Polybrominated Diphenyethers (PBDEs): Lessons Learned about Flame Retardants
Anthropogenic Biomes of the World

Urban & dense settlements
- 11 Urban
- 12 Dense settlements

Villages
- 21 Rice villages
- 22 Irrigated villages
- 23 Cropped & pastoral villages
- 24 Pastoral villages
- 25 Rainfed villages
- 26 Rainfed mosaic *villages

Croplands
- 31 Residential irrigated cropland
- 32 Residential rainfed mosaic
- 33 Populated irrigated cropland
- 34 Populated rainfed cropland
- 35 Remote croplands

Rangelands
- 41 Residential rangelands
- 42 Populated rangelands
- 43 Remote rangelands

Forestied
- 51 Populated forests
- 52 Remote forests

Wildlands
- 61 Wild forests
- 62 Sparse trees
- 63 Barren

*Mosaic: >25% tree cover mixed with > 25% pasture and/or cropland

Ellis & Ramankutty, 2008
Anthropogenic biomes

A new framework for ecology

- Only 22% of land and 11% of NPP are **wild**

- **Nature is now embedded within human systems**
  - It is no longer possible to conserve nature by avoiding human interactions

- Human interactions with the biosphere go far beyond a single dimension of impact or domination.

Natural ecosystems with humans disturbing them”, or “Human systems, with natural ecosystems embedded within them”. 
What does this mean?

• Human population density and distribution is of sufficient magnitude that product use by consumers can influence public and environmental health on a global basis.
• Green chemistry must play a key role in making safer consumer products.
Late 1960’s: Polymer Proliferation

- Fabrics
- ABS resins
- Wire & cable insulation
- Carpet
- Polyurethane foams
- TVs
- Mattresses
- Polyamides
- Vinyl
- Polystyrene
- Textiles
- Cushions

![Flammable warning sign]
Flame retardants

- All plastics and fabric burns
- Fire kills > 3,000 and injures > 20,000 annually
- $11 billion in damage
- Used in many consumer products
- USA is the leading user
- Quest for greater consumer product safety??
Safety Concerns

• The government wants you to be safe
• If you are injured, the lawyers will sue
• We need flame retardants to make you safe
• All clothing, upholstery, drapes, bedding, electronic equipment are treated.
Flame Retardant Market

Market Size: $2.4 billion

- Key FR Chemistries Leadership
  - #1 Brominated FR Marketer In World
  - #1 Mineral FR Marketer In World
  - #2/3 Phosphorus FR Marketer in World

- Innovations In 1990’s
  - Stream Of Successful New FR’s
  - Widest FR Technical Service Breadth (Halogen, Phos. Mineral)

- Best Cost/Quality/Service In Industry
  - Major FR Quality Upgrades Introduced
  - Multiple Customer Awards
  - Bromine Cost Improvements – Jordan, USA
What Type of Products are Treated with Flame Retardants in Your Home?

- Nursing Pillow
- Sleep Positioners and PJs
Overview of Combustion

"pyrolysis + Heat" leads to "gas mixture ignites Air"

Polymer $\rightarrow$ combustibles $\rightarrow$ flame combustion $\rightarrow$ Gases, liquids, char products

exothermic thermal feedback
Flame retardants

physical and chemical actions

Coating, cooling, Dilution

Phosphorous salts, Antimony oxides, Aluminum compounds

Quenching chain reactions in the flame

Brominated Flame Retardants (BFRs)
Brominated Tris Flame Retardant
Tris (2,3-dibromopropyl) phosphate

- Up to 10% of the weight of fabric
- Not covalently bonded to fabric
- Absorbed in children’s bodies; metabolite found in their urine
Flame-Retardant Additives as Possible Cancer Hazards

The main flame retardant in children's pajamas is a mutagen and should not be used.

Arlene Blum and Bruce N. Ames

Thousands of chemicals to which humans have been exposed have been introduced into the environment without adequate toxicological testing.

Some chemical flame retardants provide a good example of a technological innovation where adverse environmental effects may outweigh some of the benefits.

Until recently, little attention was paid to the long-term biological effects of these flame-retardant compounds. The main organic chemicals used in flame retardants contain bromine or chlorine or they are phosphate esters. Some have chemical structures (discussed below) that are closely related to compounds known to cause cancer or to be toxic to animals. Several compounds previously used as flame retardants have been shown to be teratogenic, carcinogenic, mutagenic, or highly toxic (4).
PBDEs have had a lot of publicity:
found in breast milk, potential human thyroid hormone disruptor and developmental neurotoxicant.

