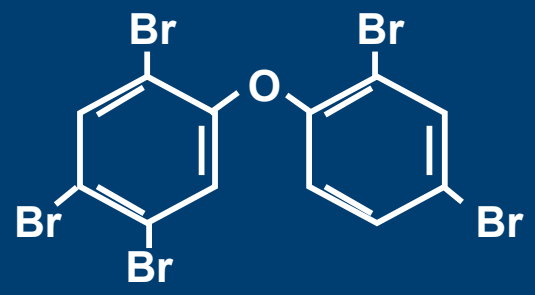
Polybrominated diphenyl ethers (PBDEs) in the San Francisco Estuary



- Added to RMP Status and Trends in 2002

Detected in:

- Water, sediment, bivalves (RMP monitoring data)
- WWTP effluent (Oros; RMP special study; North 2004)
- Sport fish (Holden et al. 2003; Brown et al. 2006; Werme et al. 2006)
- Harbor seals (She et al. 2002)
- Birds (She 2004; Davis et al. 2006; Hooper, unpublished)
- People in CA (She et al. 2002; Petreas et al. 2003; Fischer et al. 2006; Bradman et al. 2007)

Regulatory Status

- Penta- and Octa-BDE mixtures banned in CA (2006)
- Deca-BDE unrestricted use (except WA, ME…CA?)
- CA Assembly Bill 706: Would ban brominated and chlorinated flame retardants in 2010

Non-PBDE Alternative Flame Retardants

The Other Brominated Flame Retardants

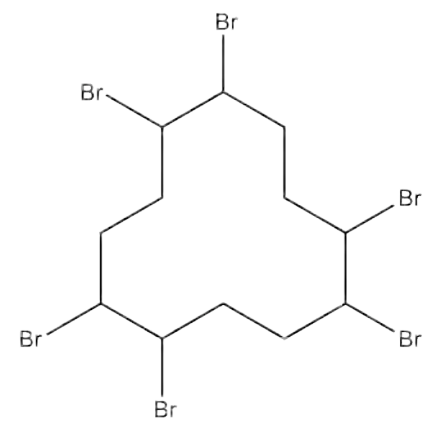
- Hexabromocyclododecane (HBCD)
- Tetrabromobisphenol A (TBBPA)
- Decabromodiphenylethane (DBDPE)
- 1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE)
- Pentabromoethylbenzene (PBEB)

Dechlorane Plus (DP)

Phosphate-based Flame Retardants

- Tributylphosphate (TBP)
- Triphenylphosphate (TPP)
- Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)

Hexabromocyclododecane (HBCD)



log K_{ow} 5.6

- Additive flame retardant; used in polystyrene foams used in thermal insulation in buildings, upholstery textiles, electrical equipment housings

Widely Used?

- High production volume chemical, primarily used in Europe
- Substitute for Penta- and Octa-BDE mixtures?

Bioaccumulative and Persistent ?

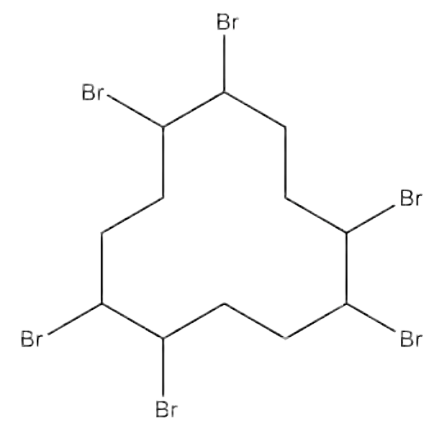
- Global contaminant, long range atmospheric transport, biomagnification
- Concentrations in N. America lower than Europe
- Increased from 0.7 to 12 ng/g wet wt. in California sea lions between 1993 and 2003 (Stapleton et al. 2006)
- Not yet measured in SF Bay Area
- Data for North America and specifically urbanized estuaries are scarce

Hexabromocyclododecane (HBCD)

Toxic?

