Brominated Flame Retardants – Another Class of Emerging Contaminants

Remediation Technologies Symposium 2016

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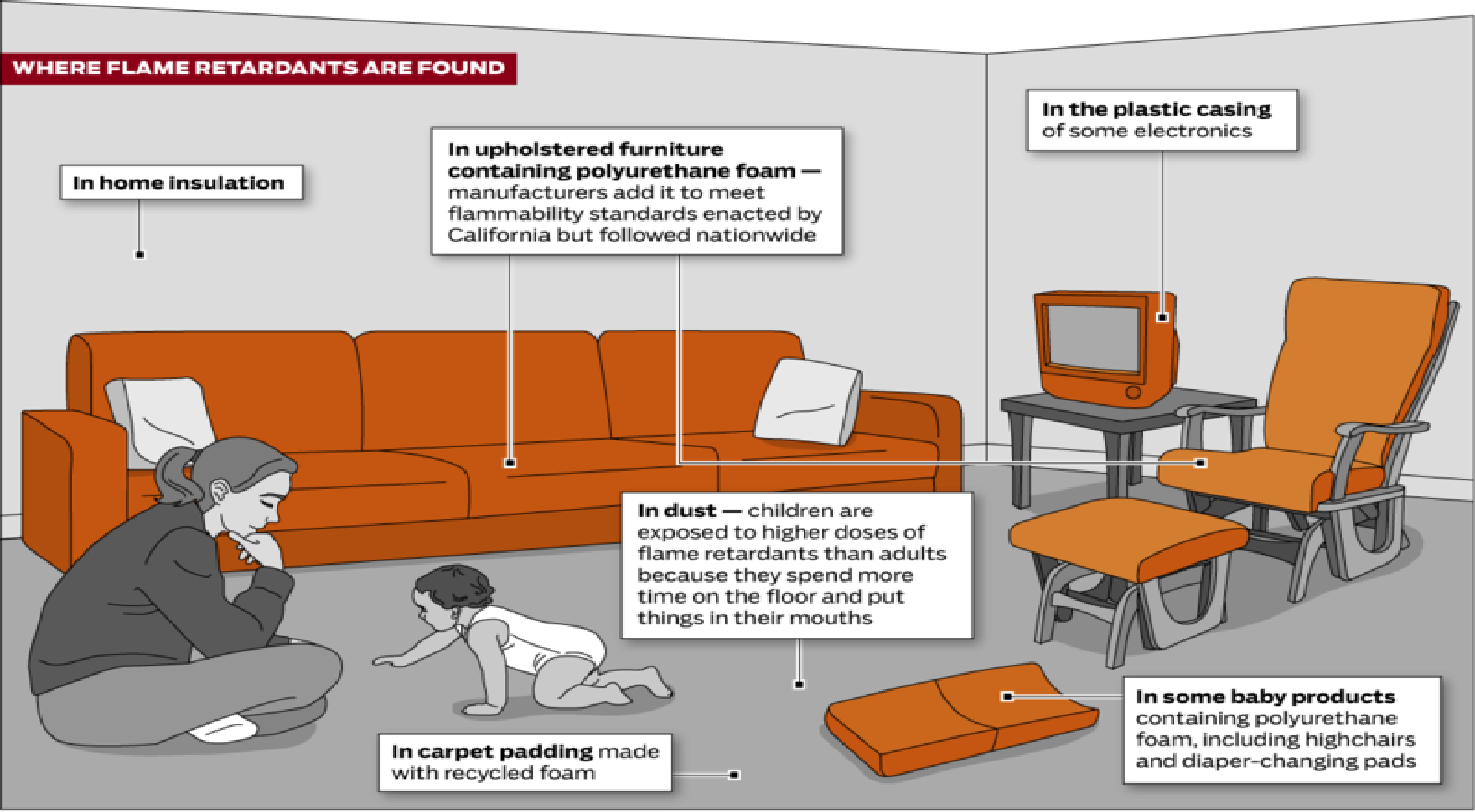


SOURCES: EPA, Tribune reporting

KATIE NIELAND/TRIBUNE

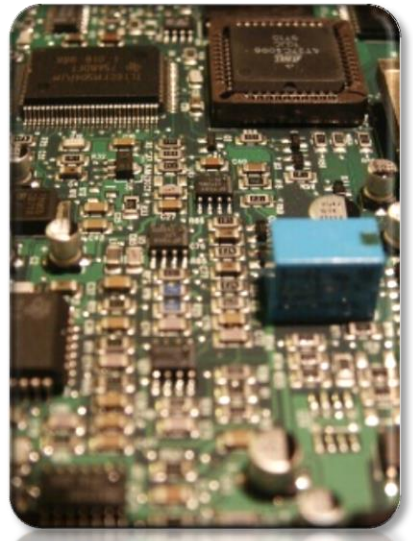
Agenda

- Why Should We Care?
- Brominated Flame Retardants (BFRs)
- Polybrominated Diphenyl Ethers (PBDEs)
- Toxicology and Environmental Issues
- What Can WEEE Do: End-of-Life Management
- Regulations
- Conclusions

Why Should We Care?

