of these bills are being developed in other states, including New York, Massachusetts and Wisconsin.

On March 31, 2004, U.S. Representatives Hilda Solis (D-CA), Lynn Woolsey (D-CA), and Diana DeGette (D-CO) introduced legislation in the U.S. Congress to ban penta- and octa-BDE nationwide and research the potential effects of deca-BDE.





## BROMINATED FLAME RETARDANTS: TIMELINE OF LEGISLATIVE INITIATIVES

Year	Country	Action
<b>1989</b>	Germany	Industrial users voluntarily agree to a phase-out of PBDEs.
<b>1989</b>	Netherlands	Industrial users voluntarily agree to a phase-out of PBDEs and PBBs.
<b>1989</b>	EU	Prohibits use of tris (2,3 – dibromopropyl)-phosphate and PBB in textiles intended for contact with the skin; implemented in 1997 in Ministry of Environment and Energy Statutory Order 1042.
<b>1992</b>	OSPAR	Places BFRs on List of Chemicals for Priority Action; recommends urgent elimination of PBDEs and PBBs.
<b>1993</b>	Germany	PBDEs banned due to dioxin regulations.
<b>1995</b>	North Sea	Environment Ministers <sup>46</sup> commit to BFR substitution with less hazardous alternatives.
<b>1999</b>	Sweden	Swedish Chemicals Inspectorate (KemI) recommends phase-out of PBDEs and PBBs within five years with eventual phase out of all BFRs as part of a non-toxic future.
<b>1999</b>	World Health Organization	Recommends that BFRs “should not be used where suitable replacements are available.”
<b>2000</b>	OECD	Joint Meeting of the Chemicals Committee and Working Party on Chemicals accepts bromine industry’s voluntary agreement to end PBB production.
<b>2003</b>	Austria	Advocates ban on deca-BDE.
<b>2003</b>	EU	Examining possible action on HBCD and TBBPA.
<b>2003</b>	Norway	Pollution Control Authority requires companies to submit reduction and phase-out plans for BFRs.
<b>2003</b>	Netherlands	Prohibits production of bis (2,3-dibromopropyl) tetrabromobisphenol A TBBPA.
<b>2004</b>	EU	Ban on penta- and octa-BDE marketing and use in all products takes effect.
<b>2004</b>	EU	Deca-BDE currently undergoing debate decision expected late – 2004.
<b>2004</b>	Norway	Ban on penta- and octa-BDE takes effect.
<b>2005</b>	Norway	Planned ban on deca-BDE.
<b>2005</b>	Norway	Planned ban on HBCD and TBBPA if no EU action.
<b>2006</b>	EU	ROHS 1 Directive takes effect banning penta-, octa-, and deca-BDE in all electrical and electronic equipment sold or imported into the EU.
<b>2006</b>	Maine	Ban on penta- and octa-BDE.
<b>2008</b>	Maine	Ban on deca-BDE.
<b>2008</b>	California USA	Ban on penta- and octa-BDE.
<b>2020</b>	OSPAR	Phase-out goal for all brominated flame retardants.



# POLICY RECOMMENDATIONS FOR FLAME RETARDANTS IN ELECTRONIC PRODUCTS

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*Fire prevention is about much more than the heavy use of chemicals in polymers — it is a whole mindset.*

— Rof/Bjorn Albinson, Swedish Rescue Services Agency (equivalent of US fire marshals)

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There is universal agreement that preventing fires and reducing burn time is critical to providing safe environments in our buildings, transportation vehicles, and products. As such we need corporate and government policies that support the development of electronic products that not only meet stringent fire safety codes, but also respond to data revealing the disturbing and often irreversible effects that persistent, bioaccumulative substances have on human health and the environment.

Fortunately, there are new materials and product design techniques available on the market today that can replace the use of many harmful materials. The following policy recommendations will help spur the rapid adoption of currently available safer materials and catalyze the ongoing development of more environmentally compatible flame retardants.

**State and federal governments should make phase out of Deca-BDE and all other PBDEs a priority.**

As a priority, we recommend a ban and phase-out of deca-BDE use in manufacturing products, since penta-BDE and octa-BDE are already being phased out of most consumer products. The United States is lagging behind other countries in banning deca-BDE even though significant levels of deca-BDE have been found widely in the US public and environment. The United States needs to catch up with the global leaders on this issue—the European Union is banning all PBDEs from electronic products starting in 2006. Furthermore, progressive companies in the high tech sector have already researched and implemented alternatives, not only for deca-BDE, but for all brominated flame retardants.

