Barbie-burn-tronics
Even with flame retardants, plastics can burn - Pic by tronics on flickr

Brominated Flame Retardants (BFRs) in e-waste

June 8, 2011

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What are brominated flame retardants and why are they a problem?

Brominated flame retardants (BFRs) are **bromine-based flame-retardant formulations** which are used in several industrial and commercial applications for the purpose of fire prevention. They are **applied to over 2.5 million tons of polymers annually**.

Approximately **70 brominated flame retardant chemicals account for a global consumption of over 300,000 tons per annum** . Besides this, large quantities of BFRs are produced for use in **electronic equipment and building materials**. Many BFRs are also added to **textiles and other materials to prevent fires.**

They are normally additives and **not chemically bound** to the plastics or textiles they are added to and hence **may leach into the environment**. Some may be reactive but **may not have polymerized fully** and are also leached out. Being **lipophilic, many persist in the environment and bio-accumulate .**

Types of BFRs

There are several brominated flame retardants in use, of which Polybrominated biphenyls (PBBs), **Polybrominated diphenyl ethers (PBDEs)**, Tetrabromobisphenol A (TBBPA), Hexabromocyclododecane (HBCCD), bis(2,4,6-tribromophenoxy) ethane (BTBPE) and tris (2,3-dibromopropyl) phosphate (Tris) are **identified environmental contaminants** .

BROMINATED FLAME RETARDANTS

Flame retardants – Where?

Flame retardants in furniture

Yet they don't meet standards

PBBs were used in the 1970s for **coating Acrinonitrile Butadiene Styrene (ABS) plastics**, coatings, lacquers and polyurethane foams until they were banned when in 1973 they were **accidentally used as a feed supplement in a Michigan** cattle operation and were found to be persistent in meat, milk, eggs and in all exposed organisms. Commercially, it continued to be available as a mixture of congeners called Firemaster BP-6, which is **even now detectable in abiotic and animal tissues**.

TBBPA, the most widely used BFR as an additive and **a reactive chemical in ABS**, High-impact Polystyrene (**HIPS**) and others, with an annual estimated worldwide production of 50,000 tons per year in 2002, has an **appreciable half-life** and remains in the soil sediments for a long time.

Tris was used in **children's sleep-ware** till 1977 until it was shown that it is a potent mutagen and carcinogen in rats. It was **replaced by a chlorinated analog tris** or Fyrol FR-2 which is **equally mutagenic** and **carcinogenic**.

HBCDD is added in very low concentrations to **Polystyrene foam** which is used as thermal insulation in the building industry and at higher levels to the back of **upholstery** textiles. It is supposed to be relatively non-toxic to rodents and marine invertebrates.

BTBPEs are also used widely in the production of **plastic materials which require high manufacturing temperatures**. However, their environmental levels and acute toxicity are said to be low.

COMMON SOURCES

PBDE in electronic waste

Deca is a fire retardant, a type of polybrominated diethyl ether — PBDE — that is added to plastics used in computers, TV screens and other electronic items to prevent them from catching fire. Deca has been banned in three states in the US. Some other types of PBDEs have been banned nationwide — penta and octa — but deca has largely escaped scrutiny because its presence can be difficult to measure.

According to the Natural Resources Defense Council, first

commercial productions of PBDEs began in the 1970s in Germany. Production of PBDEs has continued until the present. There are three commercial PBDE products (i.e., penta-, octa-, and decabromodiphenyl ethers). Deca- and octa-brominated types of PBDEs are also produced outside of the United States (in China and Israel). Decabromodiphenyl ether (decaBDE) makes up 82% of these products manufactured globally. Its main use is for electronic enclosures, such as television cabinets. Octabromodiphenyl ether (octaBDE) product is used in plastics for business equipment. Pentabromodiphenyl ether (pentaBDE) product is used in foam for cushioning in upholstery

Public Health significance

US statistics

- **How Much E-waste is Being Discarded?** Whether trashed or recycled, what are we getting rid of each year in the US?
- **E-Waste in 2007 – Was it Trashed or Recycled ?**

Products	Total disposed** (million of units)	Trashed (million of units)	Recycled (million of units)	Recycling Rate (by weight)
Televisions	26.9	20.6	6.3	18%
Computer Products*	205.5	157.3	48.2	18%
Cell Phones	140.3	126.3	14	10%

- *Computer products include CPUs, monitors, notebooks, keyboards, mice, and "hard copy peripherals", which are printers, copiers, multi's and faxes.
- **These totals don't include products that are no longer used, but stored. Source: EPA

- The EPA (in report summarized above) estimates that 29.9 million desktops and 12 million laptops were discarded in 2007. That's over 112,000 computers discarded per day!

- The EPA report (above) estimates that 31.9 computer monitors were discarded in 2007 – both flat panel and CRTs.

- There are over 200 facilities in the US and at least 10,000 workers who are engaged in doing e-waste recycling in addition to at least another 10,000 workers in industries connected with further processing

What happens to PBDEs when they enter the environment?

PBDEs enter air, water, and soil during their **manufacture and use in consumer products**. When PBDEs are suspended in air, they can be **present as particles**. They eventually **return to land or water as the dust** settles and are washed out by snow and rainwater. It is not yet possible to say how long PBDEs remain in the air. **PBDEs do not dissolve easily in water, and therefore, high levels of PBDEs are not found in water**.

The very small amounts of PBDEs that do occur in water stick to particles and eventually **settle to the bottom**. Sediments at the bottom of bodies of water, such as lakes and rivers, generally act as **reservoirs for decaBDEs, which can remain there for years. Some lower brominated PBDEs (e.g., tetra- and penta-congeners of PBDE) in water may build up in fish** to low concentrations (**about 10 billionths of a gram to 1 millionth of a gram of PDBE per gram of fresh fish [or 10x10-9-1x10-6 grams of PBDE per gram of fresh fish**]).

However, **higher brominated PBDEs, such as decaBDE, are not found in fish at measurable concentrations. In general, the breakdown** of PBDEs in soil is very slow, so they may remain in soil for several years. PBDEs bind strongly to soil particles. Rainwater is not expected to spread them much below the soil surface; thus, it is **unlikely that PBDEs will enter groundwater**.

