

FLAME RETARDANTS IN SAN FRANCISCO BAY

BY CHRIS WERME, INDEPENDENT CONSULTANT, werme@sbcglobal.net

FIRE FEARS IN CALIFORNIA

Fire is a serious worry in California. We are all taught that the fires after the 1906 earthquake did more damage than the quake itself. We have memorials for the Oakland Hills Firestorm of 1991. The California Department of Forestry and Fire Protection (CAL FIRE) maintains a statewide fire map, depicting the many active and contained fires throughout every region of the state. And every year, we hold our breaths until the rainy season comes.

Because fire is a very real concern for Californians, many government agencies have responsibilities for its prevention and control. CAL FIRE alone responds to thousands of wildland fires and hundreds of thousands of other fire-related emergencies each year. California also has some of the toughest fire laws and regulations in the country. The California Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation is just one of many state agencies that, along with a host of other responsibilities, works to ensure that California residents are safe from fires that begin in the home. Since 1975, the Bureau has developed several flammability standards, set forth in a series of Technical Bulletins, providing for

testing flammability in accordance with standards developed by the U.S. Consumer Products Safety Commission. Markets across the country sell products that meet California's tough standards.

The flammability standards do not dictate the use of chemical flame retardants or other special materials. But because the standards are so strict, many manufacturers have turned to chemical methods to ensure compliance. Flame retardants used in California and across the nation comprise an alphabet soup of chemical compounds – PBDE, HBCD, DP, PBEB, DBDBE, etc., etc. – it is hard for scientists, let alone consumers, to keep them all straight.

One class of chemical flame retardants, polybrominated diphenyl ethers (PBDEs) made big news in California in 2002, when San Francisco was identified as a global PBDE “hot spot.” A study by California Department of Public Health scientists (She et al. 2002), found PBDEs in harbor seal blubber that were among the highest levels that had ever been found in wildlife samples. Especially alarming, San Francisco Bay data suggested that concentrations of PBDEs in seal blubber had doubled every 1.8 years throughout the 1990s. Even more alarming, She et al. (2002) also found high levels of PBDEs in tissue samples from Bay Area women, the highest levels ever reported in humans.

Subsequently, two of three major classes of PBDEs, penta-BDE and octa-BDE, were banned, and use of the third class, deca-BDE, began to be phased out. (The U.S. Environmental Protection Agency (USEPA) released a draft assessment of alternatives to deca-BDE in July 2012.) But restricting the use of some chemical flame retardants just meant that manufacturers turned to other chemicals to ensure they met California's flammability standards. So, it didn't take too long before those alternate compounds began to be detected in environmental surveys. Some of the alternates may be just as environmentally undesirable as the PBDEs they replaced.

RECONSIDERING FLAME RETARDANTS

One of the Technical Bulletins put out by the California Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation has received a lot of recent attention. “Technical Bulletin 117 – Requirements, Test Procedures and Apparatus for Testing the Flame Retardance of Resilient Filling Materials Used in Upholstered Furniture,” March 2000, is available at <http://www.bhfti.ca.gov/industry/117.pdf>. It requires

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SAN FRANCISCO BAY SCIENTISTS WRITE

BY CHRIS WERME,
INDEPENDENT CONSULTANT,
werme@sbcglobal.net

**“BEST PAPER
OF THE YEAR”**

Bay Area scientists were honored in 2011 to win the coveted “Best Paper of the Year” award from the prestigious journal, Environmental Science & Technology, popularly known as ES&T. ES&T is a flagship journal of the American Chemical Association, publishing 1,500 papers on a broad range of topics in 2011. It is read and cited by environmental scientists around the globe.

The paper, “Identification of Flame Retardants in Polyurethane Foam Collected from Baby Products,” was written by Heather Stapleton (Duke University) and Lee Ferguson (Duke University and serving on the RMP Emerging Contaminant Workgroup), Susan Klosterhaus (former SFEI scientist), Saskia van Bergen (formerly of EBMUD), and other scientists with flame-retardant expertise.

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that furniture be able to withstand the heat of an open flame, one of the very strict standards enforced in California that has led to use of chemical flame retardants.

In June 2012, Governor Jerry Brown recognized the growing body of evidence suggesting that flame retardants were harming human health and the environment. Governor Brown directed Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation to revise Technical Bulletin 117. A draft of the revised bulletin was released in July, http://www.bearhfti.ca.gov/about_us/tb117_finaldraft.pdf. The revisions propose a change from protection from open flames to protection from a smoldering material, such as a lit cigarette. Neither the original nor the draft revision specifically mentions chemical flame retardants, but the changes would diminish the need for including them in upholstered furniture. There is also support for exempting some baby products from the new standards.