- Persistent, bioaccumulative, long-range transport (PBT), lipophilic
- Endocrine disrupting chemicals (EDCs)
- Concentrations in environment increasing since 1970s
- Leach out of products; end up in sewage
- Find their way into food chain and human population
- End-of-life disposal implications

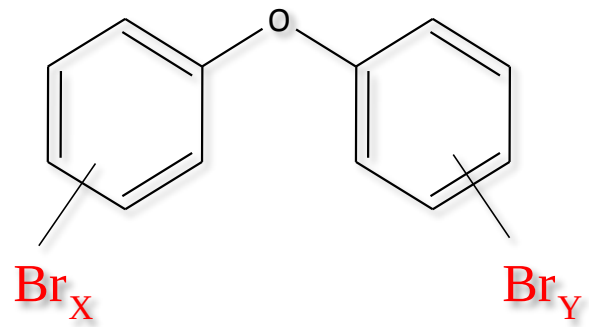
Brominated Flame Retardants (BFRs)



- ~70 different commercial products
- Applied to ~2.5 million tonnes polymers/year
- Global consumption > 300,000 tonnes/year (includes > 56,000 tonnes in North America)
- Added to polymers to enhance flame retardancy *(ABS, HIPS, PS, PC)
- Thermally stable, low cost, readily available
- Human exposure thru: diet, ingestion of indoor dust, inhalation of indoor air
- Detected from Arctic to Antarctic

*ABS: acrylonitrile butadiene styrene; HIPS: high impact polystyrene; PS: polystyrene: PC: polycarbonate

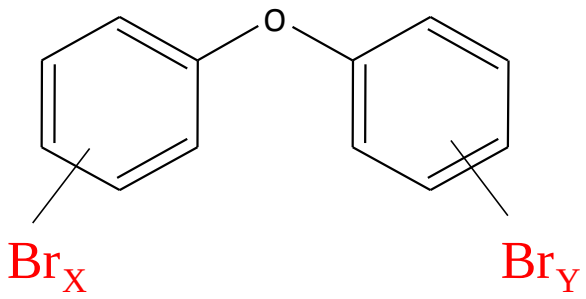
Brominated Flame Retardants (BFRs):
Polybrominated Diphenyl Ethers (PBDEs)



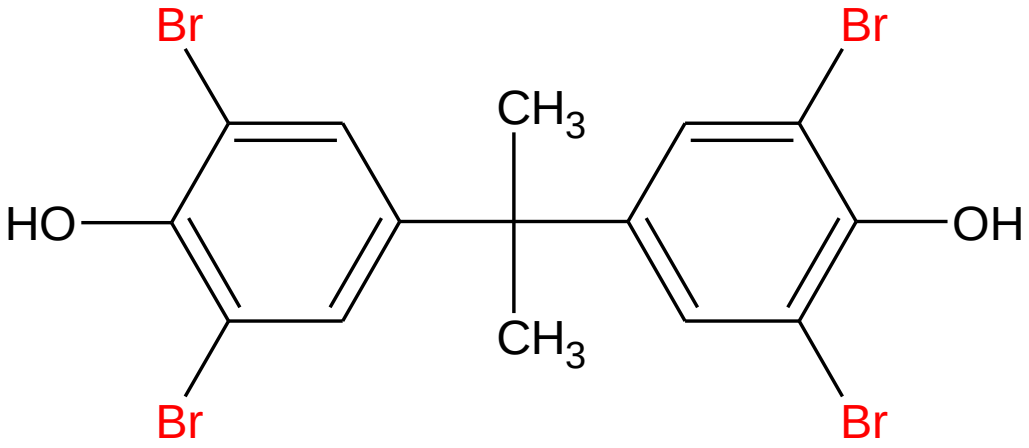
Polybrominated diphenyl ethers (PBDEs)

- Electric and electronic equipment (EEE), carpets, polyurethane foam in sofas, vehicle interiors, cotton & synthetic fibre for clothing, carpets, curtains, sofas
  - ➢ Additive or reactive flame retardant
  - ➢ Persistent, bioaccumulative, long range transport (LRT)
  - ➢ Added to products to reduce ignition

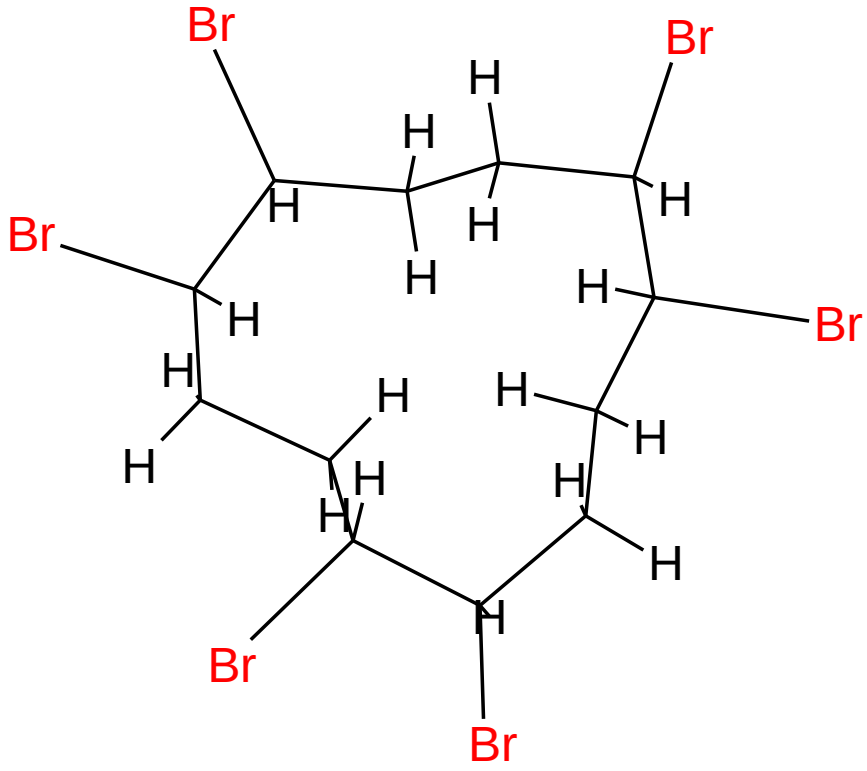
Brominated Flame Retardants



Polybrominated diphenyl ethers (PBDEs)