Source: Oros D R, Hoover D, Rodigari F, Crane D, Sericano J Levels and distribution of Polybrominated Diphenyl Ethers in Water, Surface Sediments, and Bivalves from San Francisco Estuary; Environmental Science and Technology 39, 1 (2005), 33-41; American Chemical Society

Wang Y, Li X, Li A, Wang T, Zhang Q, Wang P, Fu J, Jiang G; Effect of Municipal Sewage Teeatment Plant Effluent on Bioaccumulation of Polychlorinated Biphenyls and Polybrominated Diphenyl Ethers in the Recipient Water; Environmental Science and Technology 41, 17 (2007) 6026-6032; American Chemical Society

Schecter A, Papke O, Tung K

PBDE IN THE ENVIRONMENT

Being susceptible to **several metabolic processes** like **oxidative debromination, reductive debromination, oxidative CYP enzyme-mediated** biotransformation and/or Phase II conjugation (**glucuronidation and sulfation**), the **breakdown products of BFRs known as congeners.**

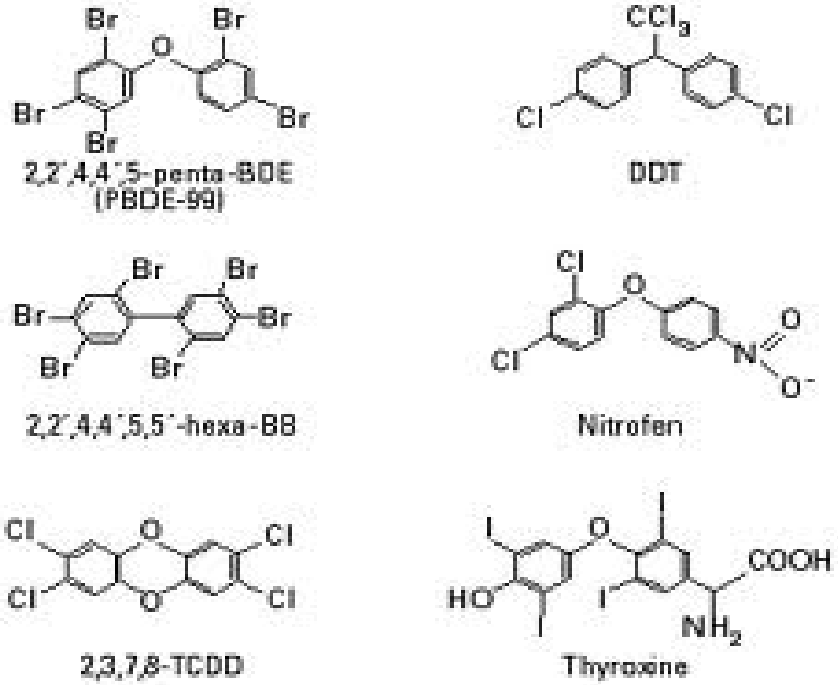
They are **ubiquitously found in human tissues and wildlife, a rising cause of concern in several parts of the world**. For instance, from PBDEs, technically 209 congeners are possible, but only a few of them such as **BDE 28, BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 183 and BDE 209 are found as contaminants** in tissues of exposed organisms.

Source: Hakk H, Letcher R J; Metabolism in the Toxicokinetics and fate of brominated flame retardants – a review; Environment International 29 (2003) 801-828 Elsevier

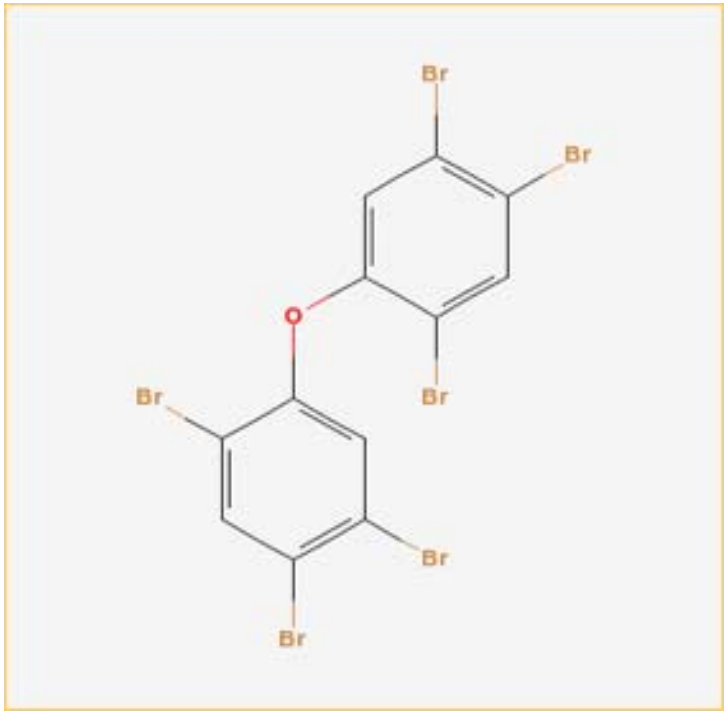
PBDE METABOLISM

PBDE congeners and other similar molecules

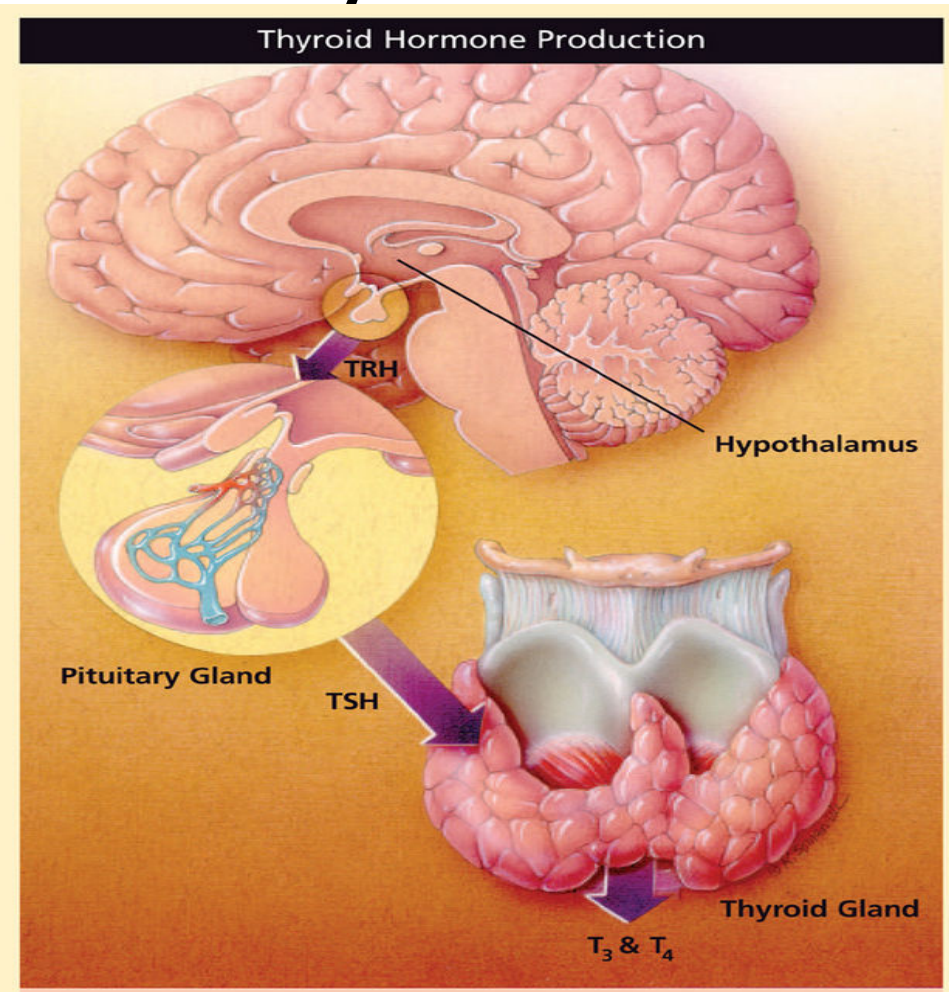
Structural similarity between Thyroxine, PBDE, its congeners and other organics



