Persistent, Bioaccumulative, Toxic Chemicals: Why the Concern?

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Persistent, bioaccumulative, and toxic chemicals (PBTs)

- Toxic, long-lasting substances that can build up in the food chain and general environment to levels that are harmful to human and ecosystem health.
- Generally applies to organic compounds; inconsistencies among agencies as to how to classify metals (e.g. lead, cadmium, mercury)

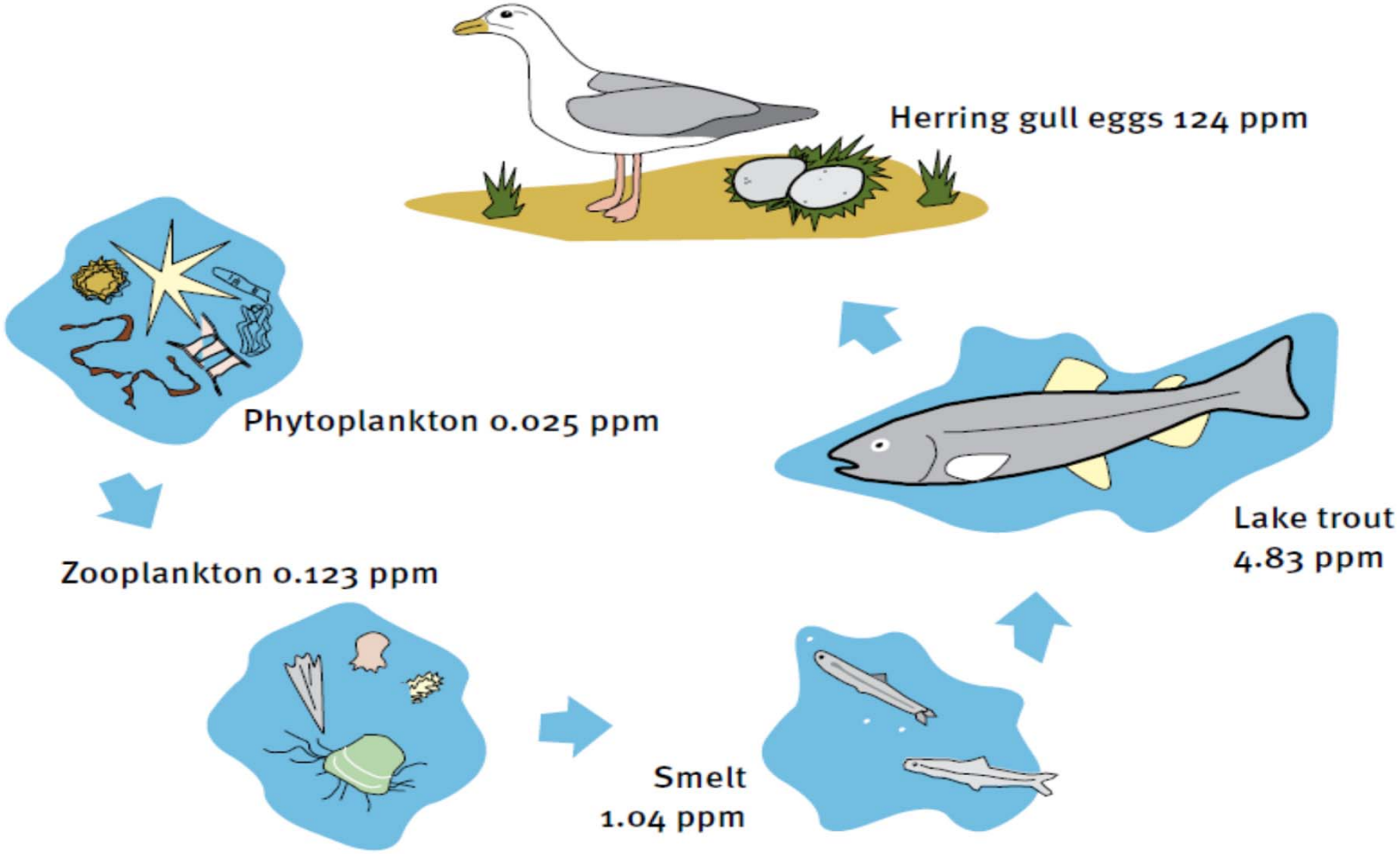
Persistent, BT

- Persistence:
  - half-life > 60 days in water, soil, sediment; > 2 days in air
  - Depends on intrinsic properties of the chemical and to some extent, on environmental conditions