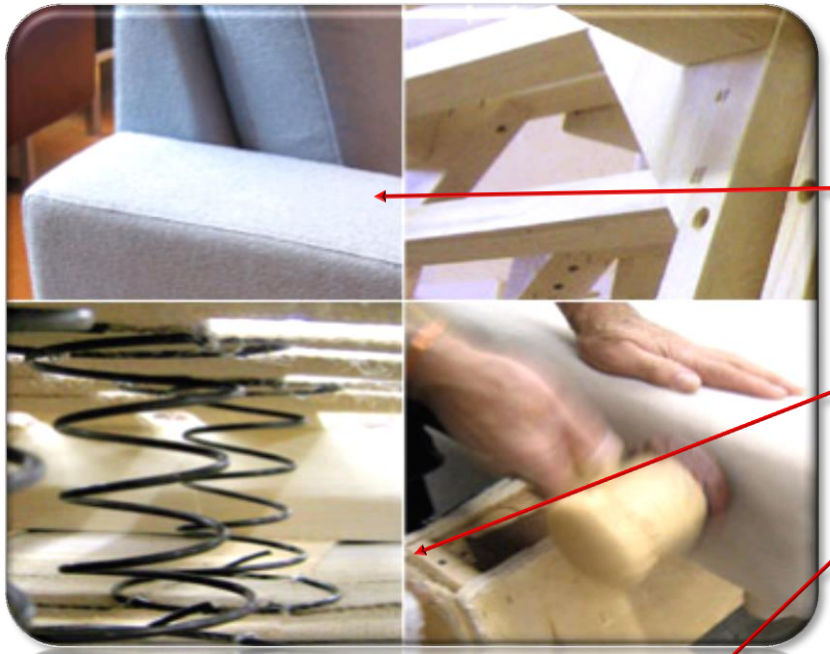


Tetrabromobisphenol A (TBBPA)



Hexabromocyclododecane (HBCD)

We have BFRs in…

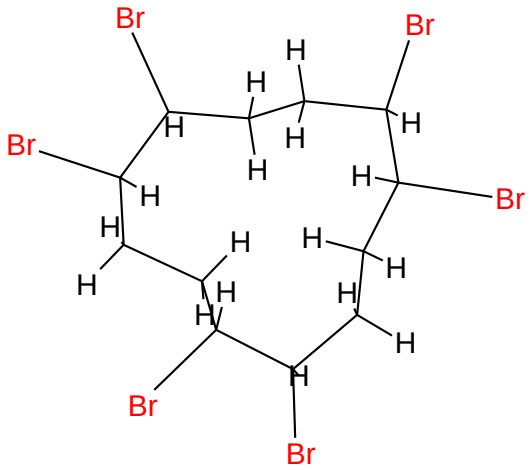


- upholstery
- mattresses
- electronics
- white goods
- vehicle parts
- auto shredder residue

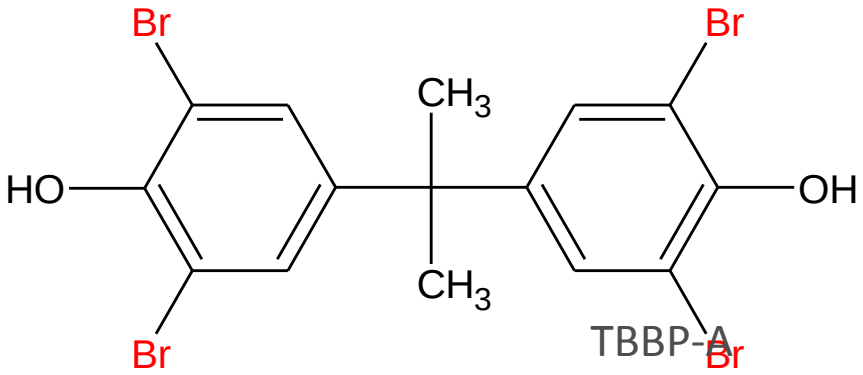
Source: Alex Stone, WA Department of Ecology

Brominated Flame Retardants (BFRs): HBCD and TBBP-A

- Hexabromocyclododecane (HBCD)
  - Thermal insulation in buildings (PS or polystyrene)
  - Backcoating of textiles in upholstery (extruded PS, foam)
  - Electric & electronic equipment (EEE) (High impact PS)
  - High bioaccumulation potential, additive flame retardant
- TBBP-A
  - Uses: laminates for printed circuit boards in electronics; additive in ABS (acrylonitrile butadiene styrene) polymer; intermediate with other BFRs
  - Short half life

