

2008 Pilot Study: Alternative Flame Retardants in San Francisco Bay

Susan Klosterhaus, SFEI

Heather Stapleton, Duke University

Alex Konstantinov, Wellington Laboratories

Francois Rodigari, East Bay Municipal Utility District

Saskia van Bergen, East Bay Municipal Utility District

Aaron Peck, Skidaway Institute of Oceanography

Denise Greig, The Marine Mammal Center

Emerging Contaminant Workgroup Meeting, April 3rd 2008



Why do we 'need' flame retardants?

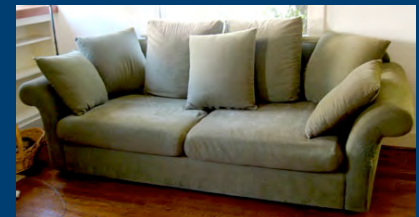
CA Furniture Flammability Standard (TB 117, 1975)

National Mattress Flammability Standard (July 2007)

National Furniture Flammability Standard (2007 drafts)

IEC Open Flame Standard for Electronics (pending)

CA Bed Clothing Flammability Standard (TB604, pending)



Draft data – do not cite or quote

Regulatory Status of PBDEs

PBDE Mixture	Primary Application	Regulatory Status
Penta-BDE	Polyurethane Foam	Banned in EU (2004) Production ceased (2004) Restricted in CA (2006)
Octa-BDE	Thermoplastics	Banned in EU (2004) Production ceased (2004) Restricted in CA (2006)
Deca-BDE	Thermoplastics	Banned in Sweden, WA, ME (2006-2007) Banned in Europe (April 2008) No other restrictions in US

Alternatives are inevitable...

Chemical	2002 Prod. Vol. (lbs)	Accumulates	Persists	Eco Tox	Mam Tox
Tris(1,3-dichloro-2-propyl)phosphate (TDCPP)	10-50M	?	M?	M	H
Triphenylphosphate (TPP)	10-50M	H?	L?	H	?
Bis(2-ethylhexyl) tetrabromophthalate	1-10M	?	?	H?	?
Tetrabromobisphenol A (TBBPA)	100-500M	L	M	H	H
Hexabromocyclododecane (HBCD)	10-500K	H	H	H	H
Decabromodiphenylethane (DBDPE)	?	L	H?	?	?
1,2-Bis(2,4,6-tribromophenoxy)ethane (BTBPE)	1-10M	H?	M?	?	?
Pentabromoethylbenzene (PBEB)	0	M?	M?	?	?
Dechlorane Plus (DP)	1-10M	L	H	?	?

Draft data – do not cite or quote

Chemicals Used to Meet CA Furniture Flammability Standard

Firemaster 550[®]

- Triphenyl phosphate
- 2 brominated compounds (proprietary)

Chlorinated 'tris'

- Tris(1,3-dichloro-2-propyl)phosphate
- Phased out of use in children's sleepwear in 1970s due to toxicity

**Another Flame Retardant, Tris-(1,3-Dichloro-2-Propyl)-
Phosphate, and Its Expected Metabolites Are Mutagens**

**Gold, Blum, and Ames
Science 200:785-787 (1978)**

What's in my couch?