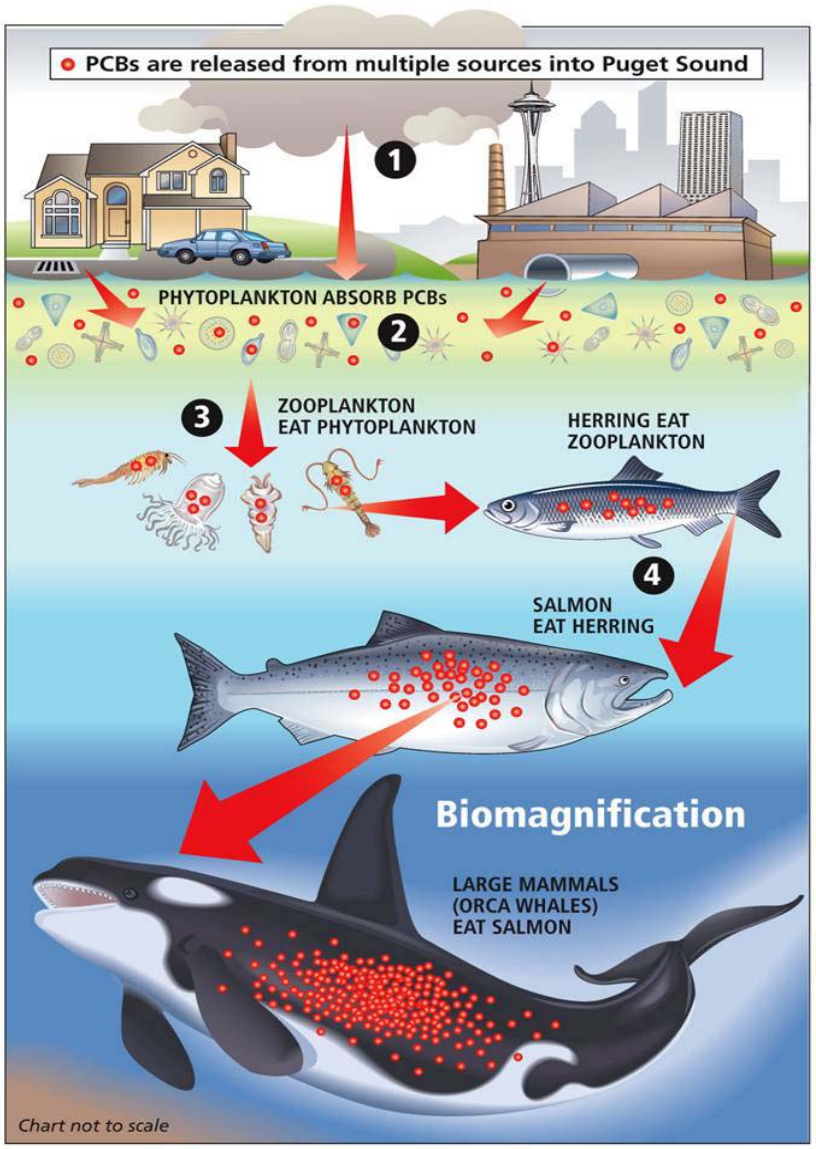
P, Bioaccumulative,T

- Bioaccumulation:
  - Bioconcentration factor or Bioaccumulation factor > 1000 (EPA)
  - BAF = Ratio of the concentration of a substance in an organism to the concentration in water, based on uptake directly from the surrounding medium and food
  - BCF = Ratio of the concentration of a substance in an organism to the concentration in water, based only on uptake directly from the surrounding medium
- Many PBTs are fat soluble; octanol: water coefficient can be used to predict BCF