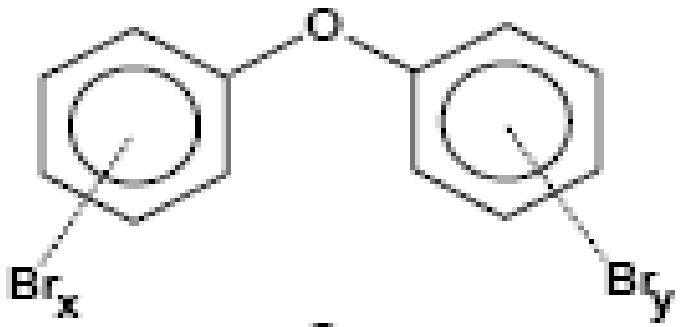


HBCD

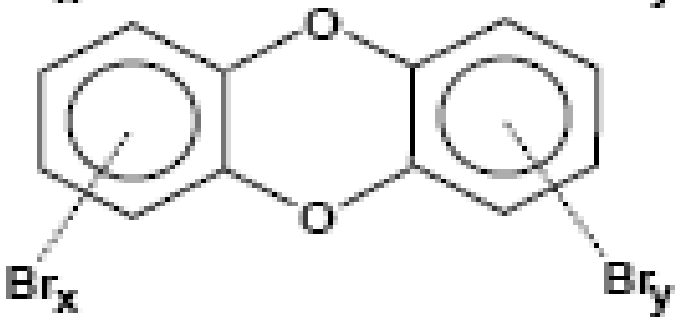


TBBP-A

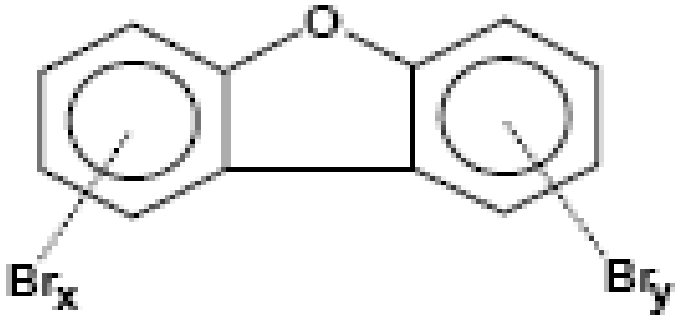
Organic Chemistry 101



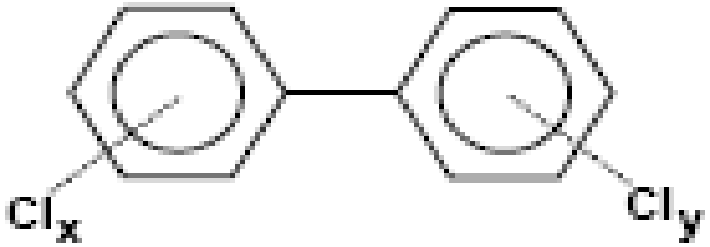
Polybrominated Diphenyl Ether (PBDEs)



Polybrominated Dibenzo-p-dioxin (Dioxin)

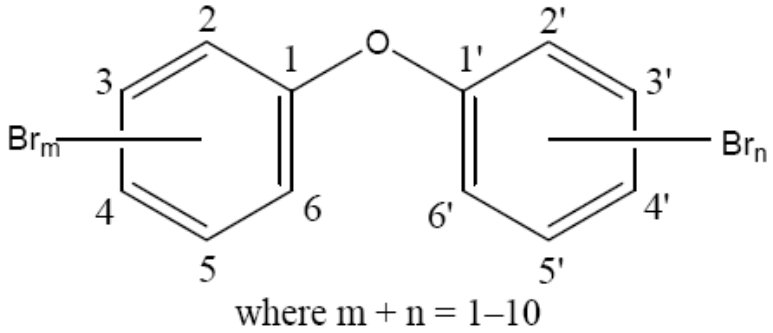


Polybrominated Dibenzo-furan (Furan)



Polychlorinated Biphenyl (PCBs)

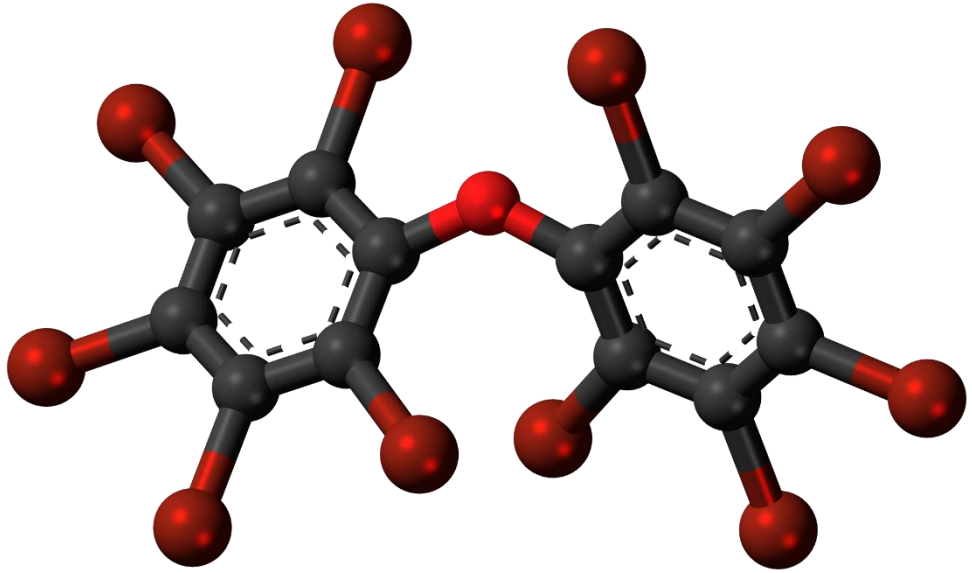
PBDEs



- PBDEs *added* to products to reduce ignition
- Highly toxic, persistent; endocrine-disrupting chemicals, with potential for long-range transport
- PBDE *levels* in environment *increasing*; widespread in the world, including Arctic and Antarctic
- Solid waste including e-waste *(~85%)* ends up in landfills
- Expensive and *challenging* to analyse
- Persistent organic pollutants (POPs), added to Stockholm Convention (2009)

