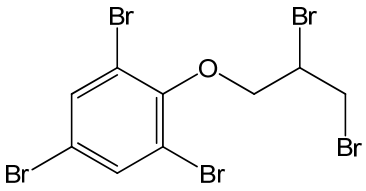
BROMINATED AND CHLORINATED ORGANIC CHEMICAL COMPOUNDS USED AS FLAME RETARDANTS

Additional Information on Four Flame Retardants

Materials for the March 2-3, 2009 Meeting of the California Environmental Contaminant Biomonitoring Program (CECBP) Scientific Guidance Panel (SGP)

For the December 4-5, 2008 SGP meeting, CECBP staff provided materials on brominated and chlorinated chemical compounds used as brominated flame retardants (BFRs) and chlorinated flame retardants (CFRs). The December 2008 document contained overviews of 13 flame retardants (available at: http://oehha.ca.gov/multimedia/biomon/pdf/120408flamedoc.pdf). In addition to these 13 chemicals, a list of some other BFRs and CFRs was included on page 32 of the document. The material that follows expands on the earlier document, by providing overviews of four additional flame retardants from that list.

2,3-Dibromopropyl-2,4,6-tribromophenyl ether [CAS No. 35109-60-5]



Use and extent of exposure:
2,3-Dibromopropyl-2,4,6-tribromophenyl ether (DPTE) has reported use as a flame retardant in extrusion grade polypropylene (ICPS, 1997). No information was identified as to whether DPTE is used as an additive or reactive flame retardant (Fisk et al., 2003). No information was found on the U.S. production/import volume. A 1997 article reported findings of DPTE in sewer slimes in Germany (as reported in NIEHS, 2002). Recently, DPTE was identified as the predominant organic bromine compound in blubber and brain samples of hooded seals and harp seals from the Barents and Greenland Seas. Levels in blubber and brain samples were as high as 470 and 340 µg/kg wet weight, respectively (Von der Recke and Vetter, 2007).

Known or suspected health effects:
DPTE contains substructures similar to both 2,3,-dibromo-1-propanol and 2,4,6-tribromophenol. 2,3-Dibromo-1-propanol is listed under Proposition 65 as known to cause cancer. Research findings indicate that 2,4,6-tribromophenol is a thyroid hormone disrupting chemical (Hamers et al., 2006; Suzuki et al., 2008). DPTE was identified as potentially meeting the criteria for designation as a chemical that is persistent, bioaccumulative and toxic (PBT) (Fisk et al., 2003).

Potential to biomonitor:
Physical and chemical properties:
Vapor pressure: 6.22×10^{-7} [predicted, U.S. EPA, 2008]
Water solubility: 0.0883 mg/L [predicted, U.S. EPA, 2008]
Octanol/water partition coefficient: Log K_{ow} = 6.341 [predicted, U.S. EPA, 2008]
Bioaccumulation: BCF 15,000 [predicted, PBT Profiler]
Persistence: Half-life in soil 360 d; in sediment 1600 d [predicted, PBT Profiler]

Availability of analytical methods: GC-MS methods are being developed.

Availability of adequate biospecimens: Serum.

Incremental analytical cost: Analysis can be bundled with other BFRs.

References:
Fisk et al. (2003). Prioritisation of flame retardants for environmental risk assessment. Produced for Environment Agency, United Kingdom. Available at: http://ec.europa.eu/environment/waste/stakeholders/industry_assoc/ebfrip/annex2.pdf

Hamers et al. (2006). *In vitro* profiling of the endocrine-disrupting potency of brominated flame retardants *Toxicol Sci* 92:157-173.

IPCS (1997). Flame Retardants: A general introduction. *Environmental Health Criteria* 192. International Program of Chemical Safety. World Health Organization. Available at: http://www.inchem.org/documents/ehc/ehc/ehc192.htm.

NIEHS (2002). Tetrabromobisphenol A bis (2,3-dibromopropyl ether) [21850-44-2]. Review of Toxicological Literature . Prepared for National Institute of Environmental Health Sciences. Contract No. N01-ES-65402. Research Triangle Park, NC. Available at:

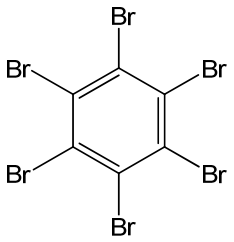
PBT Profiler. Developed by Environmental Science Center for the Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency. Available at: http://www.pbtprofiler.net/

Suzuki et al. (2008) Identification of brominated and chlorinated phenols as potential thyroid-disrupting compounds in indoor dusts. *Environ Sci Technol* 42:1974-1800.

US EPA (2008). Estimation Programs Interface Suite™ for Microsoft® Windows, v 3.20. United States Environmental Protection Agency, Washington, DC, USA. Available at: http://www.epa.gov/oppt/exposure/pubs/episuite.htm

Von der Recke and Vetter (2007). Synthesis and characterization of 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE) and structurally related compounds evidenced in seal blubber and brain. *Environ Sci Technol* 41:1590-1595.