My couch, purchased
June 2007

4% bromine



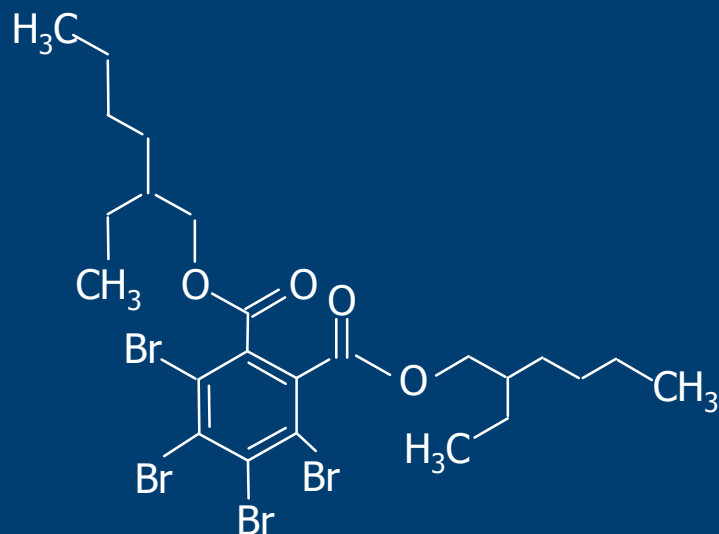
Arlene Blum with XRF

(Photo: Barry Bergman, UC Berkeley News)

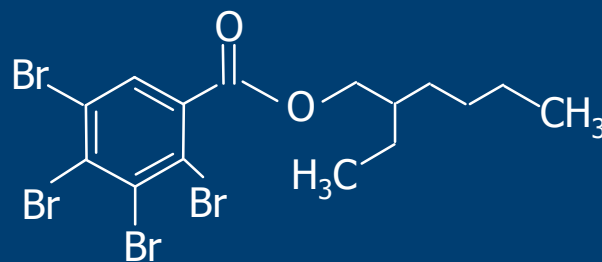
Draft data – do not cite or quote

Brominated compounds in Firemaster[®] 550

Alex Konstantinov, Wellington Laboratories, Guelph, Ontario
Heather Stapleton, Duke University



Di(2-ethylhexyl)
Tetrabromophthalate
(TBPH)

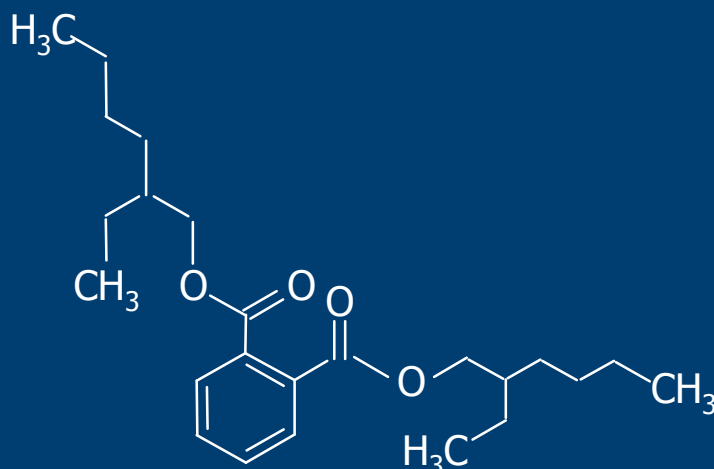


2-ethylhexyl
2,3,4,5-tetrabromobenzoate
(TBBZ)

Detected in Boston house dust (Stapleton et al. 2008)

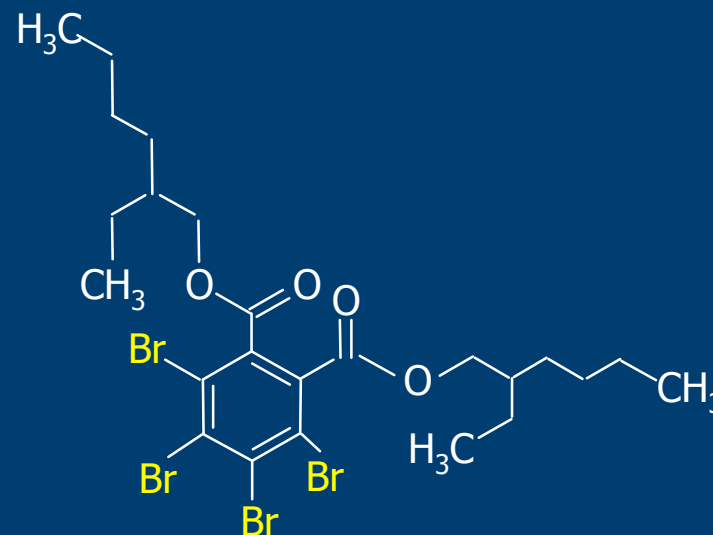
Draft data – do not cite or quote

TBPH is the brominated analogue of DEHP



Di(2-ethylhexyl) phthalate
(DEHP)

