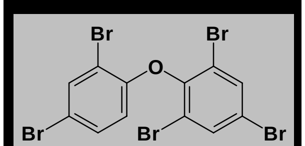

POLYBROMINATED DIPHENYL ETHERS: RECOMMENDATIONS TO REDUCE EXPOSURE IN CALIFORNIA

A Report of the Cal/EPA PBDE Workgroup

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California Environmental Protection Agency
Sacramento, California

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Executive Summary

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

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

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

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

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

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

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

Main Recommendations to Reduce PBDE Exposures[1]

Outreach and Education

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

Pollution Prevention

- Encourage the purchase of PBDE-free products.

Measurement and Monitoring[2]

- Conduct human biomonitoring to evaluate the effectiveness of the pentaBDE and octaBDE prohibition and other PBDE reduction efforts.

- Conduct environmental monitoring to identify sources, pathways and trends in PBDE levels, and to characterize the environmental fate of decaBDE.

Regulatory Initiatives

- Develop health guidance levels (e.g., reference exposure levels) for PBDEs to aid in establishing acceptable environmental levels.

- Assess the need for further regulation, such as the development of hazardous waste criteria and management and disposal requirements and practices for PBDE contaminated waste, an Airborne Toxic Control Measure, the addition of PBDEs to the Air Toxics “Hot Spots” list, and the need to limit the use of decaBDE.

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

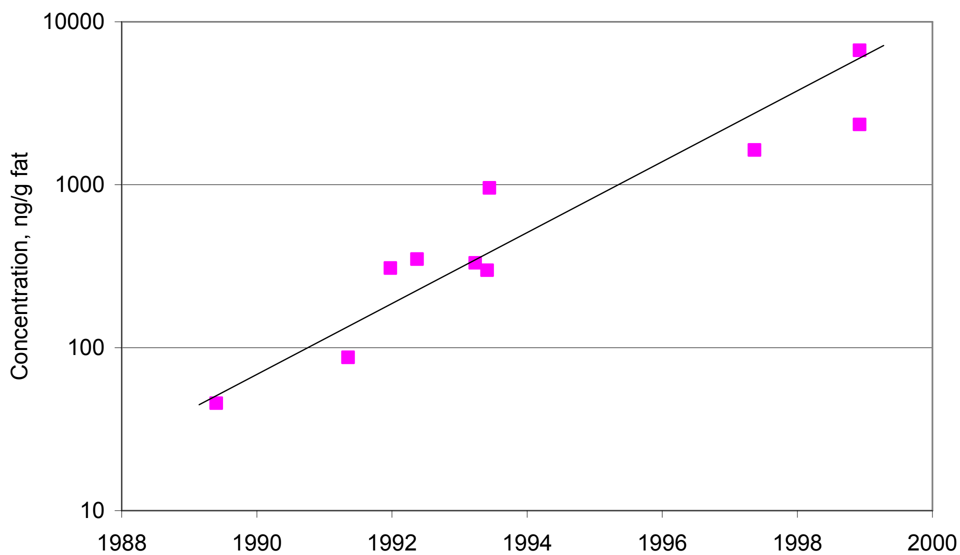
Recommendations include near-term actions intended to reduce PBDE exposures through outreach and education, and voluntary pollution prevention. Longer-term recommendations include further environmental monitoring of PBDE levels to increase the scientific base for decision-making, and consideration of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

Introduction

With the passage of Assembly Bill 302 (2003 Legislative Session, chaptered as California Health and Safety Code (H&SC) Sections 108920-108923, California became the first state in the nation to prohibit the use in commerce of products containing pentabrominated diphenyl ethers (pentaBDEs) and octabrominated diphenyl ethers (octaBDEs). PentaBDEs and octaBDEs are two of the three common commercial mixtures of polybrominated diphenyl ether (PBDE) flame retardants. PentaBDEs and octaBDEs were originally scheduled for phase-out in California in 2008. In 2004, the Legislature accelerated the timeframe for the PBDE phase-out by prohibiting the use of pentaBDEs and octaBDEs as of June 1, 2006. No product may be manufactured, processed or distributed in commerce in California after that date if it contains more than 0.1% of pentaBDE or octaBDE; only products manufactured after June 1, 2006, are subject to the prohibition. However, use of the third major PBDE mixture, decabrominated diphenyl ether (decaBDE), has not been restricted by this or any other legislation in California.

This legislation was prompted by the findings that exposures to PBDEs are widespread, and that levels of these compounds have been doubling in human tissues and breast milk every few years. Some of the highest levels of PBDEs measured worldwide have been in California human and wildlife populations. Figure 1 shows the high and increasing levels measured by DTSC in Harbor Seals in the San Francisco Bay.

Figure 1. PBDEs in San Francisco Bay Harbor Seals*



* Source: She et al. 2003

Exposures to PBDEs in the womb or early in life have affected the developing nervous system, and caused thyroid hormone disruption and male and female reproductive toxicity in animal toxicology studies (McDonald, 2005). PBDEs have not been adequately studied for their potential to cause cancer, but some evidence suggests they may have carcinogenic potential. Human tissue and blood levels of PBDEs measured in the U.S. and Canada during the past few years have typically been at least 10 times higher than those in Europe, where both the European Union (EU) and Scandinavian countries have prohibited the use of pentaBDEs and octaBDEs. Therefore, there is reason for concern about their potential health risks in humans.

Although products containing pentaBDEs and octaBDEs produced after June 1, 2006, will be prohibited from commerce after that date, exposure to them will continue due to their presence in hundreds of consumer products in homes, workplaces and motor vehicles. Further, the continued use of decaBDE may pose health risks either directly or through breakdown products. The Cal/EPA Secretary directed the formation of a workgroup of Cal/EPA Boards, Departments and Office (BDO) representatives to consider the nature and extent of the PBDE problem and to recommend actions Cal/EPA could take to mitigate the exposure to PBDEs. The California Department of Health Services (DHS) contributed expertise and provided representatives to the Cal/EPA PBDE Workgroup as well.

This report of the Cal/EPA Workgroup provides information on PBDEs and makes recommendations to characterize the extent to which Californians are exposed to PBDEs and to reduce those exposures. Specifically the Workgroup:

- Summarizes what is known about decaBDE toxicity and environmental and human tissue concentrations, as well as its potential to breakdown to more hazardous chemicals;
- Summarizes environmental measurements in California of pentaBDEs and octaBDEs;
- Characterizes the problem posed by legacy pentaBDEs and octaBDEs and continued use of decaBDE;
- Outlines ongoing activities of Cal/EPA BDOs and DHS; and
- Recommends further actions Cal/EPA can take to limit PBDE exposures in California.

This report presents neither a comprehensive literature review nor a risk assessment for PBDEs. Rather it summarizes information from the scientific literature to provide a context for the recommendations that follow.

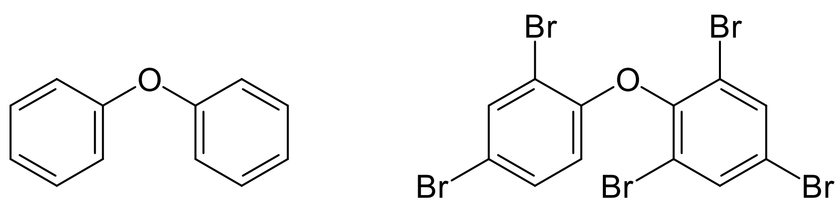
In developing these recommendations, the Workgroup did not address the availability of state resources for implementation. The majority of these recommendations cannot be acted upon by individual Cal/EPA BDOs without the provision of additional resources for this purpose. This is a serious constraint that must be addressed as Cal/EPA evaluates, prioritizes and chooses recommendations for implementation.

Background

PBDEs: Chemical Identities, Production and Use

PBDEs are diphenylethers with bromines attached, as illustrated in Figure 2 below. The number and the placement of the bromine atoms determine the type of PBDE. Figure 2 shows a non-substituted diphenyl ether and then as an example, one congener with five bromine atoms attached, 2,2',4,4',6-pentabromodiphenylether. There are 209 individual chemical congeners within the chemical class of PBDEs.

Figure 2. Diphenyl ether structure



Diphenyl ether

2,2',4,4',6-Pentabromodiphenylether
(PBDE-100)

The chemical properties depend on the number of bromines, other substituents, and their ring positions. PBDEs have been widely used as flame retardants: The bromine atoms in the PBDEs quench flames by scavenging electrons. Historically, three commercial mixtures of the PBDEs have been manufactured and used – the penta, octa, and decaBDE formulations. Among the several different PBDE congeners found in the pentaBDE formulation, the average number of bromines is five. Similarly, the average number of bromines is eight among the congeners present in the octaBDE formulation. DecaBDE (i.e., “PBDE 209”) is a diphenylether that is fully substituted with bromines, although the commercial decaBDE formulation also contains other congeners.

PBDEs have been widely used in consumer products, including electronic equipment, fabrics, and polyurethane foam. When used as flame retardants, PBDEs are not chemically reacted with or bound to the product (e.g., polyurethane foam, plastics). Thus, they can and are readily released from these products.

