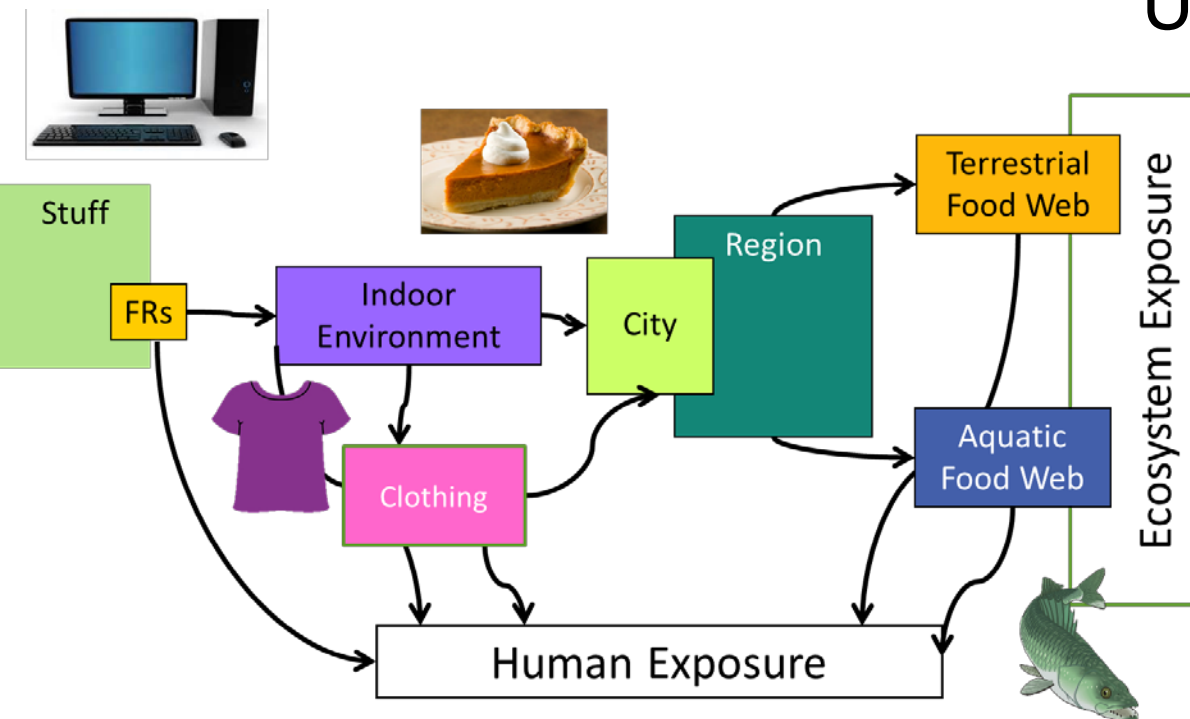


Exposures from Home and Office: the Complicated World of Flame Retardants


Miriam Diamond

University of Toronto

Oct 16, 2015




FLAME RETARDANTS-ONLINE

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The International Electrotechnical Commission IEC and 2010 fire safety activities



Founded in 1906, the International Electrotechnical Commission (IEC) is composed of 82 National Committees, (59 members and 22 associate members) representing all industrial countries in the world. IEC prepares and publishes international standards for all electrical, electronic and related technologies. These serve as a basis for national standardization and as references when drafting international tenders and contracts. The IEC's multilateral conformity assessment systems, based on its international standards, are global in concept and practice, and reduce trade barriers, thus helping industry to open up new markets. One of the most important conformity assessment systems is the CB Scheme. It is based on the principle of mutual recognition by means of certification through the use of internationally accepted standards. With 53 member countries, the International Electrotechnical Committee for Conformity Testing to Standards for Electrical Equipment (IECEE) is a global network of National Certification Bodies (NCBs) that has agreed to mutual acceptance of CB test certificates and reports. The Scheme is based on the use of international (IEC) Standards.

The CB-Scheme applies to many specific product categories established by the IECEE, for example IEC 60065 "Audio, video and similar electronic apparatus - Safety requirements", or IEC 60335 "Safety of household and similar electrical appliances". If a product is already UL-Listed, Classified, Recognized or has a test mark, such as a German GS- or VDE-Mark, these tests are usually

05.01.2015

December – The month of fires

Fire risk is particularly high in December. In Germany, during the adv... more...

03.12.2014

Busses - Fire Safety Requirements tightened, but not enough

Compared to other transportation means, the fire safety requirements f... more...

04.11.2014

Fire safety requirements and tests for railway vehicles in China

In China, fire safety requirements for railway vehicles have basically... more...

06.10.2014

Workshop on flame retardants and presentation of German AIF research projects at the Fraunhofer LBF in Darmstadt, Germany, on 18 September 2014

The Working Group Fire Safety of the plastics section in the Fraunhofer... more...

15.09.2014

Revision of the UK 1988 Furniture and Furnishings (Fire) (Safety) Regulations

The UK 1988 Furniture Fire Safety Regulations set levels of fire resis... more...

10/16/2015

<http://flammschutz-online.com/web/en/news/index.htm?showid=277>

Benefits



<http://flameretardants.americanchemistry.com/>

Risks of mortality, morbidity and costs from fires

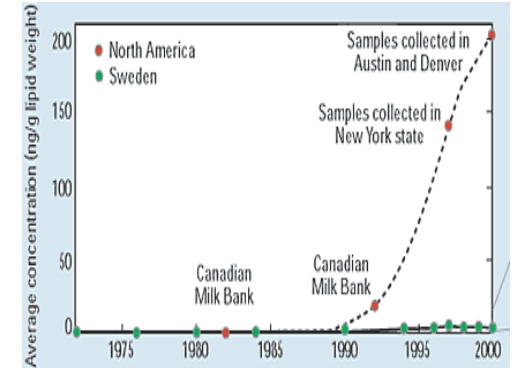
Benefits of reducing fires

Risk management: add flame retardants (FRs) to product

Benefit-Risk Dilemma



<http://flameretardants.americanchemistry.com/>



Betts 2002 *Environ Sci Technol* 36:50A-52A.

Risks of mortality, morbidity and costs from fires

Benefits of reducing fires

Risk management: add flame retardants (FRs) to product

Risks of morbidity and costs from FRs

Benefits from reduced contaminant burden

Risk management: Chemical Management Plan



TRIBUNE WATCHDOG PLAYING WITH FIRE

Chemical companies, Big Tobacco and the **toxic products** in your home

5.6k

Like

The average American baby is born with 10 fingers, 10 toes and the highest recorded levels of flame retardants among infants in the world. The toxic chemicals are present in nearly every home, packed into couches, chairs and many other products. Two powerful industries — Big Tobacco and chemical manufacturers — waged deceptive campaigns that led to the proliferation of these chemicals, which don't even work as promised.

► **Watch the introduction**



INDUSTRY DECEPTION



Part one: Torching the truth

As evidence of health risks piled up, makers of flame retardants created a phony consumer watchdog that misled lawmakers and the public by stoking the fear of fire. **Read »**

■ **Tests call effectiveness of flame retardants into question**

TOBACCO'S CLOUT

Graphics

May 2012

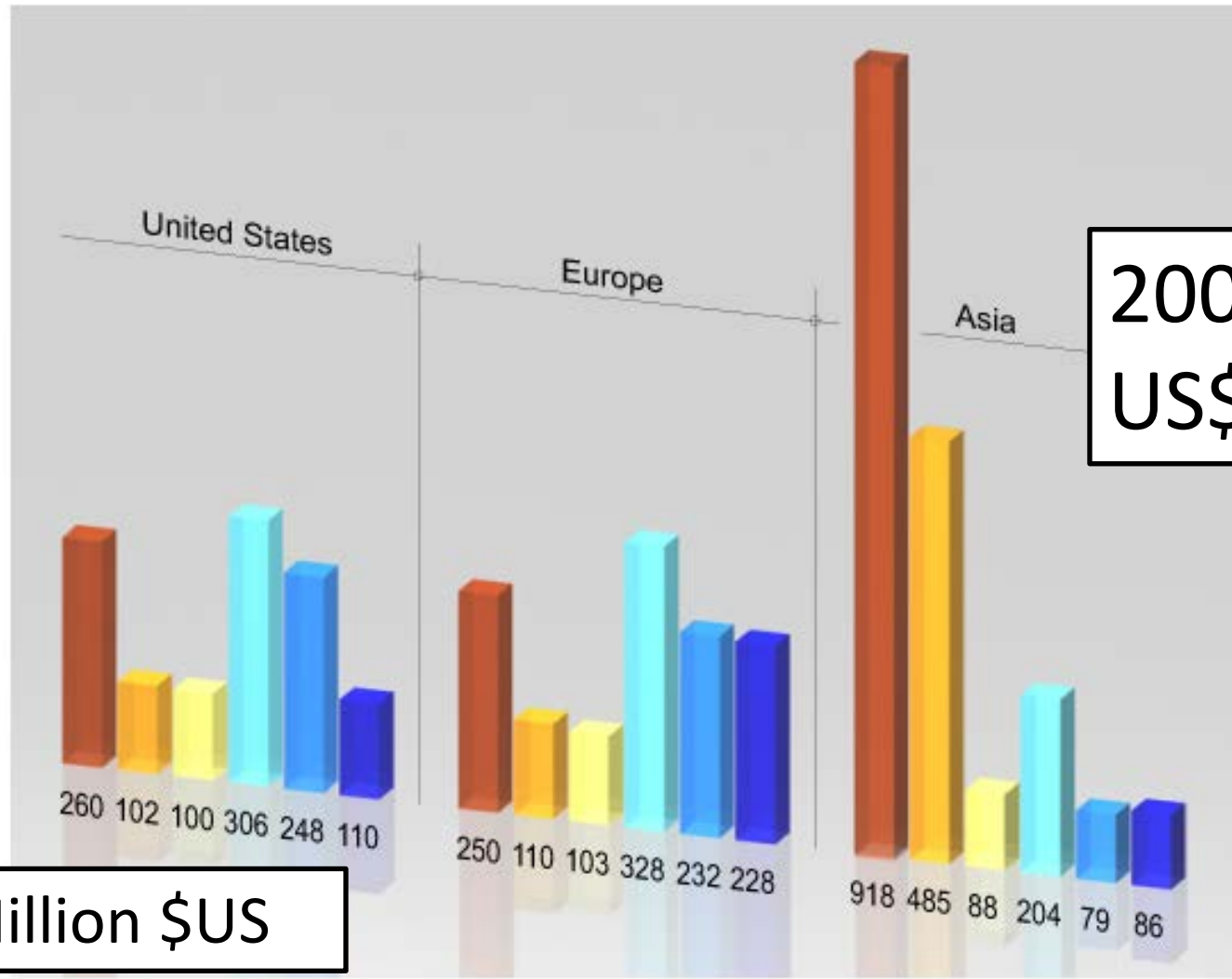
Outline

- Flame retardants & mode of action
- Human biomonitoring & health effects
- Exposure pathways
 - Product \Rightarrow Emission \Rightarrow Exposure
 - Role of Clothing
- Interventions & mitigation: flammability standards

Flame Retardants are Lucrative

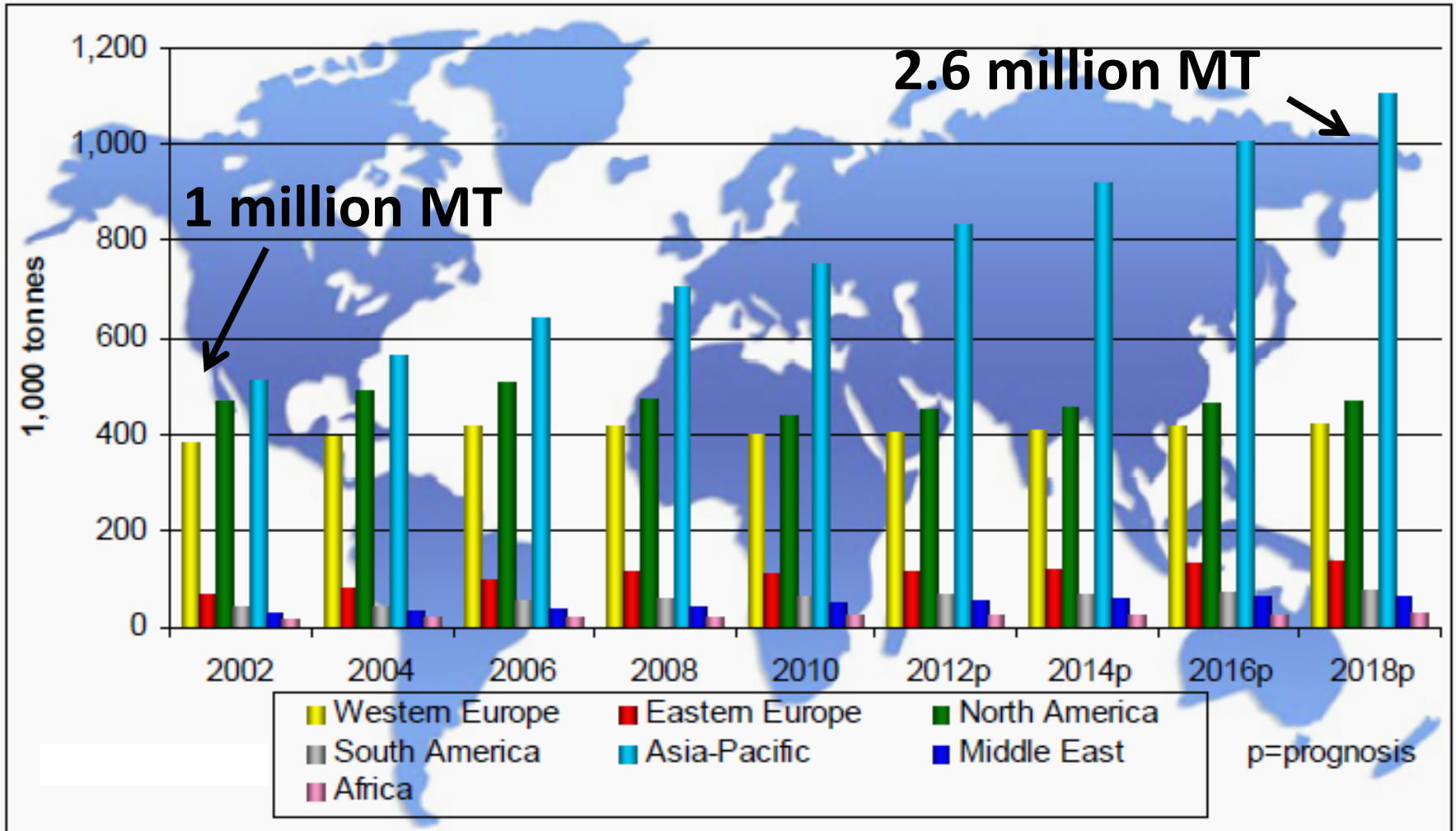
2007: Total
US\$ 4.2 billion

Million \$US



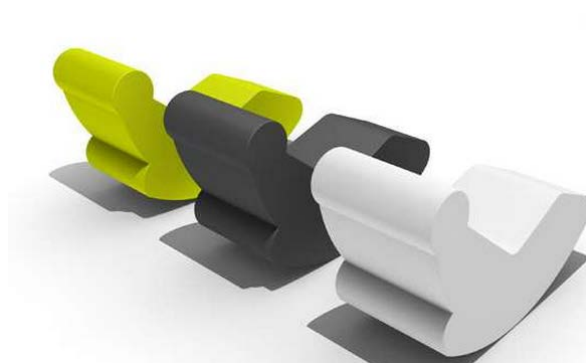
Brominated Antimony Oxides Chlorinated Organo Phosphorus Aluminium Hydroxide Other

FRs Global Market Demand



A Quick History of Flame Retardants

- Chemicals added to materials to reduce flammability
- More stuff
- More synthetic materials
- Chemical “intensification” (UNEP Global Chemicals Outlook 2013)



Tobacco Lobby



<http://everyonegoeshome.com/news/smokinghomefires.html>

A screenshot of an MSNBC news article. The article title is "Smokers burned over 'fire-safe cigarettes'" and the subtitle is "Self-extinguishing smokes sweep the country, but many say they taste bad". The author is listed as "By M. Alex Johnson, Reporter". The article was updated on 1/27/2009 at 8:31:09 AM ET. There are social media sharing buttons for Facebook, Twitter, and YouTube, and a "Jump to discuss comments below" button. A date box on the right side of the screenshot contains the text "2009-2010".

2009-2010

B. O'Malley. 1979. Cigarettes and sofas: how the tobacco lobby keeps the home fires burning. Centre for Investigative Reporting, Mother Jones.