Hexabromobenzene [CAS No. 87-82-1]



Use and extent of exposure:
Hexabromobenzene (HBB) has been used as a flame retardant in polymers, plastics, textiles, wood and paper. Its primary uses have been reported in the plastics, paper and electrical industries (Bruchajzer et al., 2004). U.S. production/import volume was listed as 10,000-500,000 pounds for 1998, but no information is available beyond that time (U.S. EPA, 2002). In addition to its use as a flame retardant, HBB is a thermal decomposition product of octa- and decaBDEs and hexabromobiphenyl (as cited in Bruchajzer et al., 2004). HBB was identified in scrap material in an aluminum recycling plant in Finland (Sinkkonen et al., 2004). It was detected in pooled samples of Herring Gull eggs in the Great Lakes basin (Gauthier et al., 2007). It was also frequently detected at low levels in plasma of male Glaucous Gulls from the Norwegian Arctic, and at higher levels in 100 percent of the gull egg yolk samples (Verreault et al., 2007).

Known or suspected health effects:
HBB is the fully brominated derivative of benzene. It is also the brominated analog of hexachlorobenzene, which is listed as known to cause cancer and developmental toxicity under Proposition 65. Both HBB and its major metabolite, 1,2,4,5-tetrabromobenzene, induce cytochrome P-450 monooxygenase enzymes (Bruchajzer et al., 2004).

Potential to biomonitor:
Physical and chemical properties:
Vapor pressure: not available
Water solubility: 0.16×10^{-3} mg/L at 25ºC [experimental, HSDB]
Octanol/water partition coefficient: Log K_{ow} = 6.07 [experimental, HSDB]
Bioaccumulation: BCF 9400 [predicted, PBT Profiler]
Persistence: Half-life in soil 360 d; in sediment 1600 d [predicted, PBT Profiler]

Past biomonitoring studies: HSDB notes that HBB was detected in human adipose tissue in Japan, at levels from 0.35 to 0.65 ng/g (wet weight).

Availability of analytical methods: GC-MS methods are being developed.

Availability of adequate biospecimens: Serum.

Incremental analytical cost: Analysis can be bundled with other BFRs.

References:

Bruchajzer et al. (2004). Effect of repeated administration of hexabromobenzene and 1,2,4,5-tetrabromobenzene on the levels of selected cytochromes in rat liver. *Int J Occup Med Environ Health* 17:347-53.

Gauthier et al. (2007). Current-use flame retardants in the eggs of herring gulls (*Laurus argentatus*) from the Laurentian Great Lakes. *Environ Sci Technol* 41:4561-4567.

HSDB. Hazardous Substances Data Bank. Toxicology and Environmental Health Information Program. National Library of Medicine. Available at: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB

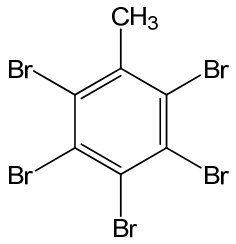
PBT Profiler. Developed by Environmental Science Center for the Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency. Available at: http://www.pbtprofiler.net/

Sinkkonen et al. (2004). Screening of halogenated aromatic compounds in some raw material lots for an aluminum recycling plant. *Environ Int* 30:363-366.

U.S. Environmental Protection Agency (U.S. EPA, 2002). Non-Confidential Inventory Update Reporting Production Volume Information. Toxic Substances Control Act (TSCA) Inventory. Available at: http://www.epa.gov/oppt/iur/tools/data/2002-vol.htm

Verreault et al. (2007). Brominated flame retardants in glaucous gulls from the Norwegian Arctic: More than just an issue of polybrominated diphenyl ethers. *Environ Sci Technol* 41:4925-2931.

Pentabromotoluene [CAS No. 87-83-2]



Use and extent of exposure:
Pentabromotoluene has been used as a flame retardant in polyester and other polymers, latex, textiles, rubbers and plastics. Information on trends in use and production volume is unavailable. No information was identified as to whether it is used as an additive or reactive flame retardant (Fisk et al., 2003). Pentabromotoluene has been detected at low levels in pooled samples of Herring Gull eggs in the Great Lakes basin (Gauthier et al., 2007). Low levels were also found in male plasma and egg yolk of Glaucous Gulls from the Norwegian Arctic (Verreault et al., 2007).

Known or suspected health effects:
Pentabromotoluene is the brominated analog of toluene, which is listed as known to cause developmental toxicity under Proposition 65. Fisk et al. (2003) identified pentabromotoluene as potentially meeting the criteria for designation as a chemical that is persistent, bioaccumulative and toxic.

Potential to biomonitor:
Physical and chemical properties:
Vapor pressure: 1.46×10^{-7} mm Hg at 25ºC [predicted, U.S. EPA, 2008]
Water solubility: 0.0176 mg/LL [predicted, U.S. EPA, 2008]
Octanol/water partition coefficient: Log K_{ow} = 6.99 [predicted, U.S. EPA, 2008]
Bioaccumulation: BCF 48,000 [predicted, PBT Profiler]
Persistence: Half-life in soil 360 d; in sediment 1600 d [predicted, PBT Profiler]

Availability of analytical methods: GC-MS methods are being developed.