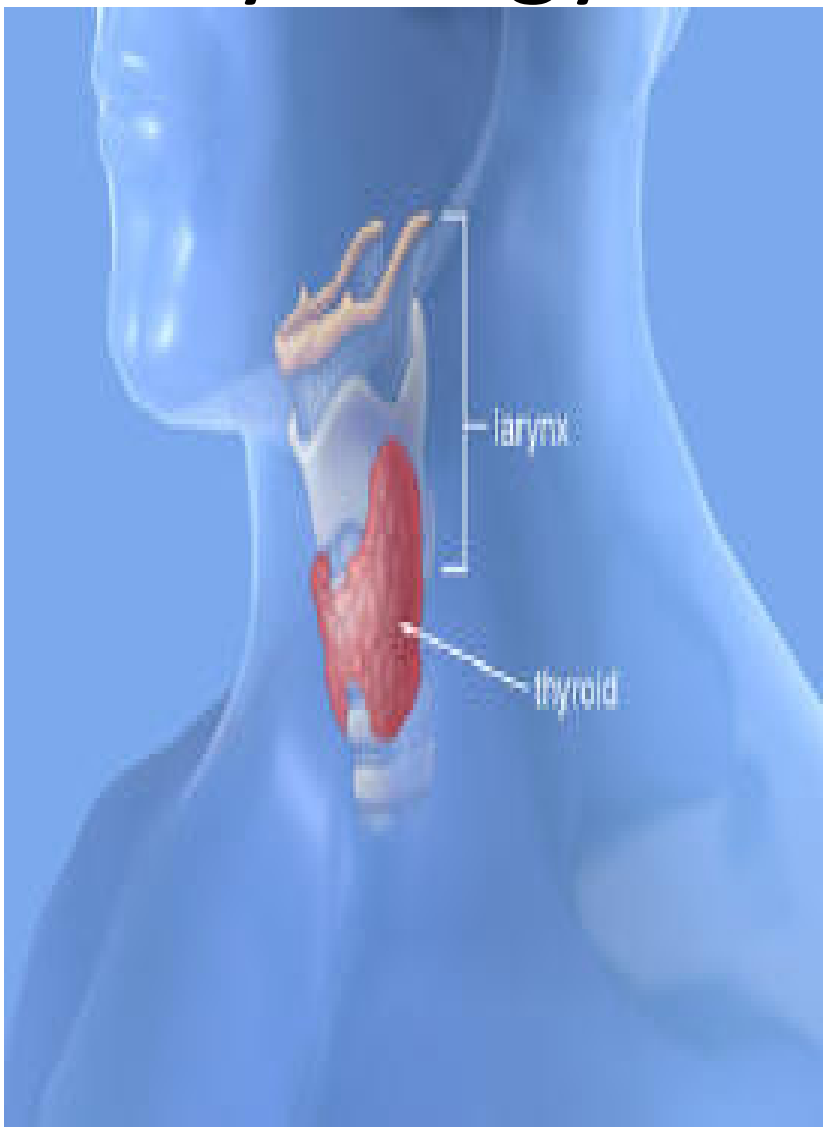
BDE 153



Thyroid Hormone Physiology



An elegant system. The thyroid regulates its hormone output with the aid of the hypothalamus and the pituitary gland. The hypothalamus secretes thyrotropin-releasing hormone (TRH), triggering the pituitary to make thyroid-stimulating hormone (TSH). TSH tells the thyroid to capture iodine from the blood to synthesize, store, and release thyroxine (T_4). When T_4 reaches target cells, it is converted to triiodothyronine (T_3). The hypothalamus and pituitary reduce their output of TRH and TSH once T_4 reaches an adequate circulating level, then resume output when the T_4 level again drops.



It has been demonstrated in a competition study using **Transthyretin (TTR), one of the thyroid hormone binding transport proteins** and BFRs, **hydroxylated brominated flame retardants are able to bind to TTR with extremely high potency** e.g. **TBBPA and PBP**.

It was also demonstrated that **hydroxylation in the para position with preferably two adjacent halogen substituents** is an essential requirement in the **binding of brominated bisphenols to TTR**. It is hypothesized that these lateral halogens (3 3', 5 5') can occupy the binding pockets of **TTR normally occupied by the di-iodo-phenolic ring of the thyroxine molecule.**

However, X-ray Crystallographic studies showed that hydroxyl group in PBP and TBP was not essential for binding to TTR. **Of the 17 PBDEs examined in this study, none of the parent compounds competed with T4-TTR**. Hence metabolic conversion is essential for displacing I-T4 from TTR.

The binding of HO-PBDEs and HO-PCBs to TTR may be involved in the facilitated transfer of compounds across the placenta and the blood-brain barrier, leading to a high level in the fetus especially in the fetal brain. Interestingly, in vivo rather than TBBPA, **metabolites of PBDE like BDE 47 compete with Thyroxine for the TTR binding site.**

Source: Meerts H A T M, Zanden J J V, Luijks E A C, Leeuwen-Bol I V, Marsh G, Jakobsson E, Bergman A Brouwer A; Potent competitive interactions of some Brominated Flame retardants and related compounds with human Transthyretin in vitro; Toxicological Sciences 56, (2000) 95-104; Society of Toxicology

COMPETITIVE MECHANISM OF BFRS

Autism Spectrum Disorder (ASD) among humans is characterized by **social and communication deficits, various degrees of cognitive impairment, repetitive behaviors and in some cases frank neurological motor and seizure** disorders. Recent increases in the prevalence of ASDs that do not appear to be due to increased ascertainment have been documented.

