Polybrominated Diphenyl Ether (PBDE) Flame Retardants

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Executive Summary

Safety concerns have been raised over the widespread use and disposal of polybrominated diphenyl ether (PBDE) flame retardants in consumer products. Commercial PBDE products are supplied as three types of mixtures: pentaBDE, octaBDE and decaBDE. PentaBDE and octaBDE were phased-out of production in North America and Europe because of concerns regarding their persistence, ability to bioaccumulate, and toxicity. DecaBDE remains in worldwide commercial use as a flame retardant. At the request of the state legislature, Oregon's Department of Human Services (DHS), Office of Environmental Public Health (OEPH) reviewed new scientific findings regarding the use and disposal of PBDE flame retardants in consumer products.

Current science suggests that decaBDE is a persistent environmental contaminant with a low to moderate ability to bioaccumulate in people and wildlife. While recent risk assessments indicate that decaBDE does not pose an immediate health hazard, there remain unresolved uncertainties regarding future trends in exposures and the adequacy of safety benchmarks.

New research suggests that decaBDE may be an endocrine disruptor and developmental neurotoxicant. The U.S. Environmental Protection Agency is currently in the process of updating the toxicological assessment for decaBDE, and results should be released during 2008. OEPH recommends that Oregon continue to review any new research and federal developments regarding children's environmental health and decaBDE.

Data were inadequate to assess the risks from the disposal of consumer products containing pentaBDE and octaBDE, but environmental releases of pentaBDE and octaBDE can occur at recycling facilities, landfills and solid waste incineration plants.

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I. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of chemicals used as flame retardants in some plastics, fabrics and foams. A variety of consumer products may contain PBDEs including computers, televisions, coated wires, upholstered furniture, mattresses, carpet padding and automobiles. Flame retardants are added to consumer products to reduce the likelihood that these materials will catch fire and to slow the rate that these materials burn. In the event of a fire, flame retardants can provide people extra time to escape a dangerous situation.

Commercial PBDE products are supplied as three types of mixtures (pentaBDE, octaBDE and decaBDE), each containing a different number of bromine atoms per PBDE molecule (i.e., on average pentabrominated products contain 5 bromines, octabrominated products contain 8 bromines and decabrominated products contain 10 bromines). By 2004, pentaBDE and octaBDE were phased-out of production in North America and Europe because of concerns regarding the chemicals persistence, ability to bioaccumulate, and toxicity (EPA 2006). DecaBDE remains in worldwide commercial use as a flame retardant.

In the interest of protecting public health, the Oregon Department of Human Services (DHS) is required by law (Or. Rev. Stat. § 453.095 (2005)) to biannually (a) summarize relevant new studies and federal regulations regarding the use of decaBDE and (b) make recommendations regarding disposal restrictions for products containing pentaBDE and octaBDE. This legislative authority will be repealed on December 31, 2008.

A variety of documents were reviewed in preparation for this report including: new peer-reviewed scientific literature on decaBDE; peer-reviewed scientific literature on risks from the disposal of pentaBDE and octaBDE products; current health effects criteria from the US EPA’s (Environmental Protection Agency) IRIS (Integrated Risk Information System) database; the toxicological profile for PBDEs published by the Agency for Toxic Substances and Disease Registry (ATSDR 2004); and the National Academy of Sciences report titled “Toxicological Risks of Selected Flame-Retardant Chemicals” (NRC 2000).

Except for reviewing the NRC (2000) report, which identified decaBDE as one of the safest chemical alternatives among 16 flame retardants evaluated, no attempt was made to compile current information on alternatives to decaBDE use. DHS is aware that flame retardant technology is evolving rapidly and safer alternatives to decaBDE may exist for some applications (Lowell Center for Sustainable

Production 2005). While DHS recognizes the importance of evaluating safer alternatives to potentially persistent, bioaccumulative and toxic chemicals, such an approach requires unique resources, interagency collaborations and cross-sector cooperative efforts that were unavailable at the present time. For example, industry expertise is often necessary to identify and gather safety information on new effective alternatives.

This report is organized around the express requirements of the Oregon Revised Statutes. It is hoped that this report provides an objective science-based framework to guide future research needs and legislative decisions.

II. Decabrominated biphenyl ether

DecaBDE (CAS # 1163-19-5) is a large chemical (molecular weight 959) that exists as a white to off-white powder (Figure 1). DecaBDE has a low water solubility (< 0.1 µg/L at 25^{o}C) and low volatility (vapor pressure = 4.63 x 10^{-6} Pa at 21^{o}C) (NRC 2000).

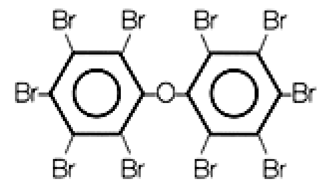

Figure 1. Chemical structure of decabromodiphenyl ether.

