Out with the old, in with the new: BFRs in Toronto

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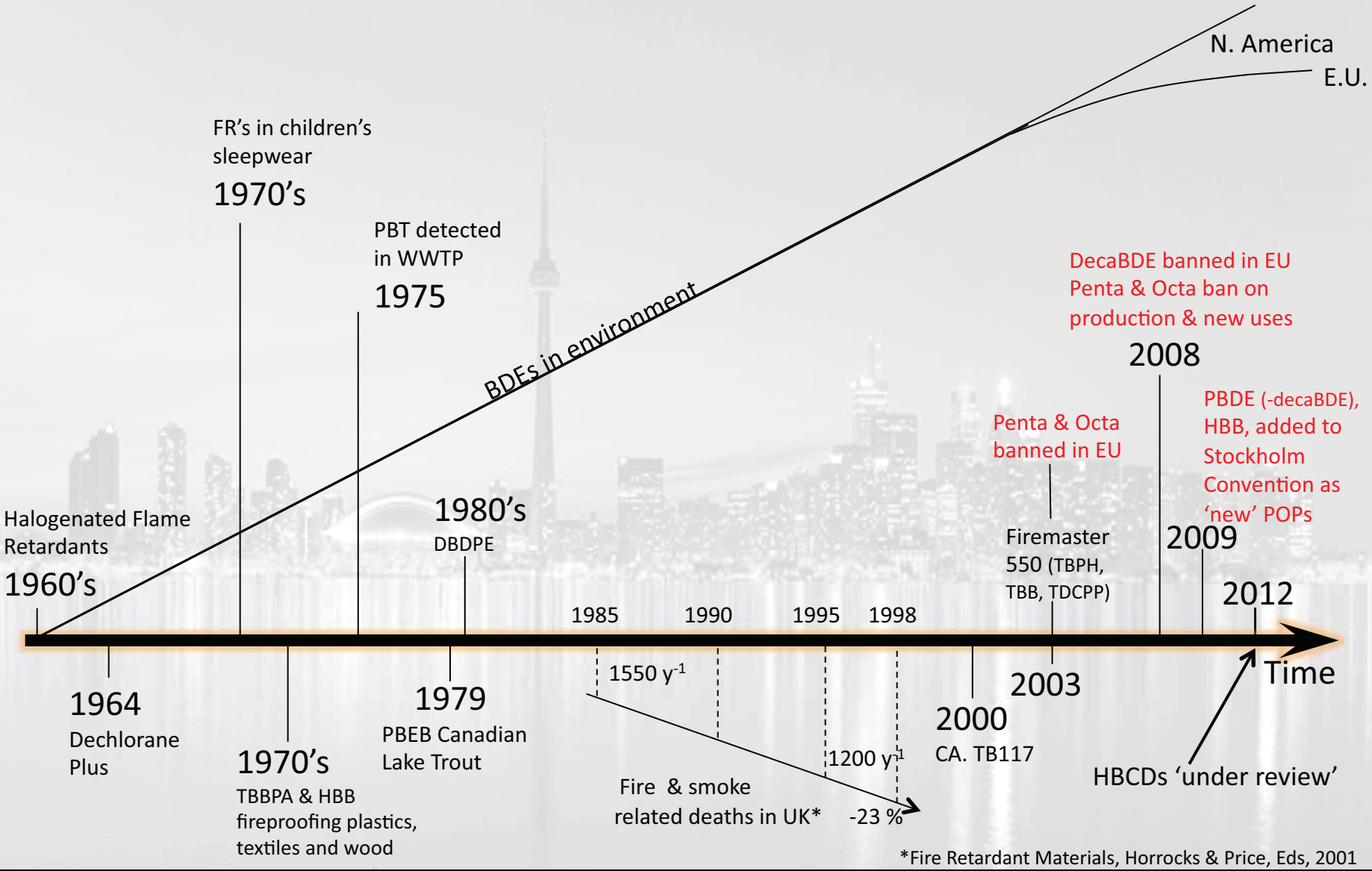
Contents

- Out with the old in with the new
- Current work
  - Results
  - Comparison of PBDEs and NFRs
- Model Framework
- Concluding remarks

Out with the old in with the new:



*Fire Retardant Materials, Horrocks & Price, Eds, 2001

BDEs & NFRs:

'certain organic flame retardants'
- *Chemicals Management Plan* (CMP) to address legacy of unassessed chemical substances in Canada
- significantly reduce potential risks to human health and the environment.

- New flame retardant (NFRs) are in some cases chemicals and formulations that may have had previous alternate uses.

- Common products being used being marketed to provide flame retardancy include **pesticides** and **insecticides** (phenols and phosphates), **plasticizers** (Lindol, tetrabromophthalate), prior **chemical warfare agents** (phosphoric acid, triethyl ester), as well as many halogenated phosphate esters and phthalates.

- The global volume of use of brominated flame retardants in 2005 was 311,000 metric tonnes with approximately one third of this volume consisting of NFRs (Harju, et al., 2008).