USEPA is also paying attention to flame retardants. On the national level, the attention is focused on inadequacy of the Toxic Substances Control Act (TSCA) to protect human health and the environment. When TSCA was enacted in 1976, it grandfathered 62,000 chemicals that were already in use. No toxicity testing was required for any of these chemicals. Since then, another 22,000 chemicals have been listed under TSCA, but only a few have been studied.

In July 2012, USEPA representative James Jones testified before the U.S. Senate, laying the blame for inadequate regulation of flame retardants on the lack of testing required or completed under TSCA and urging Congress to enact a more protective law (http://www.epa.gov/ocir/hearings/pdf/2012_jjones_testimony1.pdf).

PBDEs – CONTAMINANTS OF DIMINISHING CONCERN

PBDE flame retardants came into use in the 1970s. At that time, they were unregulated and rarely included in environmental assessments. During the 1980s and 1990s, there began to be reports, mostly from northern Europe and Canada, of PBDEs in fish and human milk and blood. It was the She et al. report in 2002 that really launched a focus on them in San Francisco Bay. The high and rapidly increasing levels of PBDEs in marine mammals and humans from the Bay Area were particularly alarming, because it seemed the PBDEs could become the next “PCB-like problem” for the Bay.

The Regional Monitoring Program for Water Quality in the San Francisco Estuary (RMP) has included PBDEs in its monitoring programs since 2002. PBDEs attracted attention in the sport fish monitoring program a little earlier, in 2000, when they were unexpectedly detected in analyses for PCBs and DDT. The good news is that, unlike the PCB problem, there are some indications that concentrations of PBDEs are declining promptly in the wake of bans.

Concentrations of PBDEs appear to be falling in Bay water (FIGURE 1, TOP). The maximum concentration of BDE-47, an abundant PBDE used as an index of the sum of all compounds occurred in 2004 and Bay-wide averages have since declined. Declines are not so apparent in sediment samples, where Bay-wide concentrations of BDE-47 have remained relatively constant (FIGURE 1, BOTTOM). There have also been no changes in sediment concentrations of BDE-209, which represents the one class of PBDEs that has not been banned. However, San Francisco Bay sediments were considered to be only in the medium range of PBDE concentrations among the 122 sediment samples collected at US coastal sites in a recent National Oceanic and Atmospheric Administration (NOAA) Mussel Watch Program survey (Kimbrough et al. 2009). San Francisco sediment concentrations were comparable or lower than those in other urbanized estuaries such as the Hudson-Raritan Estuary in New York and New Jersey, Galveston Bay in Texas, and Narragansett Bay in Rhode Island.