Approximately 67,500 metric tons of PBDEs are manufactured annually worldwide, with North America accounting for much of the world’s PBDE use. DecaBDE is the most widely used PBDE formulation globally, with annual demand of 24,500 metric tons in the American market. The pentaBDE formulation has been used almost exclusively in North America, at a rate of approximately 7,100 metric tons per year. Use of the octaBDE formulation has been considerably less than that of the pentaBDE formulation. In the U.S., manufacture of the pentaBDE and octa BDE formulations stopped in 2005.

The pentaBDE formulation contains the four congeners thought to be most bioaccumulative (PBDE 47, 99, 100, 153). These four congeners have become ubiquitous in the environment worldwide, and are found in wildlife and human tissue.

PentaBDEs and OctaBDEs: Concentrations and Toxicity

Environmental Levels and Human Exposure to PentaBDEs and OctaBDEs

PBDEs have become ubiquitous in air, sediments, wildlife and human tissues. Levels of pentaBDEs are consistently observed in breast milk, serum and adipose tissue throughout the world. The highest levels have been measured in the U.S. and Canada. Estimates of the half-lives in humans for these congeners range from 3.5 to 7.2 years. This in part explains the steady increase in human tissues over time of these PBDE congeners.

In 2004, the Air Resources Board (ARB) conducted ambient air monitoring for PBDEs, including a tetraBDE (PBDE 47) and a pentaBDE (PBDE 99) congener, at six urban sites within California (Los Angeles, Oakland, Richmond, Riverside, San Jose, and Wilmington). Appendix I summarizes the findings of ARB's air monitoring effort. Concentrations of the tetraBDE ranged from 7-170 pg/m^3. Concentrations of the pentaBDE ranged from 3-332 pg/m^3. For comparison, outdoor concentrations of various PBDE congeners have been found to range from 5-300 pg/m^3 in other parts of the world.

In 2004, the ARB contracted with the University of California at Davis (UCD) to conduct indoor air monitoring for PBDEs inside a computer training room containing 13 personal computers manufactured before 2000 (See Appendix I). Indoor air concentrations of PBDEs, mostly PBDE 47, ranged from 4-1,600 pg/m^3 in this room. For comparison, other researchers have measured indoor air concentrations of PBDEs up to 1,800 pg/m^3 (Hites, 2004). Analysis of dust from the room's carpet indicated that PBDEs were present in the dust at 10 ppm, and that decaBDE was the predominant congener.

Toxicity of PentaBDEs and OctaBDEs

Because of the structural similarity between PCBs and PBDEs, toxicological studies of PBDEs have focused on endpoints known to be induced by PCBs. For one pentaBDE congener, dioxin-like effects of metabolic enzyme induction and specific effects on the liver, thymus and immune systems were found to occur only at relatively high doses in rats (Fowles et al., 1994). In contrast, effects on thyroid are seen at fairly low doses (e.g., 0.8 mg/kg) (Zhou et al., 2001; Fowles et al., 1994). Estrogenic activity is also been observed for pentaBDEs and hexaBDEs (Meerts et al., 2001), and testicular and ovarian effects have been reported at a low dose (0.06 mg/kg) for a pentaBDE (Kuriyama et al., 2005; Talsness et al., 2005). The tissue concentration in rodents associated with this low dose was relatively close to that observed in some humans. Effects on the developing nervous system of mice have been observed after exposure to several PBDEs (Viberg et al., 2003a and b; Viberg et al., 2002; Eriksson et al., 2002). HexaBDE and pentaBDE had greater potency than tetraBDE and decaBDE.

Estimated ratios of tissue concentrations producing effects in rodents compared to those in highly exposed people in the U.S. tend to be small for the penta isomer PBDE 99 (McDonald, 2004, 2005). In other words, the levels of PBDEs detected in the tissues of people most exposed overlap with those seen in experimental animals in which toxic effects have been observed. This is in part due to its considerably longer half-life in humans compared to rodents (3-7 years versus 24-42 days). Several other PBDEs have relatively long half-lives in humans.

Carcinogenicity testing of additional PBDE congeners (PBDE-47, PDBE 153) and of the pentaBDE technical mixture is presently in the planning phase at the National Toxicology Program (under the auspices of the National Cancer Institute). Based on the structural similarities of PBDEs to certain other polyhalogenated organic compounds, some pentaBDEs and other PBDEs are expected to possess carcinogenic activity.

DecaBDE: Concentrations, Toxicity and Breakdown Products

Use of decaBDE, the most widely used PBDE, is not addressed by California H&SC Sections 108920 *et seq*. Prohibition of certain uses of decaBDE has been proposed within the EU, but thus far the EU has not limited its use. These decisions reflect a lower concern for the toxicity of decaBDE, although toxicity testing of this congener has been limited and uncertainties remain. DecaBDE does break down in the environment to more toxic chemicals; however, the identities, rates of formation, and toxicities of decaBDE breakdown products have not yet been adequately characterized. What is known about the possible exposures in California and health risks of decaBDE is summarized below, along with information on its breakdown into more hazardous lower brominated congeners.

Environmental Levels of DecaBDE

In 2004, the ARB conducted ambient air monitoring of decaPBDE at the same six urban sites for the two congeners mentioned previously (see Appendix I). Concentrations of the decaBDE congener ranged from 7-72 pg/m^3, with an average monitored concentration of 23 pg/m^3. Thus exposure to the general population from breathing outdoor air may be low (e.g., <10^{-5} µg/kg-day).

Working with UCD, the ARB also found decaBDE as the major component in air samples in the vicinity of two facilities: an indoor electronics recycling facility without air pollution control equipment, and an outdoor automobile shredding facility (see Appendix I). Inside the electronics recycling facility, air concentrations of PBDEs, mostly decaBDE, ranged from 5 – 830,000 pg/m^3 (the highest concentration is associated with a dose of roughly 0.1 µg/kg-day for workers in the facility). Outdoor concentrations ranged from 1 – 11,000 pg/m^3. For comparison, other researchers have measured up to 200,000 pg/m^3 inside a Canadian electronics recycling facility. At the automobile shredding facility, fence-line air concentrations of PBDEs, mainly decaBDE, ranged from 0.2 – 1,900 pg/m^3 (upper bound dose < 0.001 µg/kg-day). The scientific literature does not contain any similar studies on autoshredder operations for comparison.

Additional contract studies with UCD were conducted in 2004 by the ARB, measuring PBDE concentrations in the air and carpet dust of a computer training room containing 13 personal computers manufactured before 2000 (See Appendix I). While PBDE 47 was the predominant PBDE in indoor air samples, decaBDE was predominant in carpet dust. The carpet dust contained 10 ppm total PBDEs, which is consistent with findings of other researchers (EWG, 2004). A new piece of the same type of carpet was analyzed and found to contain 0.1 ppm of decaBDE. ARB is currently conducting chamber studies to more accurately characterize the release of PBDEs from personal computers.

PBDEs are present in house dust and clothes dryer lint, with the most abundant congener found being decaBDE. Young children, and in particular, toddlers, are among those most likely to receive the highest exposure to the house dust through floor activities and hand-to-mouth behaviors. If one makes high end assumptions for dust consumption by toddlers and assumes a dust concentration of 10 ppm decaBDE, an estimated dose for toddlers of 0.2 µg/kg-day for decaBDE from dust is obtained, which is comparable to occupational exposures at the electronics recycling facility noted above. Further assessment of the potential for decaBDE exposure via house dust is needed, particularly for young children.

DecaBDE has also been found in foods, including fish and soy milk, at relatively low levels. DecaBDE has been measured in wildlife throughout the world, including birds and bears from polar regions, Swedish peregrine falcon eggs, freshwater fish, Belgian foxes, and rats at an urban dump site. These data demonstrate the potential for decaBDE to distribute throughout the food web.

DecaBDE has been measured in non-occupationally exposed individuals' blood and breast milk. Given the relatively short half-life in humans (15 days) estimated for decaBDE (Thuresson et al., 2006), these observations suggest that exposure to decaBDE occurs on a regular basis in the general population. DecaBDE has also been measured in the blood of electronics dismantling workers. Still the highest decaBDE level measured in 23 breast milk samples in Texas was 8.24 ng/g lipid; decaBDE was not detected in 16 of the samples (Schecter et al., 2003). At the highest value measured, the Workgroup estimates that a young infant would consume an amount of 0.07 µg/kg-d decaBDE through nursing.

Toxicity studies of DecaBDE

DecaBDE has been assessed in animal studies investigating potential impacts on the developing nervous system and birth defects and other fetal harm. In one study, decaBDE given to mice caused irreversible changes in brain function which worsened with age. The effect was observed in mice given the compound on the third day after birth, but not on the 10^{th} or 19^{th} day after birth. The dose of 20,100 µg/kg-day caused the effect but not a dose of 2,200 µg/kg. DecaBDE was less potent in causing this effect than tetraBDE, hexaBDE or penta BDE (Viberg et al., 2003b; Viberg et al., 2002).