**Governments should require that all brominated flame retardants are replaced with safer non-halogenated alternatives.**

The bromine industry is proposing other bromine substitutes that they believe have a lower potential for dioxin/furan formation, such as 1,2-bis(pentabromophenylethane). These bromine alternatives share similar chemical structures that make the PBDEs a public health

concern. The bromine industry has not provided comprehensive data showing that these chemicals are indeed safe for consumers or the environment.

Many chemicals that have before proven to be persistent, bioaccumulative and/or toxic in the environment are halogenated chemicals. Brominated flame retardants are halogenated chemicals and have been used for decades without prior testing for environmental or human health risks. Brominated chemicals pose risks throughout their lifecycle including the probability of brominated dioxin formation when incinerated or combusted. We have enough evidence to act and indeed progressive industries are moving to non-halogenated alternatives. To avoid the use of chemicals with the potential to persist, bioaccumulate and or be toxic to living things, we call for a phase out of all halogenated flame retardant use in electronic equipment. In particular this means a phase out of the production and use of TBBPA, the most widely produced brominated flame retardant.

State and federal initiatives need to promote green chemistry and the Substitution Principle that gives priority to the development and adoption of safer substitutes. To ensure safer alternatives are used, an assessment of non-halogenated substitutes must be done and data gaps filled. At a minimum, these assessments need to include a screening methodology<sup>47</sup> that looks at:

- Accumulation potential in environmental media (occurrences in humans and environment)
- Persistence
- Chronic toxicity- carcinogenicity is a top priority
- Acute toxicity — in contact with skin and the post application process during disposal and recycling
- Recycling impediments
- Emissions tendency (production, use and waste disposal)
- By-products of fire (smoke density, smoke gas toxicity, and corrosiveness and fire extinguishing water loads, etc)

**States should require electronics manufactures to take back products for recycling to encourage (Design for Environment) better product design.**

Product design plays a very important, but often ignored role in fire prevention. Material choice (i.e. nonflammable materials) and the way in which products are designed can greatly reduce and in some cases eliminate the need for hazardous chemical additives.

Producer responsibility for the entire life cycle of their products forces holistic thinking about material choice and end-of-life product management. Producer take-back practices encourage the use of less hazardous and more recyclable materials. When a manufacturer

is financially responsible for recycling their products at end-of-life, they have a financial incentive to design products that contain fewer toxics and are more easily recyclable. In the case of post-recycled plastic, which contains brominated flame retardants, the plastic has less value and quality than non-brominated plastics.

Producer take-back laws would therefore stimulate the adoption of non brominated flame retardants as well as encourage the use of materials which are naturally flame retardant. Sony Europe's adoption of metal housings for laptops and NEC's adoption of non-halogenated flame retardants are only two examples of how environmentally advanced companies are moving to safer materials. At the state and eventually federal level, take-back laws need to be adopted for all electrical and electronic equipment at end-of-life with a requirement to phase out the use of halogenated chemicals in products. Please see CTBC's model legislation at [www.computertakeback.org](http://www.computertakeback.org).

**State and federal governments should implement recycling guidelines for electronic products to ensure that BFRs are not continually put into new products and that workers are protected.**

Materials containing brominated compounds need to be separated from end of life electronic products to reduce contamination of those materials that can be recycled and reused in new products. New technologies are emerging to de-brominate plastics prior to recycling and these must be given priority over landfilling or combustion of plastics with brominated compounds since this is likely to generate brominated dioxins in both incineration and smelting processes.

**Government purchasing guidelines should include criteria for electronic products that do not contain PBDEs and phase out other brominated fire retardants.**

To support companies who are already moving away from BFRs and other harmful flame retardants, state and local government purchasing agencies as well as institutional buyers should specify products that do not contain BFRs.

Please see model procurement guidelines developed for health care institutions at <http://www.hcwh.org/goingGreen>

**Federal and state governments need to implement new chemical policies. Such policies would require safer substitutes, the phase-out of persistent, bioaccumulative, or highly toxic chemicals; full access to chemical information in the workplace and in products, reaction to early warnings, and comprehensive toxicity data from the chemical industry for all their chemicals in commerce.**

The continued use of brominated flame retardants in consumer products, such as personal computers, is symptomatic of a larger problem in the United States – the lack of a sustainable chemical policy. Chemicals that persist in the environment and in our breast milk, blood, livers and thyroids should not be allowed in commerce. For this reason, many states, such as Maine, Washington, Massachusetts and California, have taken an important step forward by working to eliminate broad classes of chemicals that persist and bioaccumulate in the environment and/or are known to be toxic to living things.

For too long we have been exposed to chemicals in common household products with little or no information. This situation can not continue. The national regulatory system has failed to protect consumers, citizens and children from the unintended consequences of exposure to small doses of harmful chemicals from multiple sources.