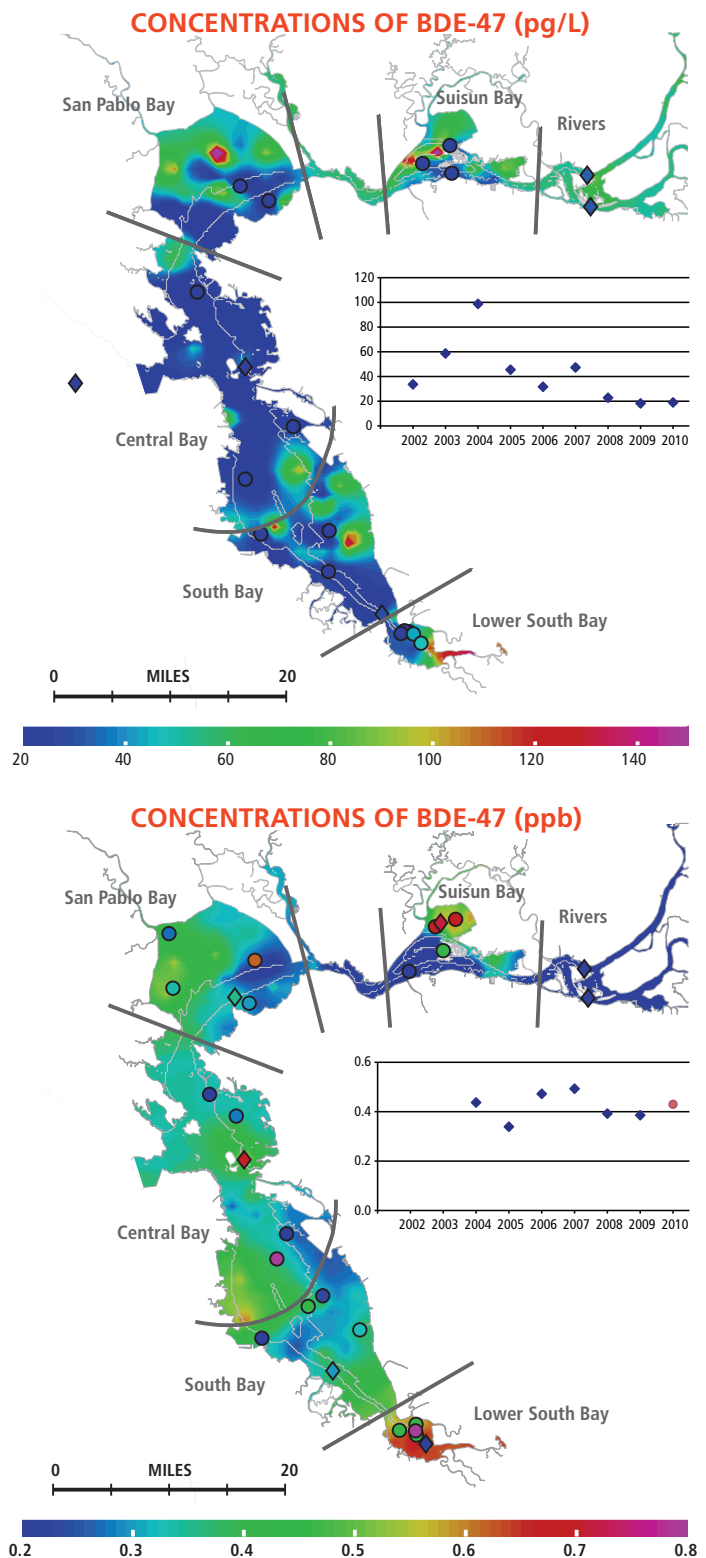


FIGURE 1. BDE-47 in water (top) and sediment (bottom) in San Francisco Bay in 2010, with annual mean concentrations in 2002–2010. Concentrations in the water have been consistently highest in Suisun Bay, while concentrations in the sediment are highest in Lower South Bay. There is evidence for a general decline in PBDE concentrations in the water column over time, but concentrations in the sediment have remained relatively constant. (BDE-47 is one of the most abundant of PBDEs and is often used as an indicator of total PBDE compounds.)

The NOAA Mussel Watch Program has found that mussels within San Francisco have some of the highest concentrations of PBDEs in California, but that the mussels from southern California coastal sites have similarly elevated concentrations (Kimbrough et al. 2009). Mussel Watch shellfish samples from the Bay have lower levels than similar samples from the Hudson-Raritan Estuary.

The RMP has monitored PBDEs in shellfish since 2002. Levels have typically been highest at the most upstream river sites where the waters from the Delta enter the Bay and relatively lower in the San Pablo, Central, South and Lower South bays. There have been steady declines in PBDE concentrations in bivalves from all Bay stations, particularly at the Rivers sites, although the Rivers sites remain higher than the other Bay segments (FIGURE 2).

Similarly, PBDE concentrations may be declining in sport fish tissues (FIGURE 3, Davis et al. 2011). The Bay-wide average concentrations of PBDEs in shiner surfperch in samples from 2009 were lower than the averages observed in 2003 and 2006. While encouraging, these results may also reflect changes in methods that were adopted in 2009, so continued monitoring will be necessary. Regardless of whether there are declines in concentrations in sport fish, the good news is that PBDE concentrations in all samples were well below the lowest California Office of Health Hazard Assessment (OEHHA) thresholds, indicating that PBDE concentrations in Bay sport fish are not a concern for human health. OEHHA had no PBDE thresholds until 2011, an indication of how difficult it is to make assessments of the risks posed by the many chemical compounds entering the Bay.

There are also encouraging results from bird studies. Some PBDE congeners readily accumulate in food chains, and monitoring studies have demonstrated that they are present in bird eggs. She et al. (2004) measured high PBDE levels in 45 individual tern eggs from the Bay Area, and the RMP has documented PBDEs in cormorant eggs (Davis et al., 2006). But a recent study suggests that tern embryos may be more tolerant of at least one commercial PBDE mixture, DE-71 (Rattner et al. 2011).

