

# ***Learning from Chemical Flame Retardants: The Life Cycle Questions We Need to Answer***



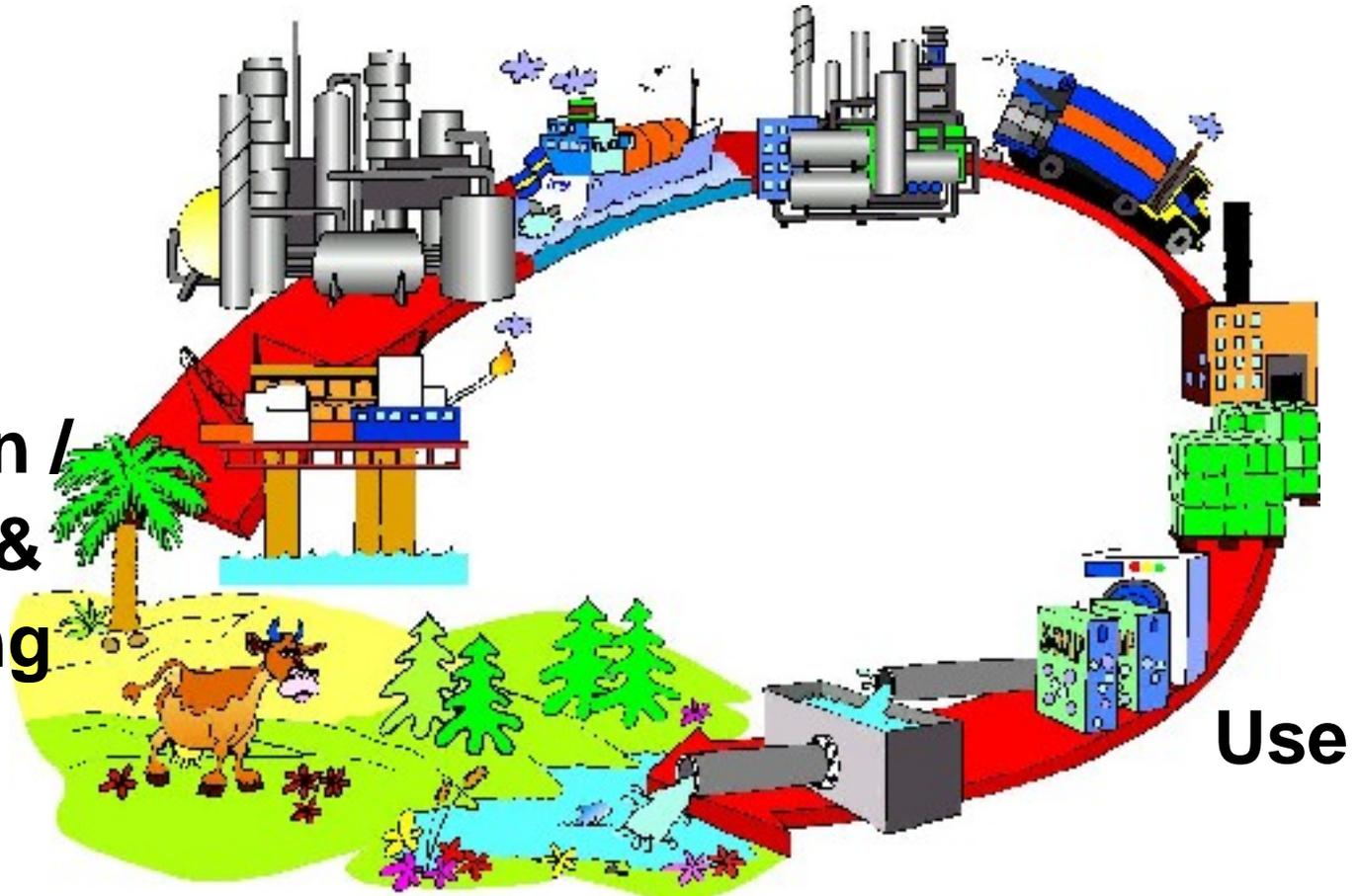
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Research Director