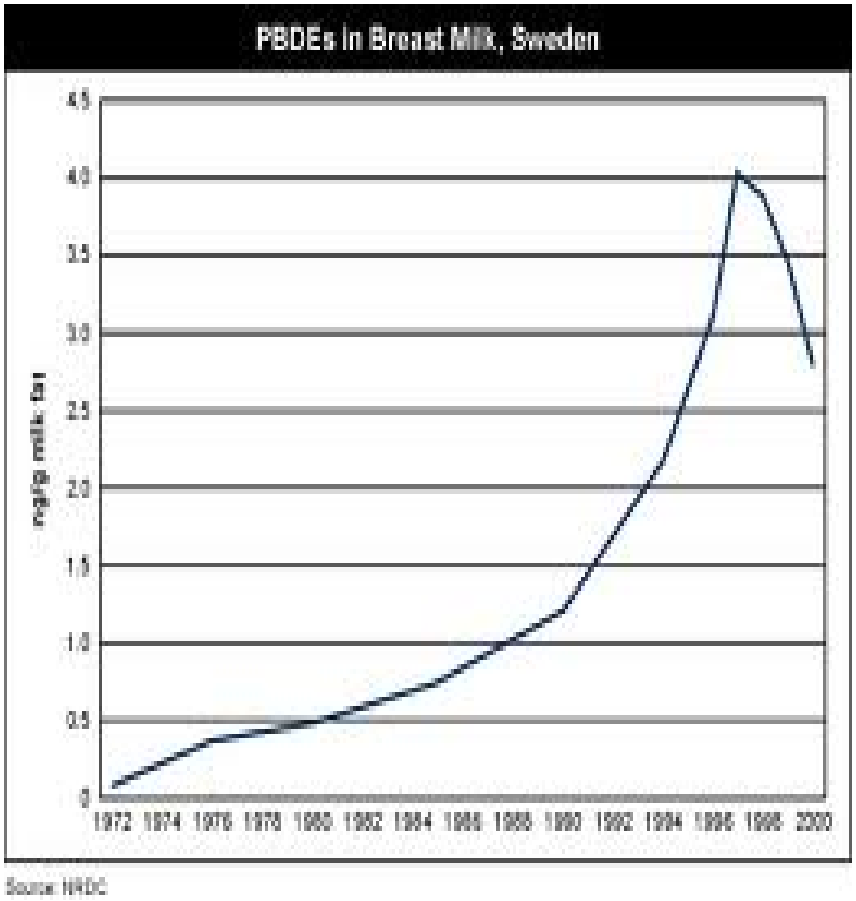
Although there are genetic factors that are responsible for developmental brain defects, there has been **significant increase over the timeframe** observed. During a similar period**, change in the tonnage of brominated flame retardants (BFR) chemicals in the environment** have also been **increasing**. Levels in human milk, maternal and fetal blood especially in the US suggests that these could be acting as **hormone mimetics and affecting the thyroid hormone, a major timing factor for the precise regulation of brain cell growth and connectivity** that is aberrant in ASD.

PBDEs, because of their structural similarities have shown to **disrupt thyroid hormone transport receptors and androgen and estrogen receptors**. Gestational exposure may occur via ingestion by mother during **pregnancy, breast-feeding, from food, indoor household dust and others.**

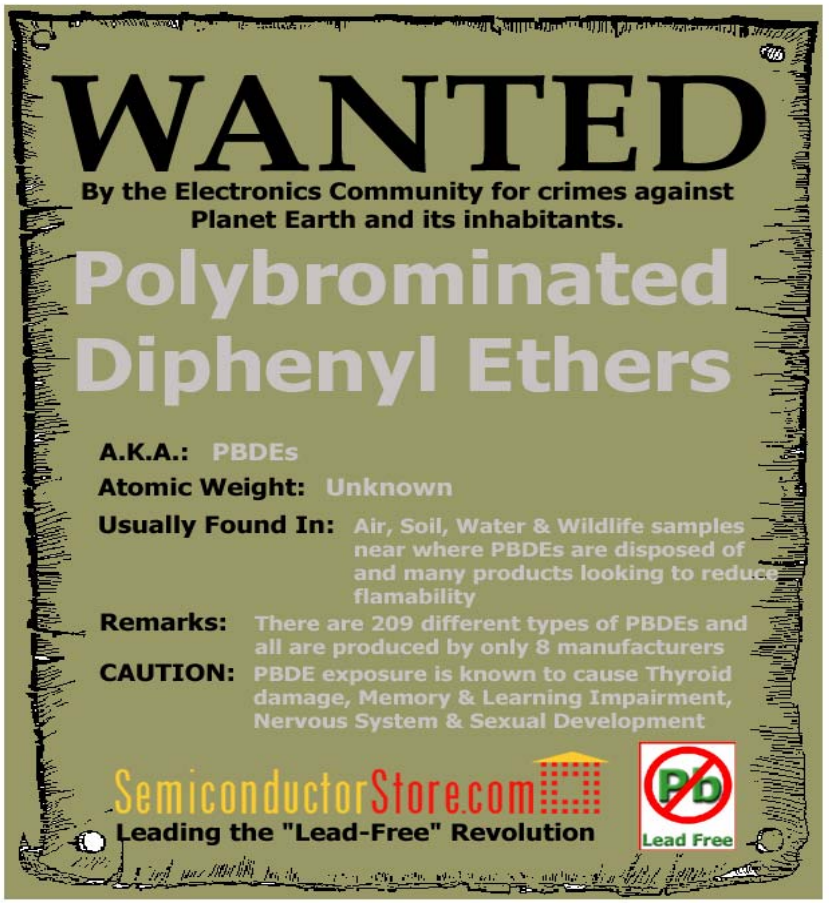
Source: Messer A, Mini-review: Polybrominated Diphenyl Ether (PBDE) flame retardants as potential autism risk factor; Physiology and Behavior; 100 (2010) 245-249