Exposure of pregnant rats to 1,000,000 µg/kg body weight of decaBDE caused delayed hardening of bones in their offspring (Norris et al., 1975). Other studies of developmental (Hardy, 2002), subchronic and chronic toxicity (National Toxicology Program, 1986) essentially reported no non-cancer effects of decaBDE when tested at relatively high doses (up to 1,000,000 µg/kg body weight).

Thus, for non-cancer toxicity studies conducted to date, the dose causing an effect in the most sensitive study (Viberg et al., 2003b) was 20,100 µg/kg-day and no effects were seen at 2,200 µg/kg-day.

Based on the structural similarity of PBDEs with polybrominated biphenyls (PBBs) and other structure-activity considerations, decaBDE would be expected to be one of the least active congeners with regard to carcinogenicity. Further, decaBDE is not readily absorbed by the body, in contrast to the lower brominated

PBDE congeners, which are readily absorbed and also have a longer half-life in the body.

DecaBDE has been tested for carcinogenicity by the National Toxicology Program (NTP, 1986) and Dow Chemical (Norris et al., 1975). In the Dow Chemical studies in rats no significant tumor findings were observed. In the subsequent NTP studies conducted at higher doses, decaBDE induced non-malignant liver tumors in rats of both sexes, and NTP concluded this provided "some evidence" of carcinogenicity in these animals. NTP (1986) concluded that there was "equivocal evidence" of carcinogenicity in male mice based on findings of thyroid and liver tumors that were marginally significant statistically. In female mice, there was little evidence of carcinogenicity. The NTP study is discussed in greater detail in Appendix II.

In reviewing the carcinogenicity evidence for decaBDE, the International Agency for Research on Cancer concluded that there is "limited evidence" for the carcinogenicity of decaBDE in animals (IARC, 1990), essentially due to the 1986 NTP findings.

To facilitate screening analyses, the Workgroup calculated an upper bound cancer potency for decaBDE from the NTP study (i.e., 0.00108 $(mg/kg\text{-}day)^{-1}$; see Appendix II).

Screening Level Risk Considerations for Direct DecaBDE Exposures

While the exposure and toxicity data are limited for decaBDE, it is still instructive to compare doses causing effects in the sensitive animal experiments to human dose levels from environmental and occupational exposures. For non-cancer effects, the decaBDE dose observed to cause no effect in the most sensitive experiment to date - that on the developing nervous system (2,200 µg/kg) - can be compared to doses associated with human exposures. The experimental dose causing no effect is roughly 30,000 times the dose calculated for a day of breast feeding by human neonates (0.07 µg/kg-d, see above); the value is 10,000 times that associated with toddler consumption of dust contaminated at 10 ppm on a given day. Further characterization of the predicted doses to nursing human neonates and dust intake relative to the doses at which toxicity was observed in animals would be included in a more detailed assessment.

Assuming chronic exposures to levels observed in ambient air, inside recycling facilities, or outside near recycling facilities results in cancer risk estimates below 10^{-6}, and large margins of exposure when compared with doses causing effects in animal studies. This suggests that, given the current state of scientific knowledge, directly breathing decaBDE is not likely to be a significant health concern for workers or the general public. Levels received via food or mother's milk also appear to be relatively low. However, a more reliable assessment comparing tissue concentrations in laboratory animals and humans is needed. Also, other exposure scenarios, such as exposures of the general population and young children to house dust, require a more in-depth evaluation.

Breakdown of DecaBDE

The studies of ARB and others establish that consumer products containing decaBDE result in release and dissemination of the chemical through the environment. Further, a number of studies indicate that decaBDE loses bromine atoms in the environment by the action of ultraviolet light, heat, and bacteria, forming more persistent and toxic lower brominated compounds, such as nonaBDEs, which are further debrominated (Soderstrom et al. 2004; Gerecke et al. 2005). Research presented at the Dioxin 2005 Meeting in Toronto indicates that decaBDE in sewage sludge may be broken down under anaerobic conditions by bacteria to octaBDEs and nonaBDEs. The researchers hypothesize that these debromination reactions also occur in sewage treatment facilities and in anaerobic soils and sediments. Other studies have demonstrated the ability of anaerobic bacteria to debrominate decaBDE to nonaBDEs and octaBDEs, and octaBDEs to lower brominated congeners.

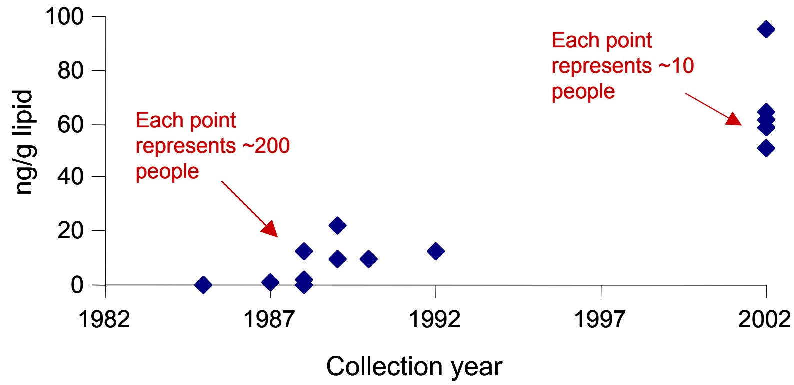
Research also indicates that decaBDE is metabolized in fish, including rainbow trout, and in chickens, to lower brominated congeners (e.g., nonaBDEs, octaBDEs, and heptaBDEs). Another potential environmental health concern, apart from debromination of decaBDE, is the formation of brominated dioxins and dibenzofurans from decaBDE during combustion (e.g., disposal via incineration of plastics).

Nature and Extent of the PBDE Problem

Continuing Exposures

PBDEs are ubiquitous substances present in homes, offices, and other buildings, and in transportation vehicles, including cars, trucks, planes and mass transit vehicles. The general population comes into contact with materials containing PBDEs in nearly every indoor microenvironment through the use of PBDEs in building materials, carpets, textiles, electronics, flooring, mattresses, foam furniture, and high temperature plastics. As a consequence of the pervasiveness of PBDEs in the indoor environment, people are directly exposed to these bioaccumulative chemicals for that portion of time spent indoors, which has been estimated by the ARB to range from 85% - 90% of each day. Thus, these direct human exposures make PBDEs strikingly different from other recognized persistent bioaccumulative chemicals, for which diet represents the primary route of exposure. PBDEs are measured in indoor air, and in house and office dust. PBDEs have been detected in some foods, and in ambient air, especially near e-waste recycling and autoshredder facilities.

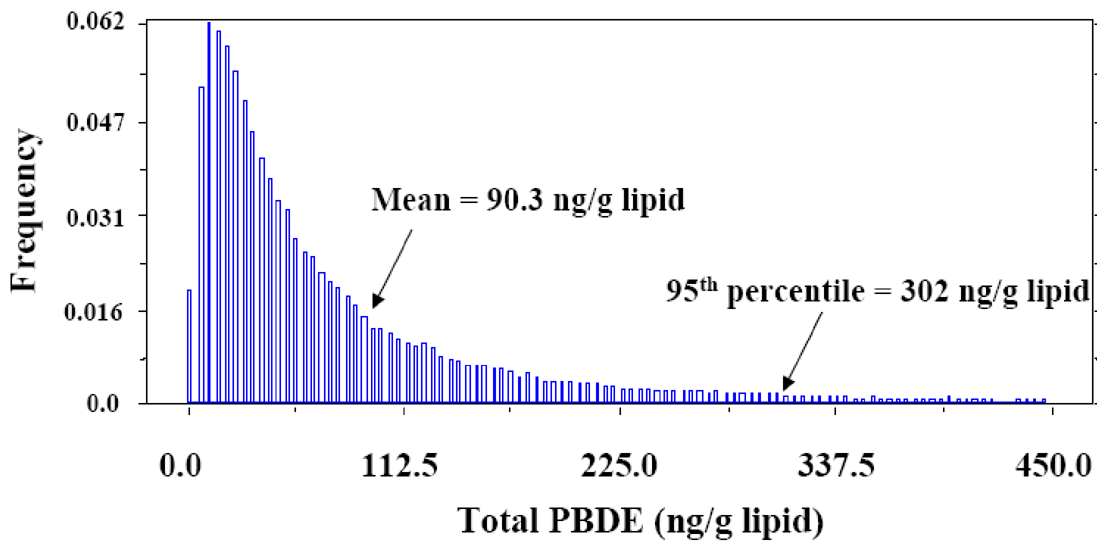
Figure 3. Increasing PBDE Human Serum Levels in the U.S.*



*Source: Sjodin et al., 2003

Recent scientific reports have shown that PBDEs are rapidly accumulating in human tissues (Figure 3). This was first observed in 1998 in Sweden, which has a national breast milk monitoring program. Based on several small studies, the levels of PBDEs measured in humans in Canada and the US are typically 10 times or more greater than in Europe (Table 1; Figure 4), and appear to be doubling every few years.