The Toxic Substance Control Act needs to be replaced with a policy vehicle that will<sup>48</sup>:

- Require Safer Substitutes — reduce toxic chemical use and emissions by altering production processes, substituting chemicals, redesigning products, or changing activities. This includes an obligation on the part of the public and private sectors to invest in research and development for sustainable chemicals, products, and materials.
- Phase-out Persistent, Bioaccumulative, or Highly Toxic Chemicals -- sunset the use and emission of chemicals that are slow to degrade, accumulate in fatty tissues, or are highly toxic to humans or the environment. The sunseting process should ensure the participation and protection of affected workers and communities.
- Give the Public and Workers the Full Right-To-Know -- disclose all materials and chemicals intentionally added to products and packaging, list quantities of chemicals used in manufacturing facilities, and provide public access to toxicity data on chemicals.
- Act on Early Warnings -- act to prevent harm when credible evidence exists that harm is occurring or is likely to occur, even when the exact nature and magnitude of the harm is not proven.
- Require Comprehensive Toxicity Data -- for a chemical to be on the market in the year 2020 comprehensive toxicity data must be publicly available. An estimated 95% of chemicals in commerce today lack some basic testing data on potential health and environmental impacts. Comprehensive toxicity data must become a pre-condition for having a chemical on the market. This is the principle of “No Data, No Market”.

# APPENDIX: COLLECTION PROTOCOL

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## 1.0 SCOPE:

To create a sampling procedure that will allow the collection of brominated flame retardants/ TetrabromobisphenolA from indoor surface of computer monitors, where potential exposures may exist for individuals working in a computerized environment.

## 2.0 RESPONSIBILITIES

It is the responsibility of the individuals performing the sampling to assure that the steps of this procedure are followed.

## 3.0 REFERENCES

Not applicable to this procedure.

## 4.0 PROCEDURE

### 4.1 Materials:

4.1.1 4" x 4" 6-ply cotton sponge dressing (Johnson&Johnson Sof-Wick)

4.1.2 One pair green nitrile gloves

4.1.3 One vial containing 3mLs of clean water

4.1.4 One glass sample container with Teflon lined lid (250mL)

### SAMPLING INSTRUCTIONS:

1.1.1 The laboratory recommends that prior to any sampling, the top surface of the computer monitor should not be dusted for a period of five days.

1.1.2 Make sure to turn the computer and monitor off before beginning the sampling procedure.

1.1.3 Measure the top surface of the computer monitor (length and width in inches or centimeters).

1.1.4 Place the green nitrile gloves on each hand and remove one sponge from the sterile package provided. At this point, care should be taken not touch any other surfaces.

1.1.5 Open the small glass vial containing water and pour the entire contents onto the sponge dressing. Fold the dressing approximately four times over and lightly squeeze in order to maximize the surface area contact of the sponge with the water.

1.1.6 Unfold the sponge back to it original size. Notice that the sponge has six layers to it. Using one sweeping continuous motion from left to right, begin wiping the top surface of the computer monitor, making sure that you expose a clean layer of the sponge

between each wipe. Wipe only the area of the monitor that was measured in step 4.2.2.

- 1.1.7** When you have completed the task of wiping the surface of the monitor, place the now sampled sponge dressing into the large 250 mL glass container and close the container with the Teflon-lined lid provided.
- 1.1.8** Place the chain of custody seal across the top of the lid, making sure the seal comes in contact with the sides of the glass as well as the lid. Write Sample ID, and Date and Time of Collection on label affixed to the glass container.
- 1.1.9** In addition, please fill out the chain of custody form provided. On the custody form be sure to fill in the Sample ID, Sample Collection Date and Time, Matrix Type, Sample Type, Number of Containers, and Analysis Requested. You do not have to fill out the Temperature (Temp:) and Thermometer number:(Therm#). Refer to the example chain of custody provided to see how the form should be filled out. **BE SURE TO SIGN THE "RELINQUISHED BY" LINE.**
- 1.1.10** There will be one trip blank provided for this project. The individual who receives this trip blank should identify it on the chain of custody form.
- 1.1.11** The sampling of the computer monitor surface is now complete and the sample can now be shipped to Southwest Research Institute Laboratory. Be sure to ship using next day air service.

## **5.0 MAINTENANCE**

Not applicable to this procedure.

## **6.0 SAFETY**

Safety is performed in accordance with requirements of the Chemical Hygiene Plan for Chemistry and Chemical Engineering Division (CHP-008).

## **7.0 RECORDS**

Applicable records generated by the processes of this procedure shall be maintained in accordance with Division 01 SOP-01-4.2.4, Storage and Maintenance of Quality Records.

## **LAB METHODOLOGY TO EXTRACT CHEMICALS FROM DUST<sup>1</sup>**

The methodology for this project was divided into three parts: sample extraction, cleanup, and analytical.