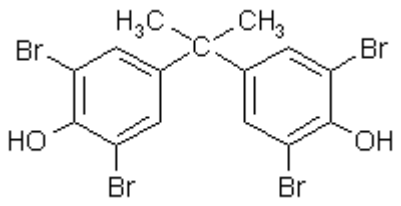
- Mammalian toxicity: P450 enzyme induction, carcinogenic, thyroid hormone interference, developmental neurotoxic effects
- Aquatic toxicity data limited (NOEC for daphnia 3.1 μg/L; LC50 for rainbow trout 2.5 μg/L)
- No chronic toxicity data
- EU risk assessment ongoing (expect early 2008)

Analytical methods established? Yes



log K_{ow} 5.6

Tetrabromobisphenol A (TBBPA)



log K_{ow} 4.5

- Reactive flame retardant in circuit boards, with some use as an additive flame retardant in plastic housings

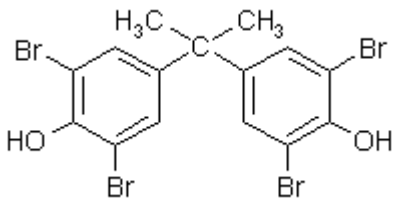
Widely Used?

- Highest volume brominated flame retardant in production

Bioaccumulative and Persistent ?

- Detected in soils and sediments, fish, predatory birds, and human serum
- Slightly lipophilic; susceptible to degradation and metabolism, short half-life
- Compared to PBDEs and HBCD, potential for biomagnification appears to be lower?

Tetrabromobisphenol A (TBBPA)



log K_{ow} 4.5

Toxic?

- Structure similar to the thyroid hormone thyroxine (T4)
- Endocrine disruption in mammals and fish
- Immunotoxicant, interferes with cell signaling pathways in both vertebrates and invertebrates
- Acutely toxic to fish at high concentrations (LC50s 0.4-3 mg/L)
- Chronic toxicity?

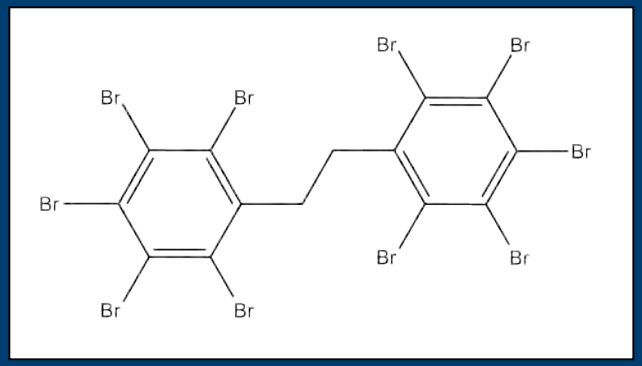
Nominal ~25 µg /L (0.047 µM) exposure to zebrafish (Kuiper et al. 2007)

- Decreased egg production
- Effects on egg production, juvenile survival, and gender development of offspring at body burdens of 5-7 µg/g lipid
- Concentrations in wild-caught fish several orders of magnitude lower (Morris et al. 2004; others?)

- EU risk assessment ongoing (early 2008)

Analytical methods established? Yes

Decabromodiphenylethane (DBDPE)



Widely Used?

- Introduced in early 1990s, applications similar to Deca-BDE
- Current production volume unknown

Bioaccumulative and Persistent ?

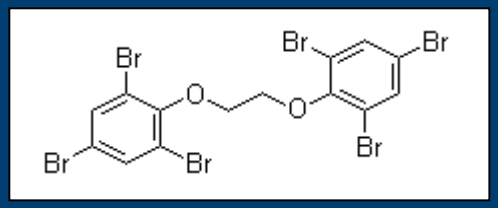
- 10-100 ng/g dry wt in sewage sludge from Sweden and Canada (Kierkegaared et al. 2004; McCrindle et al. 2004)
- Great Lakes air (Hoh 2006), tree bark in North America (Zhu and Hites 2006), Lake Winnipeg food web (Law et al. 2006)

Toxic? We don't know

Analytical methods established? Yes

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

Widely Used?



- Replacement for Penta- and Octa-BDE?
- Current production volume unknown

Bioaccumulative and Persistent ?