Changes in the concentration of PBTs as they move up the food chain



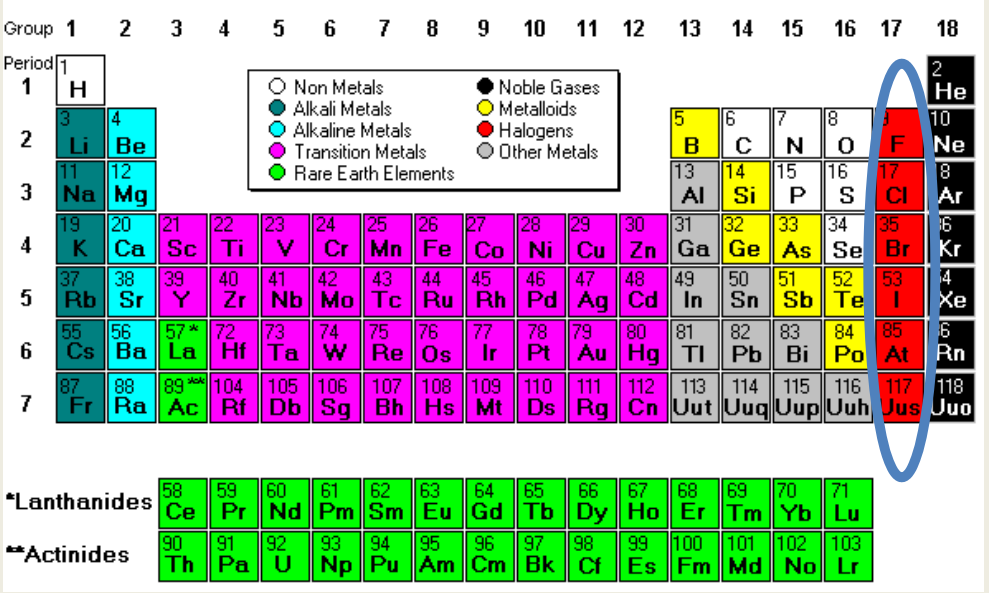
ppm = parts per million. Adapted from: US Environmental Protection Agency.


PCBs are released from multiple sources into Puget Sound
1
PHYTOPLANKTON ABSORB PCBs
2
3
ZOOPLANKTON
EAT PHYTOPLANKTON
HERRING EAT
ZOOPLANKTON
4
SALMON
EAT HERRING
Biomagnification
LARGE MAMMALS
(ORCA WHALES)
EAT SALMON
Chart not to scale

Adding halogens (particularly fluorine, chlorine, bromine atoms)

- Tends to increase fat solubility (there are exceptions)
- Create strong chemical bond with carbon; increases resistance to metabolic breakdown

Outer shell of halogens contains 7 electrons (unstable); by attracting an additional electron and filling the outer shell, becomes more stable