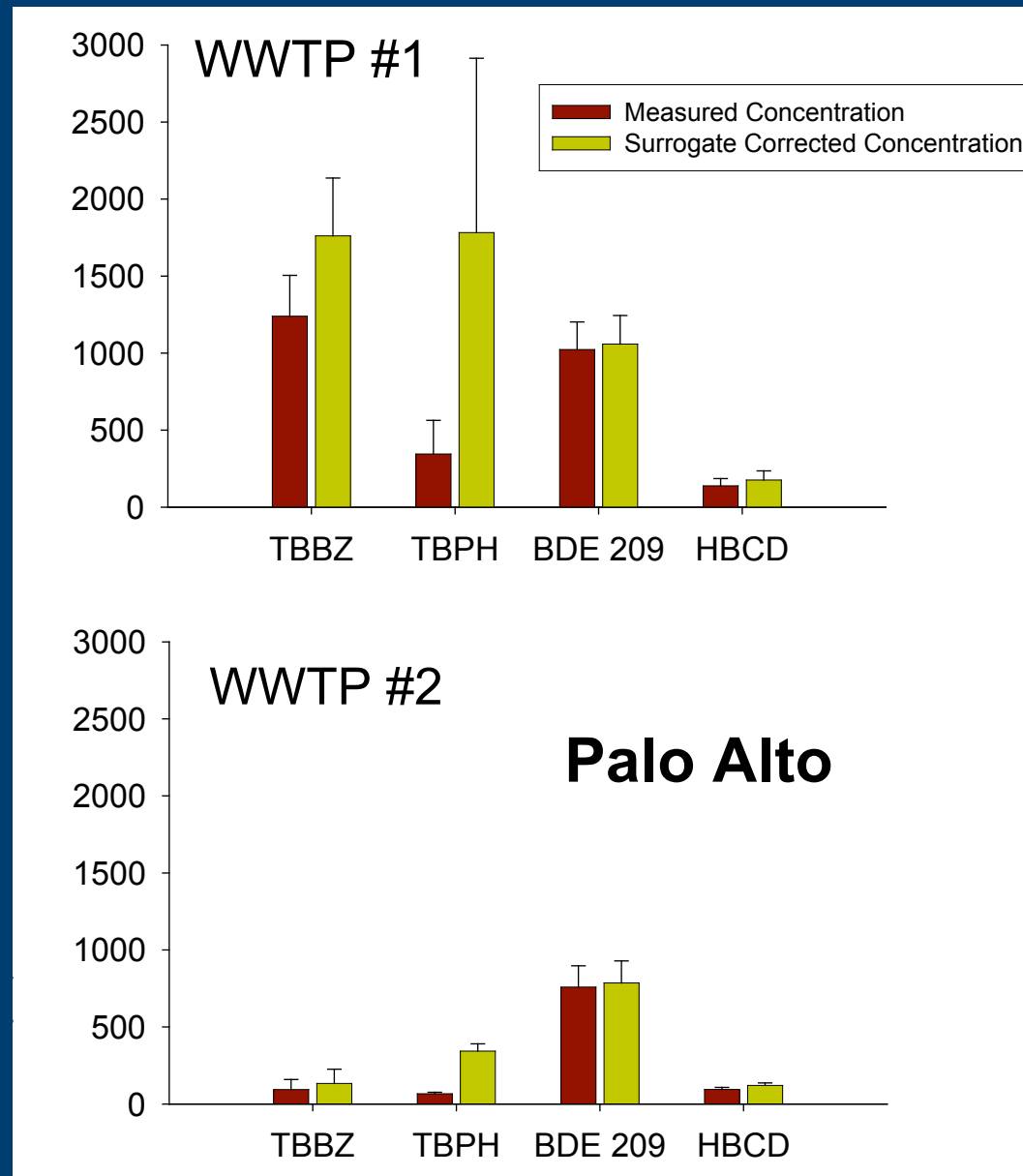
- $\log K_{ow}$ 4.9
- Reproductive, developmental toxin; carcinogen
- Bioaccumulative, persistent



Di(2-ethylhexyl) tetrabromophthalate
(TBPH)

- $\log K_{ow}$ 12 (EPIWIN estimate)
- Toxic?
- Bioaccumulative?
- Persistent?