Figure 4. Distribution of PBDE levels among U.S. women*



*Source: McDonald, 2005

Biomonitoring data indicate that individuals have measurable levels of decaBDE in their blood. Unlike most of the PBDE congeners, the fully brominated decaBDE does not bioaccumulate. Thus, the finding of decaBDE in blood samples obtained from the general population indicates that people experience repeated continuous exposures to decaBDE. In addition, Cal/EPA scientists have found the highest tissue concentrations of PBDEs in the world in California wildlife (shorebird eggs and fish), and have reported rapid accumulation of PBDEs in the tissues of San Francisco Bay harbor seals (Figure 1 above).

Table 1. Mean Concentrations of PBDEs in Humans in the U.S. and Three European Countries

Country	Mean PBDE body burden (ng/g lipid)	References
United States	90.3	McDonald 2005
Sweden	6.03	Bavel et al. 2002
Spain	4.12	Meneses et al. 1999
Finland	2.30, 11.7	Strandman et al. 1999, 2000

With the coming prohibition in California of products manufactured on or after June 1, 2006 containing pentaBDEs and octaBDEs, exposures to these PBDEs should decrease over time but will nonetheless continue for many years through the continued use of existing building materials, furnishings, and consumer products. Recycling and disposal of materials containing pentaBDEs and octaBDEs will also result in continuing exposures.

It should be noted that the June 1, 2006 prohibition, while banning the introduction of new sources of pentaBDEs and octaBDEs into the state, will not alter exposures arising from materials and consumer products currently in use. In fact, exposures will continue for years. Moreover, it is possible that new sources of pentaBDEs and octaBDES will continue to be introduced into California after the effective data of the ban because California H&SC Sections 108920 *et seq.* do not specify how the pentaBDE and octaBDE prohibition will be enforced. In such cases, the Attorney General's Office usually assumes the responsibility of enforcement; however, at this time it is not clear whether the Attorney General's Office has the resources to enforce the relevant statutory provisions. Nor is it clear whether the Attorney General's Office would require the technical assistance of any of the Cal/EPA BDOs in this regard. As noted above, tissue PBDE concentrations producing effects in rodents overlap with existing human tissue concentrations, indicating the potential for human health effects and an urgent need to reduce human exposure.

DecaBDE is not affected by any legislation and its use and release into the environment will continue unabated. Preliminary analyses suggest that breakdown of decaBDE to more toxic forms is a more important concern than direct exposure to decaBDE, although this requires further study. While exposures to decaBDE are continuous in the indoor air in homes and offices, the airborne concentrations are quite low. Exposure to dust in these settings may result in higher doses to, for example, young children, as described above. Further characterization of dust as a source of exposure requires a more detailed assessment. Levels of decaBDE found in sewage sludge suggest that decaBDE from the indoor environment and perhaps laundering finds its way into municipal sewage systems and is further dispersed in the environment. This is an example whereby decaBDE enters the outdoor environment, and moves into the food chain and into aquatic and terrestrial wildlife, along with the debrominated forms it gives rise to. A growing body of data indicates that decaBDE undergoes debromination to lower brominated forms through sunlight, heat, bacteria, and through metabolism as it progresses through the food web. Several of these lower brominated forms are bioaccumulative.

Co-Exposures to PCBs and similar classes of chemicals

PBDEs have structural similarity to PBBs, PCBs, and certain other persistent polyhalogenated organic pollutants. In the limited toxicity testing to date, PBDEs have produced some of the toxic effects and physiologic changes seen with many persistent polyhalogenated organic pollutants, in particular the PBBs and PCBs. These effects include developmental and nervous system toxicity, as well as mimicry of estrogen and interference with the activity of thyroid hormone. These observed similarities in the toxicological profiles suggests that PBDEs, PBBs, PCBs, and certain other persistent polyhalogenated organic pollutants may induce toxic effects via common mechanisms of action. The general population is exposed on a daily basis not only to PBDEs, but also to these other chemicals, primarily via their presence in the diet. Given this, there are concerns that co-exposures to PBDEs and certain of these other persistent polyhalogenated organic pollutants may be additive, and that total levels of exposure to these compounds may be close to the point where frank developmental toxicity may occur in more highly exposed individuals (McDonald, 2005). To date, only one study has investigated the effect of co-exposures in animals. In this study a greater than additive effect of PBDE 99 and PCB 52 was observed for effects on the developing nervous system (Eriksson et al., 2003).

Waste Disposal/Recycling Issues

Assembly Bill 2587 (2004 Legislative Session, chaptered as California H&SC Sections 108920-108923) does not restrict the disposal of waste containing PBDEs. Other countries that have restricted the use of PBDEs have not addressed waste disposal. To date, the Workgroup has not identified any measures or procedures that have been implemented for PBDE waste disposal by other countries. California should continue to monitor future activities of others with regard to PBDE waste disposal.

Nonetheless, there is a need to identify the waste streams containing PBDEs, and determine which contribute to release of PBDEs into the environment. Measurement and monitoring studies are needed to investigate this. While Assembly Bill 2587 prohibits the processing of products manufactured on or after June 1, 2006 that contain more than one-tenth of one percent pentaBDEs or octaBDEs, it does allow metallic recyclables containing PBDEs (pentaBDEs and octaBDEs) to be processed for recycling or reuse, which includes automobiles, metal furniture, major appliances, and electronic products. Studies to date suggest that e-waste recycling facilities are significant sources of PBDEs released into the ambient air. Autoshredder facilities have also been shown to release PBDEs into the ambient air. California should characterize these exposure pathways more fully.

Another need is to investigate the fate and transport of PBDEs via municipal waste water systems and the use of sewage sludge, especially regarding releases into the aquatic environment.

In addition to autoshredder and e-waste, PBDEs released from the processing and disposal of a variety of products should also have their exposure pathways characterized. PentaBDEs are found in mattresses, foam packaging, cushioned furniture, and carpet padding; octaBDEs acrylonitrile butadiene styrene (ABS) plastic, housings for fax machines, computers and other electronic equipment, telephone handsets, small electronics parts, and electric cable; decaBDE is found in housings for TVs, and other electronics, textile backings (curtains, upholstery covering), electrical boxes, wiring, and high impact polystyrene (HIPS) plastic.

In summary, exposures of the general public to PBDEs occur through the use of consumer products and furnishings in homes, offices, cars and schools. As these consumer products are used and after they are discarded, PBDEs are released into the environment where they can bioaccumulate in wildlife and food animals.

Cal/EPA Entities and DHS Past and Ongoing Activities

Air Resources Board

As described in Appendix I and elsewhere in this report, ARB has conducted air monitoring to aid the characterization of PBDE pathways of exposure and the extent of exposure to total PBDE and the different PBDE congeners. ARB has reviewed its regulatory authority and found that PBDEs fall within the class of polycyclic organic matter, which has been designated as a Toxic Air Contaminant under H&SC sections 39660 *et seq*.

Department of Toxic Substances Control

DTSC's Hazardous Materials Laboratory has pioneered measurements of PBDEs in human tissue and wildlife in the U.S. DTSC first reported the exponential increase of PBDEs in harbor seals from the San Francisco Bay that occurred between 1988 and 1998 (She et al. 2002). Moreover, DTSC reported that levels of PBDEs in California human adipose and serum samples obtained in the late 1990s were 30 times higher than human tissue levels reported during the same time period from Europe and Japan (Petreas et al. 2003). The absence of PBDEs in California serum dating from the 1960s reflects the recent introduction of PBDEs into commerce and the environment (Petreas et al. 2003). Because PBDE concentrations did not correlate with PCB concentrations, that study also suggested that other exposure pathways, such as indoor air may be significant. Additionally, DTSC reported that levels of PBDEs measured in California marine fish and seabird eggs are among the highest in the world (Holden et al. 2004; She et al. 2004; Brown et al. 2006). Currently, DTSC is completing a study of breast milk, the first such study specifically designed to identify PBDE sources of exposure. In addition, in an effort to identify major waste streams of concern, DTSC is measuring PBDEs in e-waste and autoshredder waste (Petreas et al. 2005) as well as consumer products, using both chemical methodologies and an XRF screening tool (Petreas et al. 2006). DTSC has been hosting a Technical Working Group where scientists from government, industry, and non-governmental organizations present and discuss the latest information on PBDEs and other brominated flame retardants. DTSC publications on PBDEs are included in Appendix III.

DTSC plans to:

- Complete ongoing PBDE research
- Seek/obtain funds for further research
- Develop integrated research plan with DTSC regulatory programs
- Define waste stream management alternatives
- Define/assess current PBDE disposal/destruction options
- Explore changes in regulations to define PBDEs as hazardous waste
- Develop an integrated approach to biomonitoring with Cal/EPA and DHS

Integrated Waste Management Board

The CIWMB has authority to regulate nonhazardous solid waste handling, transfer, composting, transformation, and disposal. The CIWMB does not characterize waste and does not restrict the handling and disposal of waste containing PBDEs. DTSC determines if a waste is hazardous and what management standards are required. The SWRCB/RWQCB determines if any constituents of concern contained in a waste would affect water quality and if specific management standards are required. At this time, no restrictions have been identified by DTSC and the SWRCB/RWQCB for wastes containing PBDEs.