10/16/2015

A Quick History of Flame Retardants

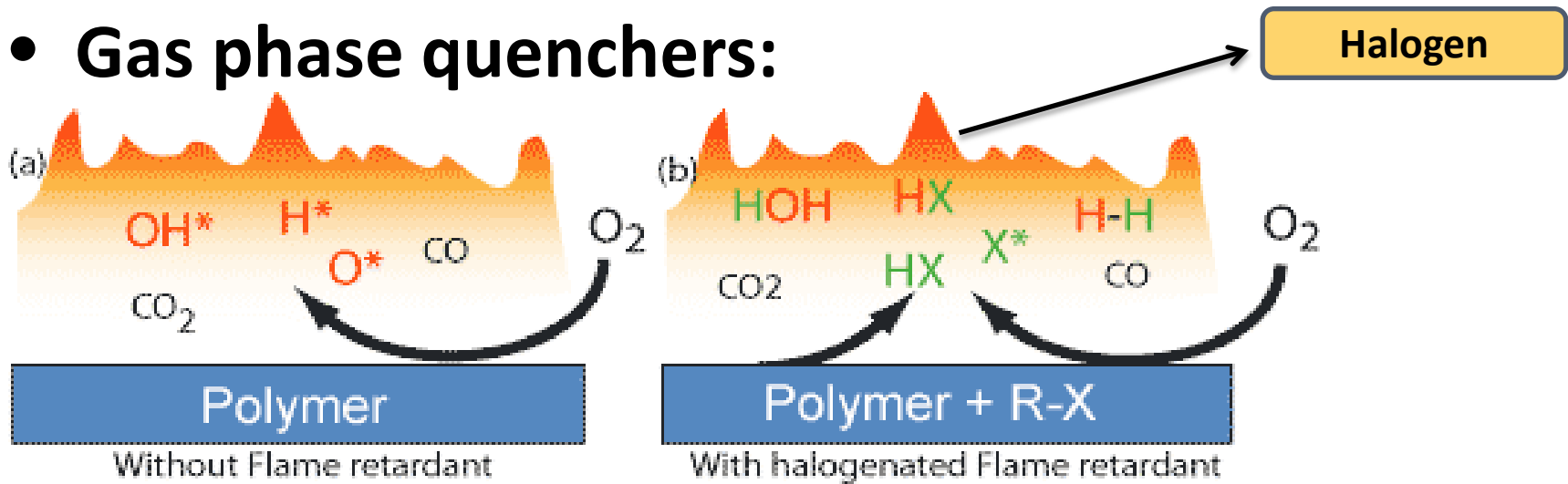
Electrical devices

- Asia & Europe: 220 volts
 - High voltage \Rightarrow Shock
- North America: 110 volts
 - Low voltage, higher resistance \Rightarrow Overheating

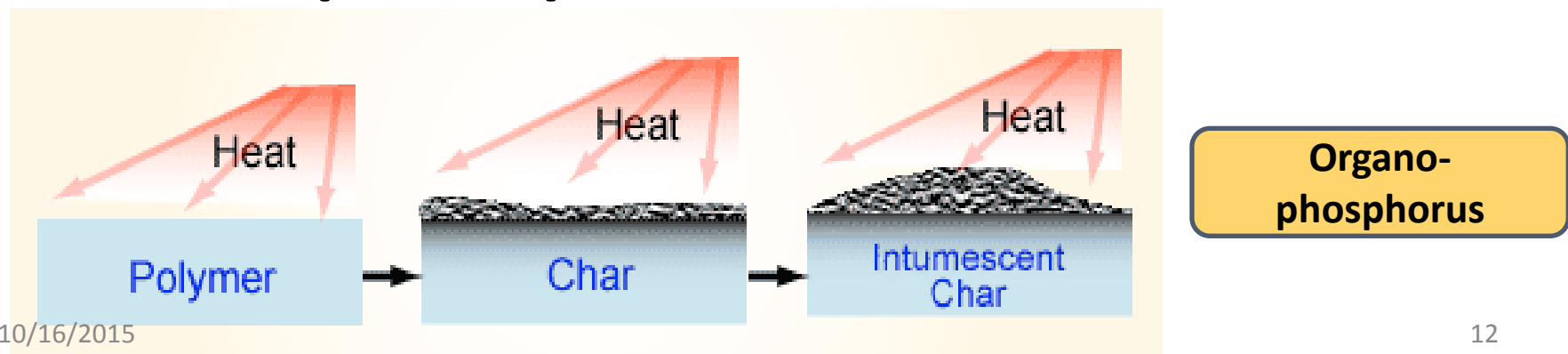


Mode of Action

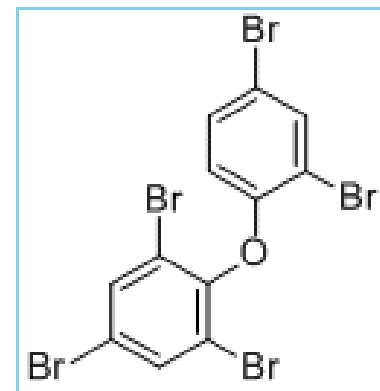
- **Gas phase quenchers:**



- **Particle phase quenchers:**



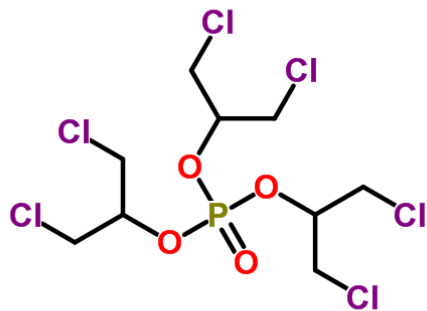
Halogenated Organics



Polybrominated diphenyl ethers (PBDEs)

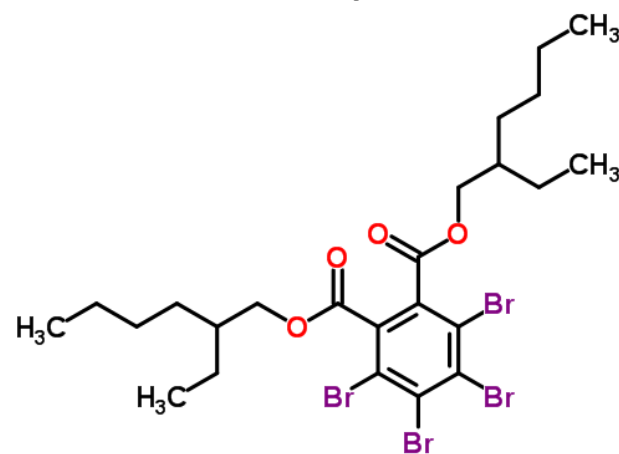
http://www.chemicalbook.com/ChemicalProductProperty_EN_CB7841510.htm

- Gas-phase quenchers
 - Halogen (Br, Cl) react with free radicals from fire
- Most are additive FRs (vs reactive)



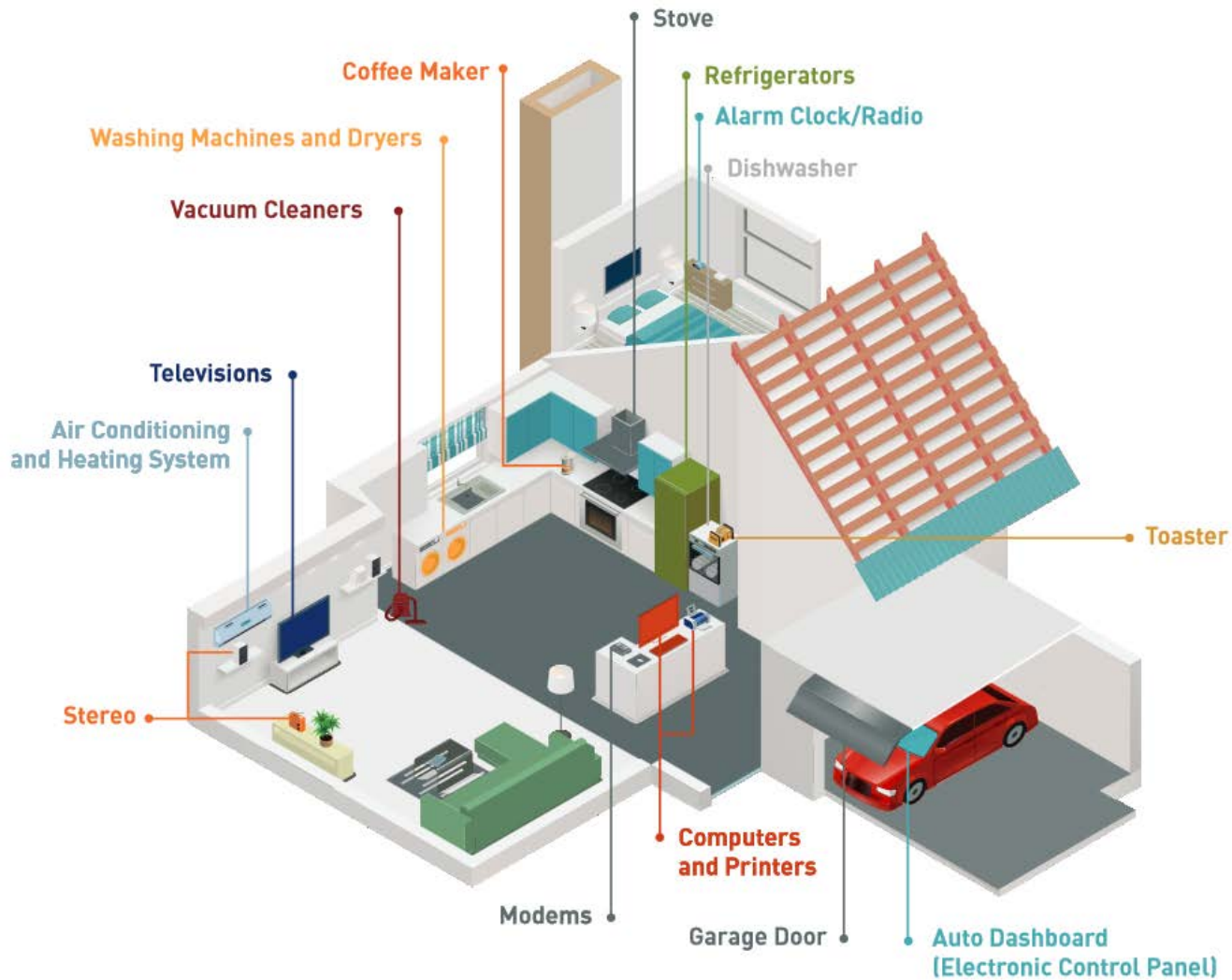
TDCPP (tris(1,3-dichloro-2-propyl) phosphate)

<http://www.chemspider.com/Chemical-Structure.24388.html?rid=255c355c-ef17-4fca-aae9-a5fa21b6c281>



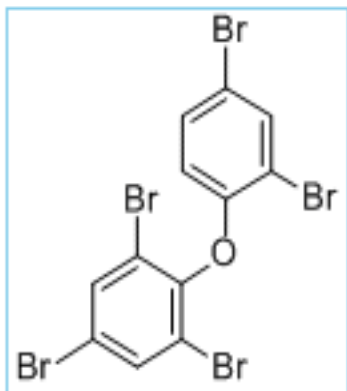
Tetrabromophthalate

<http://www.chemspider.com/Chemical-Structure.104816.html>

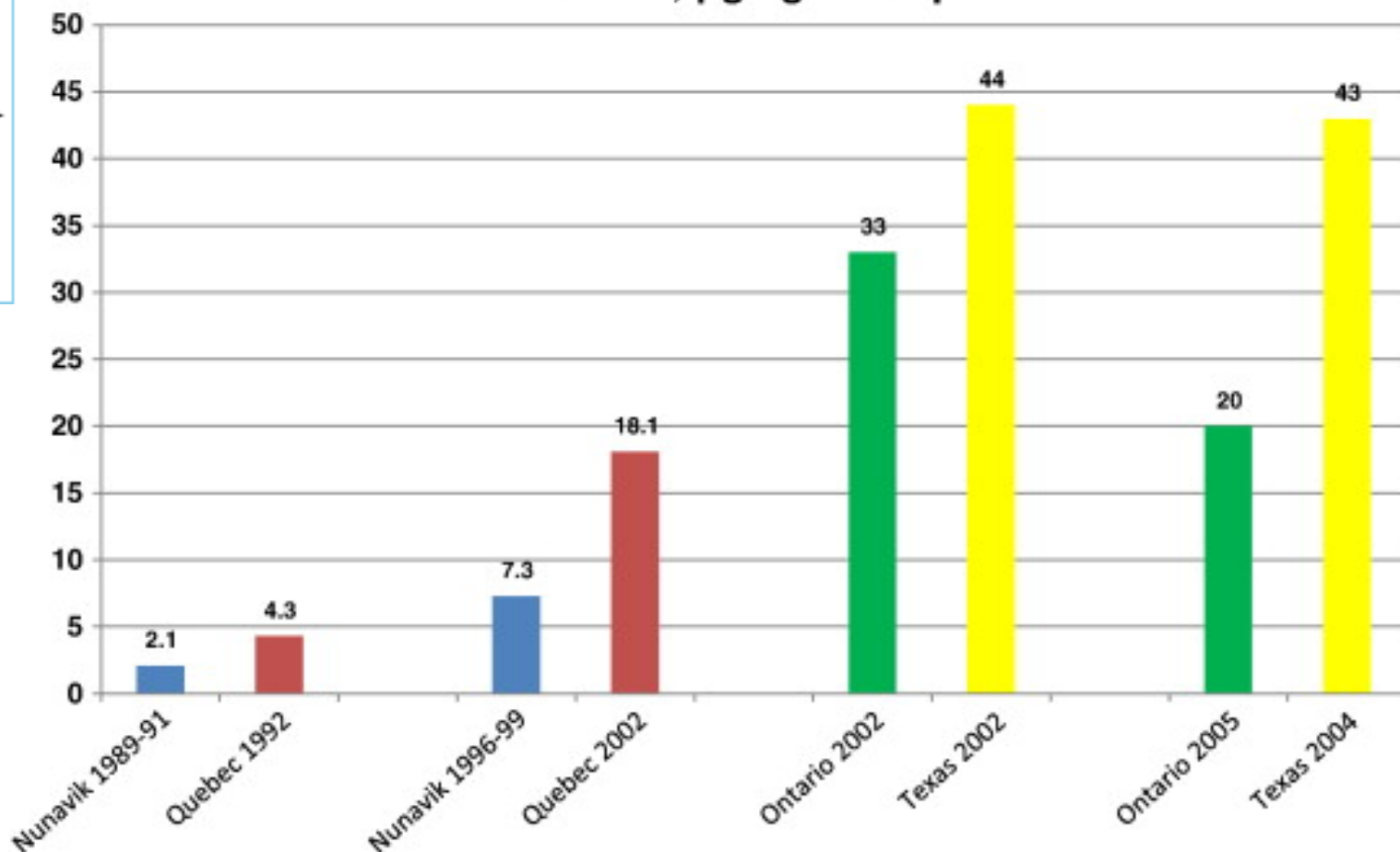


BENEFITS OF ELECTRONIC FIRE SAFETY TOOLS IN THE HOME & OFFICE

Flame retardants are added to different materials or applied as a treatment to materials (e.g. plastics) that are used in electronics and electronic appliances to prevent fires from starting, limit the spread of fire and



Σ -PBDE; $\mu\text{g}/\text{kg}$ milk lipid

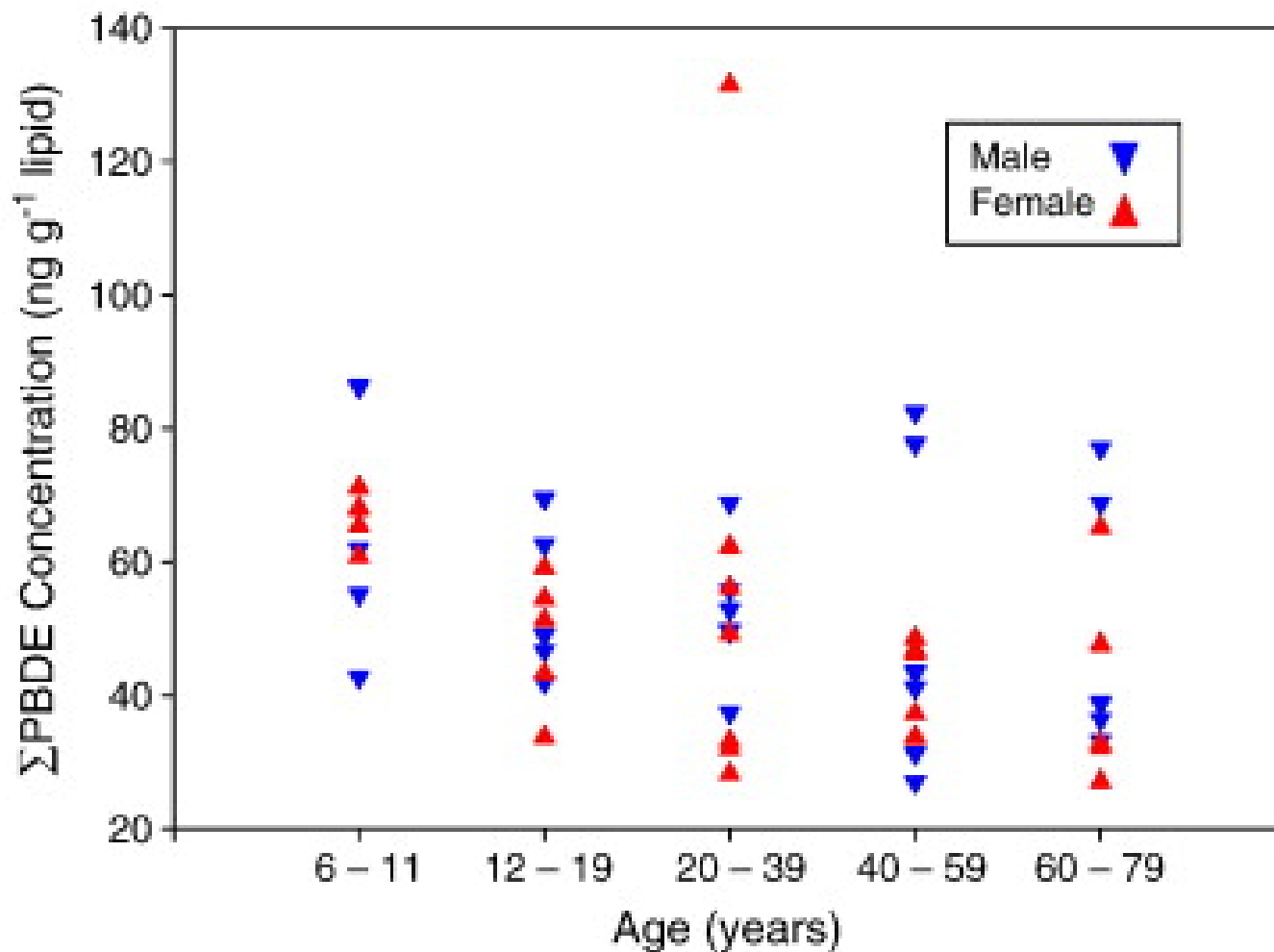


Comparison of Σ -PBDEs in individual milks by latitude for Quebec/Nunavik for 1992/2002 and by country for Canada/USA for 2002/2005.