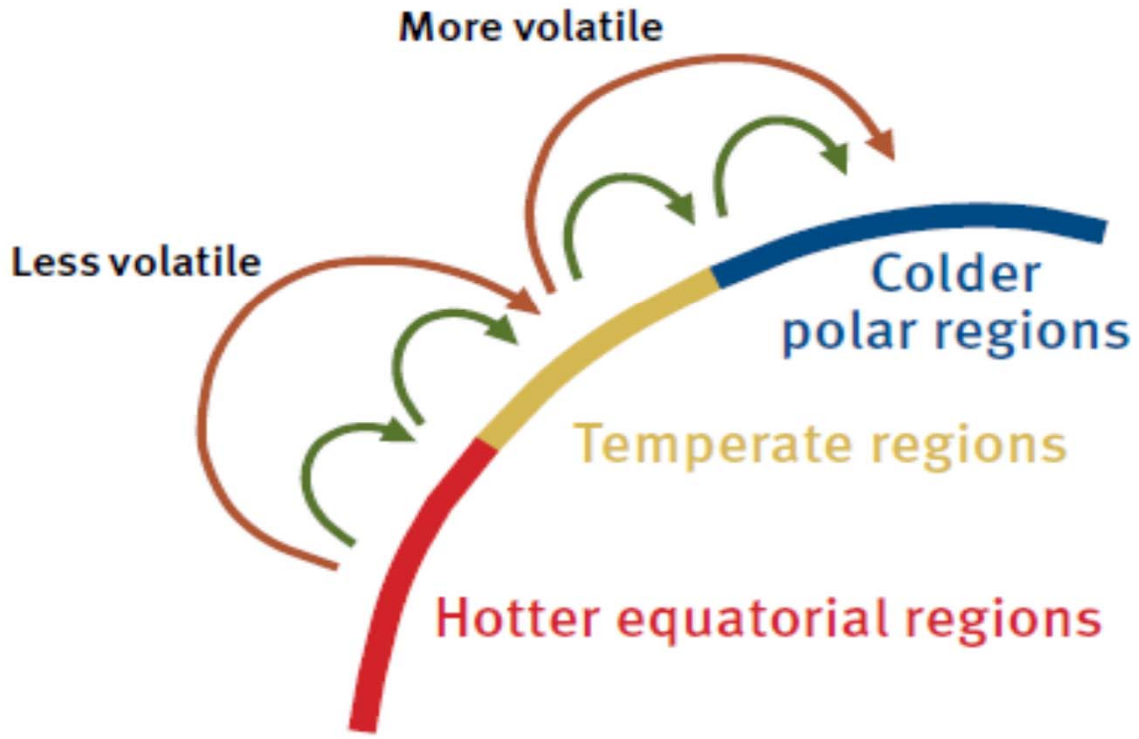
PB,Toxicants

- Associated with a range of adverse human and wildlife health effects, including effects on:
  - the nervous system, (e.g. mercury compounds; lindane)
  - the endocrine system (e.g. TBBPA; flame retardant; thyroid disruption)
  - the immune system (e.g. some brominated flame retardants)
  - reproductive and developmental toxicity (e.g. PBDEs)