Because PBDEs are ubiquitous substances that have been used for more than 30 years as flame retardants in home and office building materials, motor vehicles, electronics, furnishings, textiles, high temperature plastics and polyurethane foams, they are common in the waste stream. The presence of PBDEs in waste materials cannot be readily discerned by solid waste facility operators. Should the disposal of wastes containing PBDEs eventually be restricted, some method for identification would need to be devised to let the solid waste facility operator know if the waste contains PBDE. This is especially important in light of the fact that diverting waste from landfills through reuse and recycling is a major requirement of the Integrated Waste Management Act (Act), and the operator needs to be able to discern when a waste has restricted handling.

Nonhazardous solid waste landfills are prohibited from accepting hazardous wastes with few exceptions. One exception is treated wood waste, which can be disposed in a composite-lined portion of a solid waste landfill. Another exception is asbestos containing waste, which can be disposed in a designated disposal area at a landfill. Asbestos containing waste is cradle-to-grave manifested; treated wood waste is not manifested or labeled, which has the potential to be a problem for operators who cannot readily discern if the waste is treated or non-treated wood waste. Neither asbestos containing waste nor treated wood waste can be processed prior to disposal. To conserve landfill space, most landfill operators divert wood materials from disposal and typically ground and screen the wood before marketing it for reuse as a landscape product, compost feedstock, biomass fuel, etc. Because operators may have difficulty in discerning whether a waste is treated wood waste or not, treated wood waste could end up being processed even though this activity is prohibited.

Used oil and electronic waste consisting of CRTs and monitors have been classified by DTSC as hazardous wastes and cannot be disposed in nonhazardous solid waste landfills, but they can all be recycled. The handling and management of these wastes, including recycling, fall under the authority of DTSC.

In the area of pollution prevention, the CIWMB encourages the procurement of products that do not contain PBDEs. Examples of this include the following:

- The CIWMB, working with the Department of General Services (DGS) on Strategically Sourced Statewide Contracts, added specification language as provided below:

    - Office Equipment: copiers and associated services; awarded July 2005; estimated value of contract $36 million – Specification language:

Requirement that digital copier shall contain no polybrominated biphenyls (PBB) or diphenyl ethers (PBDE).

- Computer Hardware: desktop computers and workstations, notebook computers, printers, monitors, and peripherals; awarded June 2005; estimated value of contract $116 million – Specification language: points awarded for meeting environmental requirement that electronics manufacturers should demonstrate that they are complying globally with European Union's Directive – Restriction of Hazardous Substances – which includes the phase out of certain PBDEs by 2006.

- The CIWMB adopted the Electronic Product Environmental Assessment Tool (EPEAT) rating system as environmental purchasing criteria in June 2005, which can be used by State agencies to identify electronic devices with reduced environmental impacts. The CIWMB has requested that the DGS issue a Broadcast Bulletin on the use of EPEAT by State agencies once EPEAT certified products are available.

  EPEAT is an environmental procurement tool that is designed to help institutional purchasers in the public and private sectors evaluate, compare and select desktop computers, laptops and monitors based on their environmental attributes. EPEAT was initiated through a cooperative agreement between the Zero Waste Alliance and US EPA Region 10. To qualify for EPEAT, a product must conform to 22 mandatory criteria, including compliance with provisions of the European Directive for the Restriction on use of certain Hazardous Substances in electronic products (RoHS Directive) that requires less than 1000 ppm PBDE within homogeneous materials.

- The CIWMB is working with DGS on implementing the recently developed environmentally preferable purchasing (EPP) standards for carpet, called "the California Gold EPP Carpet Criteria." The specifications include a requirement that the carpet contain no PBDE.

Office of Environmental Health Hazard Assessment

OEHHA has followed the emerging scientific information on the toxicity of PBDEs, and OEHHA staff have published several reviews and analyses of the available toxicity data in scientific journals. Evaluation of the available toxicity data on the PBDEs, including decaBDE, is ongoing, and an assessment of the health risks from exposures to PBDEs is underway.

State Water Resources Control Board

The SWRCB has reviewed its authority and that of the Regional Boards to regulate PBDEs. Bioaccumulative chemicals that are harmful to aquatic organisms at detected levels can be regulated by the Regions. Chemicals in waters at levels harmful to humans can also be regulated. Further, PBDEs are listed in DHS' draft groundwater recharge regulations with a number of other emerging chemicals because they are endocrine disruptors, found in wastewater treatment plant effluents (i.e., the source of recharge water), and are ubiquitous. The identification of acceptable sampling and analytical protocols for PBDEs would facilitate SWRCB efforts, as well as values for maximal allowable concentrations in drinking water and ground and surface waters.

Department of Health Services

Activities of DHS have included the following:

- Developing over the past two years a proposal to establish a human biomonitoring program in California, with a strong emphasis on PBDEs.
- Along with DTSC staff, preparing and presenting a briefing on PBDEs to the Secretary of Cal/EPA and senior management of the Cal/EPA BDOs.
- Assisting Kaiser's Women's Health Research Institute in developing *Developmental Toxicants and Healthy Childbearing*, a physician's guide that includes information on health effects, exposure sources, and exposure prevention recommendations for PBDEs, and other toxicants. The purpose of the guide is to increase physicians' awareness of developmental toxicants and to assist them in taking relevant histories, and in addressing their patients' concerns.
- Participated in the Technical Working Group on PBDEs convened by DTSC's Hazardous Materials Laboratory.
- Conducted a qualitative assessment of workplace exposures to lead, PBDEs and other toxicants at a computer recycling facility.

Workgroup Recommendations

The Workgroup identified a number of recommendations that should lead to reductions in exposures to PBDEs as well as facilitate compliance with California H&SC Sections 108920 *et seq*. For each of the recommendations identified, estimated timeframes for implementation are provided. In instances where completion of one recommendation is necessary before other recommendations can be implemented, this is noted.

In developing these recommendations, the Workgroup explicitly did not address issues related to the availability of sufficient state resources for implementation.

The Workgroup notes that the majority of these recommendations cannot be acted upon without the provision of additional resources. This is a serious constraint that must be considered and addressed as Cal/EPA evaluates which of these recommendations to implement. It should be noted that some of these recommendations would also require the involvement of DHS as well as the BDOs of Cal/EPA. The main recommendations are given in the table below. More detailed recommendations follow.

Table 2. Main Recommendations to Reduce PBDE Exposures[1]

Outreach and Education

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

Pollution Prevention

- Encourage the purchase of PBDE-free products.

Measurement and Monitoring[2]

- Conduct human biomonitoring to evaluate the effectiveness of the pentaBDE and octaBDE prohibition and other PBDE reduction efforts.

- Conduct environmental monitoring to identify sources, pathways and trends in PBDE levels, and to characterize the environmental fate of decaBDE.

Regulatory Initiatives

- Develop health guidance levels (e.g., reference exposure levels) for PBDEs to aid in establishing acceptable environmental levels.

- Assess the need for further regulation, such as the development of hazardous waste criteria and management and disposal requirements and practices for PBDE contaminated waste, an Airborne Toxic Control Measure, the addition of PBDEs to the Air Toxics “Hot Spots” list, and the need to limit the use of decaBDE.

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

Outreach and Education

1. Educate key governmental officials and the public about the PBDE prohibition and hazards and work with them to encourage compliance with the prohibition and exposure reduction behavior.

   This would involve working with and educating state and local government, industry, public interest groups, and the general public about the PBDE prohibition and environmental concerns about PBDEs. Targeted state officials would include the State Fire Marshal and the Attorney General's Office, as well as staff in General Services and other agencies responsible for developing and implementing policies related to purchasing and recycling. Local officials could include county health officers, environmental health officers and purchasing officials.

   Timeframe: These activities would begin immediately, and would continue as long as there are significant amounts of PBDEs in commerce or in the state's waste streams.
   Departments involved: DTSC, ARB, OEHHA, SWRCB, IWMB, DHS.

   a. Develop practical information on the prohibition of the use in commerce of products containing pentaBDEs and octaBDEs.

      Timeframe: Fact sheets and similar documents would be completed and distributed/available to target audiences within six months. This would include development and distribution of educational materials for businesses, government entities, and the public regarding product purchasing, use and disposal. Written information would be reviewed and updated as needed.
      Departments involved: DTSC, ARB, OEHHA, SWRCB, IWMB, DHS.

   b. Identify at-risk workers and develop a health hazard advisory/alert for workers and employers. Conduct outreach and education for workers and employers.

      Identify and target dissemination of a worker Health Hazard Advisory or Alert on PBDEs to PBDE-exposed workers, including computer recyclers, janitors, foam fabricators, computer technicians, and to their unions and community-based organizations, employers, and health care providers. Develop a Health Hazard Advisory or Alert on PBDEs for workers and employers that provides practical information on health effects, exposure sources, safe substitutes, industrial hygiene controls, the prohibition of the use in commerce of products containing pentaBDEs and octaBDEs, and additional information resources. Publicize the Health Hazard Advisory or Alert by issuing a press release.