In 2008, RMP scientists published a mass budget of PBDEs in the Bay (Oram et al. 2008), including predictions of PBDE inputs and possible rates of decline following the bans of two PBDE classes. Although there were great uncertainties, the predictions provided reasons for hope and optimism. PBDEs were unlikely to become a problem as large as PCBs, mostly because PBDEs degrade more quickly than PCBs. If loads to the Bay were reduced, the PBDE inventories would decline. The years since 2008 have provided indications that the decline is underway. Based on the available information, the Regional Board does not anticipate designating the Bay as impaired by PBDEs.

PBDE REPLACEMENTS – WHAT DO WE KNOW ABOUT ALL THESE COMPOUNDS?

With the bans on two types of PBDEs, manufacturers scrambled to find alternatives. It didn't take too long for these alternatives – organophosphates and other brominated and chlorinated flame retardants

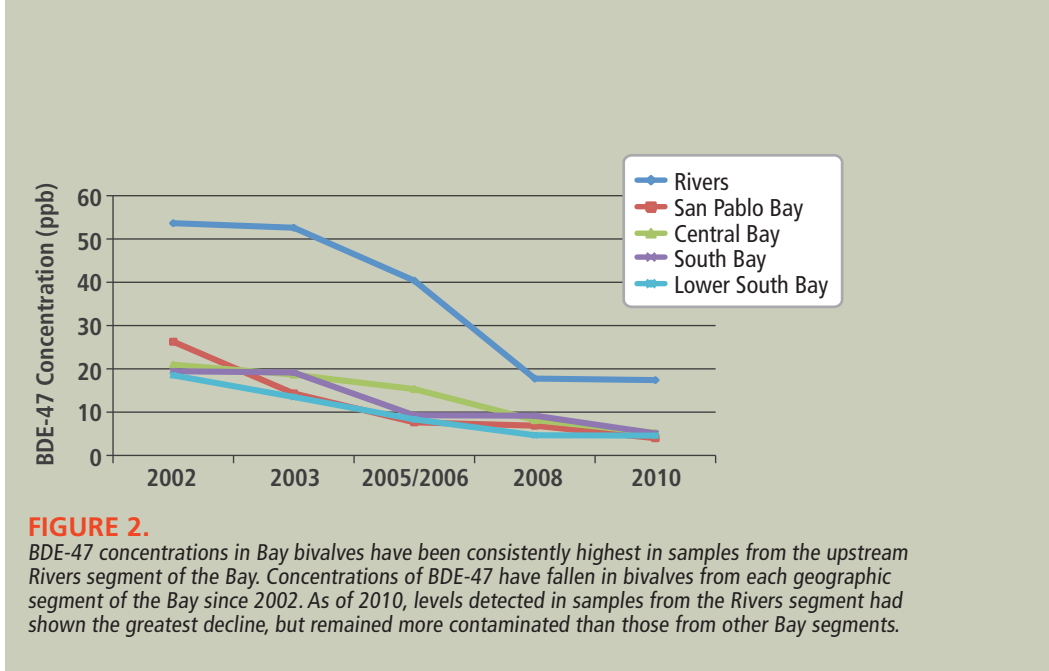


FIGURE 2. BDE-47 concentrations in Bay bivalves have been consistently highest in samples from the upstream Rivers segment of the Bay. Concentrations of BDE-47 have fallen in bivalves from each geographic segment of the Bay since 2002. As of 2010, levels detected in samples from the Rivers segment had shown the greatest decline, but remained more contaminated than those from other Bay segments.

– to start showing up in the Bay and its food web. There is not much known about these compounds yet, but the RMP is beginning to take note. There are data from some municipal treatment plant discharges, and a recent RMP study surveyed samples of Bay sediment, shiner surfperch, white croaker, and cormorant eggs for a variety of PBDE replacements (Klosterhaus et al. 2012). The study also analyzed blubber from freshly dead or euthanized, stranded harbor seals. The RMP is also examining organophosphate fire retardants in another study and has some preliminary results.

ORGANOPHOSPHATE PBDE REPLACEMENTS

Many organophosphate compounds are used as flame retardants in paints, glues, foams, rubbers, and textile coating. Many of the compounds are also used as plasticizers and softeners in synthetic rubbers and PVC piping. Some of the compounds are also used as antifoaming agents in lubricating oils and hydraulic fluids. Their use has increased greatly in recent years. Little is known about their toxicity or environmental effects. To date, organophosphate flame retardants have been detected in biosolids from Bay Area municipal treatment plants and in sediments from the Bay, and there are some indications that they are present in wildlife samples.