DecaBDE is one of the most widely used brominated flame retardants in consumer products. The 1999 market demand for decaBDE in North America was 24,300 metric tons, equivalent to 44.3% worldwide use (de Wit 2002). Since then, market demand for decaBDE may have increased because production of pentaBDE and octaBDE has been discontinued. Current commercial decaBDE products are of high purity (97-98%), but may contain some nonabromodiphenyl ethers and octabromodiphenyl ethers as impurities (de Wit 2002).

A. Relevant new scientific research

Persistence. Persistent chemicals remain in the environment for a long-time after being released to air, land or water and may build up in the environment to levels that are potentially toxic to people and wildlife. Persistence can be measured by standardized tests that determine the half-life of a chemical or the amount of time it takes for 50% of the chemical to disappear from aquatic or terrestrial environments. Chemicals are considered persistent if their half-lives exceed 2 months in water or 6 months in aquatic sediments and terrestrial soils (Lerche et al. 2002).

DecaBDE is a persistent chemical contaminant. While standardized data on decaBDE are not available at the present time, other lines of evidence strongly indicate that this chemical will persist in the environment:

- DecaBDE was designed to be persistent so that consumer products will have long-lasting flame retardant protection without the need for chemical reapplication (BSEF 2007).
- When released to air, persistent chemicals are often capable of long-range transport on a global scale. New research has documented the presence of decaBDE in arctic environments with no known local sources of pollution (Verreault et al. 2005, Su et al. 2007).
- DecaBDE may be resistant or slow to degrade by some of the more typical environmental pathways by which chemicals breakdown including hydrolysis (Boethling and Mackay 2000), photolysis (Raff and Hites 2007) and metabolism by microorganisms (Gerecke et al. 2005).

Because decaBDE is persistent and has a low volatility and water solubility, decaBDE will bind strongly to particles that ultimately end up in depositional environments such as terrestrial soils and aquatic sediments (Hale et al. 2006). Studies have detected the presence of decaBDE in household dust (Stapleton et al. 2005) and biosolids from sewage sludge (Hale et al. 2001).

There is a lack of information on the environmental fate and degradation of decaBDE. Of concern is the possibility that the breakdown of decaBDE may result in the formation of more bioaccumulative and toxic pentaBDE and octaBDE products by the process of debromination (i.e., loss of bromine atoms from the parent compound). There is evidence indicating that degradation of decaBDE by photolysis (Söderström et al. 2004) and anaerobic microorganisms (Gerecke et al. 2005) in the laboratory can lead to the formation of octaBDE. The extent to which this may occur in the environment is unknown.

Bioaccumulation. Bioaccumulation is a measure of the potential for a chemical to accumulate in living organisms relative to its concentration in the surrounding environment. Chemicals that bioaccumulate are typically those that partition preferentially into fat versus water. Highly fat-soluble chemicals can move easily across cell membranes, which are also composed of fat, and enter our bodies. Additionally, fat has a low turnover rate in our bodies compared to water. Hence, fat-soluble chemicals are not excreted quickly and can build up in tissues to levels that are potentially toxic to people and wildlife.

One measure of a chemical’s fat solubility is the octanol/water partition coefficient (Kow). Octanol is liquid that dissolves fats. Chemicals with high Kow’s (log Kow > 5) partition preferentially in octanol versus water in experimental tests, and often have a tendency to bioaccumulate in people and wildlife (Lerche et al. 2002).

DecaBDE is a highly fat soluble chemical with a log Kow of 6.26 (NRC 2000), but current research indicates that decaBDE may only have a low to moderate ability to bioaccumulate in people (Thuresson et al. 2006) and wildlife (Verreault et al. 2005, Burreau et al. 2006). One explanation for this phenomenon is that the decaBDE molecule is too large to move readily across cell membranes by passive diffusion (Mörck et al. 2003). This phenomenon has also been suggested to occur with some highly chlorinated PCBs (polychlorinated biphenyls) (Fisk et al. 1998).

In rats, the low bioaccumulation potential of decaBDE is due to its low absorption from the gut (approximately < 1 to 26 %) and rapid excretion in feces (NRC 2000, Mörck et al. 2003, Sandholm et al. 2003, Huwe and Smith 2007). In people, the estimated half-life of decaBDE is 15 days, whereas half-lives for lower brominated BDEs are much higher (e.g., half-life for octaBDE is 37-91 days) (Thuresson et al. 2006).