AUTISM AND OTHER BIRTH DEFECTS

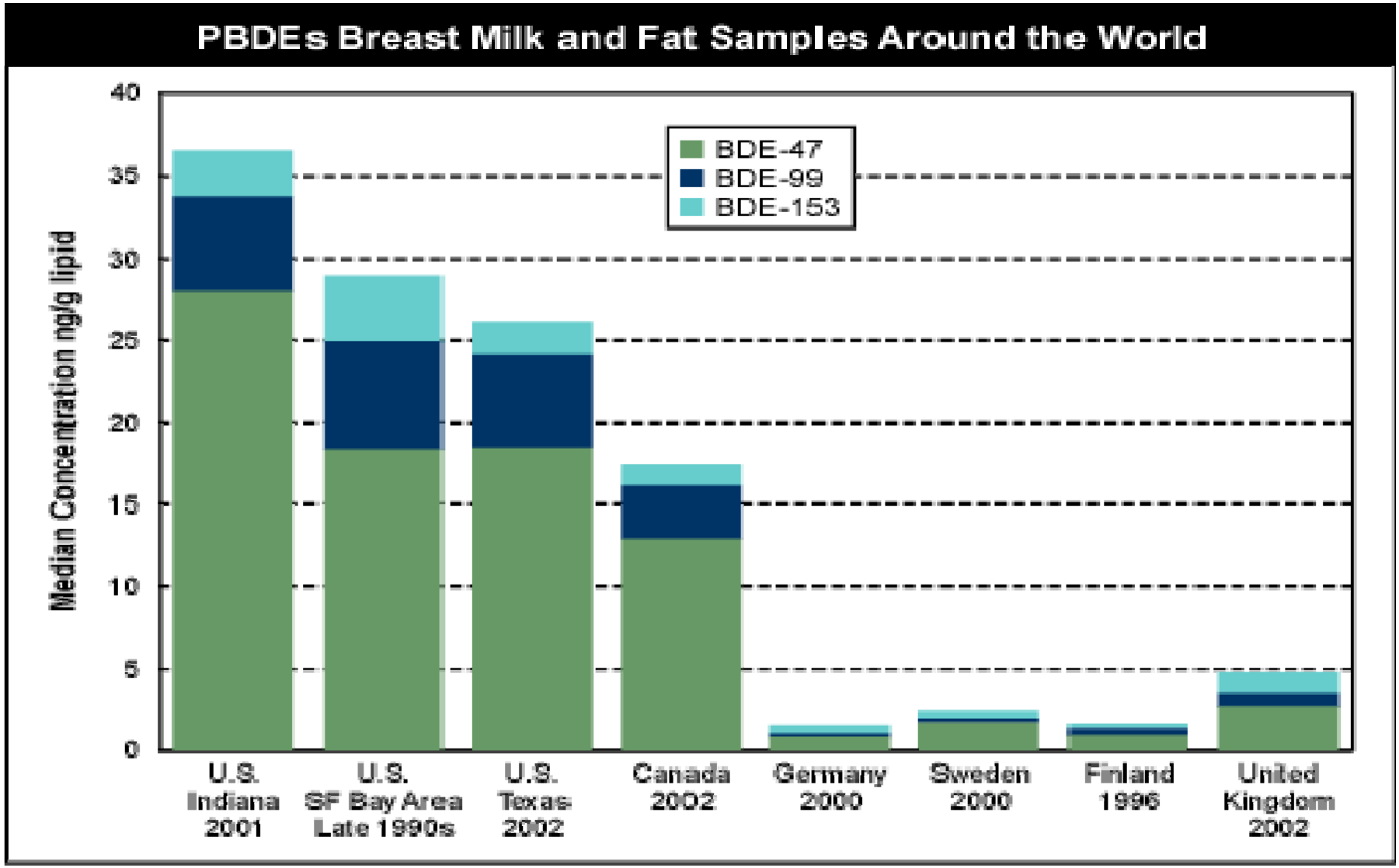
Alarm in Europe



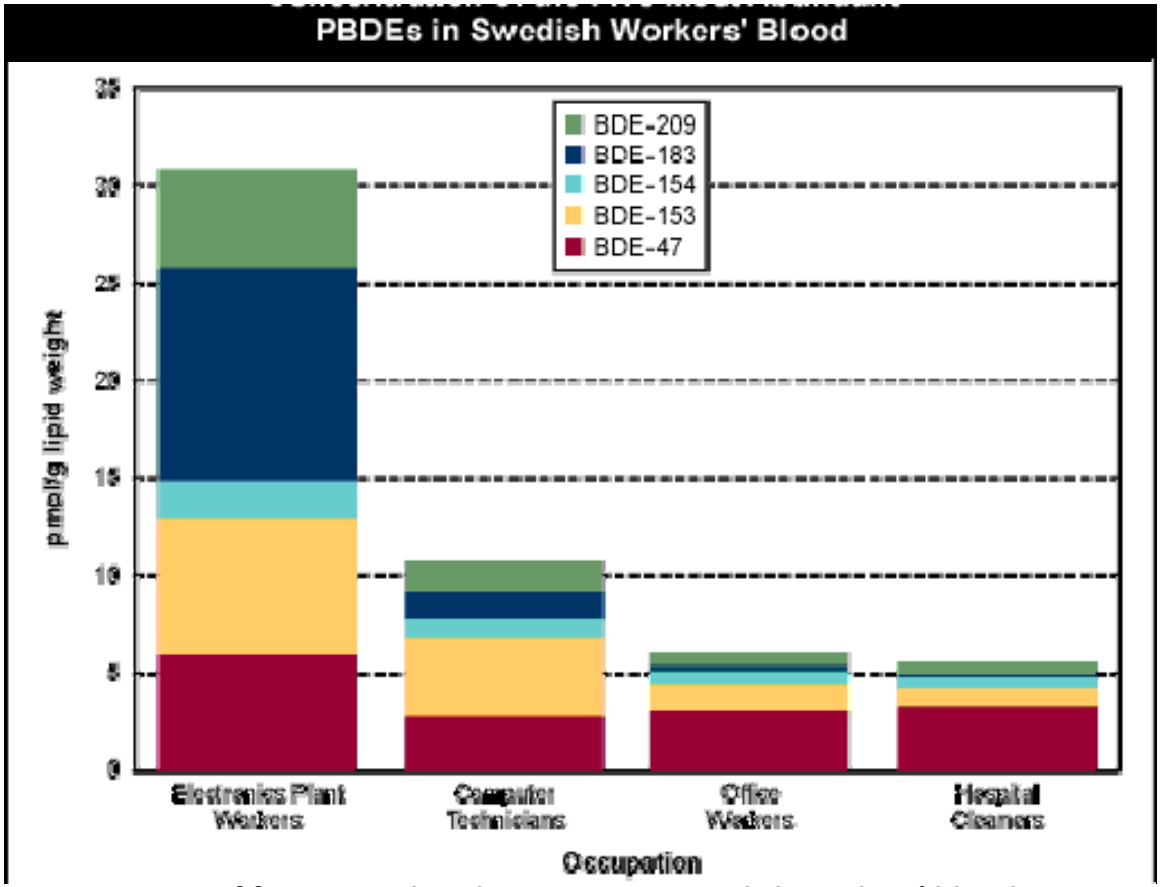
Source: NRDC



Increasing concentration in breast milk and fat samples



Source: Figure 3 in Schecter et al (EHP, August 2003), Table 1 in Mazdai et al (EHP, July 2003), and Table 1 in Kalantzi et al (EHP, July 2004)



Concentration of five most abundant PBDEs in Swedish workers' blood, **Source: NRDC**

The appearance of increasing levels of deca-BDE in workers with greater exposure to electronic equipment is particularly notable, since deca-BDE is used in far greater volumes than penta- or octa-BDEs. Deca-BDE has been considered to be less harmful than the other PBDE classes because studies have identified penta- and octa-BDEs in much higher concentrations in human and animal fat than deca-BDE, indicating higher rates of bioaccumulation. As a result, in places where PBDEs are regulated, penta- and octa-BDEs have been more stringently restricted or banned than deca-BDE.

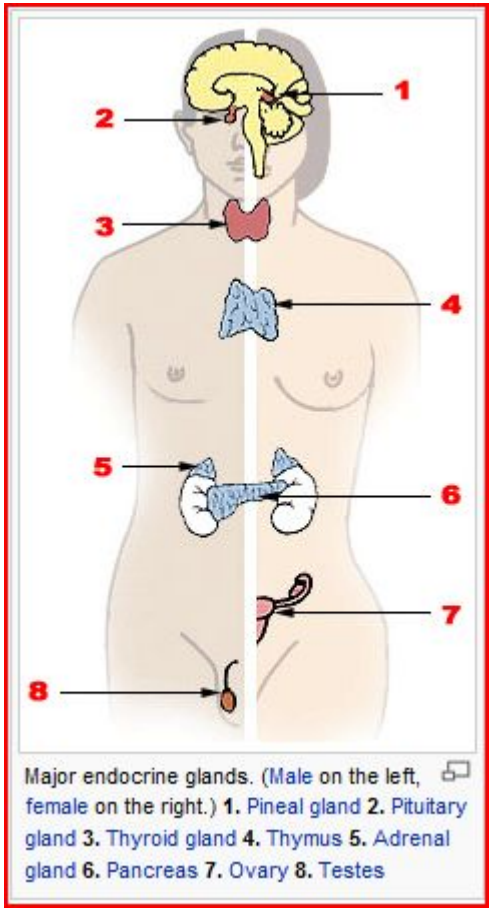
However, through studies such as these, researchers are now finding that deca-BDE is indeed absorbed into the body, though less easily than penta- or octa-BDEs. Other research suggests that deca- and octa-BDEs may also be breaking down in the environment to the more readily absorbed penta-BDEs. Further scientific inquiry is necessary to clarify these differences in occupational exposure and protect workers from PBDEs in the workplace. 'Healthy Milk Healthy Baby ' Source: Natural Resources Defense Council (NRDC), 2003

What are the consequent health effects?