TBPH and TBBZ in SF Bay Biosolids



Draft data – do not cite or quote

Chemical Analysis Plan (Summer 2008)

Analyze bioaccumulative compounds in archived samples:

- Harbor seal blubber (~10 samples; various sites; 2007-2008)
- Croaker, surfperch (~10 samples; various sites; 2006)
- Cormorant eggs (6 samples; 2 composites @ 3 sites; 2006)
- Sediment (~10 samples; South Bay, Central Bay; 2007)

Analyze non-bioaccumulative compounds in surface water:

- Lower South Bay
- 1L grab samples (10 samples; 5 sites; 2 replicates/site)

Bioaccumulative target analytes

- H. Stapleton: PBDEs
Decabromodiphenylethane (DBDPE)
1,2-Bis(2,4,6 tribromophenoxy) ethane (BTBPE)
Pentabromoethylbenzene (PBEB)
Hexabromobenzene (HBB)
Dechlorane Plus®
Di(2-ethylhexyl) tetrabromophthalate (TBPH)
2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBBZ)
- A. Peck: Hexabromocyclododecane isomers (HBCD)
Tetrabromobisphenol-A (TBBPA)
- Others?
1,2,3,4,5-pentabromo-6-chloro- cyclohexane
1,2-dibromo-4-(1,2-dibromoethyl)-cyclohexane
tetrabromodichloro- cyclohexane
Octabromoindane*
1,2,4,5-tetrabromo-3,6-bis(pentabromophenoxy)-benzene*

Surface water target analytes

Tributylphosphate

Triphenylphosphate

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

Tris(2-chloroethyl) phosphate

Tris(2-chloro, 1-methyl ethyl) phosphate

Tri(2-butoxyethyl)phosphate



Chlorinated Paraffins (polychlorinated n-alkanes)

C10 to C30; 30 to 70% Cl- by mass

Widely Used

- High temperature lubricants, cutting fluids
- Plasticizers, flame retardants in plastics, additives in sealants, adhesives, paints, rubber
- Unrestricted use; largest group of high molecular weight chlorinated hydrocarbons in commercial use

Bioaccumulative, persistent, toxic, long-range transport

- Ubiquitous
- Environmental fate, transport unknown

Draft data – do not cite or quote

Chlorinated Paraffins (polychlorinated n-alkanes)

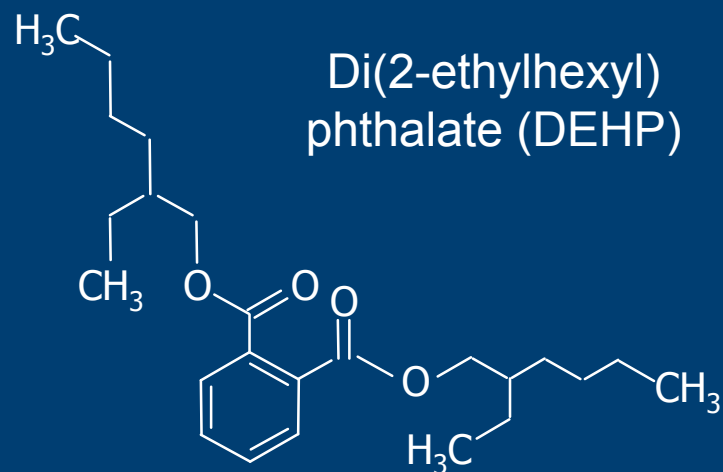
Chemical analysis is challenging

Concern for the Bay?