  - cancer (e.g. p-dichlorobenzene [mothballs, disinfectant])

PBT challenges

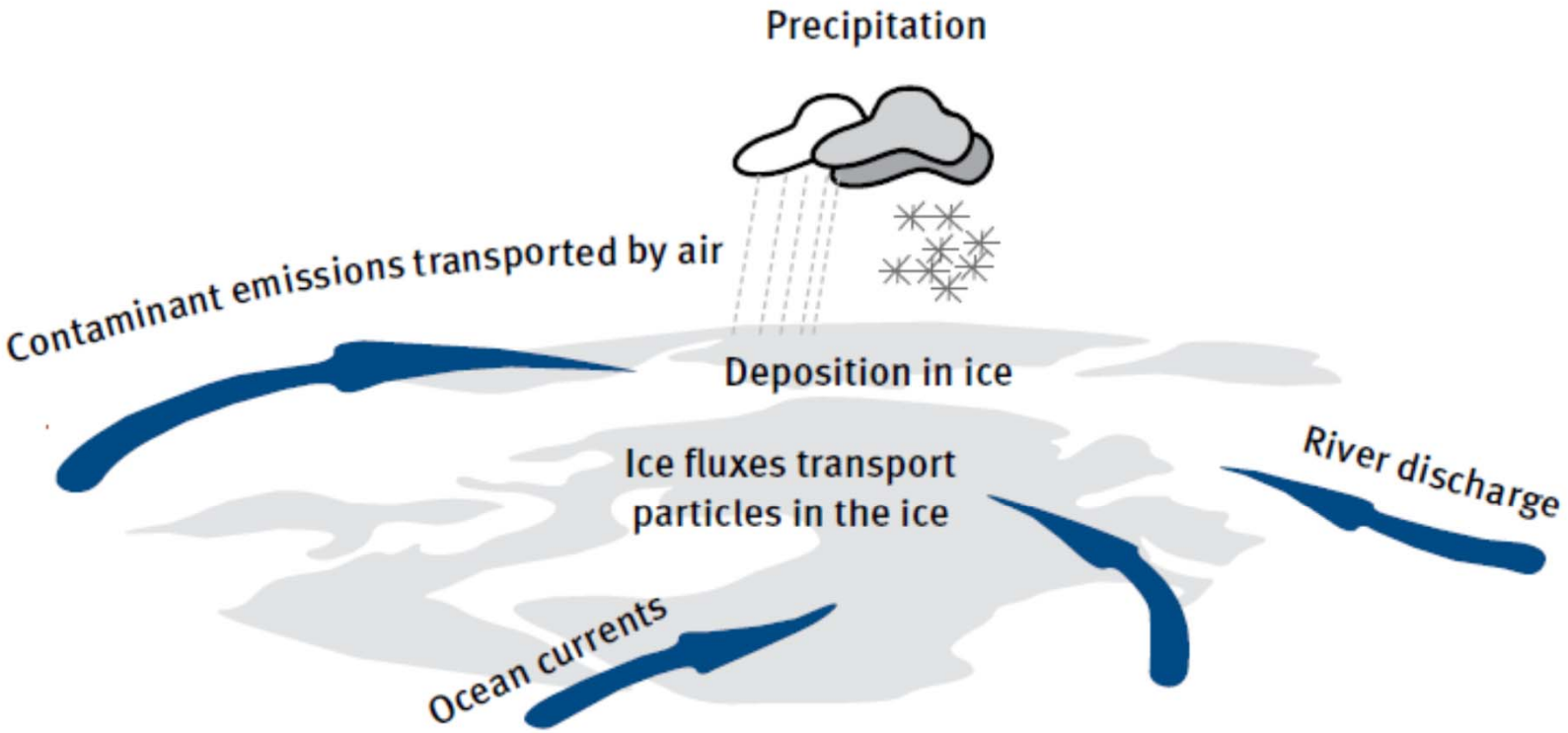
- The challenge in reducing risks from PBTs arises from their ability
  - to travel long distances,
  - to transfer rather easily among air, water, and land, and
  - to linger for generations in people, wildlife, and the environment