John Jake Ryan , Dorothea F.K. Rawn

The brominated flame retardants, PBDEs and HBCD, in Canadian human milk samples collected from 1992 to 2005; concentrations and trends

Environment International, Volume 70, 2014, 1 – 8 .doi.org/10.1016/j.envint.2014.04.020



PBDE concentrations in Canadian human serum pools distributed by age (years).

Dorothea F.K. Rawn, J. Jake Ryan, Amy R. Sadler, Wing-Fung Sun, Dorcas Weber, Patrick Laffey, Douglas Haines, Kristin Macey, Jay Van Oostdam

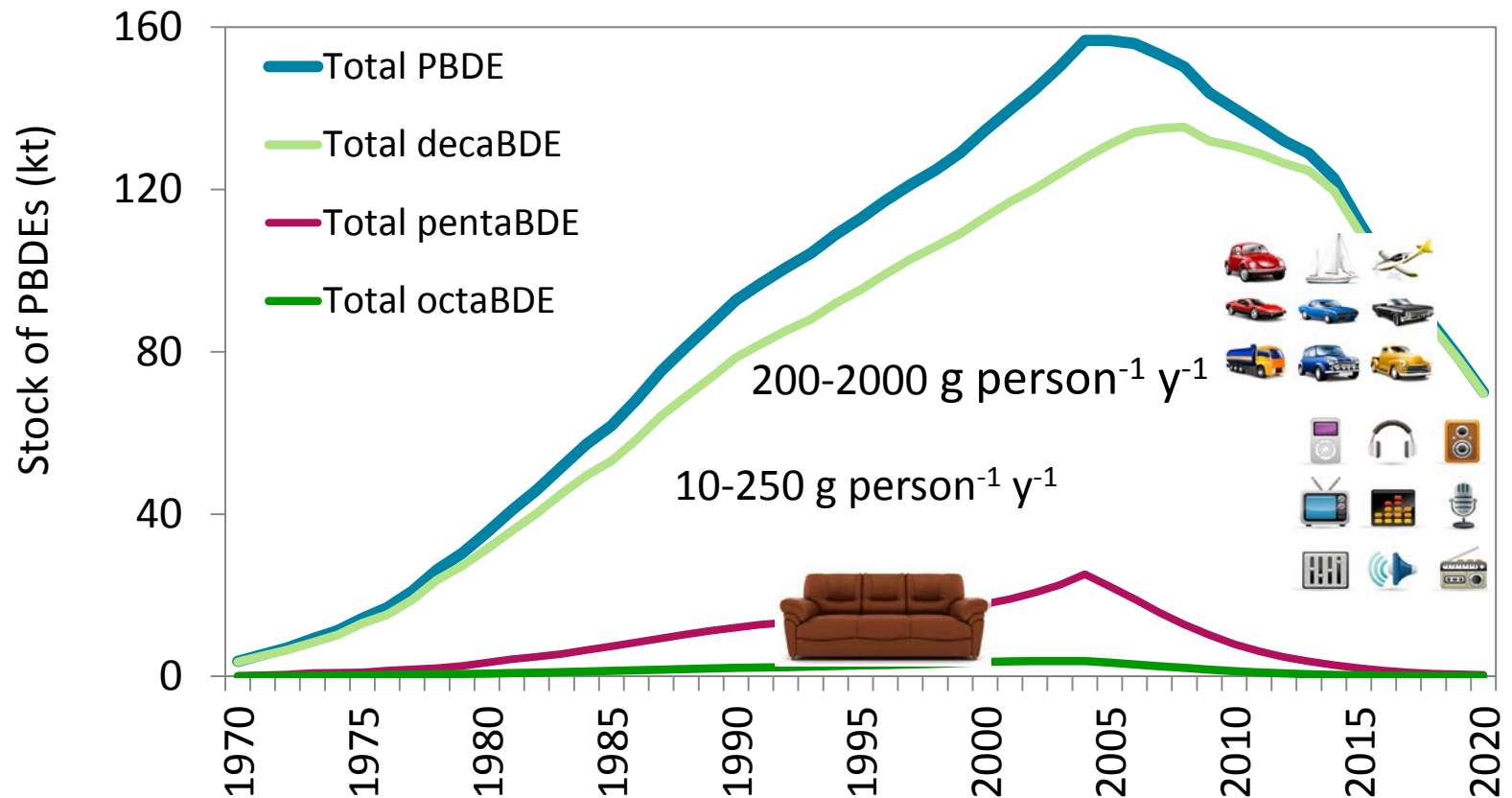
Brominated flame retardant concentrations in sera from the Canadian Health Measures Survey (CHMS) from 2007 to 2009

Environment International, Volume 63, 2014, 26–34, <http://dx.doi.org/10.1016/j.envint.2013.10.012>

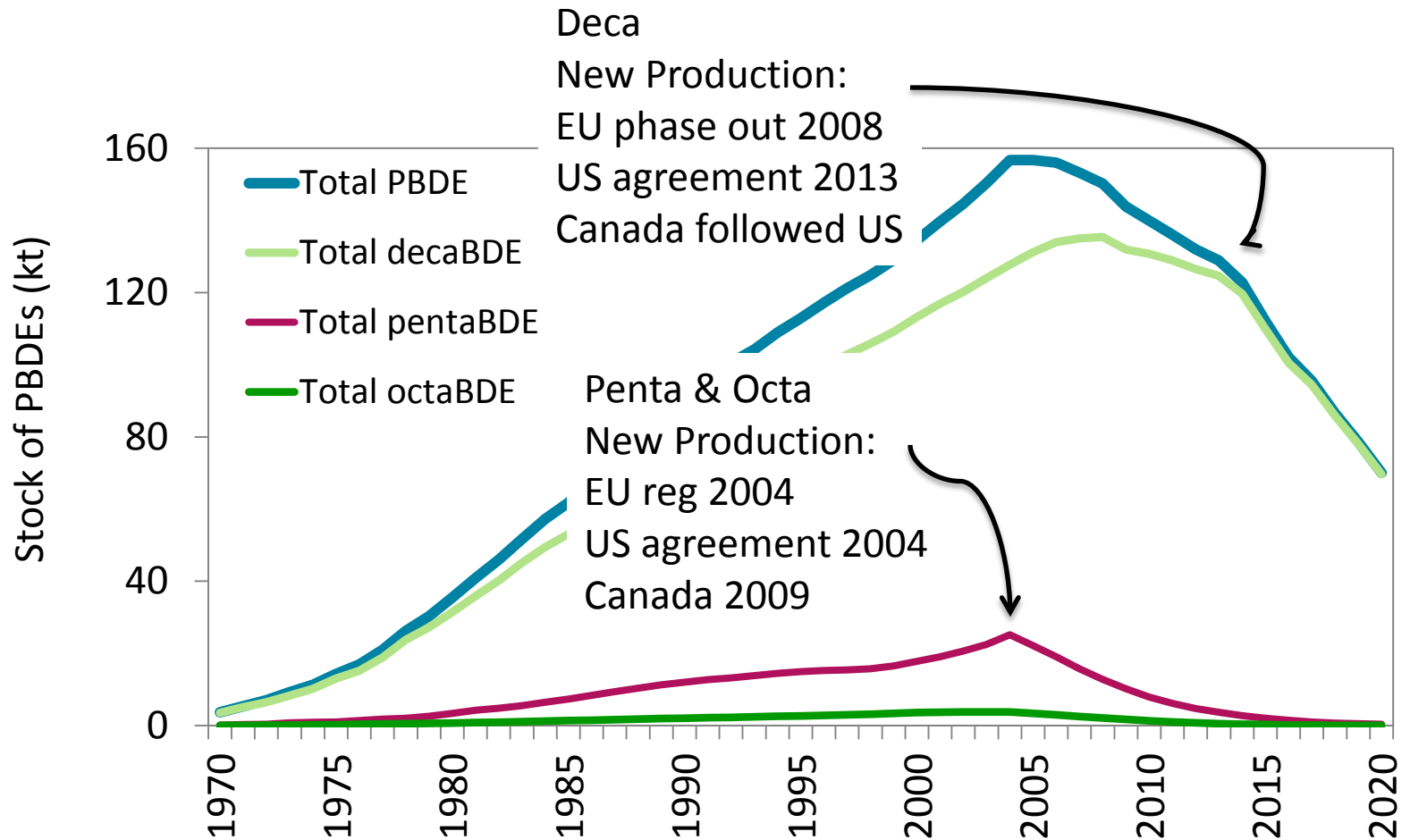
Health Effects of PentaBDE

- Endocrine modulation (Bellanger et al. 2015)
- Altered thyroid and estrogen/androgen hormones systems (Meeker & Stapleton 2009, Turyk *et al.* 2009, Ernest et al. 2012)
- Longer time to pregnancy (Harley et al. 2010)
- Developmental neurotoxicity (Herbstman et al. 2010, Eskenazi et al. 2013, Gascon et al. 2012, review by Roth & Wilks 2014)
 - ↓ motor skills
 - ↓ cognition & IQ
 - ↓ behaviour

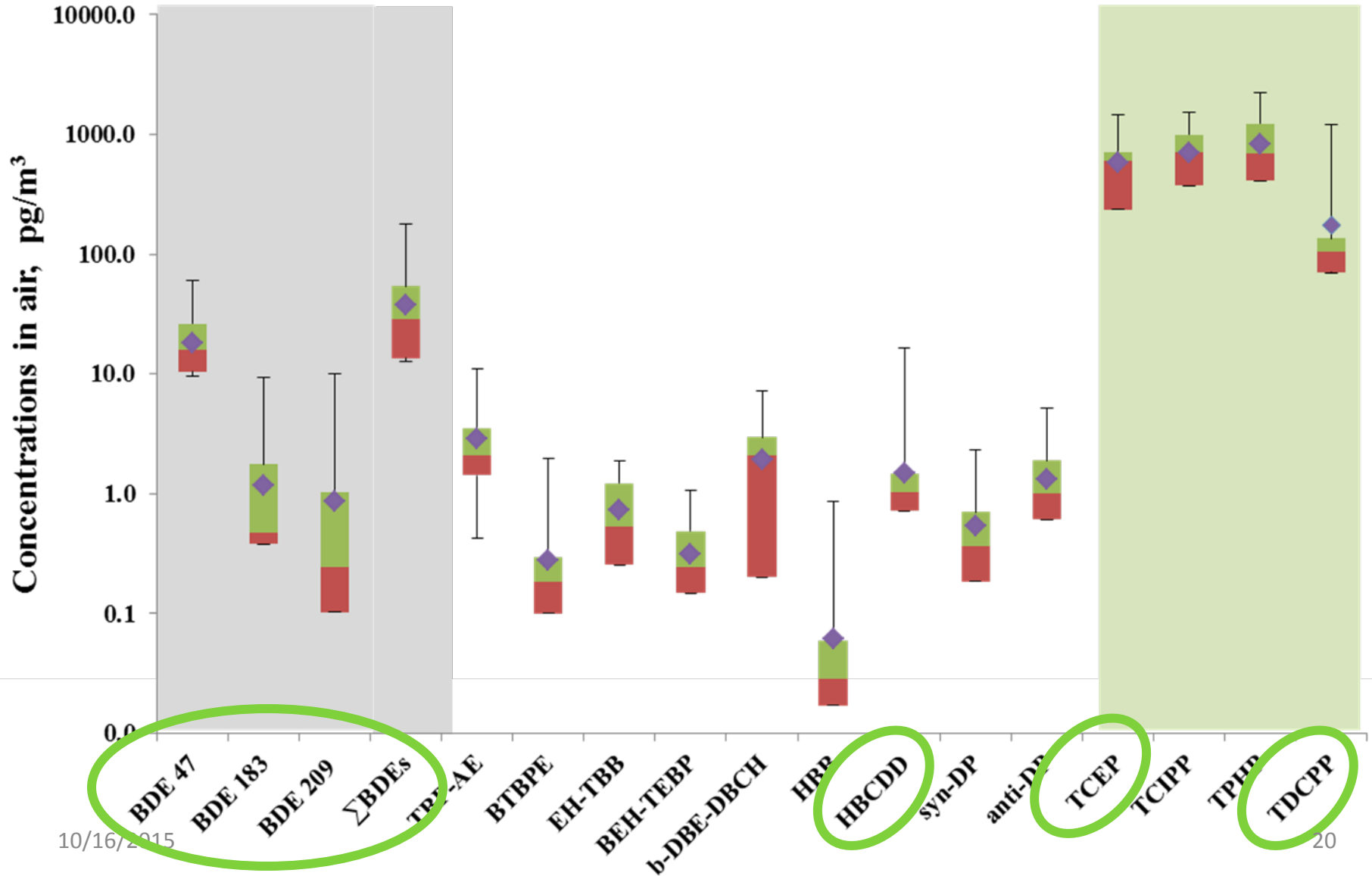
PBDE Inventory 1970-2020 (missing 2/3 deca inventory!)



PBDE Inventory 1970-2020 (missing 2/3 deca inventory!)

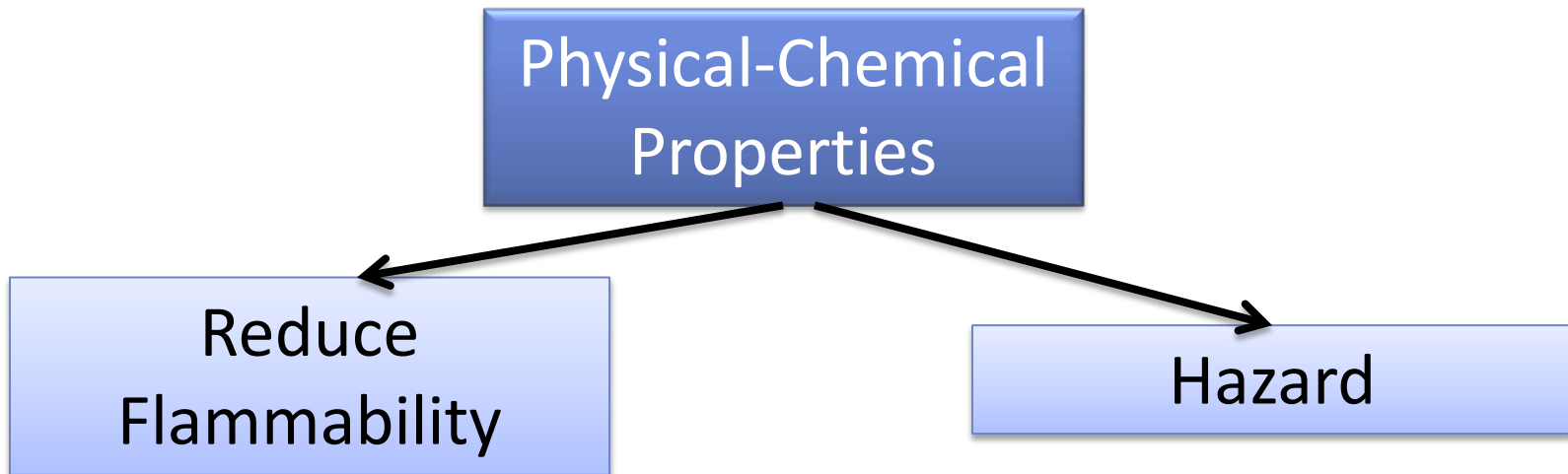


Legacy and New FRs in Toronto Air



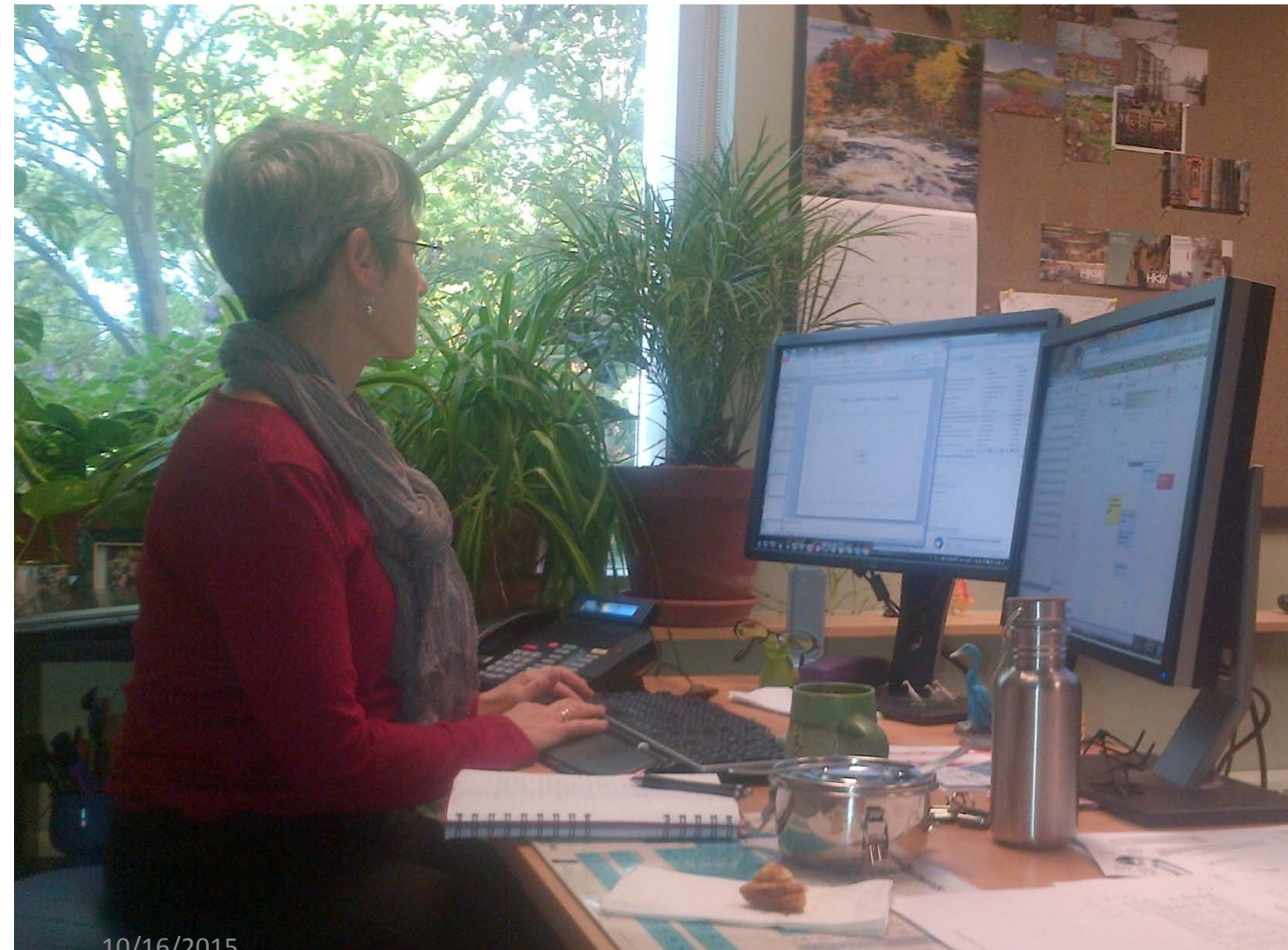
Hazards of Halogenated & P FRs

- Semi-volatile
- Halogenated \Rightarrow Persistent in environment, resistant to metabolism, toxicity
- Phosphates \Rightarrow Metabolised to potentially toxic compounds