Box 2: Health Hazards of PBDEs Identified in Animal Models

- Evidence of hormone disruption
  - Some forms are estrogen mimics (PBDE 100)
  - Some forms bind to thyroid hormone receptor or disrupt thyroid hormone pathways
- Some evidence of carcinogenicity
- Neurological and reproductive problems
  - Hyperactivity in male rats fed high or low levels
  - Hyperactivity more pronounced as animal ages
  - Spermatogenesis permanently impaired
  - Structural effects in ovaries of female rats
- Developmental defects (skeletal malformations)

Credit: Suzanne Snedeker



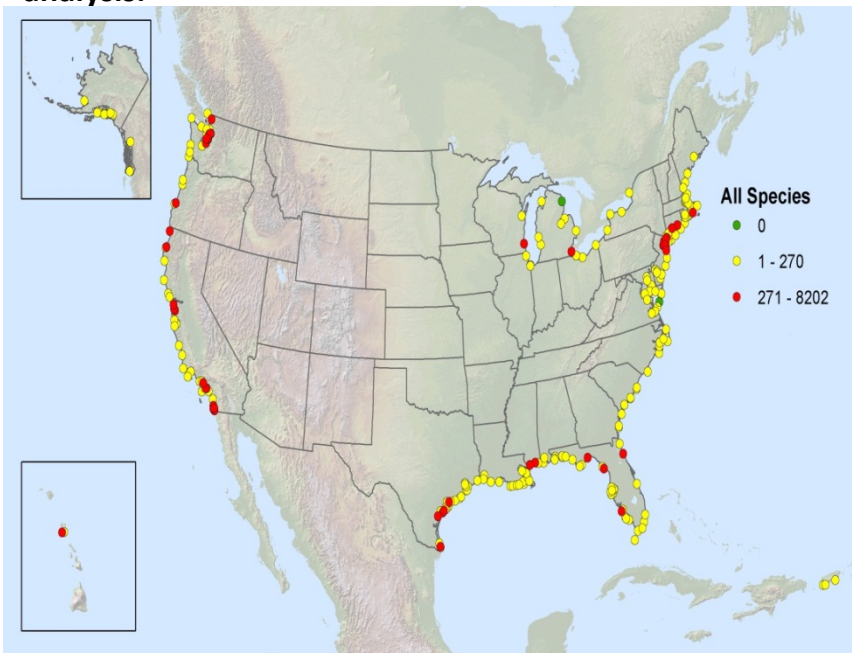
Major endocrine glands. (Male on the left, female on the right.) **1.** Pineal gland **2.** Pituitary gland **3.** Thyroid gland **4.** Thymus **5.** Adrenal gland **6.** Pancreas **7.** Ovary **8.** Testes

Accumulation of flame retardants

According to Nutrition Wonderland Sept.3, 2009, 34,000 metric tons of PBDEs are manufactured in N America every year which are applied to 2.5 million tons of plastic polymers annually

NOAA Report Calls Flame Retardants Concern to U.S. Coastal Ecosystems: April 1, 2009

National Distribution of 200X PBDE tissue concentration in parts per billion lipid weight (where 200X = between 2004 and 2007). Categories low (green dot), Medium (yellow dot), High (red dot) were determined by cluster analysis.



Residues

Butter Contaminated by PBDE Flame Retardant
Science Daily (Dec. 7, 2010)

One of ten samples of butter purchased at five Dallas grocery stores contained high concentrations of deca-BDE, a PBDE compound widely used in electronics as well as in textiles, wire and cable insulation, and automobile and airplane components.

Area oysters contain fire retardant
Two banned chemicals found in oysters from a St. Johns waterway are raising many questions

Source: The Florida Times Union, Jacksonville.com
April 20, 2009

Exposure to the next generation

Pre-natal

Post-natal

Daily dose

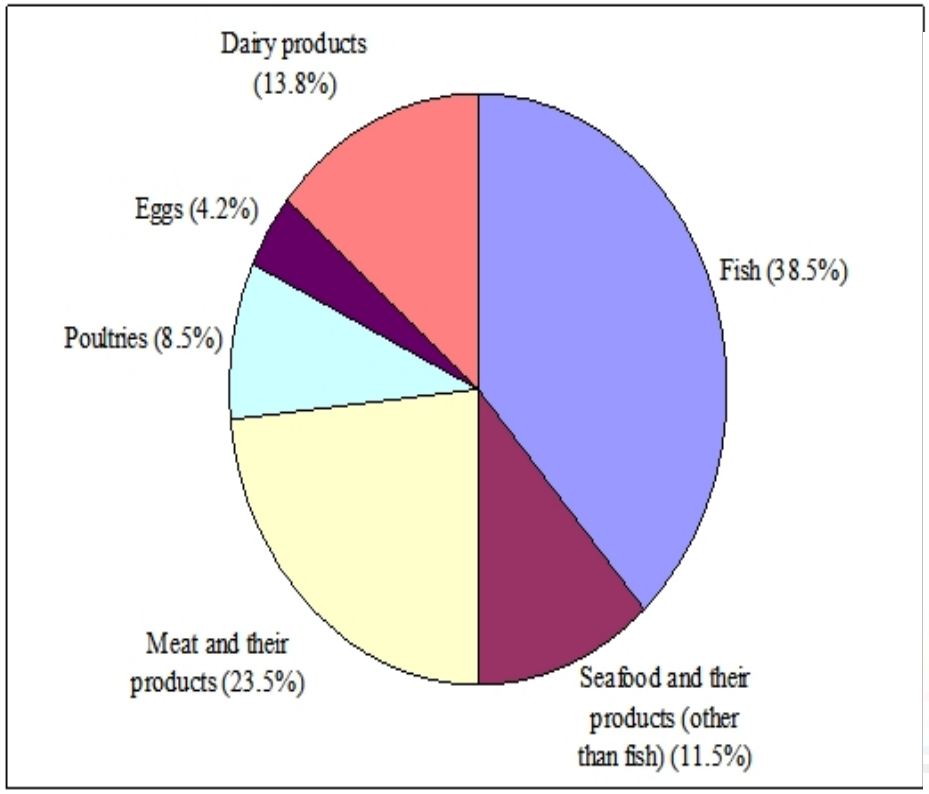


Figure 7. Major Contributing Foods to Total Estimated PBDE Dietary Exposure from Animal Origin for Average Secondary School Students

