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Editorial

A Sluggish Response to a Smoldering Problem

In late 2004, manufacturers of polybrominated diphenyl ethers (PBDEs) voluntarily discontinued the production and sales of two of their products used as flame retardants in the United States. This phase-out was due to government pressure and threatening data about the environmental fate and health effects of these compounds. It was welcomed by many, but I believe that the response was too slow, the issue was avoidable, and that sales of another PBDE should be discontinued.

Over the past two decades, PBDEs have emerged as a new class of organic contaminants joining predecessors like 1,1,1-trichloro-2,2-*bis*[*p*-chlorophenyl]ethane (DDT) and polychlorinated biphenyls (PCBs). PBDEs were used in appliances, textiles, plastics, foams, and other products where human exposure was inevitable. Like PCBs, PBDEs are composed of a group of 209 possible congeners that are hydrophobic and have a tendency to partition into fats and other pools of organic matter in the environment. They are a bit less stable in the environment than PCBs because the carbon-to-bromine bond is weaker in PBDEs than the carbon-to-chlorine bond in PCBs. This subtle difference is why PBDEs are used as flame retardants—at elevated temperatures, the bromine atoms dissociate and quench fires.

Production of PBDEs started in 1960s, and global sales were ∼70,000 metric tons by 2001. They were sold as several different types of mixtures that mainly contained either pentabrominated or octabrominated congeners (these two were the ones just phased out). The biggest seller has been a mixture dominated by the fully brominated congener, decabromodiphenylether (DecaBDE), which continues to be marketed and sold. Studies performed on laboratory animals have indicated that DecaBDE can affect thyroid activity.

Major awareness for PBDEs was raised by Meironyté and colleagues in the late 1990s when they determined that the concentration of PBDEs in Swedish breast milk began to exponentially increase in 1972 over a 25-year period, with a doubling rate of 5 years. Arnold Schecter at the University of Texas and his colleagues analyzed human breast milk collected in 2002 in the U.S. and determined that concentrations of PBDEs were 10 to 100 times greater than those found in Europe.

By examining the history of DDT, PCBs, and PBDEs, it is clear that the manufacturers of PBDEs were too slow when phasing out mixtures containing the pentabrominated and octabrominated congeners. In addition, alternatives to DecaBDE should be sought.

While working on the pesticidal properties of diphenyl-trichloroethane derivatives, Swiss chemist Paul Müller recognized the toxicity of DDT on flies in the late 1930s. Follow-up experiments were made in the field and replicated Müller's initial laboratory results. By the latter half of World War II, American forces applied large amounts of DDT to control the spread of malaria. During the 1940s and 1950s, DDT was used on numerous pests, often indiscriminately. An editorial published in 1951 in *Scientific American* called it "one of the great world necessities." Thus, within a narrow timespan of only a decade, Müller's discovery was credited with saving countless lives. He received the Nobel Prize in physiology or medicine in 1948 for identifying the insecticidal properties of DDT.

However, Rachel Carson's book *Silent Spring*, published in 1962, called attention to DDT's deleterious effects on birds, thereby creating social environmental awareness of unintended consequences. Widespread concern about DDT's impacts led the U.S. government to regulate its production and usage in the late 1960s and early 1970s. It took approximately 10 years after *Silent Spring* was published for restrictions or bans on DDT to occur in the U.S.

PCBs had a similar fate. Production of PCBs began in the late 1920s, during which they were used as industrial chemicals due to their high stability and chemical inertness, especially as insulators in electrical transformers and capacitors. In the U.S., sales paralleled the great industrial growth following World War II. In the mid-1960s, while attempting to analyze for DDT in samples, Swedish chemist Soren Jensen found PCBs in fish and bird samples. He published his first results in 1966. Jensen's work and studies by American scientist Robert Risebrough revealed by the late 1960s that PCBs were clearly organic chemicals of environmental concern. Even with these findings, sales of PCBs by Monsanto in the U.S. peaked in 1970, but eventually ceased in 1977. Again, about a 10-year lag occurred between the discovery of PCBs in the environment and a major restriction of their use.