BDEs & NFRs:

- NFRs have already been documented in indoor and outdoor environments during the last 4 years (Ali, et al., 2011) (Stapleton, et al., 2011) (Harju, et al., 2008) Venier & Hites, 2011; Stapleton et al. 2011; Vetter & Rosenfelder, 2008; Van den Eede et al 2010).
- The presence of these compounds have also been measured in remote environmental regions, suggesting an abundance of use and environmental persistence (de Wit, et al., 2010).
- Of considerable concern is the finding that two of the four components of Firemaster 550 (FM550), a pentaBDE replacement, are doubling in concentration in Great Lakes air every 1.1 years (Ma et al. 2011).
- EU and N.American restrictions of certain flame retardants has led to 'novel' flame retardant use
- Adoption of California flammability standards, notably California Bulletin 117, has led to a wide range of NFRs being introduced to the market over the past decade

Why NFRs: (http://transparency.perkinswill.com/flameretardantcategories.cshtml)

TRANSPARENCY

Flame Retardants

ALPHABETICAL CATEGORY

Brominated Flame Retardant

1,2-bis(2,4,6-tribromophenoxy)ethane	2-Ethylhexyl tetrabromobenzoate	Bis(2-ethylhexyl) tetrabromophthalate	Decabromodiphenyl ethane
Decabromodiphenyl ether (BDE-209)	Diphenyl cresyl phosphate	Hexabromobenzene	Hexabromocyclododecane
Tetrabromo-bisphenol-A			

2-Ethylhexyl tetrabromob

Where is it Commonly Found?

2-Ethylhexyl tetrabromobenzoate (TBB) is used in well as wall coverings and adhesives (Andersson polyurethane foam in furniture and juvenile produ

HEALTH EFFECT SUMMARY

No toxicity information is available on TBB alone; oral and dermal exposure, but it is a slight eye an animal studies are available for carcinogenicity, b Escherichia coli were negative. No information is chemical. An animal study indicates that the comp doses. Based on its chemical structure and prope contamination of surface waters may lead to sign

In 2004, the EPA Design for the Environment pred and persistent degradation products from TBB. C sludge, and marine mammals, suggesting that th bioaccumulating in animals (Shaw et al., 2010).

TBB is structurally similar to bis(2-ethylhexyl) tetra fish, causing significant DNA damage (increased (Bearr, Stapleton, and Mitchelmore, 2010). TBPH (Stapleton et al., 2008), which is listed under Prop developmental toxicity (OEHHA 2008). Health effe (New Materials International, 2003).

How is Proposition 65 meeting its goal of reducing exposure to hazardous chemicals in California?

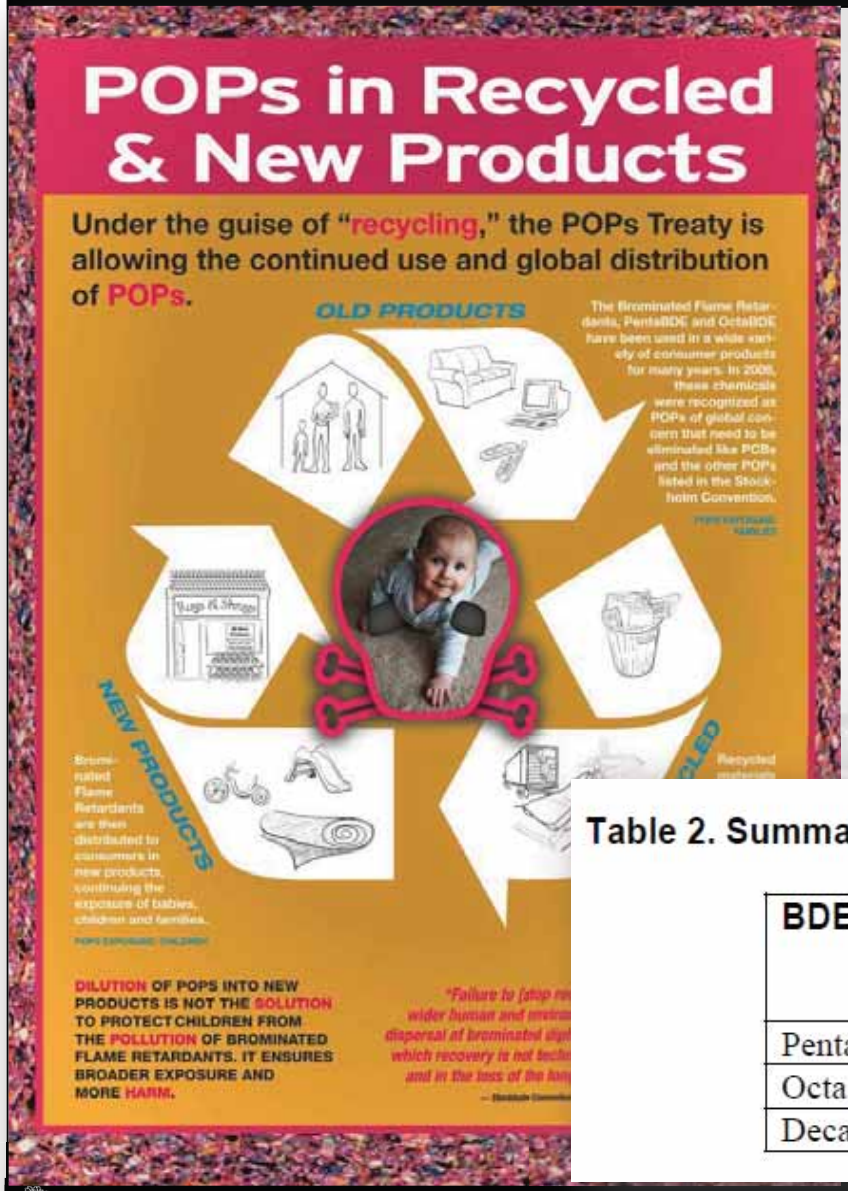
Since it was passed in 1986, Proposition 65 has provided Californians with information they can use to reduce their exposures to listed chemicals that may not have been adequately controlled under other State or federal laws. This law has also increased public awareness about the adverse effects of exposures to listed chemicals. For example, Proposition 65 has resulted in greater awareness of the dangers of alcoholic beverage consumption during pregnancy. Alcohol consumption warnings are perhaps the most visible health warnings issued as a result of Proposition 65.