Obtain California customer lists from manufacturers, importer, and distributors of PBDE-containing products and increase targeted dissemination of the Alert.

Timeframe: Initiate educational outreach to identified groups within one year, and continue educational outreach as needed.
Department involved: DHS

c. Identify especially at-risk communities and other groups in the general population. Develop health hazard advisories for dissemination to these groups.

High risk groups in the general public are identified through collaboration with community and other public interest groups, and targeted for dissemination of health advisories. Develop a health advisory on PBDEs that provides practical information on health effects, exposure sources, and safe substitutes, the PBDE prohibition, and additional information resources.

Timeframe: Work completed within two years.
Departments involved: OEHHA, DHS

2. Develop building operation and maintenance "best practices" guidelines for PBDEs for residential and business use. Incorporate these into guidelines for the public, schools, businesses, state and local agencies. Ensure that guideline information is reflected in pertinent State indoor air quality programs.

Timeframe: One year timeframe after fact sheets completed under "Outreach and Education," 1.a, and update as needed.
Departments involved: DTSC, ARB, OEHHA, IWMB, Cal/EPA, DHS

a. Develop a set of guidelines designed to reduce PBDE exposures indoors.

Based on information developed by DTSC, it appears that indoor exposure to dust adds appreciably to PBDE body burdens. ARB could develop a set of guidelines designed to reduce PBDE exposures indoors. Conceptually, the guidelines could contain recommendations, including more effective cleaning methods and vacuuming techniques and equipment to reduce exposure to PBDEs that adhere to dust. These "best practices" guidelines could be used as a model for the public, government agencies, businesses, and schools.

Timeframe: Will be completed within 18 months.
Departments involved: ARB, OEHHA, DHS

b. Work with the Collaborative for High Performance Schools (CHPS) to incorporate the new PBDEs "best practices" information developed under 2.a above into the Best Practices Manual for green buildings for schools.

CHPS, which is comprised of several state agencies, public utilities and other organizations, has developed a very comprehensive Best Practices Manual for schools on green buildings. There are multiple volumes to the Manual that include sections on design, purchasing, operations, maintenance and cleaning. The ARB could work with the Collaborative to have the new information on PBDEs incorporated into these guidelines. While the next update is scheduled for 2008, ARB could work to get this information included in the ongoing revisions to the design and construction manual to raise awareness. In addition, the ARB could also include the information in the Relocatable Classrooms volume when developed, and in training, e-bulletins, and other resources that CHPS publishes. (available at www.chps.net, see "publications").

Timeframe: Ongoing, but revisions to Best Practices Manual completed within one year.
Departments involved: ARB, OEHHA, IWMB

c. Work with the Sustainability Manager and the Real Estate Services Division of the Department of General Services (DGS) to incorporate the new PBDEs "best practices" information developed under 2.a above into DGS Management Manuals as a requirement for buildings to achieve the Silver level of certification.

DGS is developing guidelines and policies, called Management Manuals, to facilitate the implementation of Executive Order S-20-04, which calls for buildings to achieve the Silver level of certification, according to the U.S. Green Building Council's green building rating system, "Leadership in Energy and Environmental Design (LEED)." The IWMB could work with DGS's Sustainability Manager and the Real Estate Services Division to have information on PBDEs incorporated into this effort.

Timeframe: Complete within one year after fact sheets are completed under "1.a" above.
Departments involved: OEHHA, IWMB, Cal/EPA

Pollution Prevention Initiatives

1. Encourage institutions, state and local agencies (e.g., in cities and counties) to buy PBDE-free products by posting fact sheets on DTSC's and DGS's Environmentally Preferable Purchasing (EPP) Web sites that provide examples of PBDE-free products and manufacturers, including information on where such products can be purchased.

   DTSC and IWMB could work with DGS to have the fact sheets posted on the state's EPP Web site, which will help assure that state and local procurement officials know about PBDEs.

   The information used in the fact sheets would be derived from products completed under "Outreach and Education," 1.a, above.

   Timeframe: Complete within one year after fact sheets completed under "Outreach and Education," 1.a, and update lists as needed.
   Departments involved: DTSC, ARB, IWMB

2. Evaluate the use of incentives for "PBDE-free" products and product labeling by manufacturers.

   Timeframe: Complete within one year.
   Departments involved: DTSC

3. Offer "Environmental Leadership" awards for phase-out of PBDEs.

   Timeframe: Offer first set of awards within one year.
   Departments involved: DTSC, Cal/EPA

4. Compile a list of safer alternatives that have been identified by other entities (e.g., Consumer Affairs, U.S. EPA Region IX, IWMB Household Hazardous Waste (HHW) safer alternatives brochure and website).

   The list of alternatives could be promoted through the activities identified for recommendations under "Outreach and Education" and "Pollution Prevention Initiatives."

   Timeframe: Complete within one year, and update as needed.
   Departments involved: DTSC, ARB, OEHHA

5. Work with Department of General Services (DGS) and Prison Industry Authority (PIA) to encourage the purchase of PBDE-free products by all state agencies.

DTSC and IWMB could work with DGS to have information on PBDE-free products included on DGS's Environmentally Preferable Purchasing (EPP) Web site, which is part of the "Green CA" Web site, and in product catalogs used by purchasing agents. DTSC and IWMB could also work with PIA to encourage the latter organization to purchase PBDE-free products, since state agencies are required to purchase furniture and other office supplies made by the PIA.

Timeframe: Continue ongoing effort after fact sheets completed under "Outreach and Education," 1.a.
Departments involved: DTSC, IWMB

Measurement and Monitoring

1. Initiate and implement an environmental measurement program to assess the effectiveness of PBDE pollution prevention measures, remediation activities, and regulations.

   a. Convene an Inter-Agency PBDE Exposure Workgroup to facilitate implementation and coordination of the environmental measurement and monitoring conducted by Cal/EPA. This group would assist in the identification of sources and pathways of exposures, identify data gaps, and provide guidance and input to other exposure assessment activities of Cal/EPA BDOs and DHS.

      Timeframe: Initiate within three months, and continue as long as PBDE concentrations pose an environmental health threat.
      Departments involved: DTSC, ARB, OEHHA, SWRCB, IWMB, DHS

   b. Develop guidance on acceptable sampling methods and testing protocols for identifying PBDEs in environmental matrices.

      In the short term, DTSC will provide guidance on acceptable sampling methods and testing protocols for identifying PBDEs in environmental matrices of concern to the SWRCB. The SWRCB has requested this guidance in order to implement the Cal/EPA PBDE Workgroup recommendations on monitoring and measurement in environmental matrices.

      Identification by ARB and DTSC of acceptable sampling and analytical protocols for PBDEs in matrices of interest to Cal/EPA BDOs (e.g., air, ambient water, sludge, sediment, treatment plant influent, effluent). ARB and DTSC will help to ensure that the PBDE measurement and monitoring data are collected and analyzed appropriately. This guidance on PBDE sampling and analytical protocols will assist BDOs in evaluating the reliability and comparability of current and future California PBDE measurement and monitoring data.

The Environmental Laboratory Accreditation Program (ELAP) within DHS can use this guidance to develop a procedure to certify laboratories as competent in PBDE analyses. SWRCB and regional water boards require such certification of laboratories for PBDE analyses before they institute monitoring requirements for PBDEs. However, there currently are no certification programs in the U.S. for PBDEs. Therefore, the workgroup may have to develop certification criteria in conjunction with the State and Regional Water Boards, and ELAP.

Timeframe: Complete within six months to one year.
Departments involved: DTSC, ARB, SWRCB

c. Identify sources and pathways of PBDE exposure , including the importance of decaBDE.

The Inter-Agency PBDE Exposure Workgroup would assess existing information on the extent of environmental PBDE contamination in California, identify data needs, prioritize data collection, and recommend additional sampling in a pilot project, to be implemented by Cal/EPA BDOs and DHS. The pilot project would address data gaps with measurements and monitoring of PBDEs, and would include investigation into the role decaBDE plays as a source of lower brominated PBDEs present in environmental matrices. This would be used by the Inter-Agency PBDE Exposure Workgroup to characterize sources and pathways of exposure. Workplace exposures to PBDEs in targeted industries/workplaces could be investigated using the DHS's right-of-entry mandate (H&SC 105175).

Timeframe: Complete within one to three years.
Departments involved: DTSC, ARB, OEHHA, SWRCB, DHS

d. Characterize temporal and spatial in-situ PBDE levels, including decaBDE.

A monitoring program would be implemented to track in-situ levels of PBDEs, including decaBDE and its breakdown products, to assess the effectiveness of PBDE exposure mitigation measures. For example, the ARB could seek funding to conduct additional outdoor and indoor air monitoring to better characterize temporal and spatial trends in PBDE concentrations throughout the state and in different indoor settings. This monitoring could include collecting additional PBDE data from ARB's network of air toxics monitoring sites, additional near-source monitoring adjacent to probable sources of PBDEs, and additional indoor air monitoring in public buildings, schools, and homes. DTSC could seek funding to systematically characterize trends in waste streams (e.g., autoshredder, ewaste). DTSC could seek funding to expand its studies of PBDEs in human milk, adipose tissue, serum and wildlife.