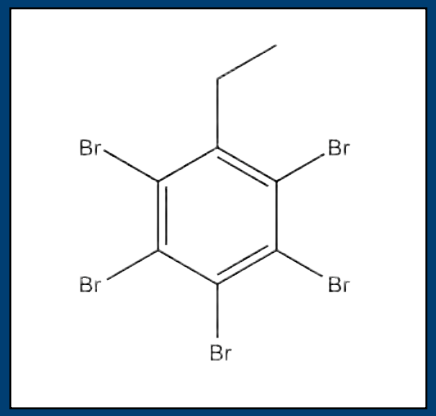
- Detected in U.S. ambient air in concentrations that approximated those of PBDEs (Hoh et al. 2005)
- Detected in sediment from the Great Lakes (Hoh et al. 2005), tree bark from North America (Zhu and Hites 2006), a Lake Winnipeg food web (Law et al. 2006), and herring gull eggs from the Great Lakes (Gauthier et al. 2007)
- Between 1979 and 1998, concentrations of BTBPE increased in Ontario lake trout and may still be on the rise (Tomy et al. BFR 2007).

Toxic?

- Thyroid interference in juvenile rainbow trout, not as potent as other brominated flame retardants (Tomy et al. BFR 2007)

Analytical methods established? Yes

Pentabromoethylbenzene (PBEB)



Widely Used?

- Additive flame retardant in the 1970s and 1980s
- Current production volume unknown

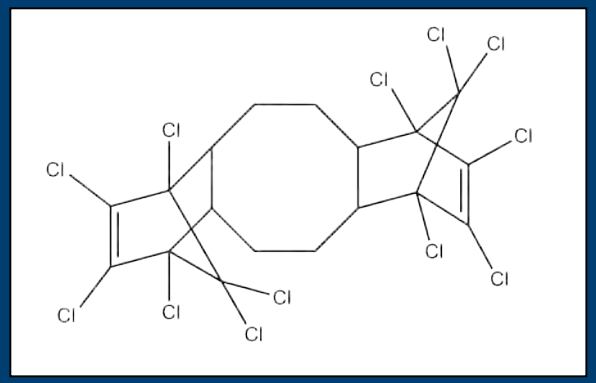
Bioaccumulative and Persistent ?

- Detected (0.03-1.4 ng/g wet weight) in herring gull eggs from the Great Lakes (Gauthier et al. 2007)
- Detected in U.S. air samples (Hoh et al. 2005)

Toxic? We don't know

Analytical methods established? Yes

Dechlorane Plus ®



Widely Used?

- Additive flame retardant; used in electrical wires and cables, computer connectors, and plastic roofing materials
- High production volume chemical, used for over 40 years

Bioaccumulative and Persistent ?

- Highly lipophilic (log Kow ~9.3), resistant to degradation, bioaccumulative

Detection in the environment:

- Air, sediment, and fish from the Great Lakes region (Hoh et al. 2006)
- Lake Winnipeg and Lake Ontario food webs; low relative to PBDEs and HBCD (Tomy et al. 2007)
- Increasing concentrations in lake trout from Ontario between 1979 and 1993 but then declined (Tomy et al. 2007)
- Low concentrations (< 2 ng/g lipid) in beluga whale blubber collected from the Canadian arctic between 1993-2005; concentrations did not vary over the time period (Tomy et al. 2007)
- Great Lakes herring gull eggs (Gauthier et al. 2007)

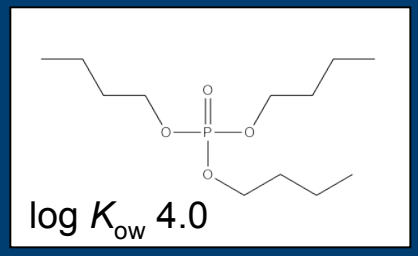
Toxic? We don't know (Oxychem only)

Analytical methods established? Yes

Phosphate-based Flame Retardants: Widely Used?

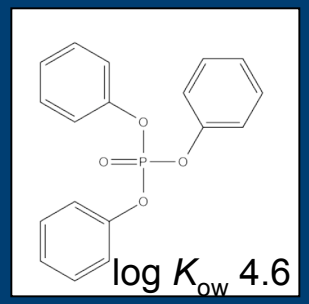
Tributylphosphate (TBP)

- Several applications including use as a solvent, plasticizer, antifoaming agent, and flame retardant in polyurethane foams
- High production volume chemical
- Replacement for Penta-BDE?