Deca-BDE (BDE-209) – the most popular

- Used in polypropylene (PP) and polyethylene (PE) for wire and cables and electronic equipment
- Legacy spare parts in auto industry (i.e. powertrain and under-hood applications, fuel hoses and tanks, air bag ignition cables, seat covers, etc.)
- Huge stockpile leads to more mobility, toxicity, bioaccumulation and potential to become chronic input to aquatic systems
- Bioaccumulation/biomagnification and debromination to lower brominated congeners



Sources of PBDEs to the Environment

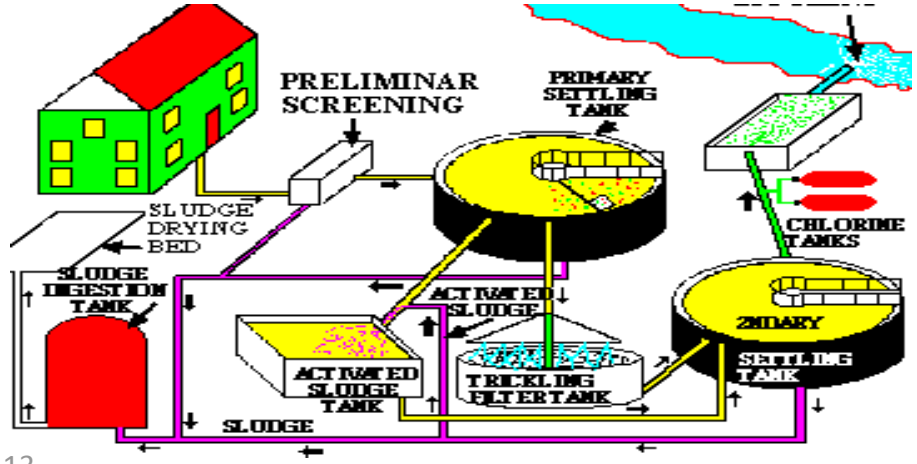
- Electronic waste

  (e-waste)

- Consumer products

  (Non electronic waste solids or NeWS)

- Wastewater or sewage treatment plants (STPs)



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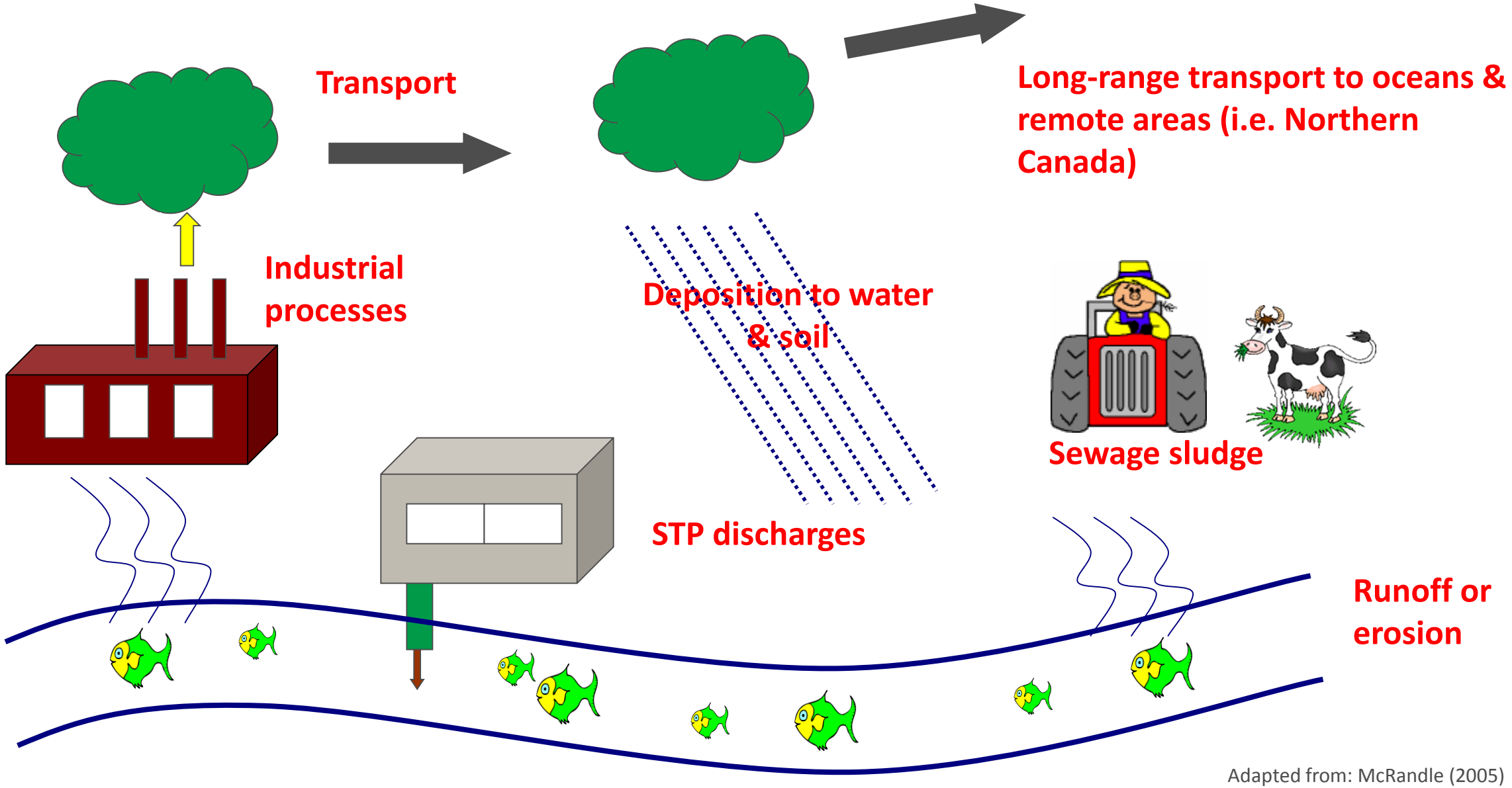
Environmental Transport of PBDEs