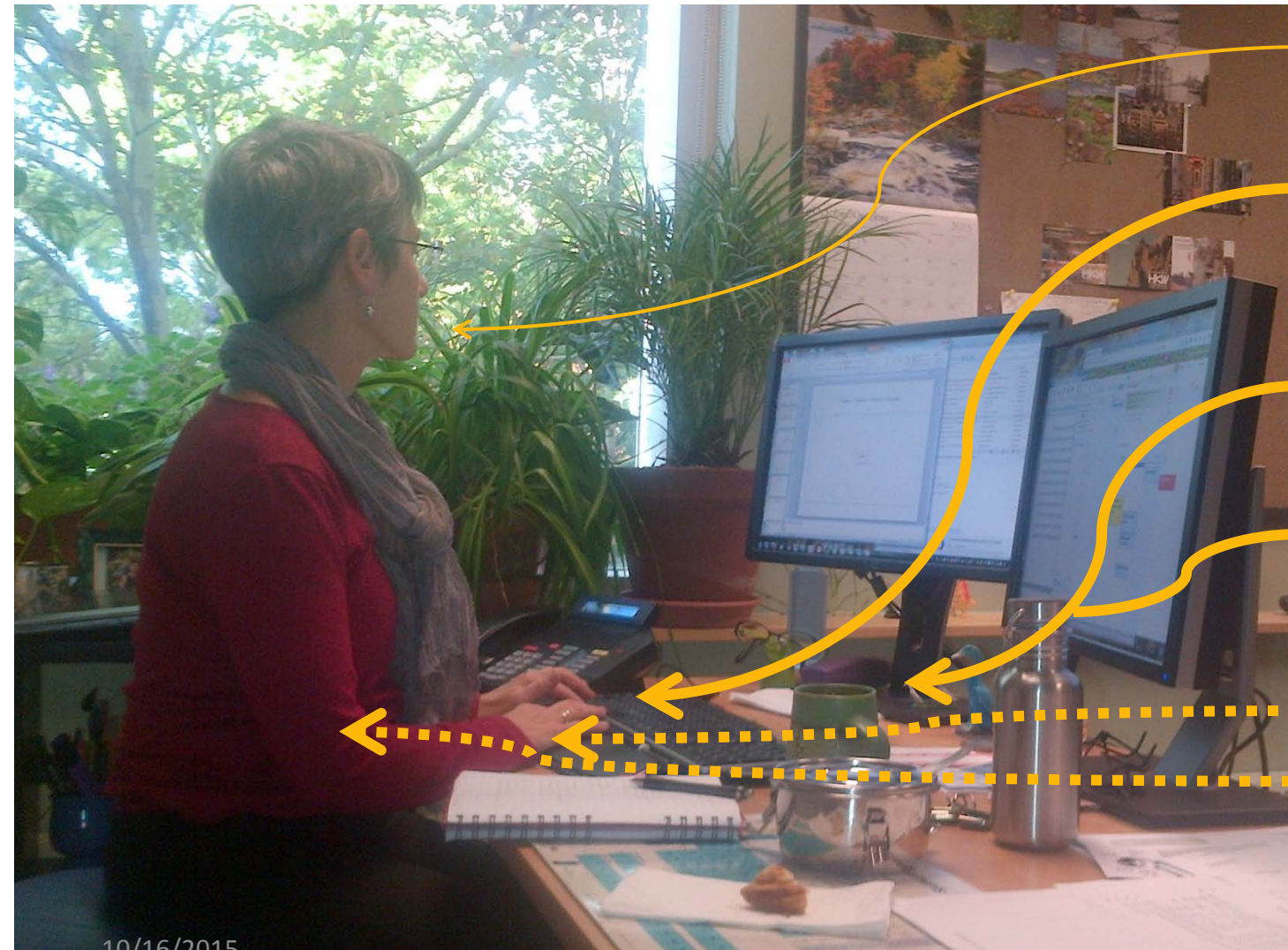
Exposure pathways

Product \Rightarrow Emission \Rightarrow Exposure



Exposure pathways

Product \Rightarrow Emission \Rightarrow Exposure



Inhalation

Direct Contact
• Hand-to-mouth

Diet

Dust Ingestion

Dermal
• From air
• Via clothing

Direct contact, hand-to-mouth
Dust

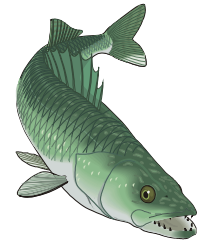


Diet via products

Dermal uptake via
clothing



Diet via food web



Human Exposure



Stuff

FRs

Indoor Environment



Clothing

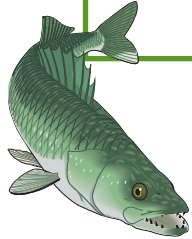
City

Region

Terrestrial Food Web

Aquatic Food Web

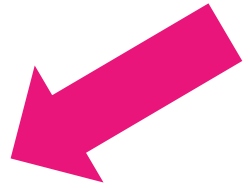
Human Exposure



Ecosystem Exposure

Persistent
High Production Volume





Stuff

FRs

Indoor Environment



Clothing

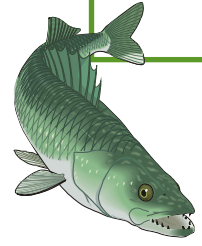
City

Region

Terrestrial Food Web

Aquatic Food Web

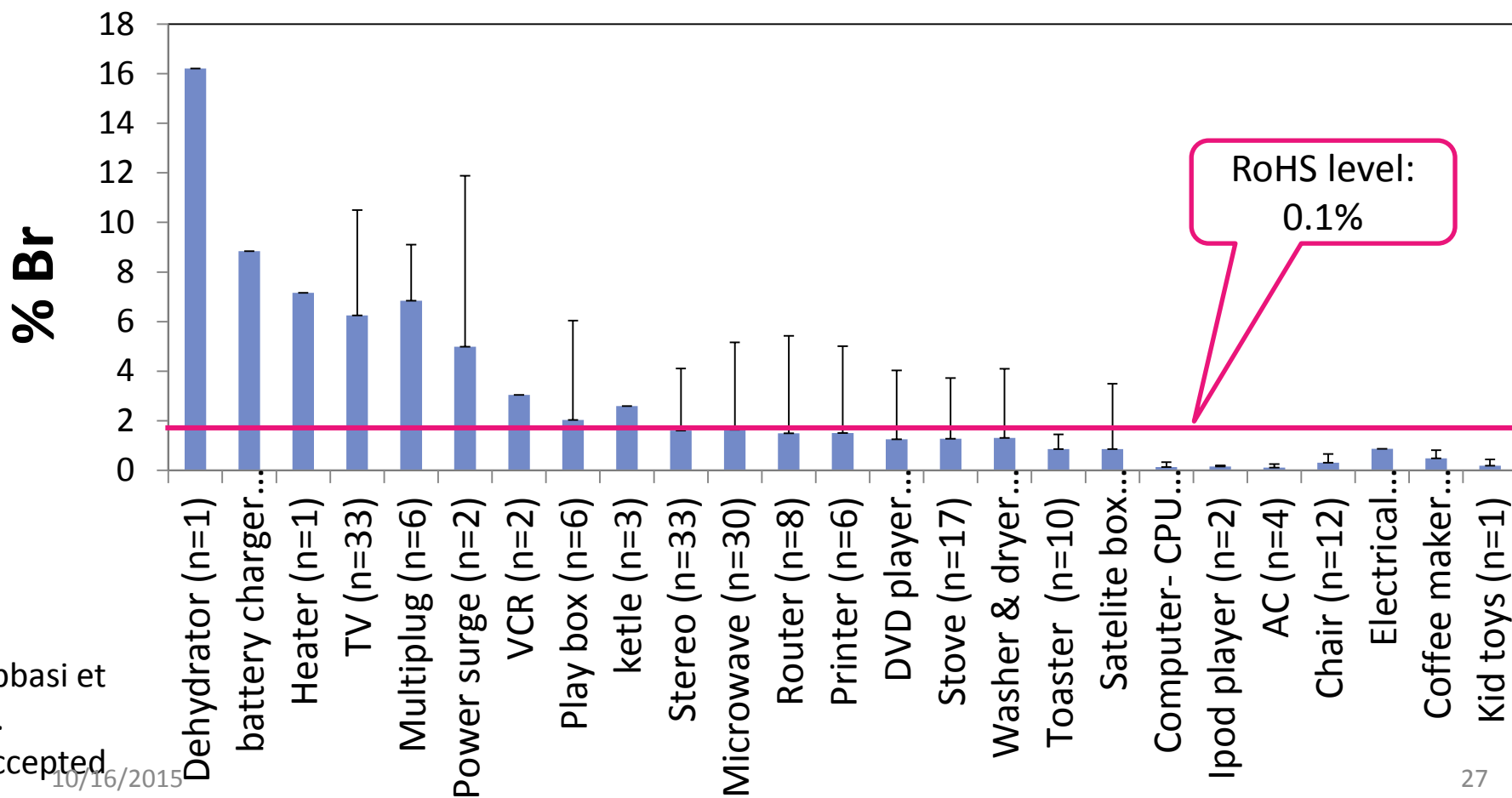
Human Exposure



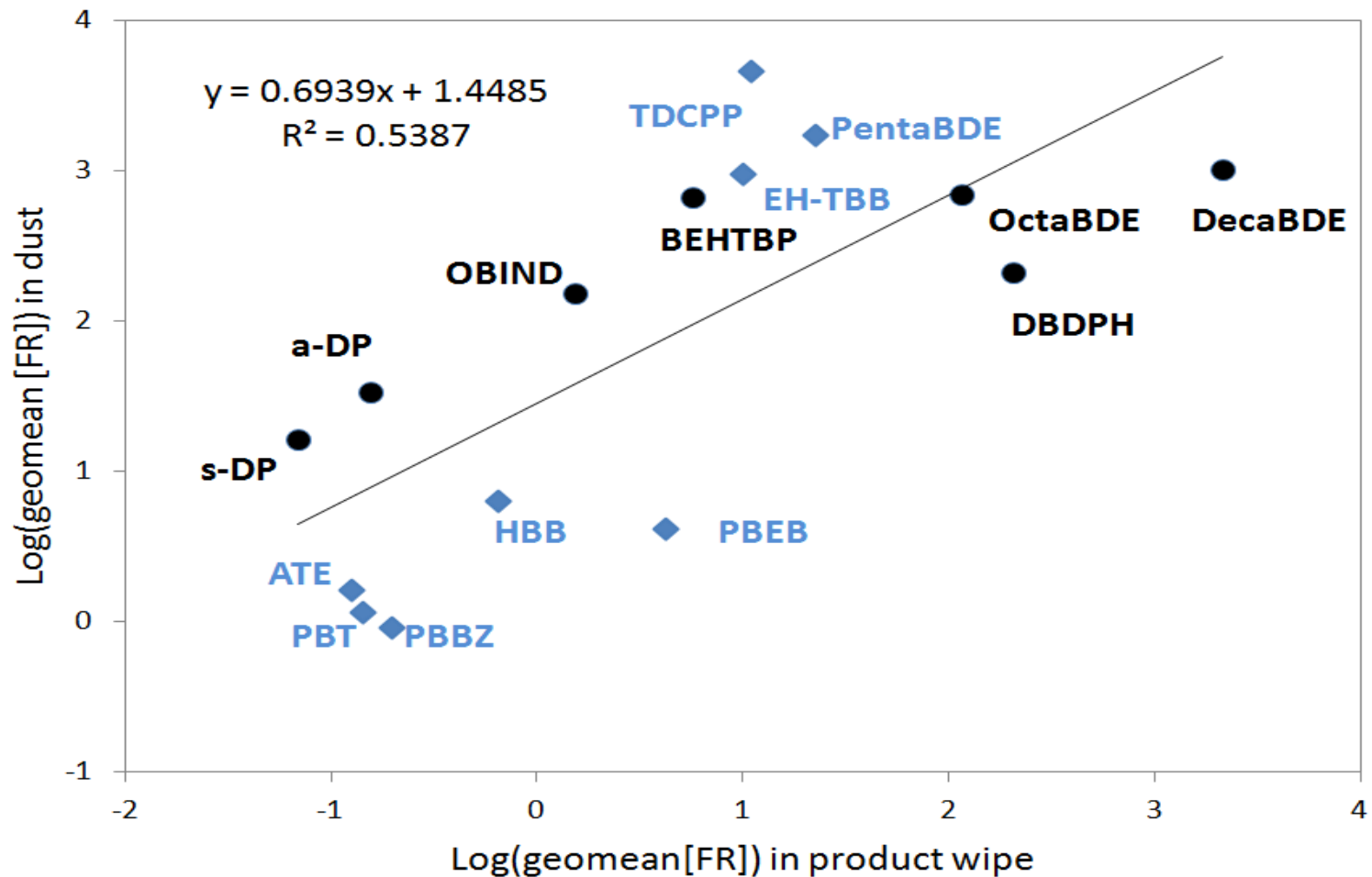
Ecosystem Exposure



Products with Brominated FRs



Correlation between FRs in Product & Product Wipe



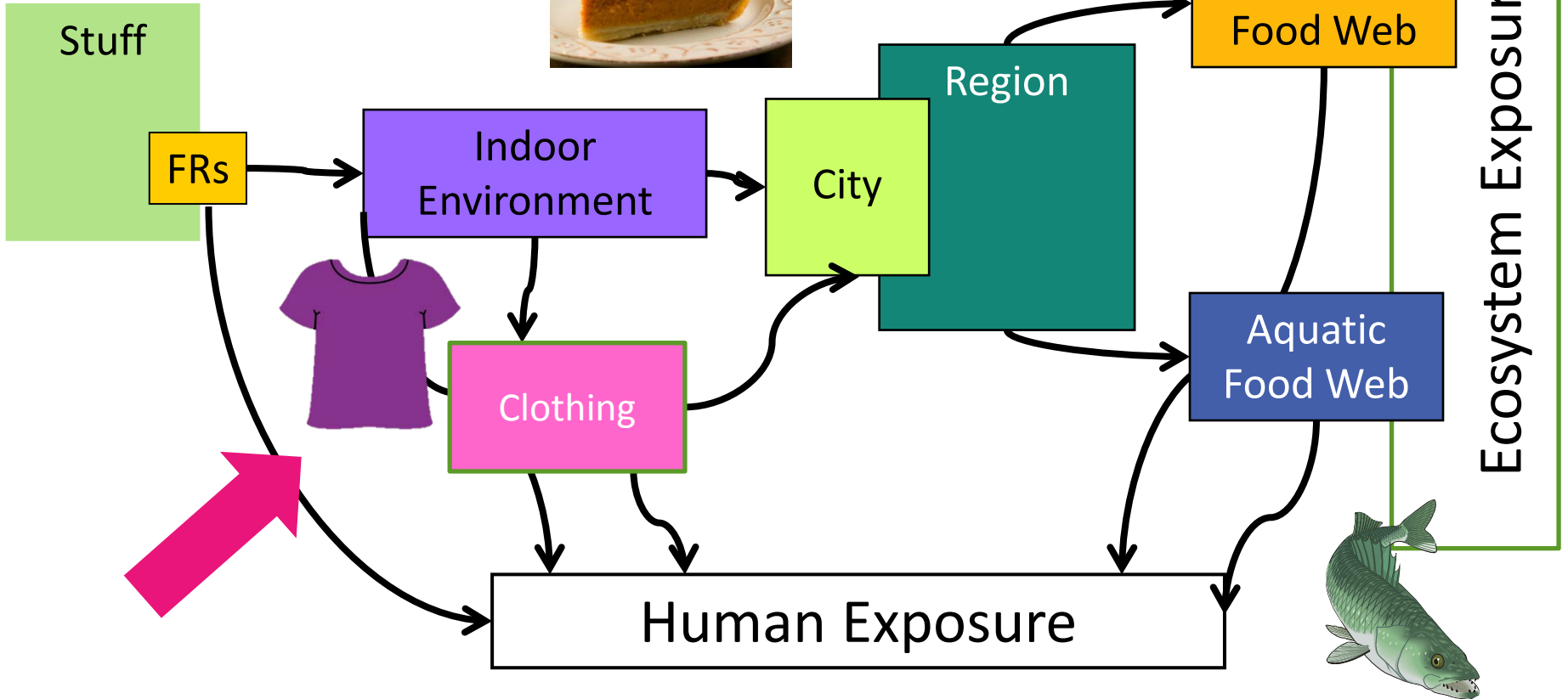
ORIGINAL ARTICLE

Associations between serum levels of polybrominated diphenyl ether (PBDE) flame retardants and environmental and behavioral factors in pregnant women