There are several important milestones that can be considered in this discussion of PBDEs, but the Firemaster incident must be highlighted. In 1973, the Michigan Chemical Corporation accidentally mixed a flame-retardant mixture of polybrominated biphenyls (PBBs) called Firemaster with another one of its commercial products called Nutrimaster, a feed additive used in farming. The tainted Nutrimaster was sold to Michigan farmers in 1973 and 1974. Dairy cows became ill. Milk and meat were then consumed, and at least 10,000 Michigan residents were exposed to PBBs. Production and sales of PBBs ceased soon thereafter. Yet, analysis of fish in the Great Lakes by Zhu and Hites at Indiana University found that these compounds continued to persist in 2000, indicating that brominated organic compounds have the potential to last in the environment for decades. Soon after the Firemaster incident, sales of PBBs were discontinued. Ironically, this event may have catalyzed increased production of PBDEs—conversely, it should have motivated industry to produce flame retardants that were less potentially persistent in the environment.

In the late 1970s and early 1980s, PBDEs began to be detected in environmental samples. Swedish scientists Andersson and Blomkvist were the first to find these compounds in lake fish far from any known chemical plants. Additional studies continued around the world in the 1980s. By 1987, Swedish chemists Jansson, Asplund, and Olsson published a manuscript entitled "*Brominated Flame Retardants—Ubiquitous Environmental Pollutants?*" in which they stated that PBBs and PBDEs can be detected around the globe and stressed that this was an important topic for future studies. Regardless of these findings and the histories of DDT and PCBs, sales of PBDEs continued through the 1980s and into the 21st century.

Only work by Meironyté and others, beginning in the late 1990s, turned the tide on the PBDEs and increased overall awareness. Because compounds from mixtures of pentabrominated and octabrominated congeners were most often measured in human samples, a voluntary phase-out began in 2004—nearly two decades after Jansson et al. (1987) was published. This, however, does little to diminish the amounts that currently exist in residential households. In 2005, DecaBDE is the only PBDE on the market. Manufacturers argue that DecaBDE is not usually detected in environmental matrices and hence not a problem. Recent evidence indicates that this issue is not so simple. Heather Stapleton and her colleagues at the University of Maryland observed that fish fed DecaBDE-doped food can create less brominated congeners, including one that is commonly detected in humans and fish.

PBDEs are life-saving organic compounds. A report prepared for the Chemical Manufacturers Association on the flame-retarding properties of DecaBDE indicated that it is responsible for saving 200 to 300 lives per year in United States. Numerous research groups and agencies are closely examining the environmental fate of DecaBDE and a wide range of possible biological effects it may exert on humans and animals. I believe these results will lead to the discontinuation of sales of DecaBDE and a switch to safer alternatives. For example, phosphorus-bromine flame retardants, which are less likely to bioaccumulate in humans and persist in the environment, will be replacing the pentabrominated mixtures of PBDEs.

A 2004 report by the United States Environmental Protection Agency concluded that less than 10% of the most highly produced industrial chemicals have been evaluated regarding their bioaccumulation, environmental fate, and toxicity. In order to avoid other foreseeable problems like the PBDEs, efforts are underway to increase testing in the United States. The European Union has gone one step further and begun a program entitled Registration, Evaluation, and Authorization of Chemicals (REACH). The latter program significantly increases the responsibilities of the chemical industry and demands that the safety of their products be evaluated. Let's hope that these efforts will catalyze all manufacturers to be more proactive while allowing society to continue to prosper.

One of the key parameters used for predicting whether chemicals will bioaccumulate is the octanol-water partition coefficient (Kow). Compounds that prefer to partition into fats like PCBs, DDT, and PBDEs have very large Kow values. The scientific concept of using Kow values to gauge bioaccumulation potential became a hot topic in the scientific literature in the late1970s to the mid-1980s. By the mid-1990s, textbooks on environmental chemistry had whole chapters devoted to this topic, which leads me to the question that I continue to ask—*why* were PBDEs used despite all of the data and scientific knowledge that was available decades ago?

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