# Life Cycle Thinking

**Manufacturing**

**Extraction /  
Growing &  
Harvesting**



**End of Life**

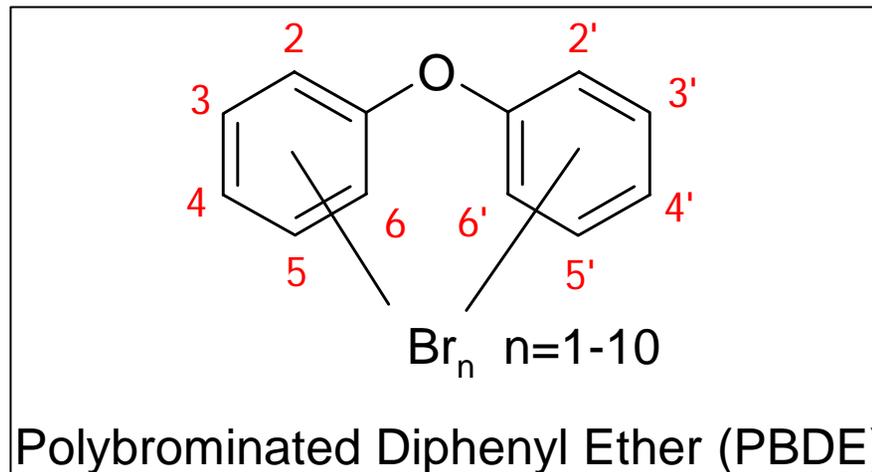
# Brominated Flame Retardants (BFRs)

## Polybrominated diphenyl ethers (PBDEs)

- pentaBDE (pentabromodiphenyl ether – “Penta”)
- octaBDE (octabromodiphenyl ether – “Octa”)
- decaBDE (decabromodiphenyl ether – “Deca”)

## Tetrabromobisphenol A (TBBPA)

## Hexabromocyclododecane (HBCD)



# Extraction / Growing & Harvesting

- **Environmental concerns from extraction have not been raised during discussions of environmental concerns with flame retardants**

***(yet, we know that the environmental impacts of mining, drilling, and agriculture need to be minimized)***

# **Manufacturing – Questions for Nanotech from FRs**

- 1. How is worker exposure to nanomaterials minimized?**
- 2. What are the emissions to the environment from manufacturing?**
- 3. Is the nanomaterial reactive or additive in polymers?**

# Manufacturing – Worker Exposure

## **Occupational Exposure to Commercial Decabromodiphenyl Ether in Workers Manufacturing or Handling Flame-Retarded Rubber**

KAJ THURESSON,<sup>\*,†</sup> ÅKE BERGMAN,<sup>†</sup> AND KRISTINA JAKOBSSON<sup>‡</sup> (2005)

“The results confirm significant uptake of BDE-209 in the workers exposed to DecaBDE and indicate the potential for in vivo formation of lower BDEs”



# Manufacturing – Emissions to the Environment – DecaBDE

## Toxics Release Inventory Data, lbs (2004)

- On-site Releases = 92,750
  - On-site Disposal = 151,040
  - Off-site Transfers = 710,697
- Total Release & Transfer = 954,487**

# Manufacturing – Reactive vs. Additive Chemistry

- **Reactive chemical**: integrated into the backbone of a polymer
- **Additive chemical**: mixed into the polymer, but not part of the polymer backbone
- Reactive chemicals are more stable – less likely to be released into the environment – than additive chemicals

*However, reactive chemistry is no guarantee to eliminating environmental release:*