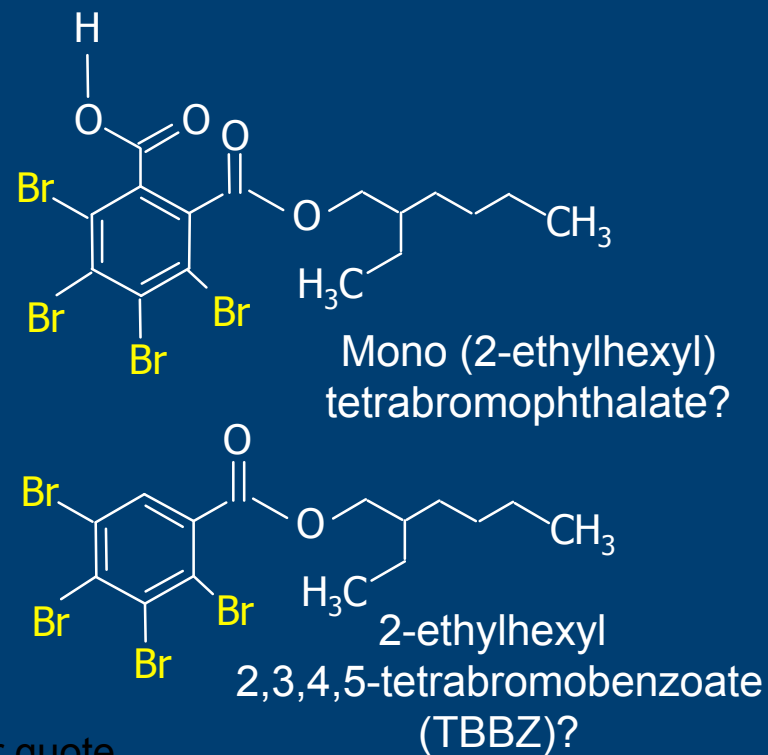
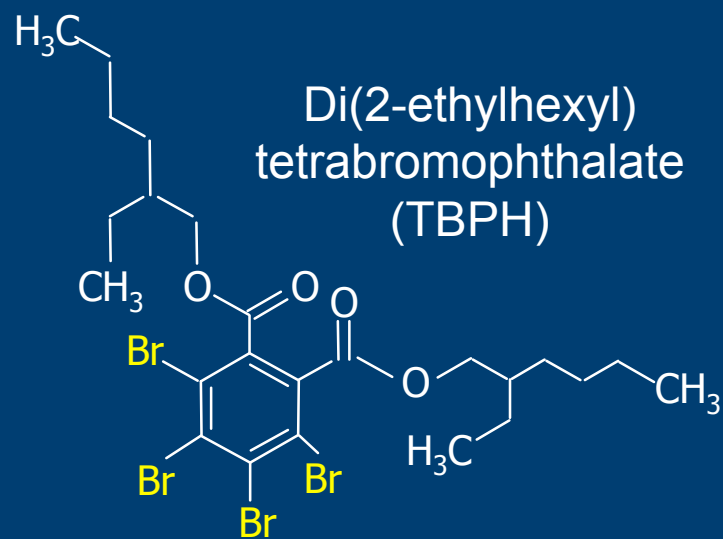
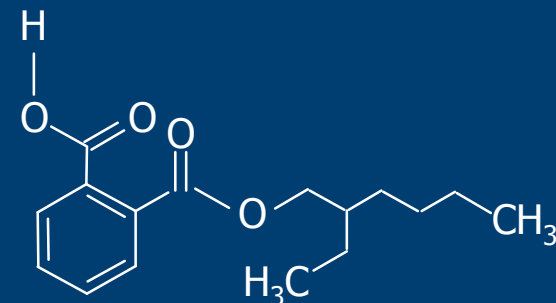
- Urban sources
- Analysis of 2006 sport fish, harbor seal blubber, cormorant eggs (Gregg Tomy, pro bono)
- Results expected April 2008



Fate of di(2-ethylhexyl) tetrabromophthalate



Mono(2-ethylhexyl) phthalate (MEHP)



Tetrabromophthalic acid?

Draft data – do not cite or quote