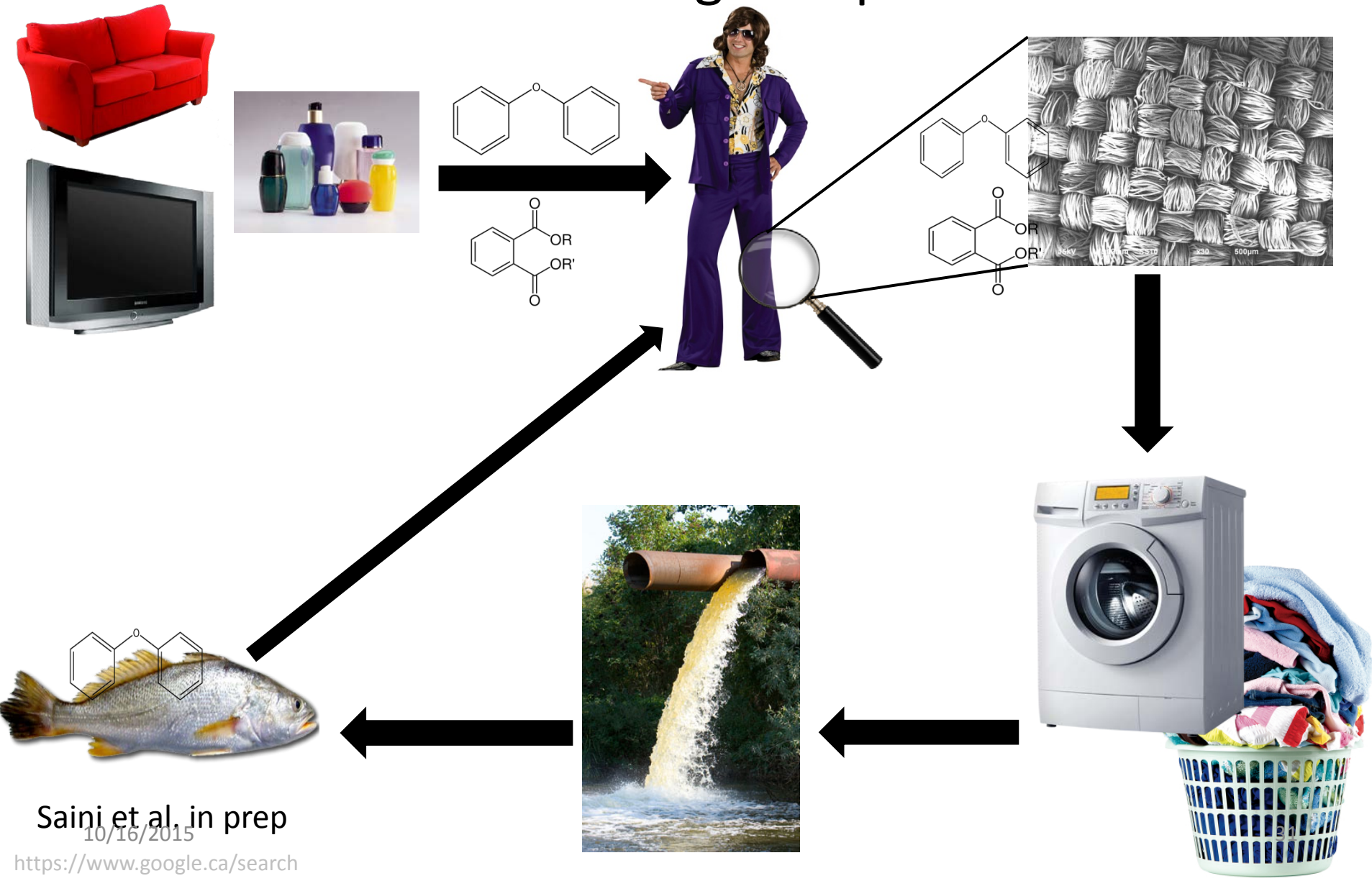
Danielle E. Buttke¹, Amy Wolkin¹, Heather M. Stapleton² and Marie Lynn Miranda³

Serum levels of PBDEs (BDE-47, 99, 100, 153)

- Association with hand-to-mouth behaviour, including nail biting & licking fingers
- Association with owning large-screen TV



Contaminant's journey indoors to outdoors: Role of clothing in exposure



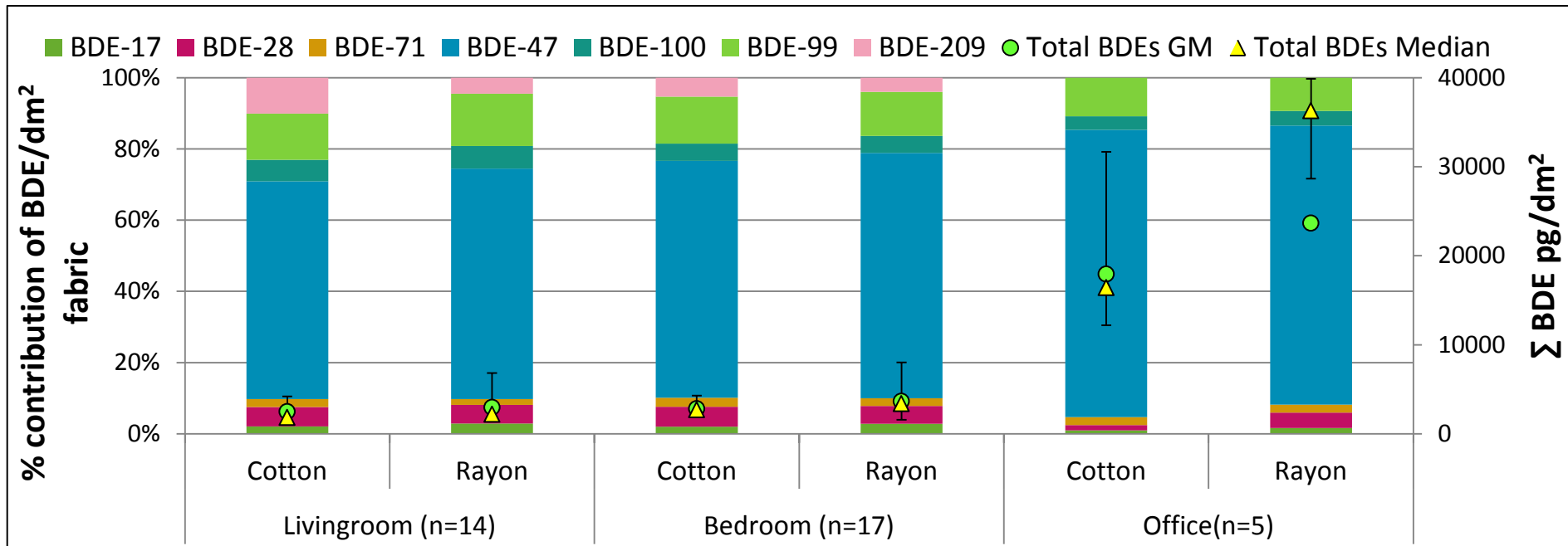
Saini et al, in prep

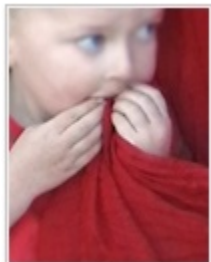
10/16/2015

<https://www.google.ca/search>



20 Bedrooms +
Living rooms
5 Offices



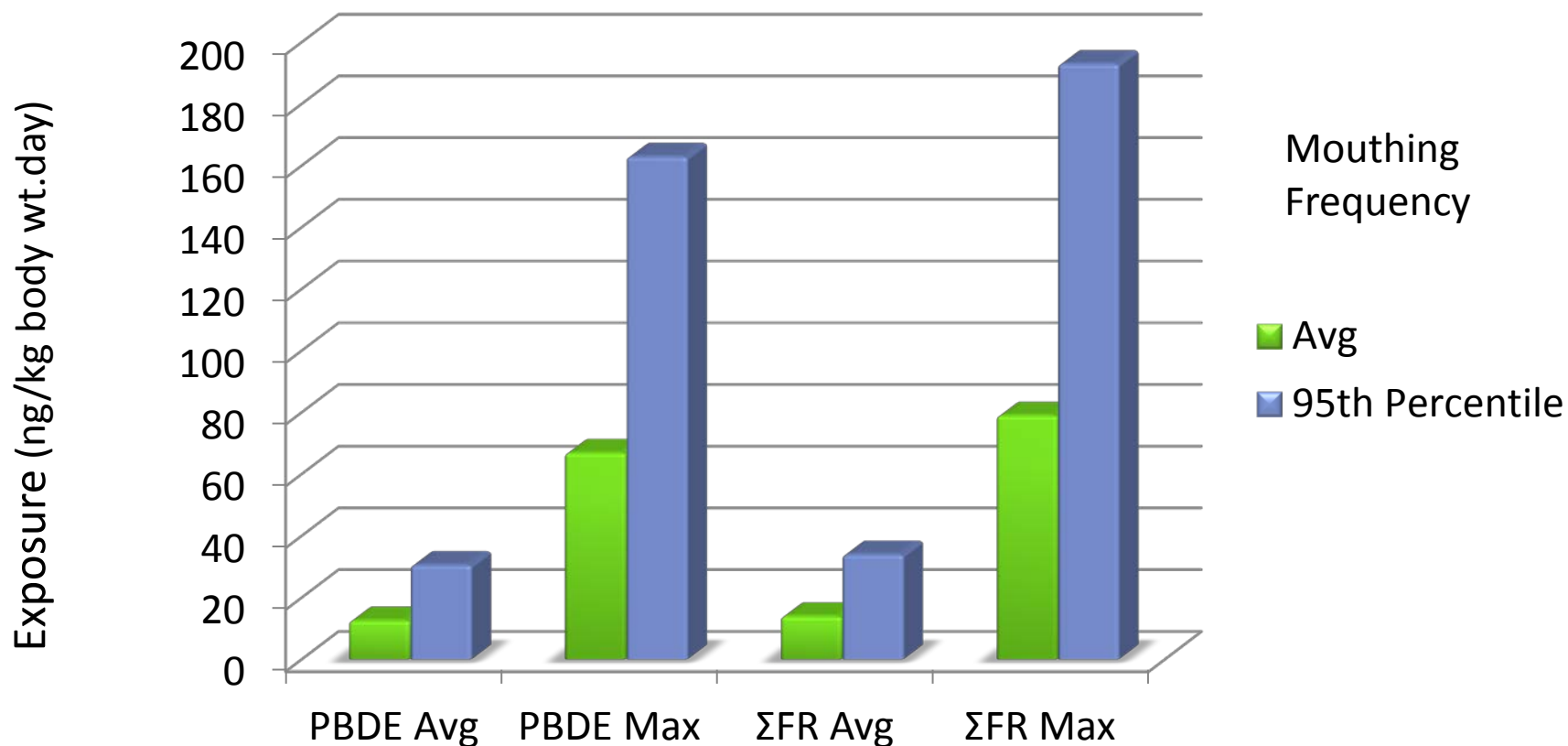


Exposure from Mouthing Fabric

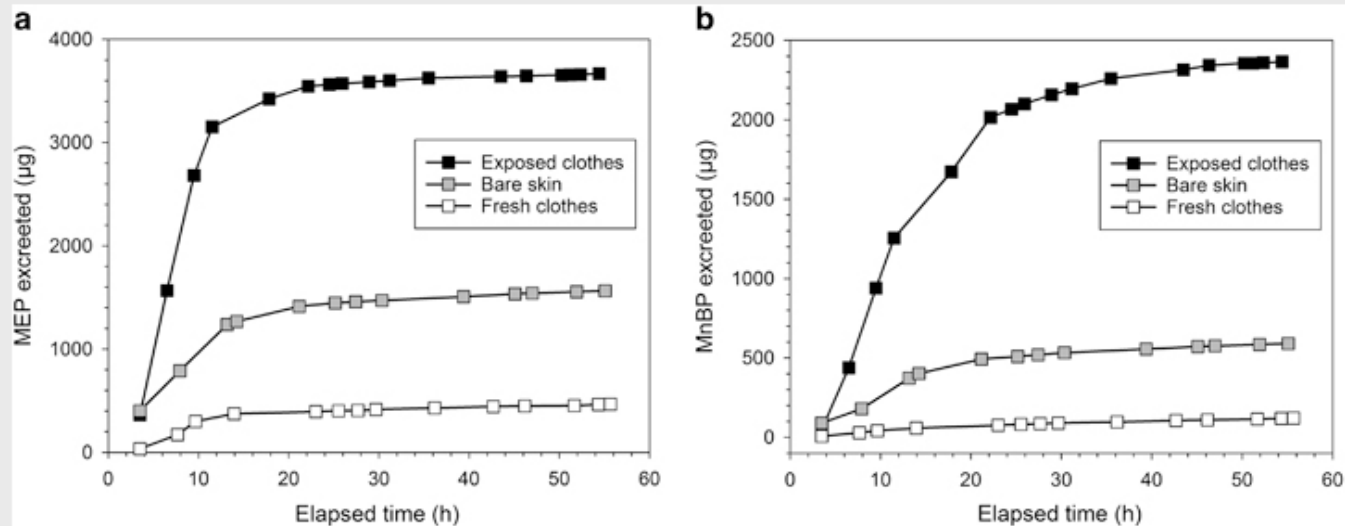
Upper Bound Estimate of Total Daily Intake, 0.5-4 yrs old
~1000 ng/kg body wt.day

Health Canada Exposure Assessment

<https://www.pinterest.com/pin/105553184986828807/>



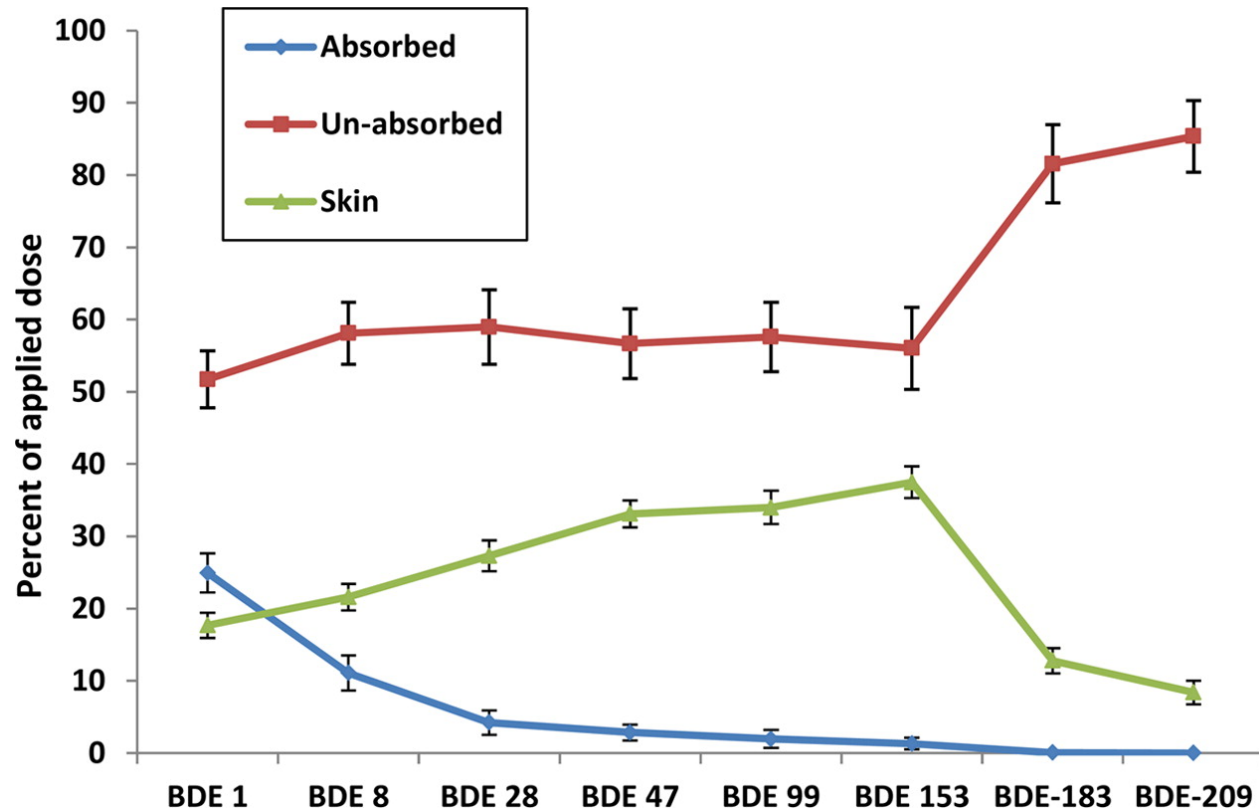
Dermal Exposure to Phthalates: Role of Clothing



Net amount of MEP (2a) and MnBP (2b) excreted from beginning of exposure until last urine sample. Results for fresh and exposed clothes are compared against the bare-skin results of the closest aged participant in Weschler et al.⁸

Morrison G. et al. 2015. *J Exp Sci & Environ Epi* doi: 10.1038/jes.2015.42

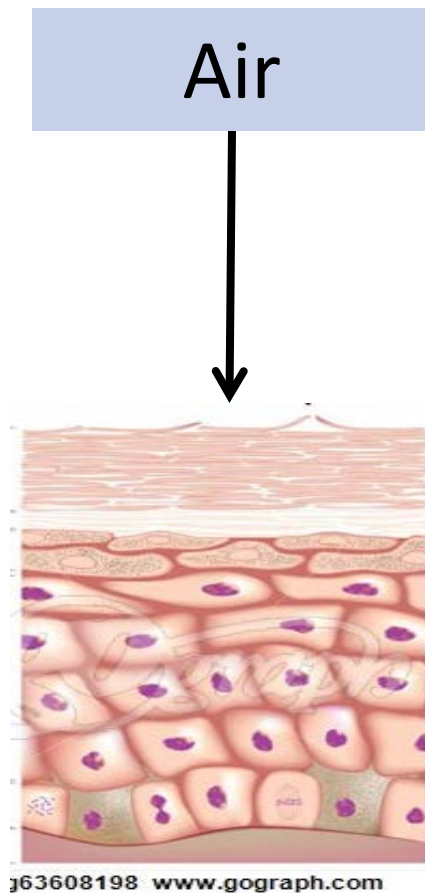
Dermal Absorption of PBDEs



Percent of applied dose (500 ng/cm²) of target PBDEs absorbed (present in the receptor compartment), unabsorbed (remaining in the donor compartment and on skin surface), and accumulated in the skin tissue following the 24 h exposure.