Tris (1,3-dichloro-2-propyl) phosphate – TDCPP or “chlorinated tris”

It has been 35 years since tris was banned from use as a flame retardant in children's pajamas, and its replacement, chlorinated tris was similarly banned soon afterwards. Yet today, chlorinated tris can be found in a range of household items, including baby strollers, pillows, and foam mattress pads. Chlorinated tris is also readily detected in household dust. It is a suspected mutagen, and in 2011, it was added to the California Proposition 65 list of suspected carcinogens, which requires businesses to alert consumers about possible risks of products they may purchase. Chlorinated tris has been found in biosolids from wastewater treatment plants and in Bay sediment samples at levels comparable to PBDEs. Chlorinated tris has not been detected in Bay wildlife tissues.

Tris (1-chloro-2-propyl) phosphate – TCPP

TCPP is used in rigid polyurethane foams. It is also used in flexible polyurethane foams for furniture and upholstery. TCPP is not acutely toxic, but the effects of long-term exposures are not known. It is structurally similar to some known carcinogens and is listed as causing cancer under California Proposition 65. TCPP has been detected in sewage biosolids and sediment samples from the Bay, at levels comparable to PBDEs. TCPP has also been detected in Bay wildlife tissues.

Triphenyl phosphate – TPP

TPP is used as a flame retardant and a plasticizer in the automotive industry, in roofing paper, and in other applications. It is considered to have relatively low toxicity, but only limited information is available. TPP has been found in Bay biosolids, sediment and bivalves.

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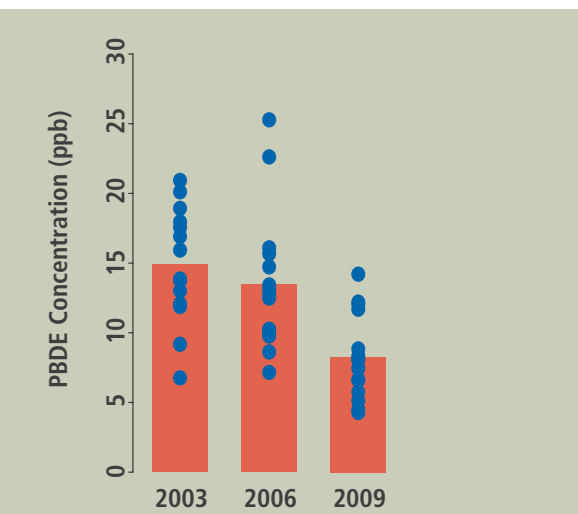


FIGURE 3. PBDE concentrations (ppb wet weight) in shiner surfperch in San Francisco Bay, 2003-2009. Bars indicate average concentrations. Points represent composite samples. Concentrations measured in 2009 were significantly lower than those measured in 2003 and 2006 and well below thresholds for concern for human consumption.

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Tris (2-chloroethyl) phosphate – TCEP

TCEP is used as both a flame retardant and a plasticizer in furniture foam, vinyl, home electronics, adhesives, plastics, paints and many other products. TCEP has been shown to cause tumors and reduce fertility in laboratory animals and is listed under California Proposition 65. TCEP has been detected in Bay cormorant eggs, at levels comparable to samples from the Great Lakes, another flame retardant hot spot (Chen et al. 2012).

Tris (2-butoxyethyl) phosphate – TBEP

TBEP is used as a flame retardant and plasticizer in floor polishes, plastics, and acrylic paints. It is considered to be biodegradable. It may affect liver function, and its long-term toxicity is unknown. TBEP has not been analyzed in Bay sediment samples but has been found in cormorant eggs.

OTHER BROMINATED AND CHLORINATED PBDE REPLACEMENTS

A wide variety of brominated and chlorinated compounds are being used as flame retardants. Their chemical structures vary widely. Some of the compounds chemically bind to the products they are treating, while others do not, leaving them free to migrate from the product and escape into the environment. Some of these varied compounds have been detected in Bay samples, but at low levels, generally about an order of magnitude lower than PBDEs.

Bis (hexachlorocyclopentadieno) cyclooctane or Dechlorane Plus – DP

DP is a chlorinated flame retardant, used in coatings for wires and cables and in plastic roofing materials for commercial buildings. It has also been used as a pesticide. DP has been in use since the 1960s, but little information is available about its toxicity. It is readily detected in foam products and dust from homes. It has been found in Bay Area sewage biosolids and in Bay sediment, mussel, fish, bird egg, and harbor seal tissue samples.