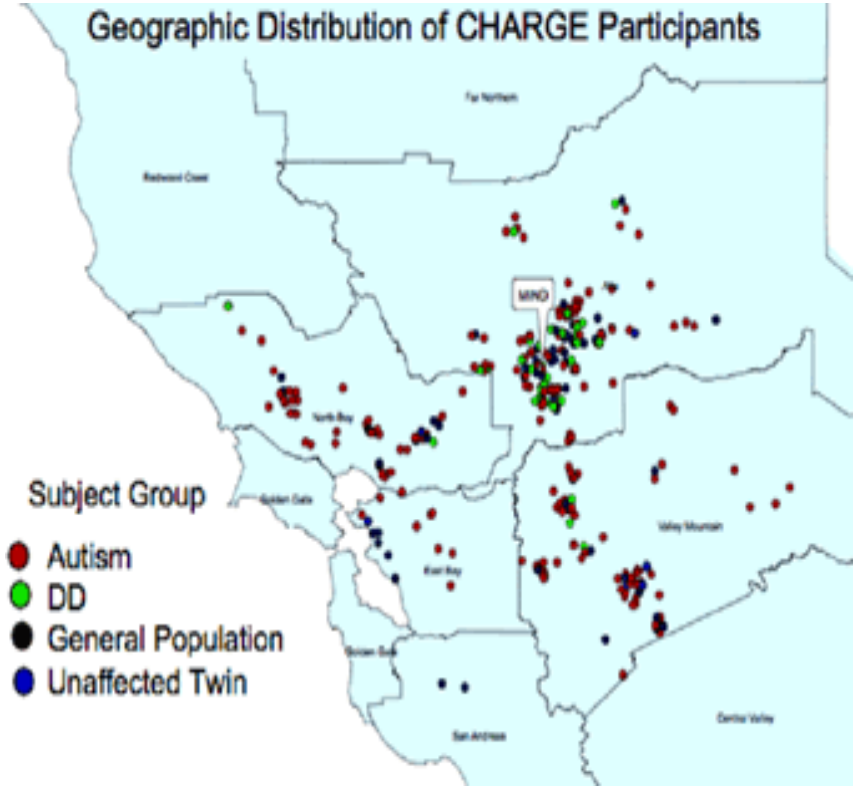
UC Davis Autism study

Groups of children with autism and with mental retardation/developmental delay (MR/DD) participating in studies at the UC Davis Children's Center are enrolled in the State of California Regional Center system (shown here), which serves individuals with developmental disabilities and their families.

UC Davis study

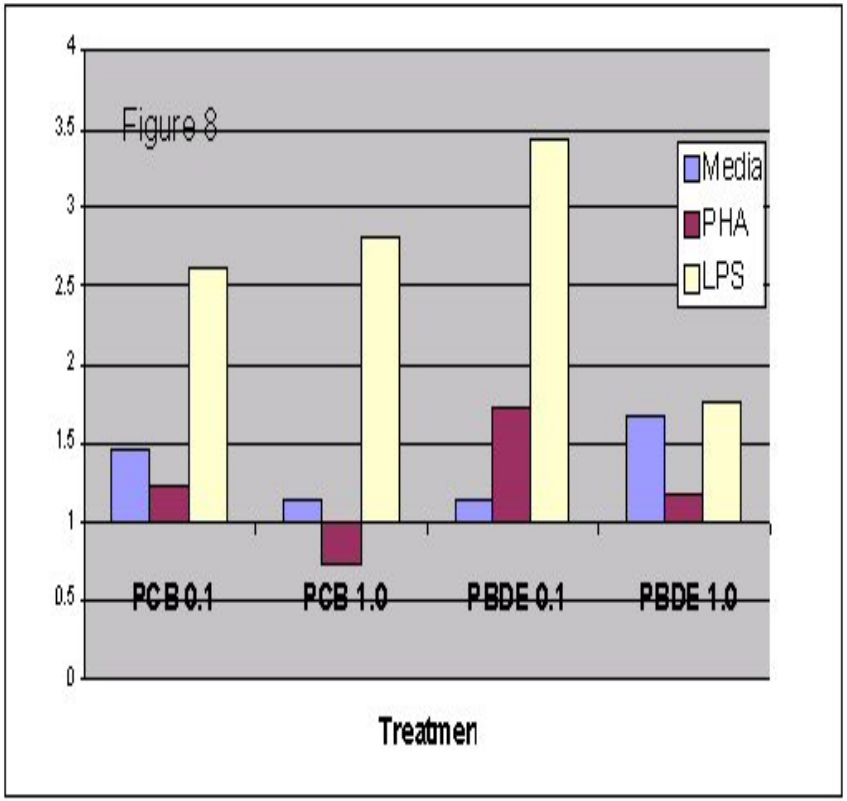
Autism in Bay area

In light of the enormous gap in our understanding of the causes of both autism and developmental delay (DD), a large epidemiologic study was initiated in 2002. The Childhood Autism Risk from Genetics and the Environment (CHARGE) study is addressing a wide spectrum of environmental exposures, endogenous susceptibility factors, and interplay between these two (CHARGE 2006). There is no conclusive evidence of association.



Source: The CHARGE study: An Epidemiologic Investigation of Genetic and Environmental Factors contributing to Autism; Hertz-Picciotto et al, July 2006

Effect of PCB 95 and PBDE 47 on cell proliferation



UC Berkeley study

Pregnant women with higher blood levels of a common flame retardant had altered thyroid hormone levels, a result that could have implications for fetal health, according to a new study led by researchers at the University of California, Berkeley.

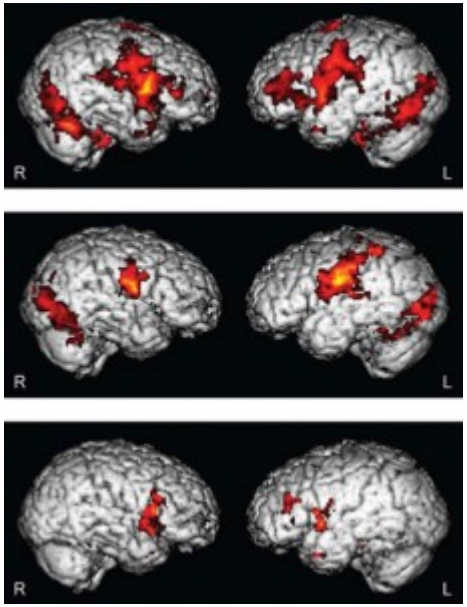
"Low TSH and normal T4 levels are an indication of subclinical hyperthyroidism, which is often the first step leading toward clinical hyperthyroidism," said study's lead author, Jonathan Chevrier.

"Though the health effect of subclinical hyperthyroidism during pregnancy is not well understood, maternal clinical hyperthyroidism is linked to altered fetal neurodevelopment, increased risk of miscarriage, premature birth and intrauterine growth retardation."

Literature: University of California – Berkeley, Flame retardant linked to altered thyroid hormone levels during pregnancy, June, 21, 2010.

The study did not find a statistically significant effect of PBDE concentrations on levels of T4. With one exception, all the women in the study with low TSH levels had normal free T4 levels, which corresponds to the definition of subclinical hyperthyroidism. The study found that odds of subclinical hyperthyroidism were increased 1.9 times for each tenfold increase in PBDE concentrations.