The grasshopper effect and global distillation



Source: Environment Canada.

Pathways of contaminants to the Arctic



Source: Arctic Monitoring and Assessment Programme.

How many PBTs are in commerce?

- Estimates vary: probably several hundred; may be 1000
- Depends on:
  - Choice of cut-off for persistence and bioaccumulation
  - Methods for determining P, B, and T; Measured? Calculated? Estimated?

The Stockholm Convention (UNEP)

- The Stockholm Convention on Persistent Organic Pollutants is a UNEP-sponsored global treaty to protect human health and the environment from some PBTs
- Adopted in 2001 and entered into force in 2004
- Requires its parties to take measures to eliminate or reduce the release of (listed) POPs into the environment.
- The US has not ratified the treaty

Stockholm Convention chemicals

- **Original 12 chemicals banned or restricted by Stockholm Convention**
  - **Pesticides**: aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, toxaphene;
  - **Industrial chemicals**: hexachlorobenzene, polychlorinated biphenyls (PCBs); and
  - **By-products**: polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF)

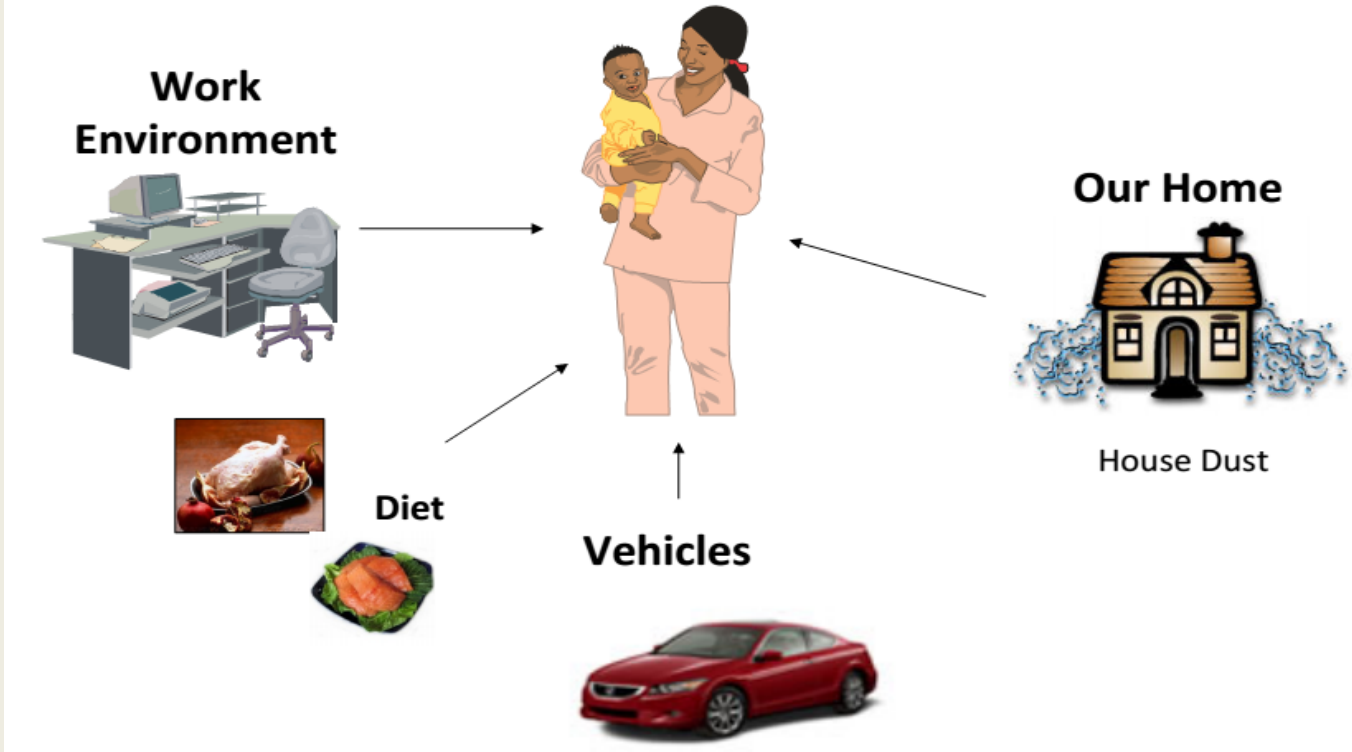
Chemicals more recently added to Stockholm Convention

- Chlordecone
- Hexabromobiphenyl
- Pentachlorobenzene
- Alpha- and beta- hexachlorocyclohexane; lindane
- Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride (PFOS)
- Pentabromodiphenyl ether; Octabromdiphenyl ether
- Endosulfan

Case Study

Flame retardants

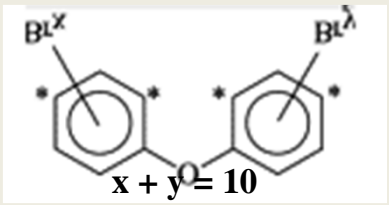
How Are We Exposed to Flame Retardants?



Flame retardants

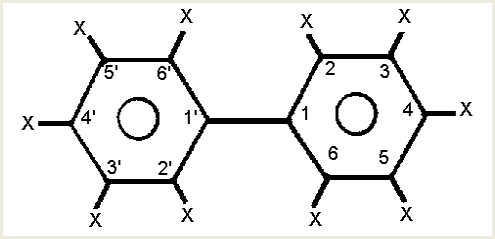
- Halogenated flame retardants (contain bromine or chlorine)
  - PBDEs, TBBPA, hexabromocyclododecane (HBCD), chlorinated tris (TDCP, TCEP), Declorane plus
- Phosphorus based
- Nitrogen based
- Inorganic (e.g. aluminum, magnesium oxides)

Polybrominated diphenyl ethers (PBDEs) resemble PCBs



PBDEs

Over 150 million pounds produced annually until recently



PCBs

Production banned in 1977 (toxicity and widespread contamination)

Neurodevelopmental toxicity studies began to surface in early 1980s;