Adapted from: McRandle (2005)

Novel BFRs (NBFRs)

- Concern for environmental impacts
- Combined with remaining inventory of ‘legacy’ BFRs
- NBFRs: 100,000-180,000 Mt/yr
- Alphabet soup*: DBDPE, BEH-TEBP, PBEB, BTBPE, EH-TBB, TTBP-TAZ

**Fine print*:

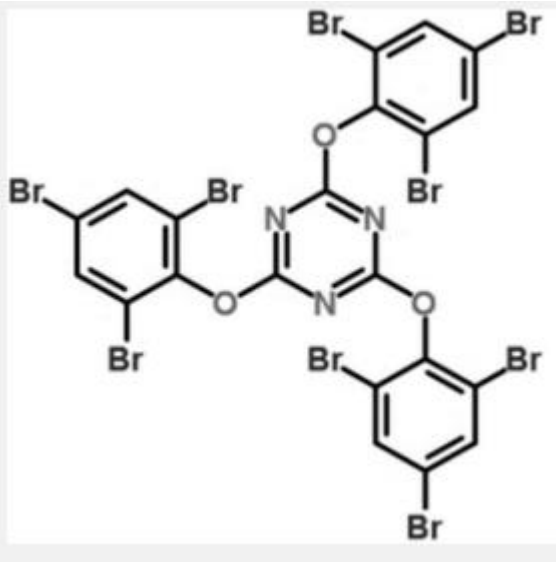
DBDPE: decabromodiphenylethane

BEH-TEBP: bis(2-ethylhexyl)-3,4,5,6-tetrabromo phthalate

PBEB: pentabromoethylbenzene

BTBPE: 1,2-bis(2,4,6-tribromophenoxy)ethane

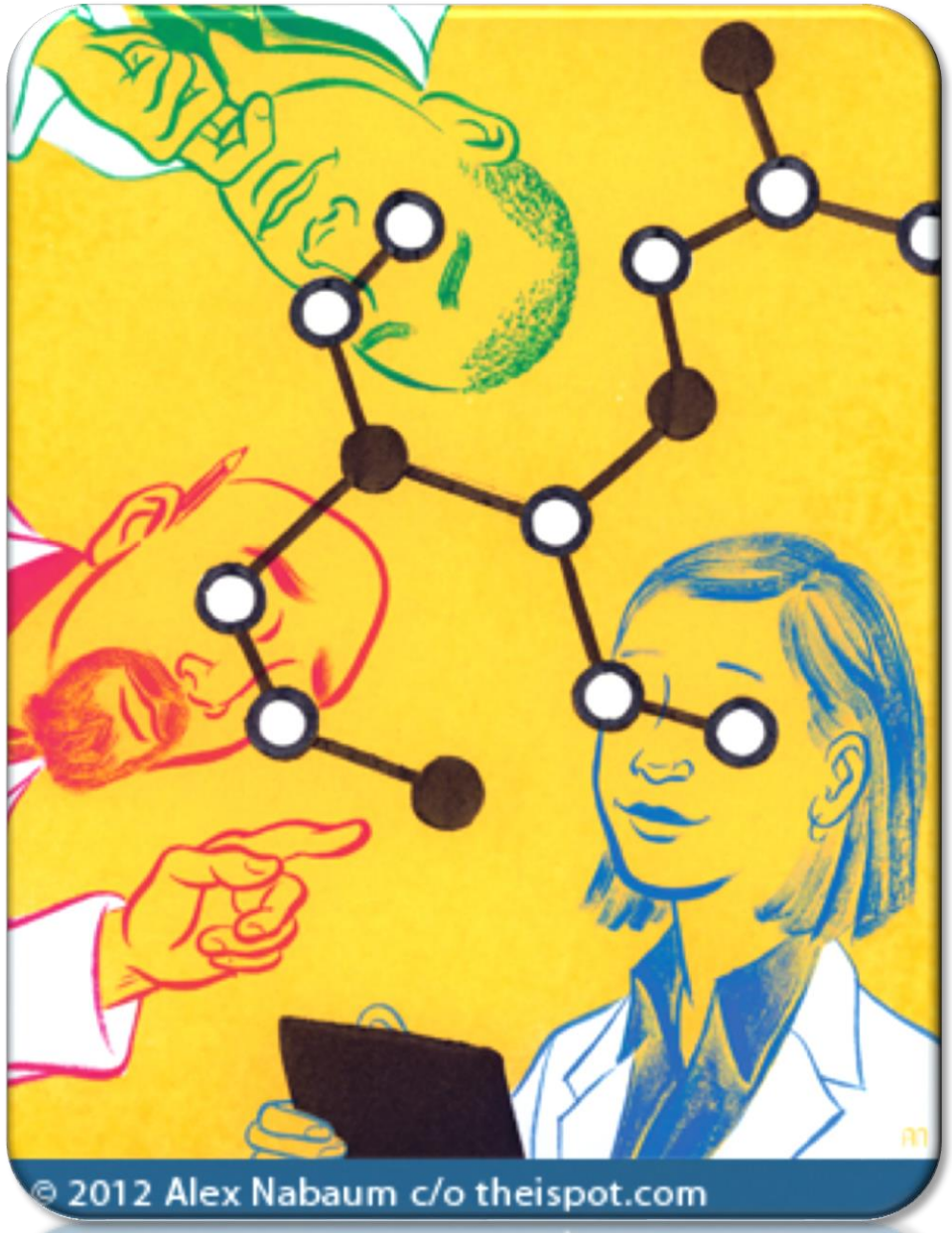
EH-TBB: 2-ethylhexyl-2,3,4,5-tetrabromobenzoate