Despite its low to moderate ability to bioaccumulate, decaBDE has been widely detected in biomonitoring studies of people and wildlife. Biological samples where decaBDE has been detected include those from fish (Burreau et al. 2006), birds (Elliott et al. 2005, Gauthier et al. 2007), polar bears (Verreault et al. 2005), dairy cows (Kierkegaard et al. 2007), cats (Dye et al. 2007) and human blood and breast milk (Schecter et al. 2005). These data may indicate that people and wildlife are being continuously or frequently exposed to decaBDE in the environment (Thuresson et al. 2006).

Human exposures to decaBDE may be high in certain occupational settings such as electronics and automobile recycling facilities (Cahill et al. 2007). For non-occupational exposures, the primary exposure pathways are thought to be the diet (fish, meats and dairy products) for adults, breast milk for infants and household dust for toddlers (Schecter et al. 2004, Wilford et al. 2005).

There is a lack of information on whether or not decaBDE concentrations are increasing in people and wildlife. Of concern is the possibility that the currently low concentrations of decaBDE in people and wildlife may eventually increase to toxic levels if the use of decaBDE continues or accelerates. Unfortunately, decaBDE has been inadequately measured in many of the biomonitoring studies that have detected increasing trends in overall PBDE concentrations, (i.e., decaBDE was either not measured in these studies, or if measured, the limits of detection were too insensitive to detect trends) (Hites 2004).

Toxicity. Screening for "highly toxic" chemicals is typically done by comparing the results from short-term, acute toxicity tests with experimental animals such as rats or fish to established criteria. DecaBDE is not a "highly toxic" chemical according to current acute toxicity criteria (Table 1).

Table 1. Acute toxicity of two commercial decabrominated diphenyl ethers produced by North American manufacturers (Chemtura 2005, Albemarle 2007a). Data are doses or concentrations lethal to 50% of experimental animals (LD50 or LC50).

Product	Animal	Exposure Route	LD50 or LC50	Criteria for "Highly Toxic" Chemicals[2]
DE-83R	Rats	Oral	> 5000 mg/kg	< 50 mg/kg
		Inhalation	> 50 mg/L	< 2 mg/L
	Rabbits	Dermal	> 2000 mg/kg	< 200 mg/kg
SAYTEX 102E	Rats	Oral	> 2000 mg/kg	< 50 mg/kg
		Inhalation	ND[1]	< 2 mg/L
	Rabbits	Dermal	ND[1]	< 200 mg/kg

[1] ND = no data
[2] Definition of "highly toxic" hazardous substances from Or. Rev. Stat. § 453.005 (2005)

Chronic toxicity tests have identified the liver and thyroid gland as important targets for the harmful effects of decaBDE during long-term exposures (NRC 2000). The current EPA IRIS health effects benchmark (oral RfD) that is expected to be reasonably safe for chronic exposures is 0.01 milligrams per kilogram of body weight per day (EPA 1995). No benchmarks have been established for inhalation exposures (RfC). DecaBDE is presently classified as a "possible human carcinogen."

New scientific research suggests that decaBDE can interfere with the nervous system and endocrine system of experimental animals and cause developmental toxicity (reviewed by Costa and Giordano 2007). While the exact mechanisms are unknown, Viberg et al. (2007) proposed that decaBDE disrupts neurons during the peak period of rapid brain growth in neonates. Also, decaBDE is similar in structure to thyroid hormones and may interfere with thyroid hormone transport proteins (transthyretin) or metabolic enzymes (UDP glucuronosyltransferase) (Costa and Giordano 2007, Rice et al. 2007). The thyroid gland is an important endocrine system that regulates development in vertebrates. Developmental toxicity is of concern because it may ultimately lead to persistent or possibly irreversible effects on such endpoints as behavior, learning and memory.

Restrictions on the use of chemicals are usually driven by data indicating that populations are exposed to or are likely to be exposed to toxic concentrations that exceed health effects benchmarks such as the reference dose established by the EPA. Recent risk assessments do not indicate that this is the case for decaBDE (NRC 2000, Wenning 2002, Hays et al. 2003). However, it is questionable whether the current reference dose is adequately protective of effects such as endocrine disruption and developmental toxicity in sensitive populations like children. Ongoing scientific research is attempting to address this important data gap in light of significant challenges posed by the lack of sensitive standardized toxicity tests for health effects research on endocrine disrupting chemicals (Brown 2003).

B. Recent regulatory initiatives

US Environmental Protection Agency (EPA). In 2006, the EPA promulgated a significant new use rule (SNUR) for PBDEs under the Toxic Substances Control Act (TSCA) that requires companies to notify the EPA prior to any new manufacturing or importing activities for many PBDEs including tetraBDE, pentaBDE, hexaBDE, heptaBDE, octaBDE and nonaBDE, but excluding decaBDE (71 FR 34015) (EPA 2006). The EPA is currently reviewing new toxicological information on decaBDE, and plans on updating the reference dose assessment in the IRIS database (EPA 2007). The EPA is also working with industry sponsors through VCCEP (Voluntary Children's Chemical Evaluation Program) to investigate the environmental fate and degradation of decaBDE in outdoor and indoor environments (EPA 2007).