BFRs do not bind chemically to polymers in textiles or plastics, they can leach out or evaporate from flame retarded products.
Structure of PBDEs

Polybrominated Diphenyl Ethers

$\text{Br}_x \xrightarrow{O} \text{Br}_y$

$X$ & $Y$ are number of Bromine atoms e.g. decaPBDE has 10 Bromines

PCBs
Uses of PBDEs

- Tetra and Penta PBDE (congeners 47 and 99)
  - Foam in furniture, mattresses, automobile seats
    8,000 tons/year worldwide; 95% used in the U.S.
- Hexa-Hepta PBDE (congeners 153, 183)
  - Plastics in electronics
    4,000 tons/year worldwide; 40% used in U.S.
- DecaBDE (209)
  - Plastics in electronics, wire/cable insulation, textiles
    49 million pounds of DecaPBDE added to consumer products in North America in 2001
- PBDEs are added to the plastic and are not part of the polymer. This makes them easily released to the environment.

(industry data for 2001)
Health Effects of PBDEs

- **PBT** (Persistent Bioaccumulative Toxicant)
- Limited human data (more in the last 3 yrs)
- Animals studies indicate
  - Effects on thyroid hormone levels
  - Neurobehavioral toxicity
    - Effects development - alters Behavior
    - Impairs memory and learning
  - Delays sexual development
PBDEs Look like Thyroid Hormones

Penta-BDE 99

Thyroid hormone

Thyroxine

- Penta and octa-BDE mixtures were banned in 2004 in Europe and CA after 30 years of use
- Deca-BDE still used today because it’s considered safe and inert. Recently banned in Michigan
PBDE metabolites likely mimic Thyroid Hormone

Example of Tetra-bromo-BDE hydroxyl metabolite

Thyroxine (T4)
PBDE Environmental Cycle

Volatilization Dust

Atmospheric Deposition

Bioaccumulation

Bioconcentration
Human Exposure


- Toddlers have three times the levels of their mothers. [http://www.ewg.org/reports/pbdesintoddlers](http://www.ewg.org/reports/pbdesintoddlers)

- Californians have higher levels in their house dust and body fluids than residents of other states. Kellyn S. Betts, Environmental Health Perspectives 116, A202 - 208, 2008

![PBDE fire retardant concentration in household dust](source)

Trends of Toxin Levels

Schecter A. et al. JOEM (2005), 47(3):199-211
PBDEs Increasing in North America 1970 - 2005

Doubling time~2-5 years

Figure: Shaw and Kannan Rev Env Health 2009

Serum PBDEs levels in pregnant women from three study populations

Zota et al., 2011
After the ban

Zota et al., 2013
Early Prenatal | Mid-Prenatal | Late Prenatal | Postnatal
---|---|---|---
Central nervous system (3wks - 20 years)
Ear (4-20 wks)
Kidneys (4-40 wks)
Heart (3-8)
Limbs (4-8wks)
Immune system (8-40 wks; competence & memory birth-10yrs)
Skeleton (1-12 wks)
Lungs (3-40 wks; alveoli birth-10yrs)
Reproductive system (7-40wks; maturation in puberty)

Developmental Origins of Disease: Developmental Stressors Lead to Disease Throughout Life

Gestation  |  Childhood  |  Puberty  |  Reproductive Life  |  Middle Life  |  Later Life

Environmental Exposures

Gestation, Childhood, Puberty, Reproductive Life, Middle Life, Later Life
Polybrominated Diphenyl Ethers

- Cryptorchidism
  - Main et al, 2007

- Reproductive Hormone Effects
  - Meeker et al, 2009: Decrease in Androgens and LH; Increase in FSH and Inhibin
  - Meijer et al, 2008: Decrease in Testosterone

- Reproductive Effects
  - Eskenazi et al, 2009: Low Birth Weight & Altered Behaviors
  - Harley et al, 2010: Increased time to pregnancy
  - Associations between PBDE exposure at birth and neurodevelopment measures in children (Roze et al., 2009; Herbstman et al., 2010);

- Neurological Effects
  - Herbstman et al, 2010: Decreased IQ

- Decreased Sperm Quality
  - Akutse et al, 2008

- Diabetes
  - Lim et al, 2008
  - Turyk et al, 2009 (only in hypothyroid subjects)

- Thyroid Homeostasis
  - Stapleton et al, 2011: T4 elevated during pregnancy
  - Chevrier et al, 2010: TSH elevated in pregnancy
  - Meeker et al, 2009: elevated T4 & TBG
  - Dallaire et al, 2009: Elevated T3 from BDE47
  - Eskenzai et al, 2009: Low TSH
Children’s Exposure to Flame Retardants

- Children are spending more time indoors
- Indoor environments are often more polluted than outdoor environments (PBDEs in Dust >>>>> PBDEs in Soils)
- Children have a high number of hand-to-mouth contacts
- Children are physically in contact with many FR treated products

PCBs: Inadequate Margin of Safety

PCB BLOOD LEVELS (ppb)

REPORTED HUMAN EXPOSURES

Great Lakes fish eaters 15
Great Lakes non-fish eaters 10
Midwest and Northeast US women
Michigan mothers
North Carolina mothers
Wisconsin women
Dutch mothers