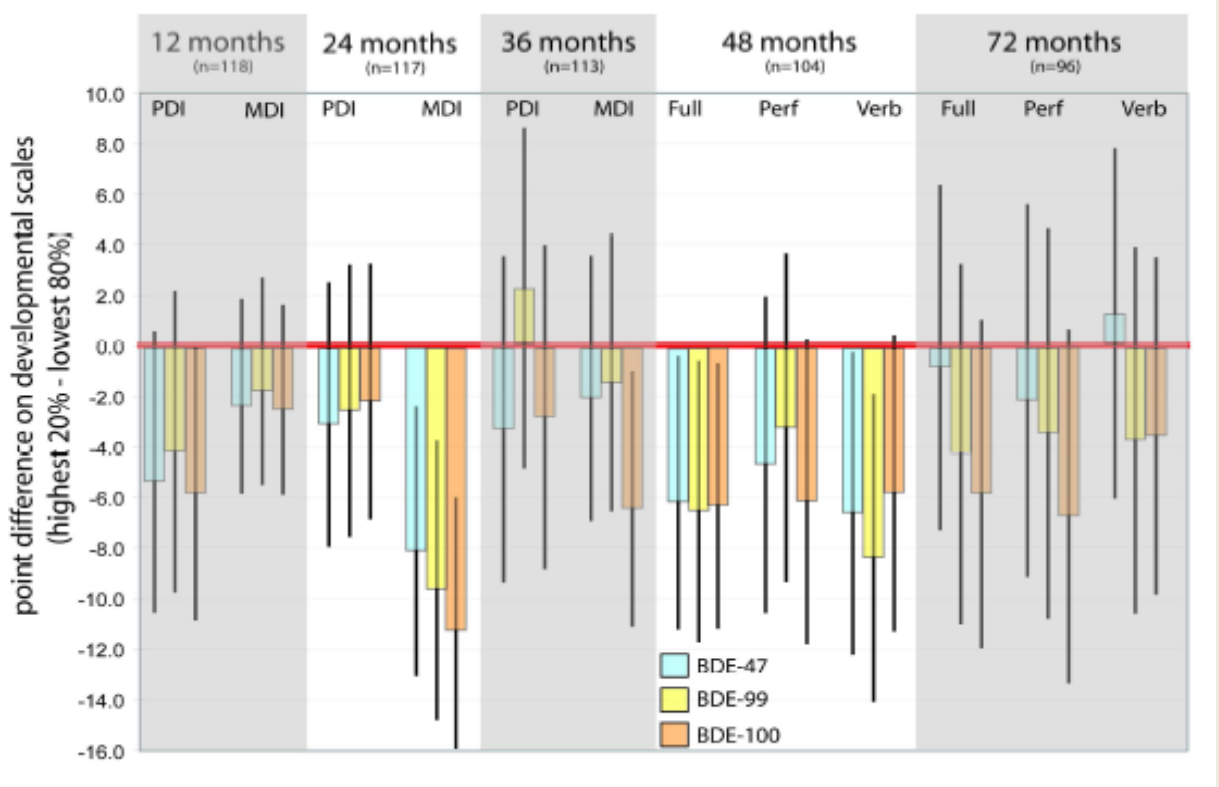
Multiple longitudinal studies in cohorts around the world confirm adverse impacts on developing brains of children

Halogenated flame retardants

- Polybrominated diphenyl ethers (PBDEs)
  - Toxicity in wildlife and lab animals demonstrated in 1990s
  - Behavioral effects in lab animals—2001
  - In humans, associations with:
    - Neurodevelopmental toxicity (Herbstman, 2010)
    - Thyroid disruption
    - Abnormal reproductive tract development (association with cryptorchidism reported; Main, et al., 2007)
    - Increased time to pregnancy (Harley, et al., 2010)
  - decaBDE: possible human carcinogen (EPA)

Prenatal exposure to PBDEs and neurodevelopment

n = 329; adjusted for multiple confounders; co-variables; effect modifiers;
Bayley Scales of Infant Development; Wechsler Scale of Intelligence



Herbstman, EHP, Jan 2010; two additional studies since 2010: Eskenazi, 2013; Chen, 2013

Replacement HFRs

- hexabromocyclododecane *(*HBCD): persistent organic pollutant (POP); developmental neurotoxicant; UN recommends phase out (used in polystyrene foam insulation; worker/occupant exposures [dust])
- Chlorinated tris and related compounds: neurotoxic, probably carcinogenic, inadequately tested (used in foam, furniture)
- Newer flame retardants showing up in household dust (Dodson, EST, 2012)
- Sources and toxicity often not well understood

Conclusions

- PBTs are toxic, long-lasting substances that:
  - travel long distances,
  - transfer rather easily among air, water, and land, and
  - linger for generations in people, wildlife, and the environment
- They build up to levels that are harmful to human and ecosystem health, causing a range of adverse effects.
- Exposures and effects are slow to reverse
- These features provide a rationale for phasing PBTs out of commerce except for uses where the use is critical or essential