European Union (EU). In 2003, the EU established a large collaborative project among academia and government research facilities called FIRE (*F*lame *R*etardants *I*ntegrated *R*isk Assessment for *E*ndocrine Effects) (Lorenz 2003, EPA 2007). The EU is currently in the process of updating a 2002 risk assessment and 2004 risk assessment addendum with new data from the FIRE project regarding decaBDE. DecaBDE products are currently exempt from the EU's 2002 RoHS directive (2002/95/EC) (*R*estriction of the Use of Certain *H*azardous *S*ubstances in Electrical and Electronic Equipment). Some decaBDE products may contain significant amounts of nonabrominated diphenyl ether impurities to qualify for RoHS restrictions (Albemarle 2007b).

III. Disposal of products containing pentabrominated and octabrominated diphenyl ethers

By 2004, pentaBDE and octaBDE were phased-out of production in North America and Europe because of concerns regarding the chemicals persistence, ability to bioaccumulate, and toxicity (EPA 2006). However, releases of pentaBDE and octaBDE to the environment still occur during the disposal of older consumer products that end up in recycling facilities, landfills and solid waste incineration plants.

Recycling facilities. PBDEs are released to the air from electronics recycling facilities and automotive shredding and metal recycling facilities (Cahill et al. 2007). Indoor air had higher levels of PBDEs than outdoor air, and the majority of PBDEs were associated with particulates. Cahill et al. (2007) suggest that relatively simple dust suppression measures could protect workers and reduce local air emissions from recycling facilities.

Landfills. PBDEs are released to water from raw landfill leachate (Osako et al 2004, Kim et al 2006). PBDEs were not detected in treated leachate, which suggests that leachate treatment processes have high removal efficiencies.

Incineration plants. PBDEs are released to the air during the incineration of municipal and industrial solid waste (Agrell et al. 2004, ter Schure et al. 2004). During incineration, PBDEs may act as precursor molecules for the formation of highly toxic PBDDs (polybrominated dibenzodioxins) and PBDFs (polybrominated dibenzofurans) (Rupp and Metzger 2005). Some companies are currently evaluating emission control technologies to determine how effective they are at removing PBDEs, PBDDs and PBDFs.

Overall, not enough information was available to characterize the risks associated with the disposal of consumer products containing pentaBDE and octaBDE. Without such information it is difficult to make specific recommendations regarding appropriate emission control measures. In general, preventing the dispersive release of pentaBDE and octaBDE to the environment may reduce exposures to people and wildlife.

IV. Major findings and recommendations

Safety concerns have been raised over the widespread use and disposal of PBDE flame retardants in consumer products. At the request of the state legislature, Oregon's Department of Human Services (DHS), Office of Environmental Public Health (OEPH) reviewed new scientific findings regarding the current use of decaPBDE in consumer products and the release of pentaBDE and octaBDE from consumer products during disposal. Listed below are the major findings and recommendations of the review.

Current science suggests that decaBDE is a persistent chemical contaminant that may accumulate in soils, sediments, household dust and biosolids from sewage treatment plants. While decaBDE has been detected frequently in people and wildlife, it does not accumulate substantially in biological tissues. Hence, the widespread presence of decaBDE in people or wildlife is likely driven by recent exposures. Data were insufficient to determine if decaBDE levels are increasing in people and wildlife, and this was identified as an important data gap in assessing future risks posed by the continued use of decaBDE.

DecaBDE is not classified as a "highly toxic" substance according to the Oregon Revised Statutes § 453.005 (2005). However, new laboratory studies indicate that decaBDE may eventually breakdown into more toxic octaBDE byproducts, which are classified as "hazardous substances" and subject to regulation. The extent to which this occurs in the environment is presently unknown.

New research suggests that decaBDE may be an endocrine disruptor and developmental neurotoxicant. The US EPA is currently in the process of updating the toxicological assessment for decaBDE, and results should be released during 2008. OEPH recommends that Oregon continue to review any new research and federal developments regarding children's environmental health and decaBDE.

Flame retardant technology is evolving rapidly and effective alternatives to decaBDE may exist for some applications. OEPH supports the use of safer alternatives in consumer products when adequate safety data are available to evaluate the risks posed by potential alternatives.

Data were unavailable to assess the risks from the disposal of consumer products containing pentaBDE and octaBDE. Environmental releases of pentaBDE and octaBDE can occur at recycling facilities, landfills and solid waste incineration plants. The degree to which this is occurring in Oregon is unknown. Without such information OEPH could not make specific recommendations regarding appropriate emission control measures.

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