Researchers Study Autism's Neural Signature



European Union study

Based on animal research, bromides have also been linked to **behavioral problems, neurodevelopment and attention deficit hyperactivity disorders** (ADD/ADHD) in children, depression & schizophrenia. **The European Union** has already banned some PBDE (polybrominated diphenyl ethers) compounds, and it is hoped that countries still allowing their use will follow suit. Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH, 2007)

food that contains these PBDEs. In the United States, the concentration of PBDEs (primarily the tetra- and penta-brominated congeners of PBDEs) in outdoor air ranges from 2 to 77 trillionths of a gram per cubic meter (or $2–77x10^{-12}$ grams/m^3), which indicates low levels of exposure of the general population to these PBDEs. Indoor air concentrations of PBDEs in lecture halls, indoor environments with computers, and rooms with computers or other electronic devices, such as television sets, also have low levels of PBDEs in suspended dust. Workers involved in the manufacture and production of PBDE-containing resins are exposed to higher concentrations of PBDEs. Occupational exposure can also occur in confined workplaces where plastic and foam products containing PBDEs are recycled, or where computer monitors containing PBDEs are repaired.

AMBIENT CONCENTRATIONS IN THE US

SOURCE: ATSDR, CDC, USA, SEPT. 2004

PBDEs can occur during the production of commercial PBDE mixtures and of PBDE-containing plastic products. Workers involved in recycling plastic products, or who repair computers in confined workplaces can also be exposed to PBDEs. If you are exposed to PBDEs while at work, you may carry them home on your clothes or body. Your occupational health and safety officer at work can tell you whether the products you work with may contain PBDEs and whether those are likely to be carried home. If this is the case, you should shower and change clothing before leaving work. Your work clothes should be kept separate from other clothes and laundered separately.

Workplace exposure

Excerpt from Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry (ATSDR), CDC, USA

September 2004

E-waste recycling

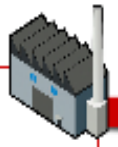
Vulnerable

Regulation

Substances banned under TSCA since 1976	Year banned
Hexavalent chromium used in water treatment in comfort cooling towers	1990
Asbestos	1989
Dioxin in certain wastes	1980
Polychlorinated biphenyls (PCBs) in response to congressional mandate	1979
Halogenated chlorofluoroalkanes used as aerosol propellants	1978

Source: Richard A. Denison, "Ten Essential Elements in TSCA Reform," Environmental Law Reporter (January 2009); Government Accountability Office, "Chemical Regulation: Options Exist to Improve EPA's Ability to Assess Health Risks and Manage its Chemical Review Program," GAO-05-458 (2005).

Sustainable E-waste Recycling



Manufacturer

Manufacturer

Designs new electronic products and consumer products using raw material from recycled waste
Incorporates sustainable design facilitating refurbishing, dismantling and recycling

Retailer

Fixes prices of products to include cost of take-back
Facilitates take-back and pay-forward schemes
Helps collect end-of-life products, electrical and electronic discards from consumers

Raw material and precious metal recovery plants

Receives shredded waste from several locations in the country and world
Uses safe processes and maximizes recovery
Adheres to environmental and occupational safety norms

Toxic Substances Storage and Disposal Facility (TSDF) & Secured Landfill

Toxics characterized, treated, encapsulated, and disposed safely
Continuous Air, Water and Soil testing around facility

Regulator

Prescribes, enforces, monitors standards
Educates public regarding e-waste
Involves public, non-profits and media to emphasize importance of compliance to standards
Supports studies and makes regulations
Recommends higher standards and provides guidelines to achieve them

Consumer

Is a green citizen! Educates self about e-waste management
Purchases safer, durable, sustainable and reusable products
Collects and stores electrical and electronic waste safely, participates in buy back schemes, drops them off regularly

End-of-life Recycling Facility

Receives, dismantles, crushes, sorts & transports end-of-life electrical and electronic products to other facilities for further processing
Adopts best practices, adheres to environmental and occupational safety norms

Is an E-steward
Printed circuit boards containing precious metals for metal recovery sent abroad
All other waste processed domestically

Drop off, Refurbishing, Repair & Dismantling Center

Operates free and cash-back incentive schemes for easy drop-off, pick-up and donations
Repairs, Refurbishes and markets functional products and handles minimal dismantling of end-of-life products

EHS,UCB Short term and Long term studies

- Based on Basel Action Network (BAN)'s request, EHS, UCB has proposed a short project (June-August 2011) to monitor PBDEs in e-waste in e-waste recycling facilities in some states in the US

- To recommend a methodology to e-waste recyclers through the e-steward document for detecting presence and concentration of PBDE congeners in vapor, dust (and possibly blood?)

- A longer project on specific PBDE congeners and analysis of various congeners in vapor, dust and blood during various e-waste recycling activities

Collaborative project between UCB, LBL and DTSC

- Sampling particles of different size (using cascade impactors) in locations within the e-waste recycling facility using pumps 9L/min (Miki Lelland) – Hammond Lab, UCB

- Sampling dust using cyclones attached to smaller pumps close to breathing zone of workers to estimate inhalable, thoracic and respirable or total dust – Hammond Lab, UCB

- Using direct reading/ real-time monitors like Grimms for peaks of specific particle size during hammering and shredding – Hammond Lab, UCB

- Analysis of dust using GC / LC against mixture of standards – Hammond Lab, UCB and LBL

Vapor and Blood sampling

- For BFR/s in gaseous / vapor phase, BFR/s to be absorbed in PUFs with XAD. Pumps required would have to draw 20L/min. Analysis to test the presence of groups of BFRs like penta, octa, deca and C13 labelled BDE 209 - LBL & Hammond Lab

- BFRs in blood of workers (especially of those whose blood samples have been analyzed previously for BFRs) / present samples to be taken as baseline – DTSC, Cal EPA, Berkeley

Number of samples for monitoring BFRs

- Besides using blanks for dust and vapor during shift times, sampling to be done during non-shift times.

- Total number of samples in each location would be: duplicates for dust (cascade impactors or TSP with similar diameter selection criteria) – ambient and on workers, one blank, one Poly-urethane foam (puf) with XAD and blank. Blood samples in triplicates.

- Therefore for shift and non-shift time, there would be 24 samples each, totaling 48 samples and in case puf cartridges are in duplicate, then there would be 54 for dust and vapor and 18 for blood.

Waiting for action

Thank you

PH Significance of Educational toolkit for India

- India's annual generation of e-waste is expected to reach 800,000 tons by 2015. In addition, nearly 50,000 to 80,000 tons of e-waste gets exported to India from various developed countries

- It is estimated that nearly 200,000 in the informal sector and about 20,000 in the formal e-waste recycling sector are exposed daily to heavy metals, solvents and BFRs while recycling e-waste

- Since only 10-12% of the workers are in the formal sector, they have access to Personal Protective Equipment but not the others

- My educational toolkit comprising a film, a poster and a manual on Safer e-mining will help workers in formal and informal sectors adopt best practices and safeguard their health and the environment