Availability of adequate biospecimens: Serum

Incremental analytical cost: Analysis can be bundled with other BFRs.

References:
Fisk et al. (2003). Prioritisation of flame retardants for environmental risk assessment. Produced for Environment Agency, United Kingdom. Available at: http://ec.europa.eu/environment/waste/stakeholders/industry_assoc/ebfrip/annex2.pdf

Gauthier et al. (2007). Current-use flame retardants in the eggs of herring gulls (*Laurus argentatus*) from the Laurentian Great Lakes. *Environ Sci Technol* 41:4561-4567.

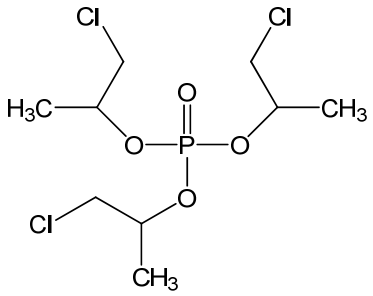
IPCS (1997). Flame Retardants: A general introduction. Environmental Health Criteria 192. International Program of Chemical Safety. World Health Organization. Available at: http://www.inchem.org/documents/ehc/ehc/ehc192.htm.

PBT Profiler. Developed by Environmental Science Center for the Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency. Available at: http://www.pbtprofiler.net/

US EPA (2008). Estimation Programs Interface Suite™ for Microsoft® Windows, v 3.20. United States Environmental Protection Agency, Washington, DC, USA. Available at: http://www.epa.gov/oppt/exposure/pubs/episuite.htm

Verreault et al. (2007). Brominated flame retardants in glaucous gulls from the Norwegian Arctic: More than just an issue of polybrominated diphenyl ethers. *Environ Sci Technol* 41:4925-2931.

Tris(1-chloro-2-propyl)phosphate (TCPP) [CAS No. 13674-84-5]



Use and extent of exposure:
Tris(1-chloro-2-propyl)phosphate (TCPP) is an additive flame retardant. It is used extensively in rigid and flexible polyurethane foam. TCPP is also used in thermoset and thermoplastic materials and in textile finishes. Annual U.S. production/import volume was 10-50 million pounds for the reporting years 1990, 1994, 1998 and 2002 (U.S. EPA, 2002). An increased use of TCPP in Europe has been linked to a decreased use of tris(2-chloroethyl)phosphate (TCEP). Studies in Sweden found high levels of TCPP in indoor environments (Marklund et al., 2005). Particularly high concentrations were found in the interiors of automobiles, buses and subway cars (Staaf and Ostman, 2005).

Known or suspected health effects:
TCPP is structurally similar to three chemical compounds that have been identified as causing cancer. Tris(2-chloroethyl)phosphate and tris(2,3-dibromopropyl)phosphate are listed as known to cause cancer under Proposition 65, and tris(1,3-dichloropropyl)phosphate was identified as a probable human carcinogen, based on sufficient evidence in animals, by the U.S. Consumer Product Safety Commission (2006).

Potential to biomonitor:
Physical and chemical properties:
Vapor pressure: 2.02×10^{-5} mm Hg [Herzke et al., 2007]
Water solubility: 1200 mg/L [Herzke et al., 2007]
Octanol/water partition coefficient: Log K_{ow} = 2.59 [Herzke et al., 2007]
Bioaccumulation: BCF 3.3 [predicted, PBT Profiler]
Persistence: Half-life in soil 120 d; in sediment 540 d [predicted, PBT Profiler]

Availability of analytical methods: GC-MS

Availability of adequate biospecimens: Serum or urine.

Incremental analytical cost: Analysis can be bundled with TDCPP and TCEP analysis. New methods development may be required.

References:
Herzke et al. (2007) A literature survey on selected chemical substances. Literature survey of polyfluorinated organic compounds, phosphor containing flame retardants, 3-nitrobenzathrone, organic tin compounds, platinum and

silver. TA-2238/2007. Norweigen Pollution Control Authority. NILU. Available at: http://www.sft.no/publikasjoner/2238/ta2238.pdf

Marklund et al. (2005). Organophosphorus flame retardants and plasticizers in air from various indoor environments. *J Environ Monit* 7:814-819.

PBT Profiler. Developed by Environmental Science Center for the Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency. Available at: http://www.pbtprofiler.net/

Staaf and Ostman. (2005). Organophosphate trimesters in indoor environments. *J Environ Monit* 7:883-887.

U.S. Consumer Product Safety Comission (2006). CPSC Staff Preliminary Risk Assessment of Flame Retardant (FR) Chemicals in Upholstered Furniture Foam. December 21, 2006.

U.S. Environmental Protection Agency (U.S. EPA, 2002). Non-Confidential Inventory Update Reporting Production Volume Information. Toxic Substances Control Act (TSCA) Inventory. Available at: http://www.epa.gov/oppt/iur/tools/data/2002-vol.htm