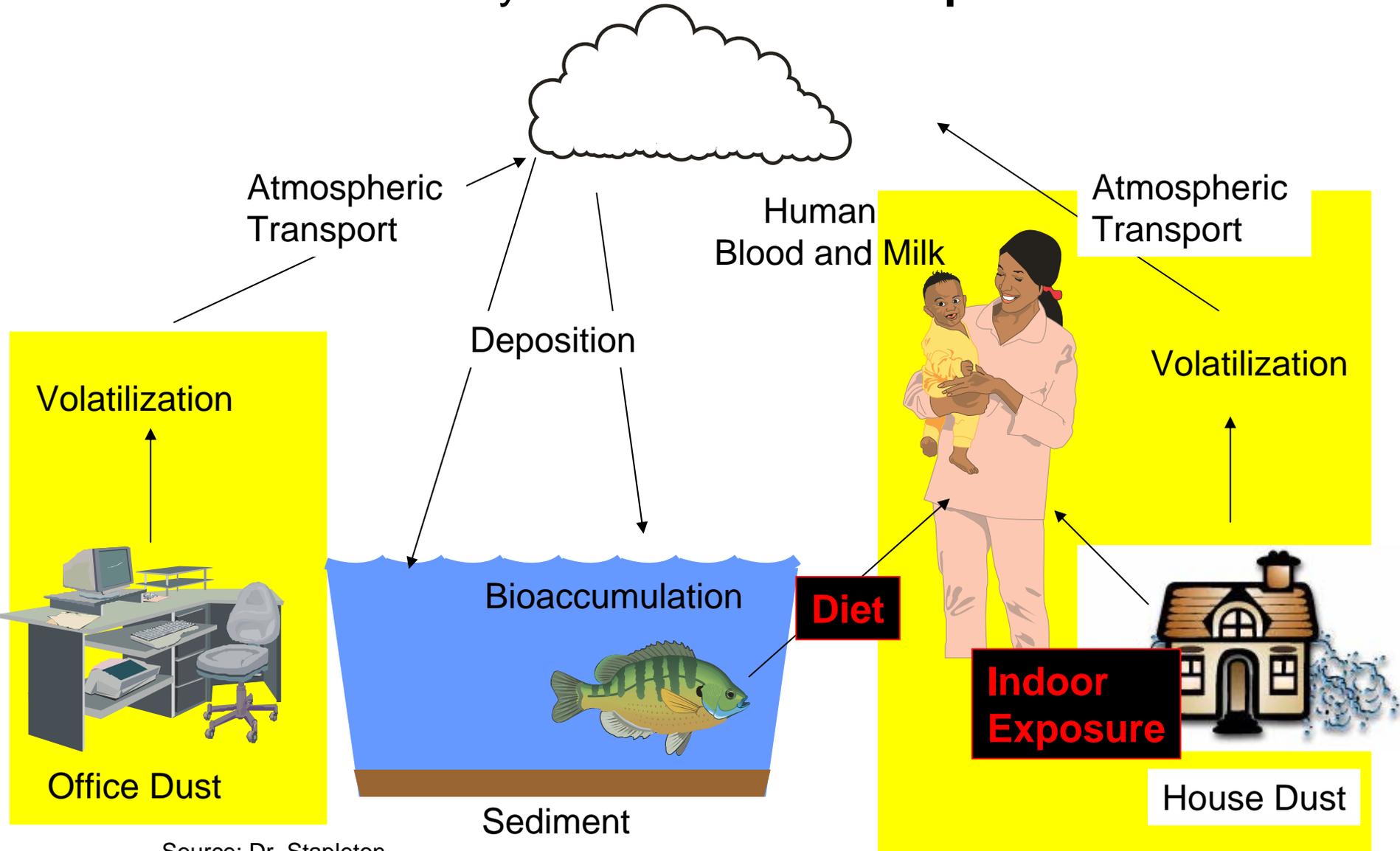
*– TBBPA, for example, is found in the environment*

# Use – Questions for Nanotech from FRs

- What happens to nanomaterials during use?
- Will exposure to light, heat, or abrasion release nanomaterials into household or office dust?
- Will nanomaterials collect in dust, to be picked up by babies and toddlers crawling on floors?

# Major Routes of Human Exposure to PBDEs?

- Likely **Diet** and **Indoor Exposure to Dust**



## A Comparison of PBDE Intake Relative to Body Weight Among U.S. Population

Exposure Route	Population	PentaBDE (ng/kg/day)	DecaBDE (ng/kg/day)	Reference
Diet	Adults	1 to 1.4	0 to 0.7 <sup>a</sup>	Schechter et al., 2006
Inhalation <sup>b</sup>	Adults	0.12 to 0.18	0.04 to 0.06	Allen et al., 2006
Nursing <sup>c</sup>	Infants	30 to 2020 Mean: 355	0 to 40 Mean 4.4	Schechter et al., 2003
Dust Ingestion <sup>d</sup>	Children 1-4 years of age	10 to 214 Mean: 46	0.2 to 4050 Mean: 30	Stapleton et al., 2005 Allen et al., 2006

a-assuming BDE 209 can be 50% of total PBDE composition in food. (**Very dependent on diet**)

b-assuming an inhalation rate of 20 m<sup>3</sup>/day.

c-assuming milk sampled is 3% lipid and that a 5 kg infant ingests 800 mL milk/day.

d-assuming that children ingest between 0.02 g to 0.2 g of dust/day and weigh approximately 13 kg.