REPORTED HEALTH EFFECTS IN OFFSPRING

Decreased reflexes, memory, IQ, attention, & visual discrimination

Decreased attention, cognitive ability, high level play, & psychomotor development;
Increased withdrawn/depressed, increased hyperactivity.
Association Between PBDEs in Pregnant Women and Thyroxine (T4)

**Same trend observed for total T4 \((r_s = 0.20; p<0.05)\)**
Do Flame Retardants Make Us Safe

• Government says they are necessary
• California says not so fast, may be some risk of fire is acceptable
• Industry says - Keep the regulations in place! “The reason people feel safe in their homes today is because fire retardants have worked for many years and improved safety.”
Fish Analysis with GC/MS
Total PBDE Congeners (±SE) in Muskegon Lake Fish

- Banded Killifish
- Bluntnose Minnow
- Round Goby
- Spottail Shiner
- Yellow Perch
- Largemouth Bass
- Northern Pike
- Walleye
- Common Carp
Mean Concentrations (±SE) of PBDE Congeners in Yellow Perch Collected from the Six Study Locations (2006).
Watershed Influence
Chemical Fate and Transport
Bioaccumulation

- Increased accumulation of chemicals in the food chain
- Not a function of active transport
- Passive diffusion and dietary intake
The curved lamellae form a basket-like sieve through which the water flows.

Cross section A...B

Primary lamella

Secondary lamellae

Blood spaces

Epithelial cells

Pillar cells

Blood flow

Water flow

Longitudinal section of secondary lamella (simplified)
Octanol-water partition coefficient (Kow)

- Kow = concentration in octanol / concentration in water
- The higher the Kow, the more hydrophobic (water hating) of the compounds. The more hydrophobic the compound, the lower the aqueous solubility of the compounds. This term is inversely proportion to the water solubility and indicates how “hydrophobic” a compound is.
- Very important for determining whether a compound will bioaccumulate.
- Example, salad dressing (oil and vinegar)
Octanol-water partition coefficient

- The solubility in water
  - generally decreases as the number of carbon atoms increases.
  - decreases as the proportion of chlorine to hydrogen increases.
- The "octanol-water partition coefficient," $K_{ow}$, is a convenient quantitative measure of the lipophilicity of a solute.

- $K_{ow} = \frac{\text{concentration of solute in octanol}}{\text{concentration of solute in water}}$
- DDT ($10^6$), polychlorinated biphenyls (PCBs) dioxins, etc.

### Table 7-3: Selected Data for Some Pesticides

<table>
<thead>
<tr>
<th>Pesticide</th>
<th>Solubility in $H_2O$ (ppm)</th>
<th>$\log K_{ow}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCB</td>
<td>0.0062</td>
<td>5.5 – 6.2</td>
</tr>
<tr>
<td>DDT</td>
<td>0.0034</td>
<td>6.2</td>
</tr>
<tr>
<td>Toxaphene</td>
<td>3</td>
<td>5.3</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>0.1</td>
<td>6.2</td>
</tr>
<tr>
<td>Mirex</td>
<td>0.20</td>
<td>6.9 – 7.5</td>
</tr>
<tr>
<td>Malathion</td>
<td>145</td>
<td>2.9</td>
</tr>
<tr>
<td>Parathion</td>
<td>24</td>
<td>3.8</td>
</tr>
<tr>
<td>Atrazine</td>
<td>35 – 70</td>
<td>2.2 – 2.7</td>
</tr>
</tbody>
</table>

Bioaccumulation

- The Bioaccumulation Factor for organic compounds in aquatic organisms is related to Kow (Mackay, 1982)
- \( \text{Log BF} = \log \text{Kow} - 1.32 \)
The basis of a cell membrane is a lipid bilayer that seals off the cell from its environment.

- A lipid bilayer consists of two layers of phospholipids.
- Each phospholipid consists of a polar head (blue) and 2 hydrophobic tails (ocre).
- The hydrophobic tails group together to form the core of the bilayer.
- The polar heads face the aqueous environments inside and outside the cell.
- Only lipophilic and small polar molecules can pass the lipid bilayer freely.
BIOCONCENTRATION FACTOR AS A FUNCTION OF THE OCTANOL WATER PARTITIONING COEFFICIENT

When log $K_{ow}$ is between 2 and 6, $K_b = 0.04 K_{ow}$
The Future

- Dow Brominated polystyrene
- Dow Brominated Butadiene/Vinyl Aromatic Copolymers
The Future

• Caseins can be exploited as new green flame retardants for cotton fabrics because of their high phosphorus content
  https://www.sciencenews.org/article/milk-protein-potential-flame-retardant

• PVS (polyvinyl sulfoinic acid sodium salt) and chitosan
  https://www.sciencenews.org/article/flame-quencher-offers-less-toxic-approach-fighting-fire