Dermal Absorption & Clothing

No Clothing



Dermal Absorption & Clothing

No Clothing

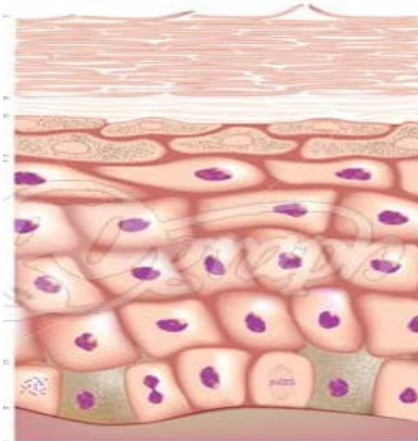
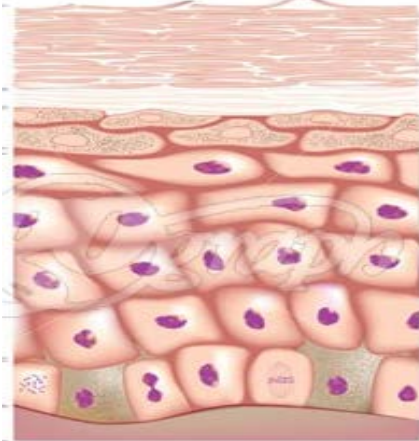
Clean Clothing

Air

Air



Barrier

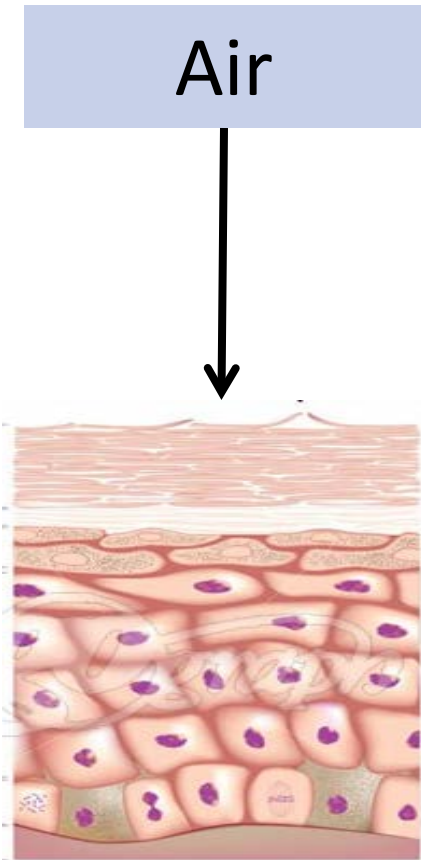


j63608198 www.gograph.com

j63608198 www.gograph.com

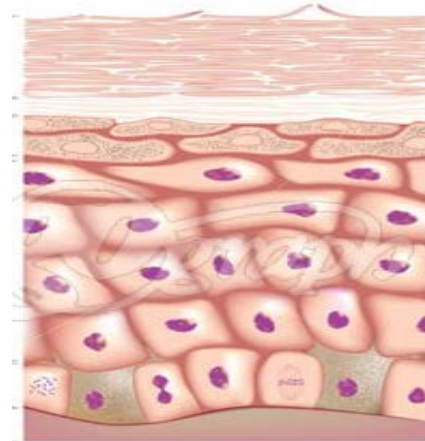
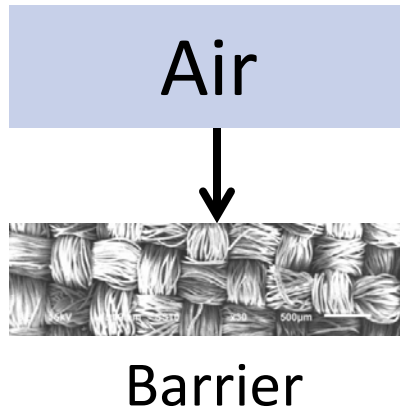
Dermal Absorption & Clothing

No Clothing



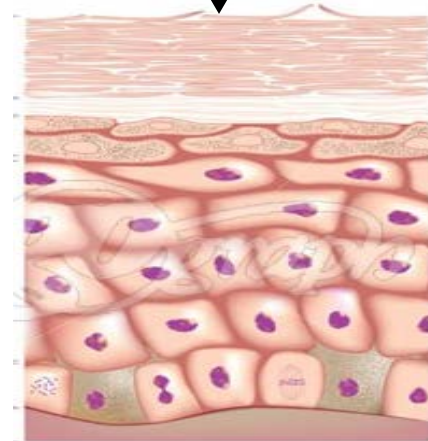
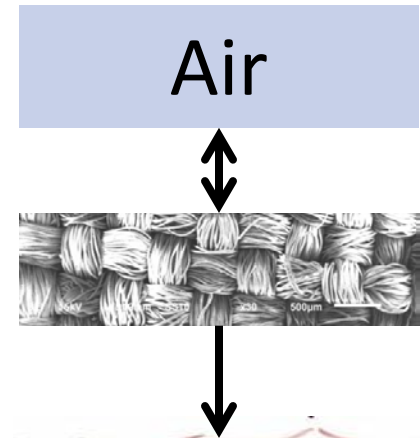
j63608198 www.gograph.com

Clean Clothing

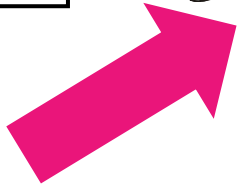
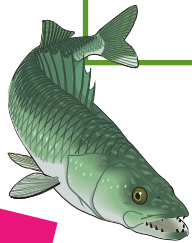
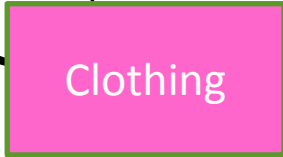
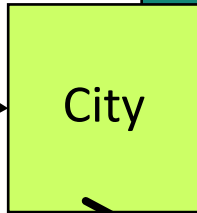