# End of Life - Recycling



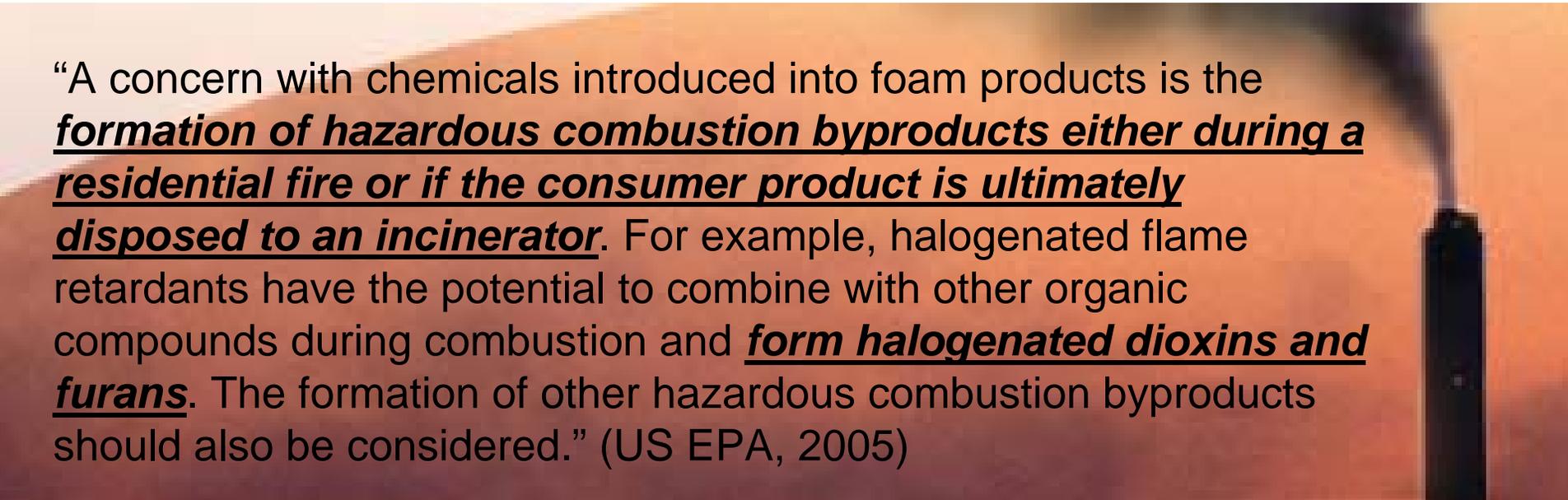
Courtesy Basil Action Network

- What happens to nanomaterials in polymers/textiles when recycled?
- How will recycling workers be protected?

# End of Life - Combustion

- What happens to nanomaterials during combustion?
- Will nanomaterials alter the formation of combustion byproducts from other chemicals in the product?