ES&T DOI: 10-201/es4057032

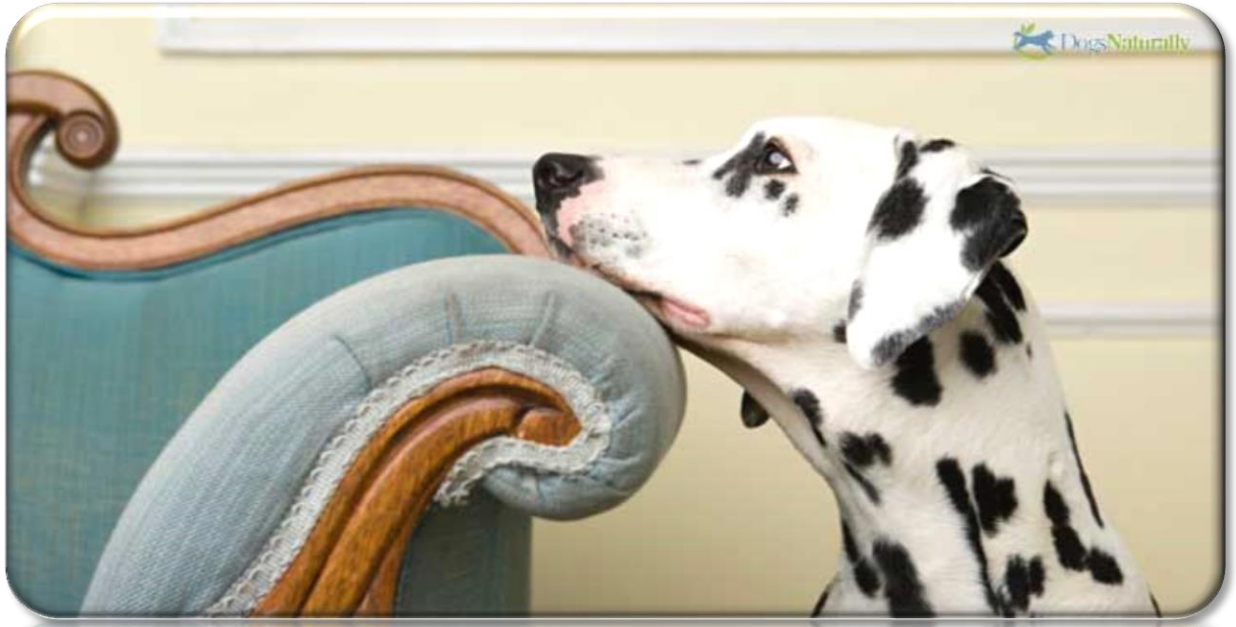
Toxicology – Human Health

- Mimics biological action of thyroid hormones
- Motor behaviour affects learning and memory
- Carcinogenicity suggested in humans
- Accumulates in fatty tissues
- Endocrine disruption, immunotoxicity



Toxicology – Animal Health

- Decreased memory, learning deficits
- Interference with thyroid hormone
- Endocrine disorders
- Obesity and diabetes
- Cancer

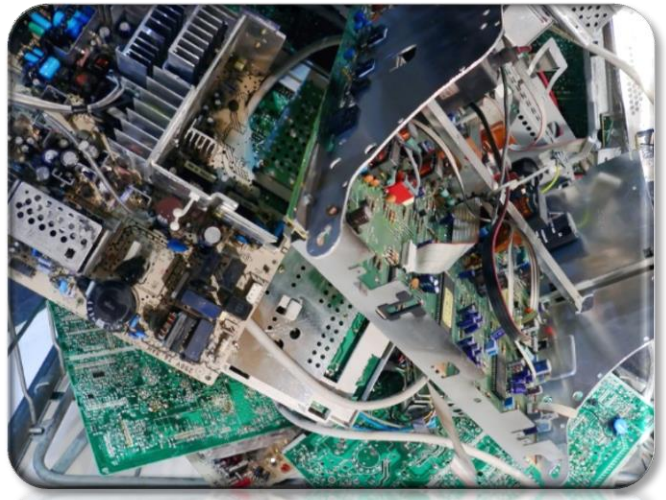


Trivia

- UK disposes of 1 million electronic waste goods/year
- WEEE man is 7 metres tall and weighs 3.3 tonnes; represents amount of e-waste 1 person will generate in their lifetime
- PCs had average lifetime of 4-5 years in 1992; in 2005 ~ 2 years; in 2016 laptop batteries last ~1 year
- 41.8 million metric tonnes (Mt) e-waste generated globally; forecast increase to 50 Mt by 2018 (2014)