j63608198 www.gograph.com

Stored or Worn Clothing



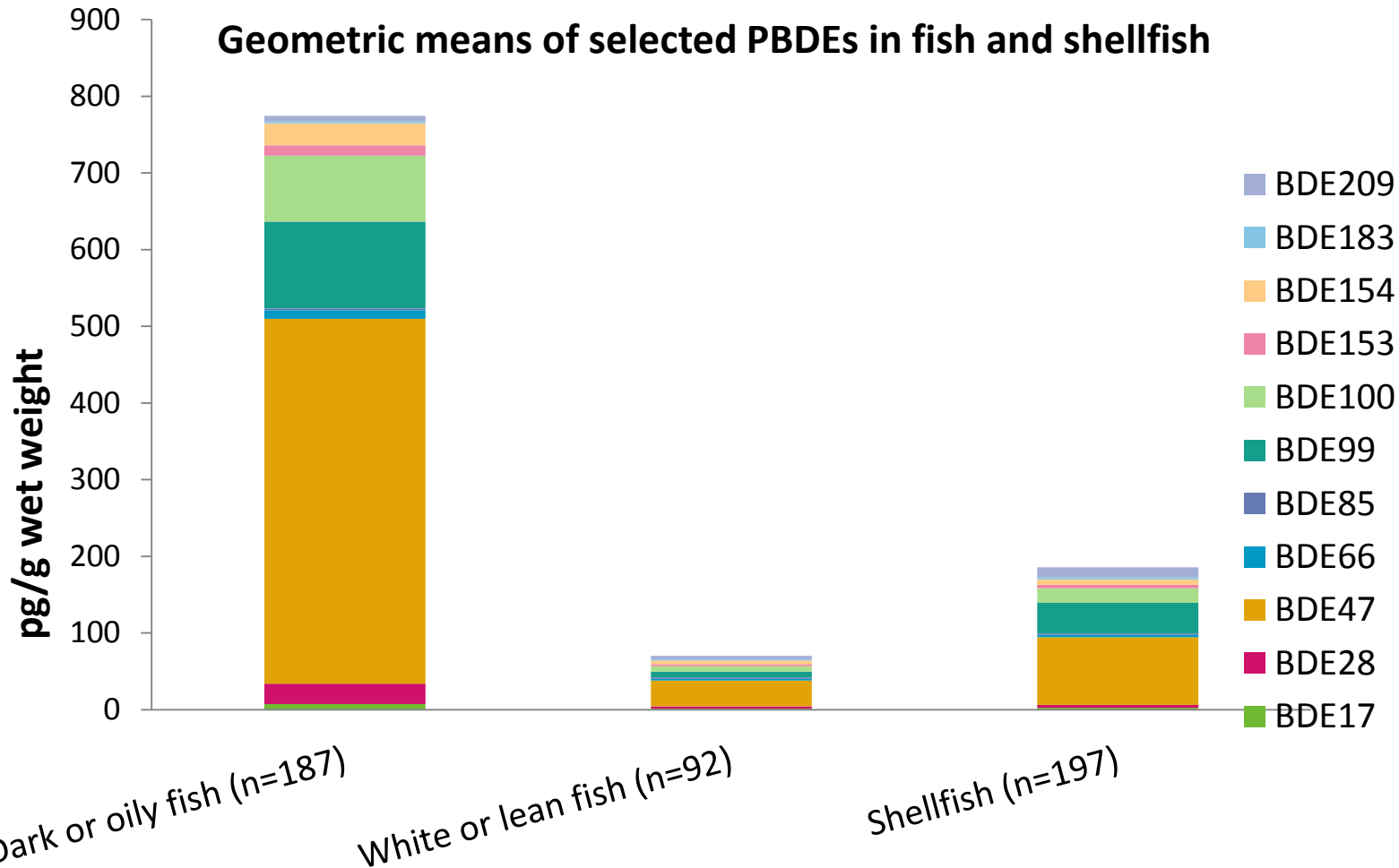
j63608198 www.gograph.com



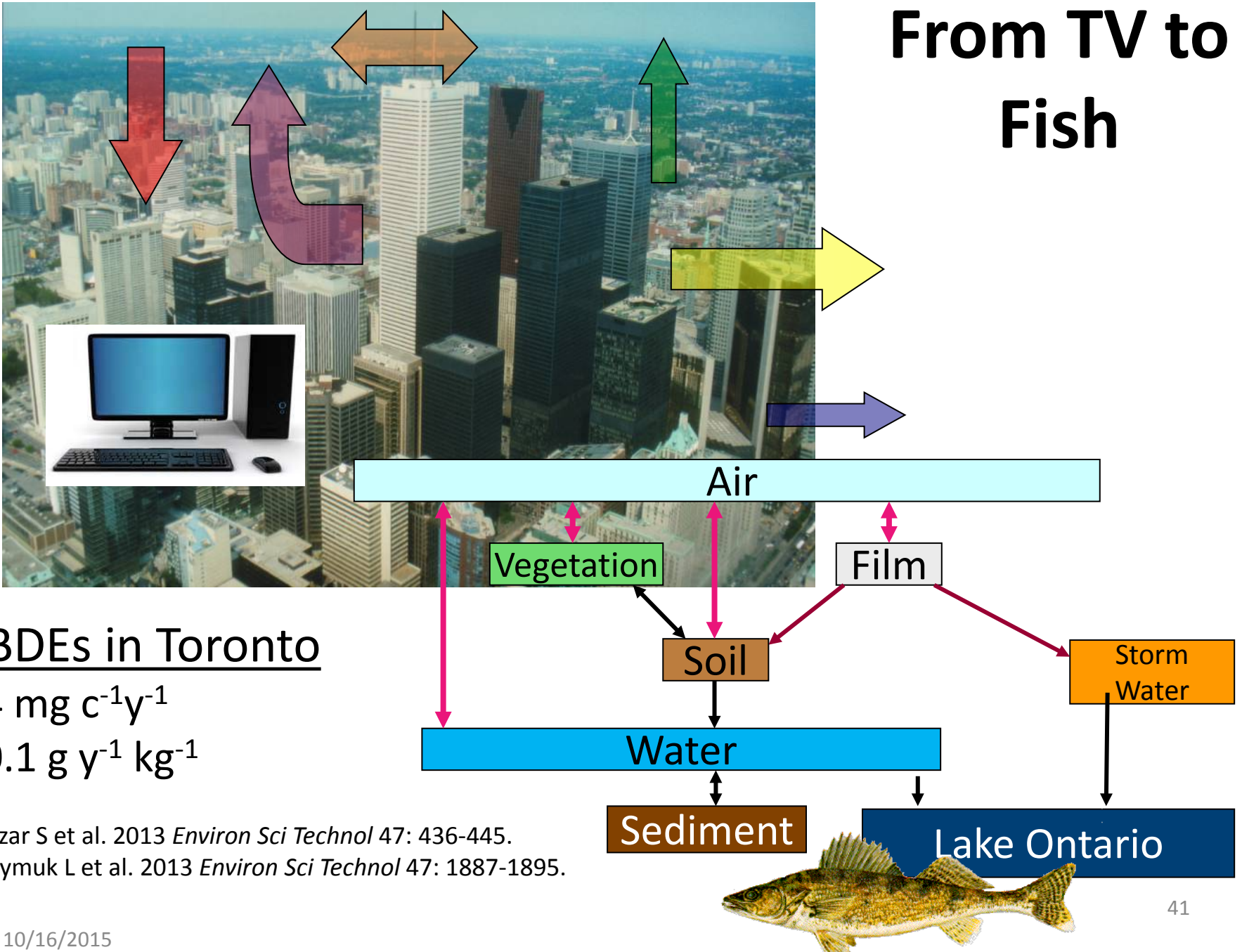
Exposure: Diet

Food Web Transfer

Geometric means of selected PBDEs in fish and shellfish



From TV to Fish



PBDEs in Toronto

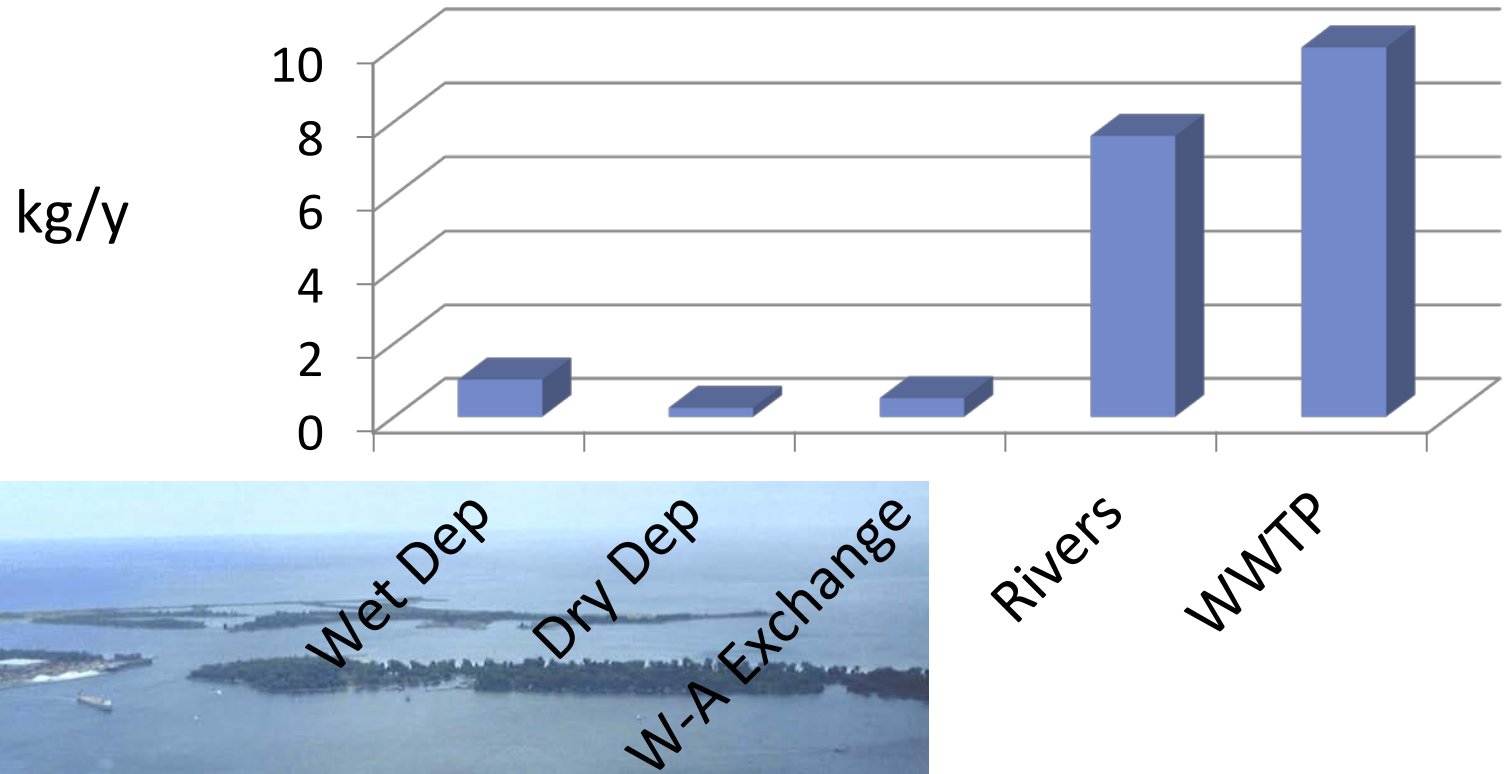
14 mg c⁻¹y⁻¹

~0.1 g y⁻¹ kg⁻¹

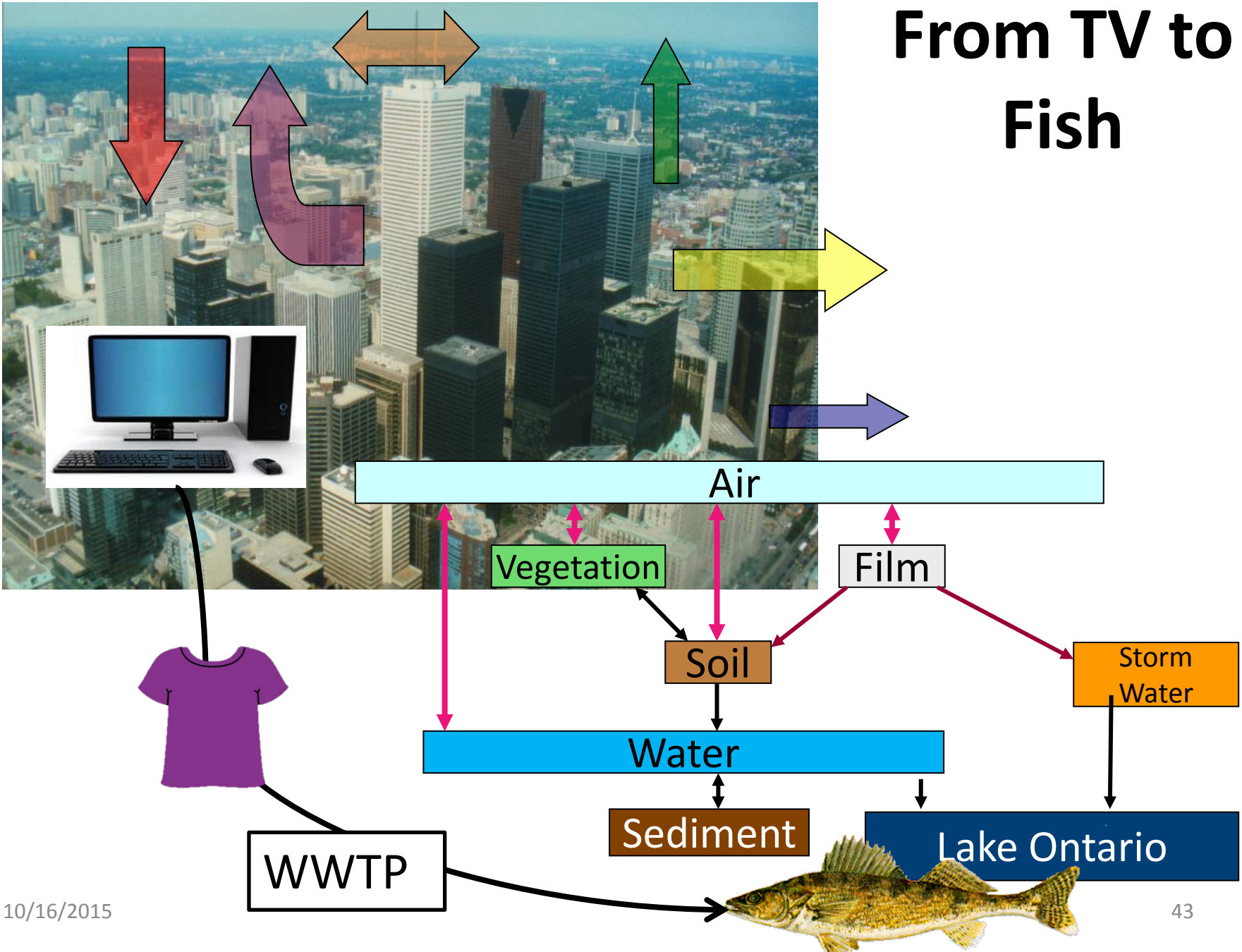
Csiszar S et al. 2013 *Environ Sci Technol* 47: 436-445.

Melymuk L et al. 2013 *Environ Sci Technol* 47: 1887-1895.

PBDE Annual Loadings to Lake Ontario



From TV to Fish

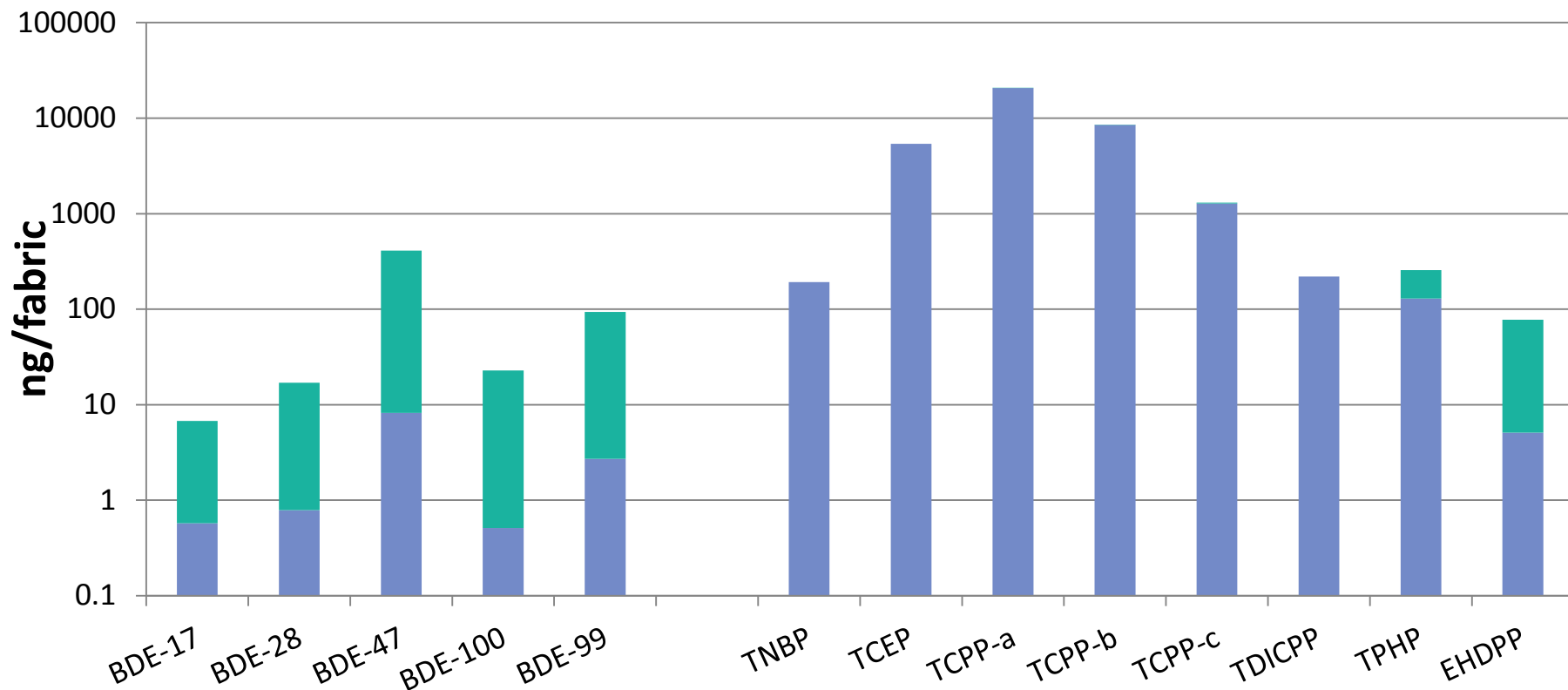




Inputs from Laundry

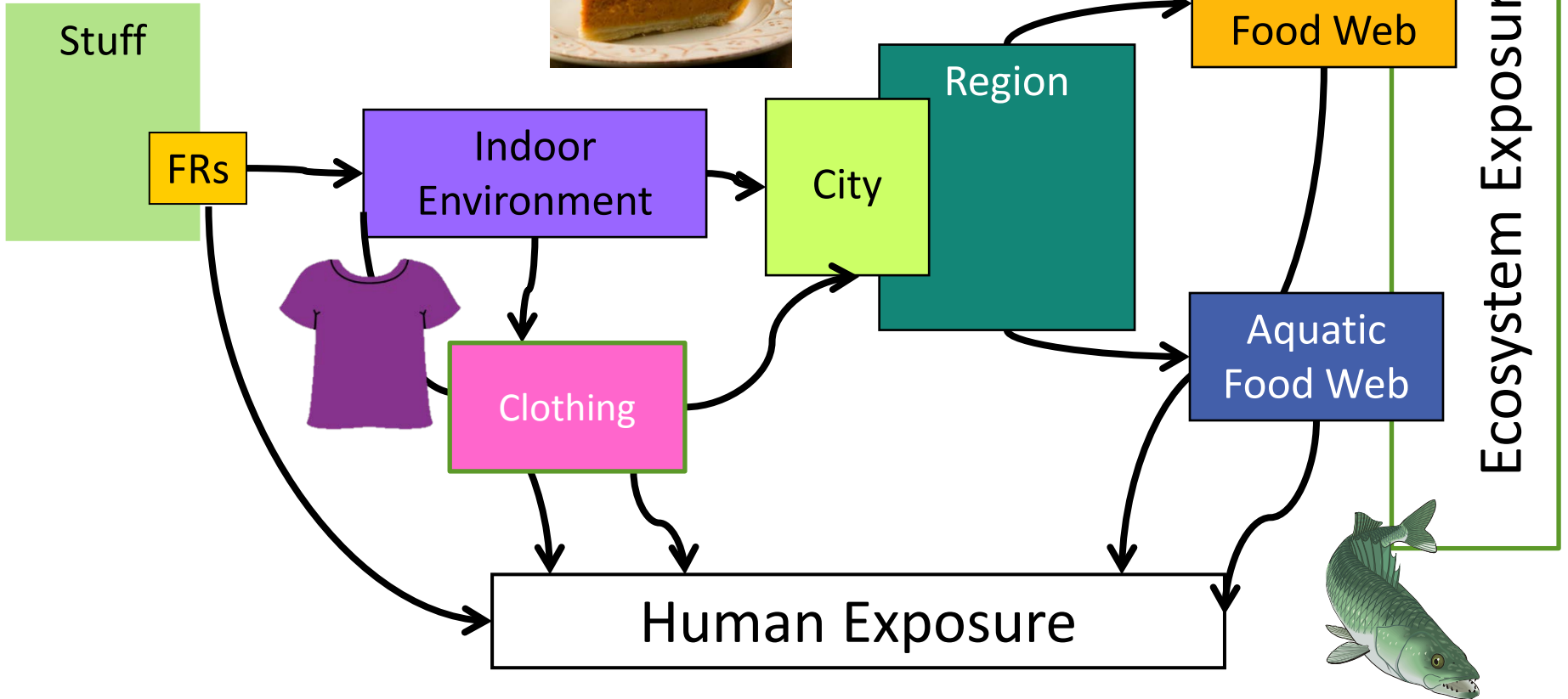
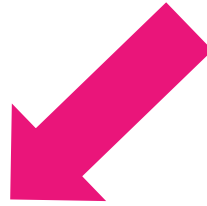
Cotton

Released in wash water Left on fabric after washing



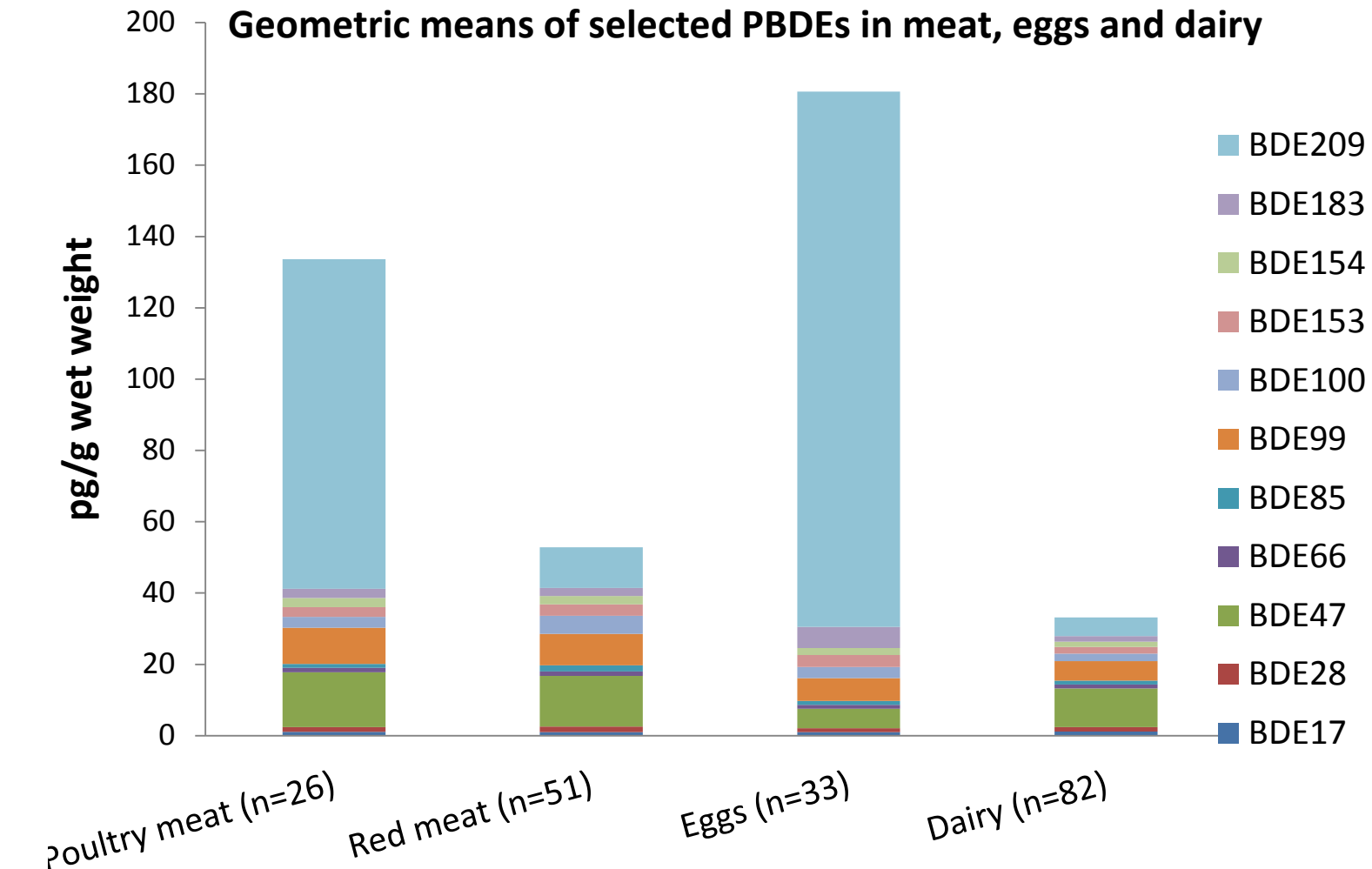
Solubility





Exposure: Diet

Animal Feed? Animal Shelter?



My Kitchen Spoons

66 ppm PBDEs + 200 ppm Pb!!

Occurrence of brominated flame retardants in black thermo cups and selected kitchen utensils purchased on the European market

J. Samsonek* and F. Puype

Institu pro testovani a certifikaci, a.s., Trida Tomase Bati 299, 764 21, Zlin, Czech Republic

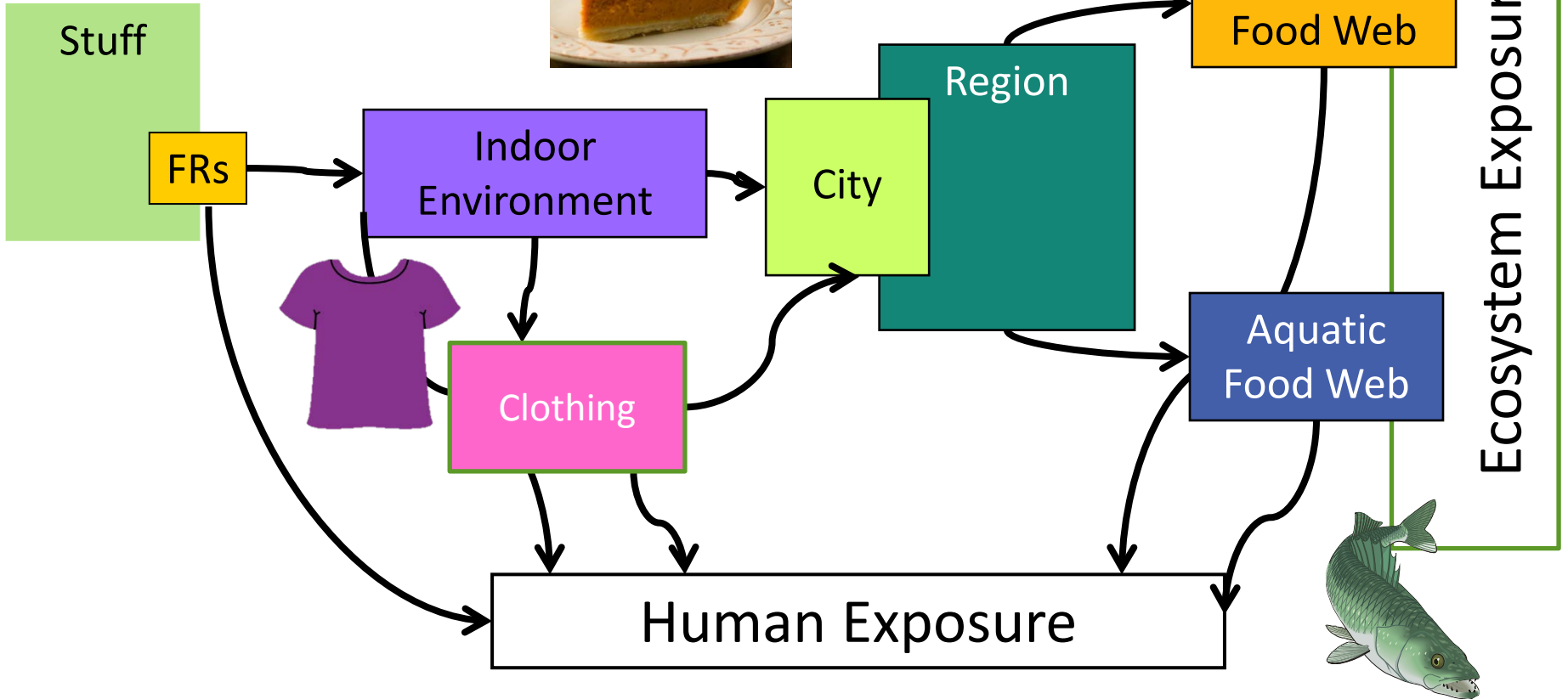
(Received 7 September 2012; accepted 22 July 2013)

In order to screen for the presence of a recycled polymer waste stream from waste electric and electronic equipment (WEEE), a market survey was conducted on black plastic food-contact articles (FCA). An analytical method was applied combining X-ray fluorescence spectrometry (XRF) with thermal desorption gas chromatography coupled with mass spectrometry (thermal desorption GC-MS). Firstly, XRF spectrometry was applied to distinguish bromine-positive samples. Secondly, bromine-positive samples were submitted for identification by thermal desorption GC-MS. Generally, the bromine-positive samples contained mainly technical decabromodiphenyl ether (decaBDE). Newer types of BFRs such as tetrabromobisphenol A (TBBPA), tetrabromobisphenol A bis(2,3-dibromopropyl) ether (TBBPA-BDBPE) and decabromodiphenylethane (DBDPE), replacing the polybrominated diphenylethers (PBDEs) and polybrominated diphenyls (PBBs), were also identified. In none of the tested samples were PBBs or hexabromocyclododecane (HBCD) found. Polymer identification was carried out using Fourier-transformed infrared spectroscopy measurement (FTIR) on all samples. The results indicate that polypropylene-polyethylene copolymers (PP-PE) and mainly styrene-based food-contact materials, such as acrylonitrile-butadiene-styrene (ABS) have the highest risk of containing BFRs.