Timeframe: Complete within one to three years.
Departments involved: DTSC, ARB, OEHHA, SWRCB

e. Archive environmental and biological samples to evaluate temporal trends, hotspots, and new chemicals.

Timeframe: Initiate within one year, and continue thereafter.
Departments involved: DTSC, ARB, SWRCB

f. Examine potential environmental and public health risks of alternatives and substitutes, based on biological and environmental monitoring data.

In examining alternatives and substitutes for PBDE flame retardants, consider information on toxicity, persistence, bioaccumulation, and potential for environmental release. Alternative flame retardants may already be in use. Consider the utility of conducting pilot biomonitoring and environmental monitoring studies to evaluate the presence and persistence of these alternatives in the environment.

Timeframe: Initiate within one year, and continue thereafter.
Departments involved: DTSC, ARB, OEHHA

2. Provide for a systematic, representative human biomonitoring of PBDEs in California, which would provide for systematic collection and chemical analysis of human biological samples to assess exposure trends and the effectiveness of the exposure reductions. This may also eventually aid in evaluating whether such exposures are associated with specific chronic diseases and, where appropriate, to inform public policy intended to prevent such diseases.

The value of biomonitoring has been demonstrated in other parts of the world, as well as in the United States. For example, biomonitoring programs in Europe found decreasing levels of dioxins, probably reflecting implementation of pollution prevention measures and emission controls.

Timeframe: Initiate within one to three years, and continue and expand thereafter.
Departments involved: DTSC, OEHHA, DHS

3. Encourage the University of California Toxic Substances Research and Teaching Program (UC TSR&TP) to emphasize research on the fate and transport of PBDEs, especially decaBDE.

   The UC TSR&TP is a University of California Multicampus Research Unit supporting research on toxic substances in the environment and teaching graduate students through funding of grants, fellowships, and lead campus programs.

   Timeframe: Initiate within one year, and continue as needed.
   Departments involved: DTSC

Regulatory Initiatives

1. Develop health values (e.g., chronic Reference Exposure Levels (cRELs)) for PBDEs.

   Completion of this recommendation is necessary before implementation of recommendations 2 and 3 can occur.

   Timeframe: Will be completed by summer 2007.
   Departments involved: OEHHA

2. Determine if there is a need to establish (1) hazardous waste criteria, and (2) management and disposal requirements and practices for PBDE-contaminated waste.

   Timeframe: Complete within three years.
   Departments involved: DTSC

3. Conduct a Needs Assessment to determine the appropriateness of developing an Airborne Toxic Control Measure (ATCM) for PBDEs, which, as polycyclic organic matter (POM), are already identified as Toxic Air Contaminants (TACs).

   Under H&SC Sections 39666 *et seq*., ARB could evaluate sources of PBDE emissions that could be controlled through development of ATCMs. In this case, ARB would prioritize sources, based on exposure and health risk characterization, and develop appropriate ATCMs to reduce exposure to PBDEs. However, before ATCMs could be developed, health values are needed to characterize health risk and allow ARB to determine the need for controls. OEHHA would develop health values.

   Timeframe: Complete within three to four years.
   Departments involved: ARB

4. Consider adding PBDEs to the Air Toxics “Hot Spots” list of chemicals.

   The Air Toxics “Hot Spots” regulation (H&SC Sections 44300 *et seq*.) applies to stationary sources and requires self-reporting. ARB could conduct a rulemaking to add PBDEs to the Hot Spots list of chemicals. Upon implementation, this may require facilities to report use and/or emissions of PBDEs.

   Timeframe: Proposed rulemaking in 2006.
   Departments involved: ARB

5. Examine evidence of toxicity and environmental fate of PBDEs, especially deca-BDE; evaluate the need for regulation or legislation.

   DHS could consider recommending an occupational health standard for the deca congener to Cal/OSHA, if warranted.

   Timeframe: Complete within one to three years.
   Departments involved: DTSC, ARB, OEHHA, DHS

6. Survey aquatic toxicity data and determine research needs for considerations of development of water quality standards.

   A critical prerequisite for implementation of this recommendation is for Cal/EPA to identify acceptable sampling and analytical protocols for PBDEs in matrices of interest (e.g., ambient water, sludge, sediment, treatment plant influent, effluent). Identification of critical pathways and waste streams contributing to PBDE contamination is also a prerequisite. Adequate funding and staff resources and Agency support would also be necessary before embarking on development of a regulatory program.

   Set up a contract with the Southern California Coastal Water Research Project (SCCWRP) to survey existing aquatic toxicity literature for PBDEs, identify data useful for developing standards, and recommend projects aimed at filling data gaps.

   Timeframe: Complete within one to three years.
   Departments involved: DTSC, SWRCB

Summary of Recommended Cal/EPA Actions

Actions	Departments					
	DTSC	ARB	OEHHA	SWRCB	IWMB	DHS
Outreach and Education 1. Educate key governmental officials and the public about the PBDE prohibition and hazards and work with them to encourage compliance with the prohibition and exposure reduction behavior. (*continuing timeframe*)	X	X	X	X	Lead	X
a. Develop practical information on the prohibition (*6 month timeframe, update as needed*)	X	X	X	X	Lead	X
b. Identify at-risk workers, develop a health hazard advisory/alert, and conduct outreach and education for workers and employers (*1 yr timeframe, with continuing outreach*)						Lead
c. Identify especially at-risk groups in the general population. Develop health hazard advisories for dissemination to these groups. (*2 yr timeframe*)			Lead			X
2. Develop building operation and maintenance "best practices " guidelines for PBDEs. *(1 yr timeframe after fact sheets completed under "Outreach and Education," 1.a, and update as needed.)*	X	Lead	X		X	X
a. Develop guidelines to reduce PBDE exposures indoors, incorporating this guidance into "Best Management Practices" guidelines for operating and maintaining buildings. *(Will be completed within 18 months.)*		Lead	X			X
b. Work with the Collaborative for High Performance Schools to have the information on PBDEs incorporated into the Best Practices Manual (BPM) for green buildings for schools *(Ongoing, but revisions to BPM within one year.)*		Lead	X		X	

Summary of Recommended Cal/EPA Actions (continued)

Actions	**Departments**					
	DTSC	**ARB**	**OEHHA**	**SWRCB**	**IWMB**	**DHS**
Outreach and Education (continued)						
2c. Work with DGS to incorporate new best practices information on PBDEs into DGS Building Manuals as a requirement to receive Silver level certification. (*Completed after one year of completion of fact sheets – per 1.a above)* (Agency level involvement needed)			X		Lead	
Pollution Prevention Initiatives						
1. Encourage institutions, state and local agencies (e.g., in cities and counties) to buy PBDE-free products by posting fact sheets on DTSC and DGS Environmentally Preferable Purchasing Web sites (*1 yr timeframe after fact sheets completed under "Outreach and Education," 1.a, and update lists as needed*)	Co-Lead	X			Co-Lead	
2. Evaluate the use of incentives for "PBDE-free" products and product labeling by manufacturers (*1 yr timeframe*)	Lead					
3. Offer "Environmental Leadership" awards for phase-out of PBDEs (Lead: Cal/EPA) *(1 yr timeframe)*	X					
4. Compile list of safer alternatives that have been identified by other entities (*1 yr timeframe, update as needed*)	X	X	Lead			
5. Work with Department of General Services and Prison Industry Authority to encourage purchase of PBDE-free products by all state agencies *(Continue ongoing effort after fact sheets completed under "Outreach and Education," 1.a, and update lists as needed.)*	Co-Lead				Co-Lead	

Summary of Recommended Cal/EPA Actions (continued)

Actions	Departments					
	DTSC	ARB	OEHHA	SWRCB	IWMB	DHS
Measurement and Monitoring 1. Initiate and implement an environmental measurement program to assess effectiveness of PBDE pollution prevention measures, remediation activities, and regulations. (*continuing timeframe*)	Lead	X	X	X		X
a. Convene an Inter-Agency Exposure Workgroup to facilitate Cal/EPA environmental monitoring and measurement *(initiate within 3 months)*	X	X	Lead	X	X	X
b. Develop guidance on acceptable sampling methods and testing protocols for identifying PBDEs in environmental matrices. *(six to 12 month timeframe)*	Lead	X		X		
c. Identify sources and pathways of exposure, including the importance of decaBDE *(1-3 yr timeframe)*	Lead	X	X	X		X
d. Characterize temporal and spatial in-situ PBDE levels, including decaBDE *(1-3 yr timeframe)*	Lead	X	X	X		
e. Archive environmental & biological samples to evaluate temporal trends, hotspots & new chemicals *(1 yr timeframe to initiate)*	Lead	X		X		
f. Examine potential environmental and public health risks of alternatives and substitutes, based on biological and environmental monitoring data *(1 yr timeframe to initiate, continuing as needed)*	X	X	Lead			
2. Provide for a systematic, representative human biomonitoring program of PBDEs in California. *(1-3 yr timeframe)*	X		Lead			X
3. Encourage the University of California Toxic Substances Research and Teaching Program (UC TSR&TP) to emphasize research on PBDE fate and transport, especially decaBDE. *(initiate within 1 yr)*	Lead					