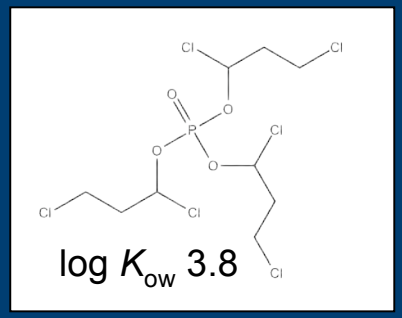
Triphenylphosphate (TPP)

- Several applications including use as a flame retardant in video monitors and as a plasticizer in pesticides, gasoline additives, synthetic motor oils, and roofing paper
- High production volume chemical



Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)

- Primarily used in polyurethane foams
- In 1994, listed as high production volume chemical (US EPA)
- Replacement for Penta-BDE (EPA website; Polyurethane Foam Association)



Phosphate-based Flame Retardants

Tributylphosphate (TBP)

- 5 - 145 ng/L in 1999/2000 SF Bay water, ND in suspended particles, sediments, bivalves
- >10,000 times less than the 48 hour LC50 for *Daphnia magna* (1580 µg/L)
- Chronic toxicity data for aquatic species are not available

Triphenylphosphate (TPP)

- 24 and 56 ng/L (2/4 sites) in 1999/2000 SF Bay water, ND in suspended particles, sediments, bivalves
- >2,000 times less than the 48 hour LC50 for *Daphnia magna* (100 µg/L)
- 2002/2003 RMP Status and Trends study : in bivalves only, 0.55 – 378 ng/g dry weight
- Chronic toxicity data for aquatic species are not available

Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)

- 5 - 76 ng/L in 1999/2000 SF Bay water, ND in suspended particles, sediments, bivalves
- Orders of magnitude less than NOEC for rainbow trout (560 µg/L) and Daphnia (1800 µg/L)
- Chronic toxicity data for aquatic species are not available
- Mammalian toxicity
- Not quantified in bivalves in 2002/2003 RMP Status and Trends study

Chlorinated and Brominated Tris propylphosphates

The Pajama Controversy in 1970s (Arlene Blum et al.):

- Both cause DNA mutations
- Brominated Tris is a potent carcinogen
- Consumer Product Safety Commission banned use in children's sleepwear

Blum: Op-Ed in NY Times (Nov. 2006)

- Chlorinated Tris is currently used in CA in furniture foam, considering use in bedding material.
- 2nd most widely used flame retardant in CA
- It's cheap
- It's toxic to mammals (causes cancer, sterility, thyroid disorders, endocrine disruption)
- Federal Safety Commission is developing a national standard for fire-retardant furniture

CA Assembly Bill 706: Would ban brominated and chlorinated flame retardants (effective 2010)

Which compounds are in commercial 'Chlorinated Tris'?

Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)?
Tris(3-chloropropyl)phosphate?
Tris(2,3-dichloropropyl)phosphate?

	Widely Used	Bioaccumulative	Persistent	Toxic	Methods Available
Hexabromocyclododecane (HBCD)	●	●	●		●
Tetrabromobisphenol A (TBBPA)	●	●	◉	●	●
Decabromodiphenyl-ethane (DBDPE)	?	◉ ?	● ?	?	●
1,2-Bis(2,4,6 tribromo phenoxy) ethane (BTBPE)	?	◉ ?	● ?	?	●
Pentabromoethyl-benzene (PBEB)	?	◉ ?	● ?	?	●
Dechlorane Plus (DP)	?	◉ ?	● ?	?	●
Tributylphosphate (TBP)	?	○ ?	○ ?	?	◉
Triphenylphosphate (TPP)	?	◉ ?	○ ?	?	◉
Tris(1,3-dichloro-2-propyl)phosphate (TDCPP) and others in 'Tris'	?	○ ?	○ ?	?	◉

● High ranking for criterion ◉ Medium ranking for criterion ○ Low ranking for criterion