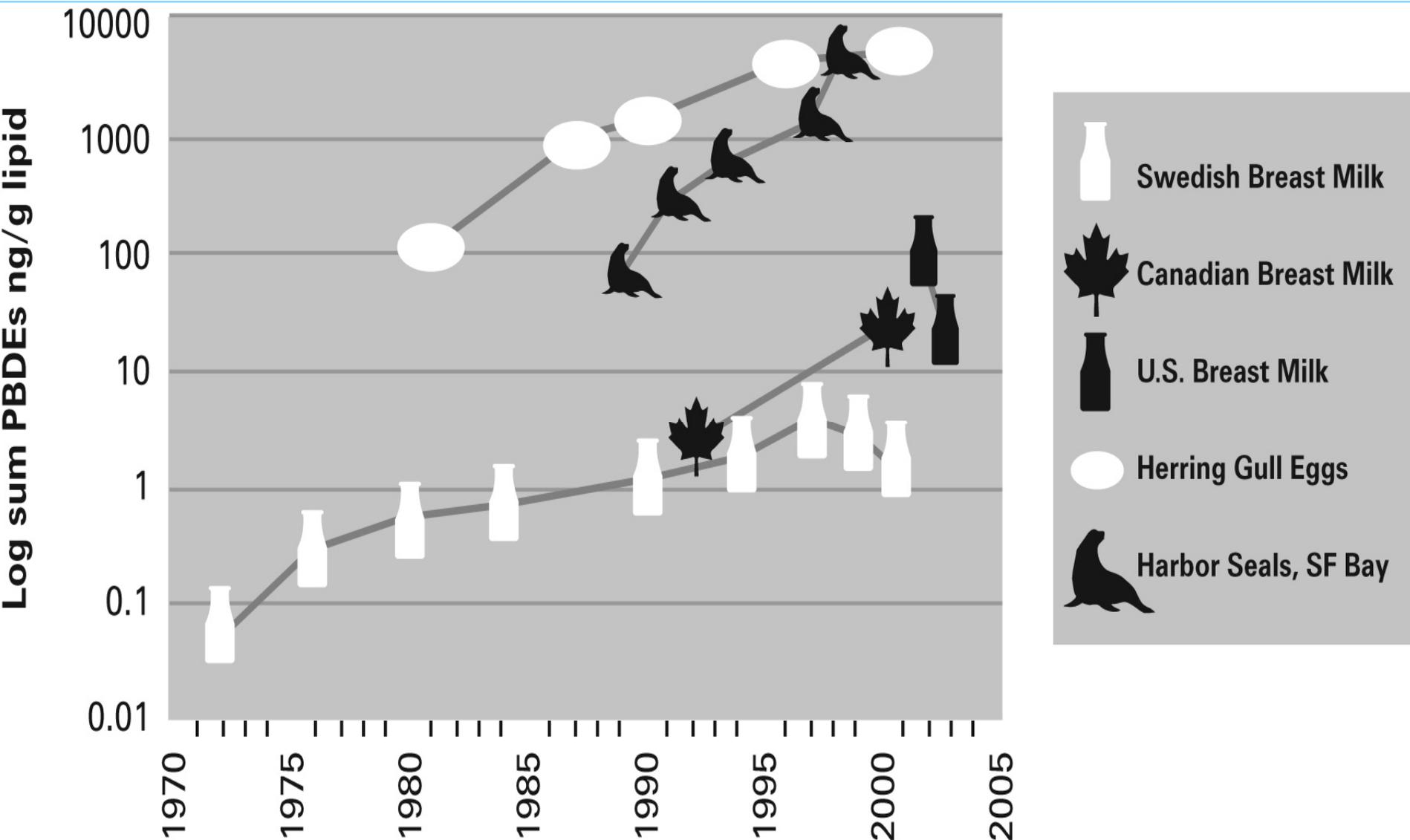
“A concern with chemicals introduced into foam products is the **formation of hazardous combustion byproducts either during a residential fire or if the consumer product is ultimately disposed to an incinerator.** For example, halogenated flame retardants have the potential to combine with other organic compounds during combustion and **form halogenated dioxins and furans.** The formation of other hazardous combustion byproducts should also be considered.” (US EPA, 2005)



# Environmental Fate & Transport

- What happens to nanomaterials in the environment?
- Are they persistent and/or bioaccumulative?
- Are they capable of long range transport?
- Are they present in the environment – water, air, soil or animals?
- Or do they safely degrade?

# Human and Wildlife Levels of PBDEs



# Toxicological Characteristics

- What are the potential toxic effects from exposure to nanomaterials?
- Have they been tested for:
  - Ecotoxicity?
  - Carcinogenicity, Mutagenicity, or Reproductive Toxicity (CMR)?
  - Sensitization of skin or respiratory system?
  - Neurotoxicity?
  - Endocrine disruption?

# Health Effects – Polybrominated Diphenyl Ethers (PBDEs)

- **Neurodevelopmental**: Exposure to PBDEs (Penta, Octa, Deca) during critical windows of brain development results in decreased memory and learning that worsens with age and is irreversible. (Viberg, 2003)
- **Reproductive development**: Penta-BDE exposure at levels similar to those found in humans was associated with decreased sperm counts in rodents. (Kuriyama, et al. 2005 and Lilienthal, et al. 2005)
- **Cancer**: US EPA considers decaBDE a possible human carcinogen.

# Environmental Impact Assessment: Summary for PBDEs

Extraction	??
Manufacturing	Concerns with: worker exposure & environmental releases
Use	Concerns: release into indoor environments, exposure of babies and toddlers
End of Life	Concerns with: exposure of recyclers & combustion byproducts
Environmental Fate & Transport	Persistence, Bioaccumulation, Long-range Transport, Presence in Environment
Toxicological Characteristics	Neurotoxicity, Reproductive toxicity, Carcinogenicity, Endocrine Disruption

# Lessons Learned from Flame Retardant (FR) Chemistry – Part 1

## Expect the Unexpected

- ***Expect chemicals or nanomaterials to “leak” into the environment***
- ***Expect degradation + exposure*** from use
- ***Expect combustion byproducts***
- ***Expect exposures and toxicological effects*** greater than anticipated

# Lessons Learned from Flame Retardant Chemistry – Part 2

## Perform an “Environmental Impact Assessment”

- *Identify potential environmental concerns at each life cycle stage*
- *Assess fate & transport potential*
- *Assess toxicological characteristics of the material -- untested ≠ safe*

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