Actions	Departments					
	DTSC	ARB	OEHHA	SWRCB	IWMB	DHS
Regulatory Initiatives 1. Develop health values (e.g., cRELs) for PBDEs *(Summer 2007)*			Lead			
2. Determine if there is a need to establish (1) hazardous waste criteria, and (2) management and disposal requirements and practices for PBDE-contaminated waste *(3 yr timeframe)*	Lead					
3. Conduct a Needs Assessment to determine the appropriateness of developing an ATCM for PBDEs, which, as POMs, are identified as Toxic Air Contaminants *(3-4 yr timeframe)*		Lead				
4. Consider adding PBDEs to the Air Toxics "Hot Spots" list of chemicals *(2006)*		Lead				
5. Examine evidence of toxicity and environmental fate of PBDEs, especially deca-BDE; evaluate the need for regulation or legislation *(1-3 yr timeframe)*	X	Co-Lead	Co-Lead			X
6. Survey aquatic toxicity data and determine research needs for consideration of development of water quality standards *(1-3 yr timeframe)*	X			Lead		

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Appendix I:

Summary of ARB PBDE Monitoring Data

During 2004, ARB measured PBDEs in ambient air, near two recycling facilities (“near-source”), and indoors. The results of these monitoring efforts are summarized below.

Ambient

ARB operates a network of air toxics monitoring sites in urban areas within California. During 2004, ARB conducted monitoring for PBDEs at six of these sites (Los Angeles, Oakland, Richmond, Riverside, San Jose, and Wilmington). At each site, integrated monthly samples for three PBDE congeners were collected. The samplers operated for five days followed by two days with the sampler shut off, for four weeks. The samples were analyzed by a contract laboratory. Below is a summary of the 2004 data from the six monitoring sites.

Congener	**Range** (pg/m^3)	**Average** (pg/m^3)
PBDE 47 (tetra)	7-170	53
PBDE 99 (penta)	3-332	52
PBDE 209 (deca)	7-72	23

For comparison, outdoor concentrations of various PBDE congeners have been found to range from 5 – 300 pg/m^3 in different parts of the world.

Near-source

Due to the growing concerns about PBDEs, ARB contracted with a group at the University of California, Davis to conduct near-source and indoor air monitoring. Near-source air monitoring was conducted at two facilities: an electronics recycling facility and an automobile shredding facility.

Several electronics recycling facilities were evaluated as possible locations for near-source air monitoring. At least one facility had installed air pollution control equipment. An electronics recycling facility without air pollution control equipment was selected for monitoring. Recycling activity consisted of shredding old electronics for metal recovery and compacting of old plastic cases. Air samples of eight-hours in duration were collected on three days during operating hours. Indoor air samples were collected near the shredding and compacting equipment. Near-source air samples were collected upwind and downwind of the facility at a distance of 15-20 meters. Indoor concentrations ranged from 15 – 830,000 pg/m^3, mostly decaBDE. Outdoor concentrations ranged from 1 – 11,000 pg/m^3, also mostly decaBDE. For comparison, other researchers have measured up to 200,000 pg/m^3 inside a Canadian electronics recycling facility.

Near-source monitoring was also conducted upwind and downwind of an automobile shredding facility. This entire operation is outdoors. Shredded metal and shredded plastics and foam (referred to as auto shredder fluff) is piled on-site following shredding, prior to removal from the facility for uses as recycled materials. Air samples of 24-hours in duration were collected on three days at the facility's fenceline (the facility operated 24 hours per day). Samples were collected at a distances of 150 – 300 meters from the shredder and piles of shredded materials. Fenceline air concentrations ranged from 0.2 – 1,900 pg/m^3, mostly decaBDE. The scientific literature does not contain any similar studies on autoshredder operations for comparison.

Indoor

Finally, indoor air samples were collected inside a computer training room that contained 13 older model personal computers (i.e., manufactured before 2000). Air samples of 24 hours in duration were collected on six days with the computers on and two days with the computers off. Concentrations ranged from 4 – 1,600 pg/m^3, mostly tetraBDEs. For comparison, other researchers have measured indoor air concentrations of PBDEs up to 1,800 pg/m^3.

The carpet within the computer training room was vacuumed for analysis of carpet dust. The carpet dust contained 10 ppm total PBDEs (mostly in the form of decaBDE), which is consistent with findings of other researchers regarding dust samples. A new piece of the same type of carpet was analyzed and found to contain 0.1 ppm of decaBDE.

Appendix II:

The NTP Cancer Bioassay for DecaBDE and Workgroup Cancer Potency Derivation

The National Toxicology Program (NTP, 1986) tested decaBDE for carcinogenicity in rats and mice of both sexes by administering the compound in the diet for two years. Absorption from the gastrointestinal tract in these studies was minimal (i.e., <1 to 2%). Male rats received average daily doses of 1,120 or 2,240 mg/kg body weight, female rats received average daily doses of 1,200 or 2,550 mg/kg body weight. The average daily doses for male mice were 3,200 or 6,650 mg/kg body weight, and for female mice were 3,760 or 7,780 mg/kg body weight. In rats, dose-dependent increases in liver neoplastic nodules (hepatocellular adenomas) were observed in males [1/50, 7/50 (p=0.003), and 15/49 (p<0.001), test for trend p <0.001] and females [1/50, 3/49, and 9/50 (p = 0.008), trend test p=0.002]. Based on these findings, NTP (1986) concluded that there was "some evidence" of carcinogenicity in male and female rats. In male mice, a statistically significant dose-dependent increase in hepatocellular adenomas and carcinomas (combined) was observed [8/50, 22/50 (p=0.002), 18/50 (p=0.02), trend test p=0.02, for control, low- and high-dose, respectively]. The incidence of hepatocellular tumors was not increased above historical controls, however. Increases in thyroid gland follicular cell adenomas or carcinomas (combined) were observed in male [0/50, 4/50, and 3/50; trend test p=0.08] and female mice [0/50, 3/50, 3/50, trend test p = 0.06], but did not reach statistical significance at the p = 0.05 level. Based on these findings, NTP (1986) concluded that there was "equivocal evidence" of carcinogenicity in male mice and "no evidence" in female mice.

The dose response data from the NTP studies in male and female rats can be used to derive upper bound estimates of human cancer potency. For regulatory purposes, the lifetime probability of dying with a tumor (p) induced by an average daily dose (d) is often assumed to be:

$$p(d) = 1 - \exp[-(q_0 + q_1 d + q_2 d^2 + \cdots + q_j d^j)]$$

with constraints,

$$q_i \geq 0 \text{ for all i.}$$

The q_i are parameters of the model, which are taken to be constants and are estimated from the data. The parameter q_0 represents the background lifetime incidence of the tumor. The parameter q_1, or some upper bound, is often called the cancer potency, since for small doses it is the ratio of excess lifetime cancer risk to the average daily dose received. Here cancer potency will be defined as q_1^*, the upper 95% confidence bound on q_1, estimated by maximum likelihood techniques. When dose is expressed in units of mg/kg-day, the parameters q_1 and q_1^* are given in units of $(\text{mg/kg-day})^{-1}$.

In the NTP studies which form the basis for the estimation of the cancer potency, the decaBDE was administered in feed, and NTP estimated the doses in units of mg/kg-day. These dose estimates are used in the potency derivation here.

Once a potency value is estimated in animals, human potency is estimated. In the absence of detailed pharmacokinetic or other data indicating otherwise, a dose in units of milligram per unit surface area is often assumed to produce the same degree of effect in different species. Under this assumption, scaling to the estimated human potency (q_{human}) can be achieved by multiplying the animal potency (q_{animal}) by the ratio of human to animal body weights (bw_h/bw_a) raised to the one-third power when animal potency is expressed in units $(mg/kg\text{-}day)^{-1}$:

$$q_{human} = q_{animal} \bullet (bw_h / bw_a)^{1/3}$$

From the male rat bioassay data, an upper bound estimate of cancer potency is 0.000200 $(mg/kg\text{-}day)^{-1}$. Assuming a bodyweight of 450 grams for test animals (see NTP, 1986, p. 33), and 70 kg for humans, the interspecies scaling factor is 5.39. The resulting upper bound estimate for human cancer potency is 0.00108 $(mg/kg\text{-}day)^{-1}$. For the female rat, the upper bound potency estimate is 9.55×10^{-5}, corresponding to an upper bound human cancer potency estimate of 5.9×10^{-4} (mg/kg-day)-1 (assuming a body weight of 300 grams for female rats [NTP, 1986, p. 34] and an interspecies factor of 6.16).

Appendix III:

Publications and Presentations by DTSC, OEHHA, and ARB: PBDE Environmental Levels, Exposures and Risks

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