Keywords: chromatography; thermal desorption; mass spectrometry; brominated flame retardants; polymer recycling; food-contact materials; waste electric and electronic equipment; waste management

Food Additives & Contaminants Part A

<http://dx.doi.org/10.1080/19440049.2013.829246>



The Source of the Problem

TABLE 21.1
California: Technical Bulletins and Some Other Fire Safety Regulations

Number	Last Issued	Withdrawn	Title
26	1987		Requirements for record keeping and prototype testing of mattresses for compliance with State and Federal Flammability Laws. Questions and Answers about the Amended Mattress Flammability Standard 16 CFR 1632 (FF 4-72)
106	1986	2007	Requirements, test procedures, and apparatus for testing the resistance of a mattress or mattress pad to combustion which may result from a smoldering cigarette
116	1980		Requirements, test procedure, and apparatus for testing the flame retardance of upholstered furniture
117	2000		Requirements, test procedures, and apparatus for testing the flame retardance of resilient filling materials used in upholstered furniture
121	1980		Flammability test procedure for mattresses for use in high-risk occupancies
129	1992		Flammability test procedure for mattresses for use in public buildings
133	1991		Flammability test procedure for seating furniture for use in public occupancies
603	2003	2007	Requirements and test procedure for resistance of a mattress/box spring set to a large open flame
16 CFR 1632	2007		Standard for the flammability (cigarette ignition resistance) of mattresses and mattress pads (replaces CA TB 106)
16 CFR 1633	2007		Standard for the flammability (open flame) of mattress sets (replaces CA TB 603)
Draft TB 604	2007		Test procedure and apparatus for the open-flame resistance of filled bedclothing
Draft TB 117 Plus	2002		Requirements, test procedure, and apparatus for testing the flame and smolder resistance of upholstered furniture
Title 19 Ch 2 Art 4	2007		Tents, awnings, and other fabric enclosures—flame resistance and labeling
Title 19 Ch 7 Art 1	2007		Standards of flammability: wearing apparel—prohibition of tris(2,3-dibromopropyl) phosphate
Title 19 Ch 7 Art 2/3	2007		Standards of flammability: hospital fabrics, sheets, and pillowcases, sleepwear

10/16/2015

Flammability
codes &
standards

Hirschler, M. M. Regulations, codes, and standards relevant to fire issues in the United States.

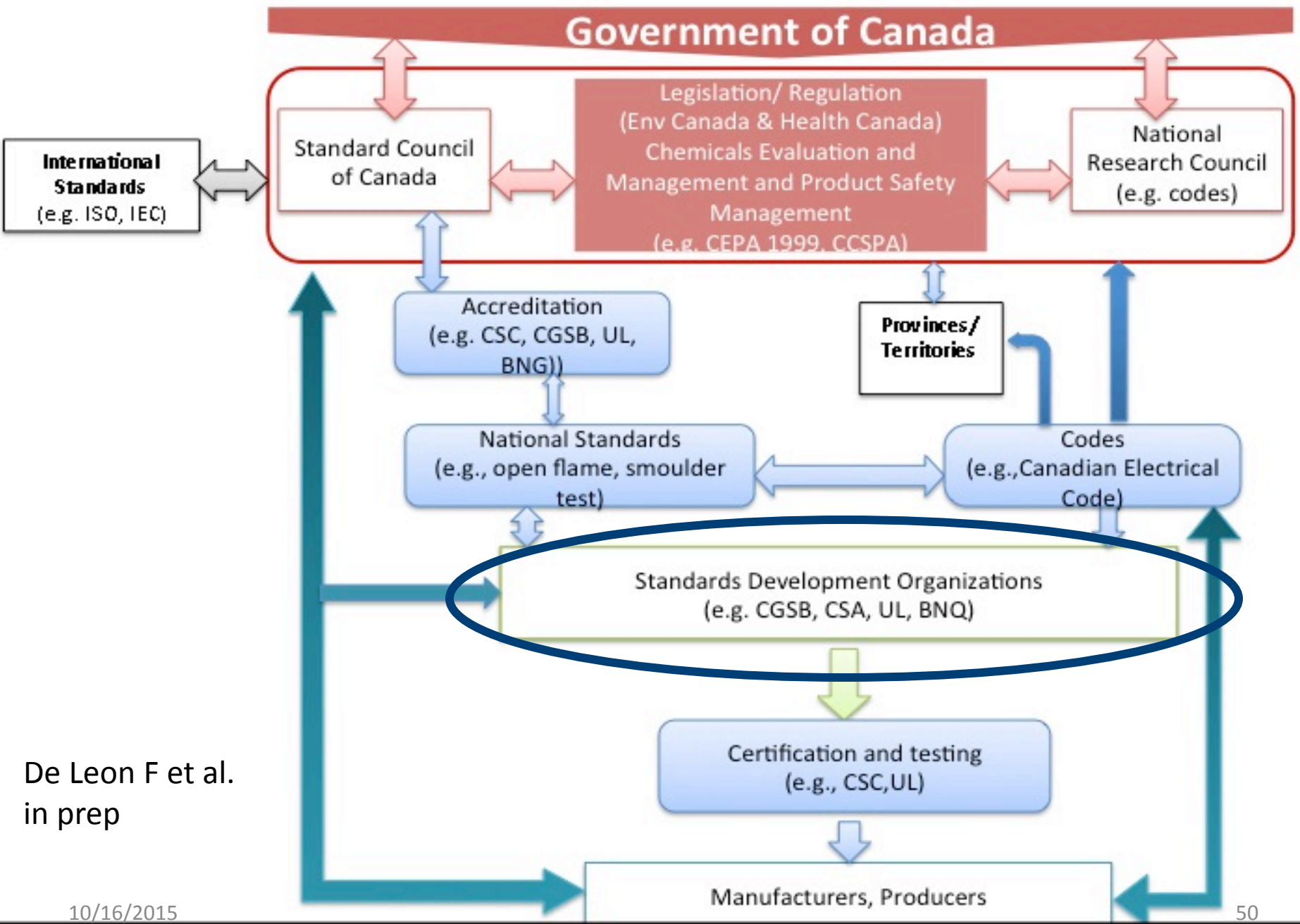
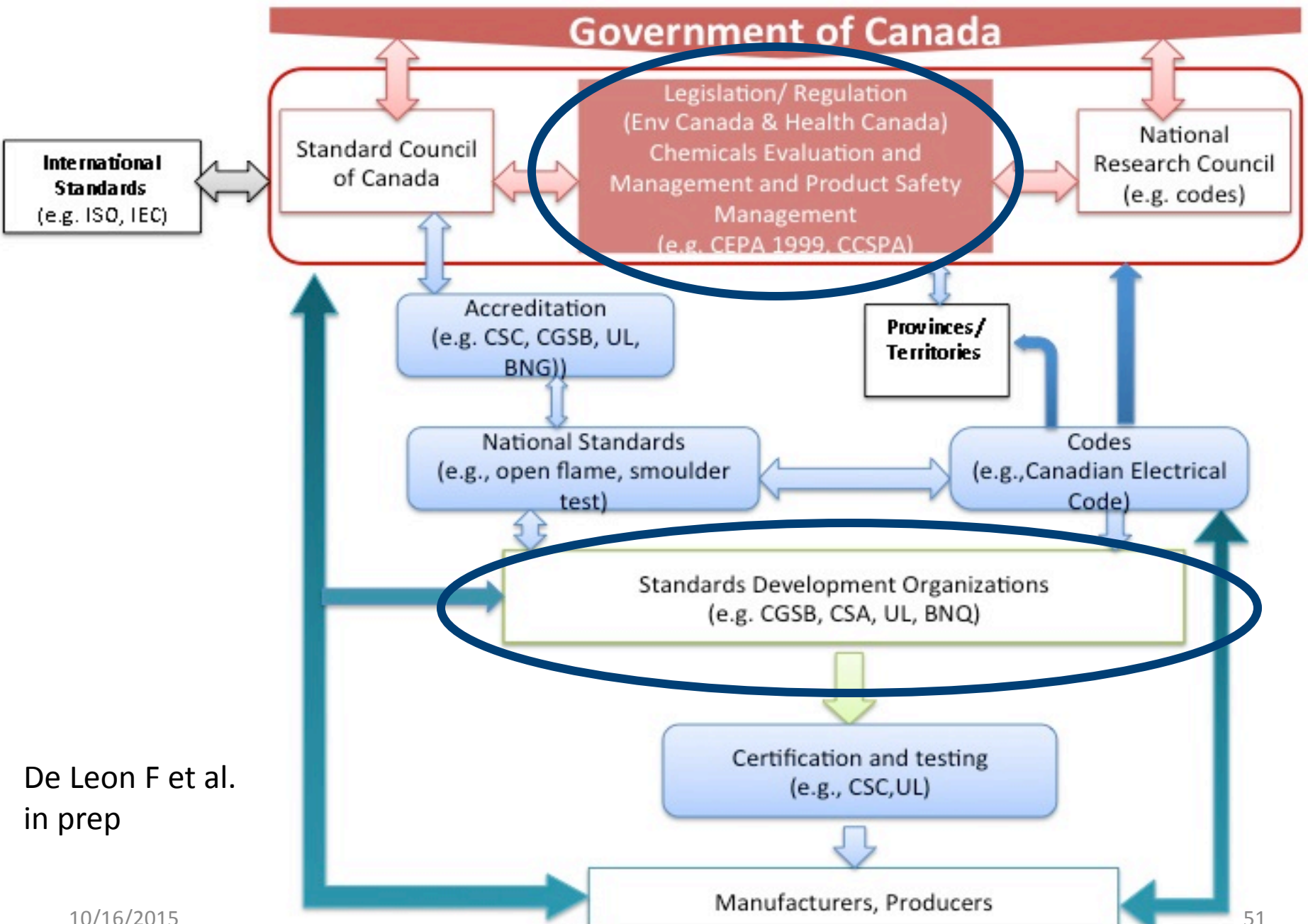


Chart 1: Flammability Standard Development for Electronic Products in Canada



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in prep

Chart 1: Flammability Standard Development for Electronic Products in Canada



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Home > Chemicals Management Plan

Main Menu
Canada's approach on chemicals
Chemicals Management Plan
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▶ Monitoring & Surveillance
▶ Resources
▶ Science Committee
▶ Stakeholders

Chemicals Management Plan

Chemicals are part of everyday life, essential to our economy, our communities and our homes. While chemicals provide benefits, they may also have harmful effects if not properly managed.

The Chemicals Management Plan (CMP) is a Government of Canada initiative aimed at reducing the risks posed by chemicals to Canadians and their environment. The Government of Canada [launched the first phase of the CMP in 2006](#) and [launched the second phase of the CMP in 2011](#). The CMP builds on previous initiatives by assessing chemicals used in Canada and by taking action on chemicals found to be harmful.

- CMP 1 in 2006: 23,000 legacy chemicals categorized, 4,300 need assessm't
- CMP 2 in 2015: 2,700 assessed
- CMP 3 by 2020: 1,600 to be assessed

<http://www.chemicalsubstanceschimiques.gc.ca/plan/index-eng.php>

http://aglayam-moroz.blogspot.ca/2012/11/fridays-mythological-creature-of-day_16.html



What data are presented as evidence?

FIRE AND MATERIALS
Fire. Mater. **24**, 53–60 (2000)

The Fire Safety of TV Set Enclosure Materials, A Survey of European Statistics

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The composition of enclosure materials used in many TV sets sold on the European market has changed significantly since the early 1990s. To determine the potential impact of this change on TV fire safety, a review of European and US TV set fire statistics has been carried out. TV set fires can have internal electrical causes due to faults not apparent at the time of manufacture, simple wear and tear, or a variety of external causes. Recent detailed statistics suggest that about one third of all TV fires are due to external ignition. Available data show that the significant drop in the rate of TV set fires experienced in Europe during the 1980s is not continuing today. In fact, the rate appears to be increasing in some countries, such as the UK and Sweden. The number of TV set fires in Europe is estimated as 100 fires per million TV sets per year due to internal ignition sources, at least an order of magnitude higher than in the USA where the fire safety classifications for TV set enclosure materials has been historically high. TV set fires have a dramatic impact on life and property. To avoid an increase in TV set fires, fire safety requirements should be increased, and public awareness of the importance of fire safety in TVs heightened. Copyright © 2000 John Wiley & Sons, Ltd.

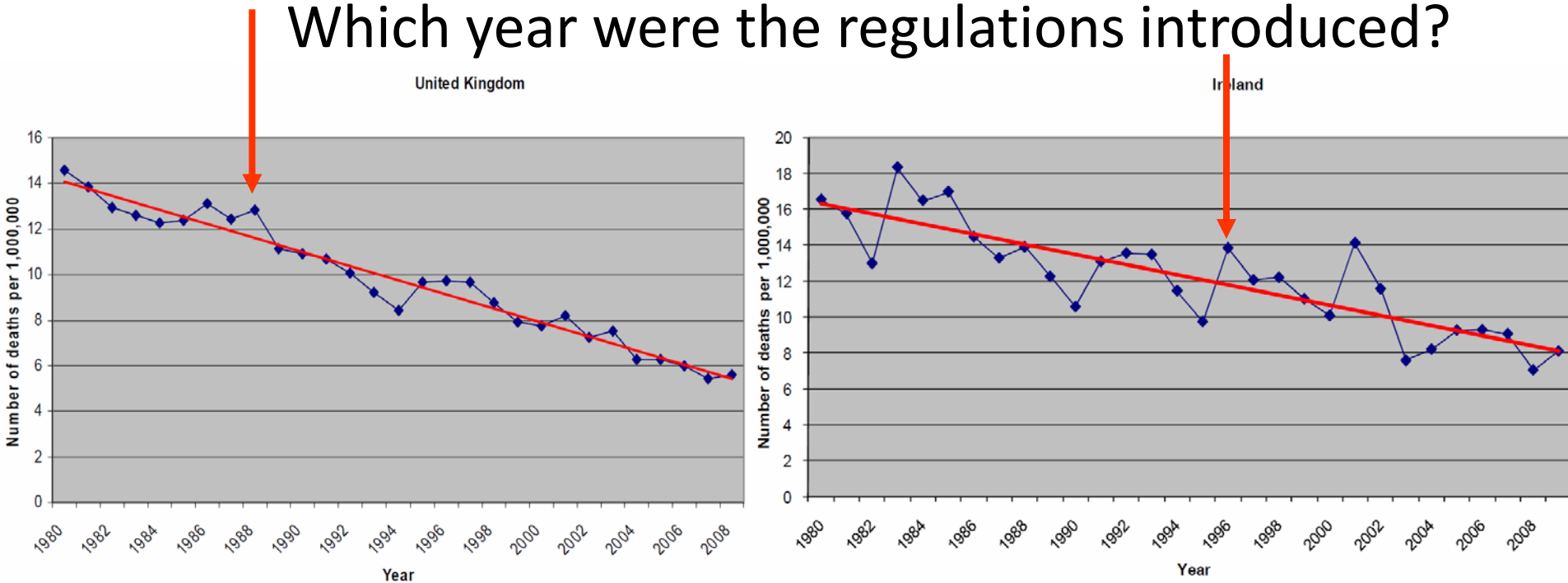
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Downward trend of fires & death & injury from fires

Fire death statistics - Quiz

Which year were the regulations introduced?



Data from Arcadis report on Flame Retardants 2011

Slide courtesy **Dr Anna A Stec & Prof Richard Hull**

Fire Toxicity Leader

Centre for Fire and Hazard Science

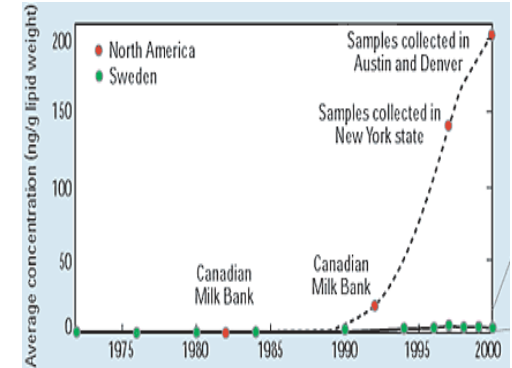
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Benefit-Risk Dilemma



<http://flameretardants.americanchemistry.com/>



Betts 2002 *Environ Sci Technol* 36:50A-52A.

Risks of mortality, morbidity and costs from fires

Benefits of reducing fires

Risk management: add flame retardants (FRs) to product

Risks of morbidity and costs from FRs

Benefits from reduced contaminant burden

Risk management: Chemical Management Plan

Benefit-Risk Dilemma



Flammability Standard Setting Process

Risks of mortality, morbidity and costs from fires

Benefits of reducing fires

Risk management: add flame retardants (FRs) to product

Risks of mortality, morbidity and costs from FRs

Benefits from reduced contaminant burden

Risk management: Chemical Management Plan



“The Tuxedo Party, which has successfully capitalized on the Internet's obsession with cats, has more than 24,000 likes on its official Facebook page. By comparison, the actual MP for Halifax, New Democrat Megan Leslie, has about 11,000.”

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