Tidbits

- Arctic/Antarctic presence: in adipose tissue of polar bears. 13% annual increase between 1991-2007
- Despite ban on PBDEs, more BFRs entering market, higher flame retardant levels in home than outdoors
- 1975-2008 (US): increased PentaBDE demand, levels off in 2000
- 1995-2008 (US): increased DecaBDE in biosolids, doubling every 5 years
- 1930-2004 (UK): nothing pre 1970s; peak mid 90s



Nuggets…more

- By 2017 volume of e-waste expected to be 33% higher than 2015, equivalent to 8 times weight of Great Pyramids of Egypt
- 70% of world's e-waste processed in China
- 5.52 Mt e-waste generated yearly in China (2013) Average Canadian generated 24 kg WEEE in 2012 or 860,000 metric tonnes, equivalent to 1700 fully loaded Boeing 747s at takeoff
- Average American generated 29 kg WEEE (2012) or 9,359 million metric tonnes

End-of-Life (EOL) Management

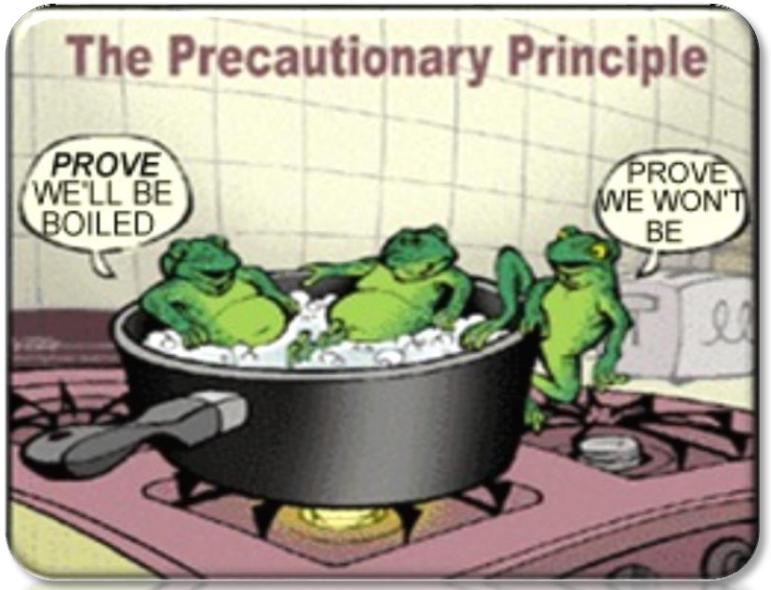
- Landfills (expensive, greenhouse gases, poor biodegradation)
- Incineration (i.e. energy recovery) – high energy value of polymers
- Chemical recovery (converts plastics to fuel for refineries)
  - pyrolysis, co-pyrolysis, catalytic cracking, hydrothermal, pyrolysis-catalytic upgrading
- Wastewater treatment
  - Granular activated carbon, reverse osmosis

End-of-Life (EOL) Management

- Recycling
  - Mechanical: sorting, dismantling (reprocessing WEEE plastics)
  - Feedstock: recovering bromine and energy in electronic equipment
- Concern with PBDD/F (dibenzo-*p*-dioxin & furan) formation
- Separate products containing BFRs prior to recycling
- Implement efficient screening and separation techniques for PBDE-containing materials

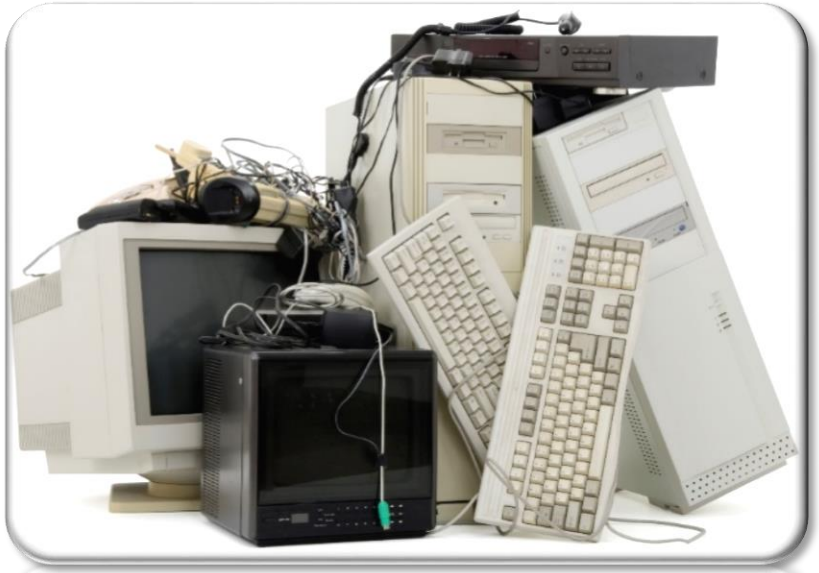
Relevant Regulations

- Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (1992)
- Directive on Industrial Emissions (IED, European Commission, 2010)
- **R**egistration, **E**valuation, **A**uthorisation and Restriction of **Ch**emicals (REACH, 2006)
- Restriction of Hazardous Substances Directive (RoHS) (EU, 2006)
- Stockholm Convention on Persistent Organic Pollutants (POPs) (2001)
- Waste Electric and Electronic Equipment Directive (WEEE, 2006)



Conclusions

- Determine *process* for leaching, degradation and spread of PBDEs from landfills
- *Improve* characterization of BFR impacts on human exposure
- BFR emissions during *open burning* of plastics not fully understood
- More *toxicology data* needed on commercial BFR products
- Focus on *challenges* associated with risk management, alternative technologies, and proper end-of-life disposal



Thank You

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