### **SAMPLE EXTRACTION AND CLEANUP**

The laboratory utilized a shake jar technique in which water along with organic solvent was added to vessels, creating a slurry containing the dust wipe samples received from specific sites across the United States. Prior to the start of the extraction procedure, the laboratory

spiked internal standards <sup>13</sup>C-Decabromodiphenyl ether-209 and <sup>13</sup>C-Tetrabromobisphenol-A to each of the dust wipe samples, method blank, and laboratory control spike sample. These internal standards were used to monitor extraction efficiency and quantify native target analytes. The pH of the slurry was basified to a pH of greater than 12 and mixed for one hour. The solution was allowed to partition for approximately 20 minutes and the organic layer was separated. This basic fraction represents the polybrominated diphenyl ethers. Fresh organic solvent was added back to the dust wipe samples and the slurry was acidified to a pH less than 2. The above-mentioned procedure was repeated, resulting in the generation of an acid fraction containing the TBBPA. The acid fraction was derivitized using diazomethane. Upon completion of the derivitization, the acid fraction was combined with the basic fraction and split fifty percent for reserve. The remaining fifty percent was passed through a cleanup procedure using combinations of silica gel and alumina. Prior to the start of the cleanup procedure, the laboratory spiked <sup>13</sup>C-Pentabromodiphenyl ether-99 to each of the samples in order to monitor cleanup efficiency. The extracts were concentrated to a final volume of 10uL and analyzed by HRGC/HRMS.

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## Analytical Methodology

The laboratory utilized a SwRI developed procedure for the analysis of polybrominated diphenyl ethers. A Micromass “M” series autospec interfaced to a Agilent 6890 GC was used to analyze the dust wipe samples. The laboratory prepared a single five point calibration curve at the following levels: 2000, 500, 100, 10, and 5 pg/uL for Octa-DecaBDE’s and 200, 50, 10, 1, and 0.5 pg/uL for TBBPA (derivitized). The native and <sup>13</sup>C mass labeled analytes were quantified using isotope dilution and internal standard methods.

The instrument was tuned to a mass resolution of 5000. The analytical sequence was as follows: Five-point calibration curve, solvent blank, method blank, samples, and laboratory control spike sample. Each analytical sequence was analyzed within an approximate twelve-hour time frame. The analytical column used was a J&W DB-5 capillary column 20 meter, 0.25mm internal diameter (ID), 0.10um film thickness.

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## Internal Standard Spike Levels

20uL was added to each sample, method blank, and laboratory control spike prior to start of extraction.

<sup>13</sup> C-TBBPA	50pg/uL
<sup>13</sup> C-DecaBDE#209	500pg/uL

Cleanup standard spike level: 10ul was added to each sample, method blank, and laboratory control spike sample prior to cleanup procedure.

<sup>13</sup>C-PentaBDE#99                      50pg/uL

Recovery Standard spike level: 10ul was added to each sample, method blank, and laboratory control spike sample prior to analysis on the HRGC/HRMS instrument.

<sup>13</sup>C-HexaBDE#                      50pg/uL

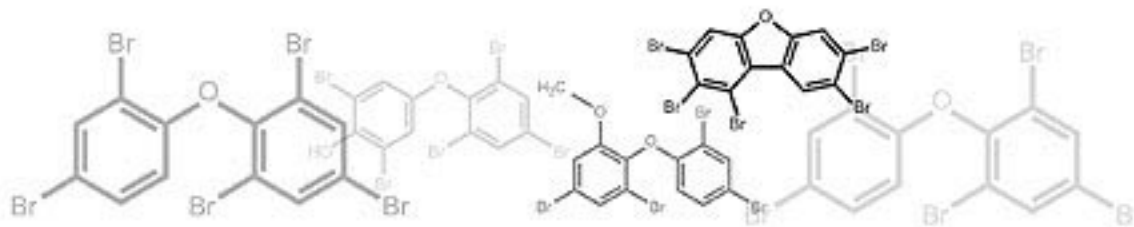
Laboratory control spike levels: 20uL was added to each laboratory control spike sample prior to extraction.

TBBPA	50pg/uL
OctaBDE#203	500pg/uL
NonaBDE#206	500pg/uL
DecaBDE#209	500pg/uL

## Observations

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The method blanks(03/04/04 and 03/18/04) contained very low levels of native analytes at or slightly above the contract required quantitation limit (CRQL). These levels equate to the laboratory's brominated flame retardant background level for these extraction batches. Values below these defined levels were not reported in any of the samples. In cases where the percent recovery for the C-TBBPA internal standard was below 10 percent, an alternate internal standard (13C-HexaBDE #154) was used to quantify the results for native TBBPA.





## ENDNOTES

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## **Production Notes**

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