Hexabromocyclododecane – HBCD

HBCD is used as a flame retardant in foams for furniture, in the automotive and electronics industries, and in polystyrene insulations in homes. It is considered to be a neurotoxin

and endocrine disruptor. It is found within indoor and outdoor environments and is known to accumulate in aquatic food webs. HBCD has been detected in sediment samples and in sport fish collected from throughout the Bay. HBCD has also been detected in cormorant eggs and in harbor seal blubber samples. Levels detected in samples from the Bay have been lower than any toxicity thresholds and about an order of magnitude lower than what has been observed in Europe.

Pentabromoethylbenzene – PBEB

PBEB is used in circuit boards, cables, and other electronics, and in textiles, adhesives, and polyurethane. Little information is available about its toxicity. It has been detected in Bay sediment, mussel, and harbor seal samples.

1,2-Bis (2,4,6, tribromophenoxy) ethane – BTBPE

BTBPE is found used in plastics that require high temperatures during manufacture, such as polystyrene, and resins. BTBPE is not considered to be highly acutely toxic. It is structurally similar to octa-BDE, which has been banned in California. Its carcinogenicity is unknown. It is a possible endocrine disruptor, as it is structurally similar to other endocrine disruptors. BTBPE has been found in Bay sediments but has not been detected in wildlife tissue samples.

Decabromodiphenyl ethane – DBDPE

DBDPE is used in polystyrene, other plastics, wires, cables, as insulation in electrical products. It is structurally similar to deca-BDE. DBDPE has been found to increase mortality in fish embryos and is a suspected endocrine disruptor. It is considered to be persistent in the

environment. DBDPE has been detected in Bay sediment samples.

Several other brominated PBDE replacements are in use but have not been detected in Bay sediment or wildlife samples. These compounds remain targets for future studies, because they are widely used as PBDE replacements and are likely to persist in the environment:

Tetrabromobenzoate – TBB

Di (2-ethylhexyl) tetrabromophthalate – TBPH

Hexabromobenzene – HBB

THE BOTTOM LINE

Overall, the monitoring of PBDE replacements is showing that, like the PBDEs they replaced, many of these compounds are finding their way from homes, businesses, and automobiles and into the Bay. Concentrations of most compounds have been lower than those measured for PCBs or PBDEs, but whether the measured concentrations pose risks to wildlife or human health is largely unknown. Little is known about the individual compounds, and even less is known about the cumulative effects of complex mixtures. Some proprietary mixtures have unknown formulations. The RMP will prioritize these compounds based on what is known about occurrence and toxicity and consider additional future monitoring to determine whether they are becoming more prevalent. The RMP will also continue to be on the lookout for flame retardants and other contaminants of emerging concern that make their way into commerce and pose threats to Bay water quality. ○

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Their study surveyed car seats, changing table pads, sleep positioners, portable mattresses, nursing pillows, baby carriers, and rocking chairs – all products containing polyurethane foam. Baby products containing polyurethane foam must meet California state furniture flammability standards, and the scientists

thought it likely that a variety of flame retardants would be found in baby products throughout the U.S. as well as California. Of the 101 foam samples they analyzed, 80 samples contained identifiable flame retardant additives. The products in all but one of those 80 samples were chlorinated or

brominated compounds. Five samples contained PBDE congeners commonly associated with one of the discontinued PBDE types, penta-BDE, showing that products sold before the bans are still in use. Other flame retardants in the samples included TDCPP (chlorinated tris), TCEP, TCP, TBB, TBPH, Firemaster 550 (a mixture), and Antiblaze V6 (another mixture), which was reported as being used primarily in the automotive industry. Many of the baby products included more than one compound. Twelve samples had compounds that could not be identified.

This paper was the first study to report on flame retardants in baby products. In addition, it identified two chlorinated organophosphate flame retardants not previously documented in the environment or in consumer products. Based on exposure estimates conducted by the Consumer Product Safety Commission, the study predicted that infants may receive higher than acceptable daily intake levels of the most commonly detected compound, chlorinated tris, a product that was discontinued in children's pajamas back in the 1970s.

The paper advocated for future studies to determine the possible health risks of this diverse chemical soup, but there were even more immediate responses. Some baby products – strollers, infant carriers, and nursing pillows – have already been exempted from the California flammability standard, and some states are proposing to completely ban chlorinated tris. Continued updates on flame retardants in baby products and other issues can be found at the California Department of Consumer Affairs, Bureau of Electronic and Appliance Repair, Home Furnishings and Thermal Insulation website, <http://www.bhfti.ca.gov/home.shtml>. ○

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4911 Central Ave., Richmond, CA 94804
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