Proposition 65's warning requirement has provided an incentive for manufacturers to remove listed chemicals from their products. For example, trichloroethylene, which causes cancer, is no longer used in most correction fluids; reformulated paint strippers do not contain the carcinogen methylene chloride; and toluene, which causes birth defects or other reproductive harm, has been removed from many nail care products. In addition, a Proposition 65 enforcement action prompted manufacturers to decrease the lead content in ceramic tableware and wineries to eliminate the use of lead-containing foil caps on wine bottles.

Proposition 65 has also succeeded in spurring significant reductions in California of air emissions of listed chemicals, such as ethylene oxide, hexavalent chromium, and chloroform.

Although Proposition 65 has benefited Californians, it has come at a cost for companies doing business in the state. They have incurred expenses to test products, develop alternatives to listed chemicals, reduce discharges, provide warnings, and otherwise comply with this law. Recognizing that compliance with Proposition 65 comes at a price, OEHHA is working to make the law's regulatory requirements as clear as possible and ensure that chemicals are listed in accordance with rigorous science in an open public process.

Mass Flow Analysis:



IPEN Community Study April 23, 2011

Table 2. Summary of PBDE levels in recycled carpet padding foam samples

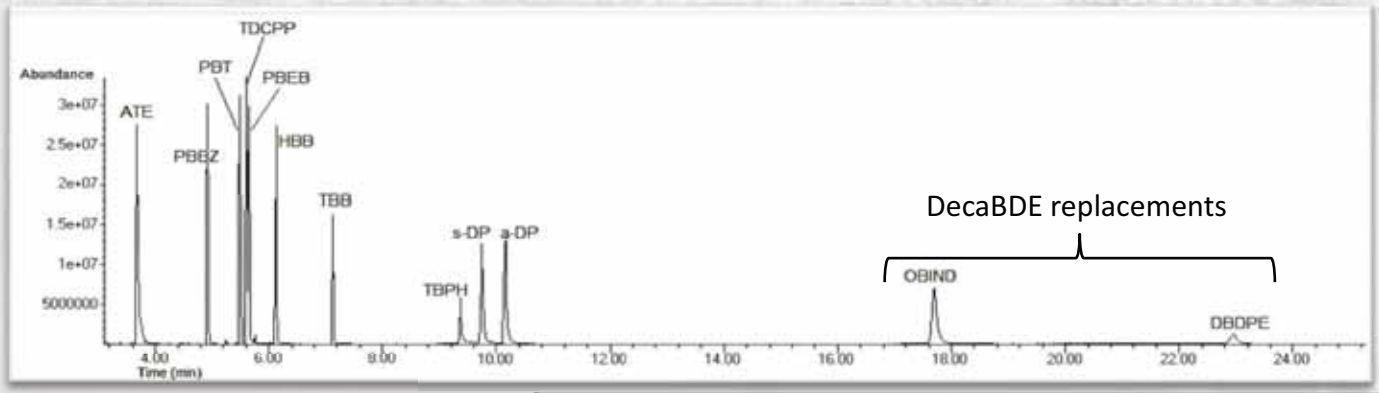
BDE	No. samples containing specific BDE	Range (ppm)	No. samples >50 ppm
Penta	20 (77%)	1 – 1130	13 (50%)
Octa	17 (65%)	1 – 263	7 (27%)
Deca	23 (89%)	1 – 166	6 (23%)

Out with the old in with the new:

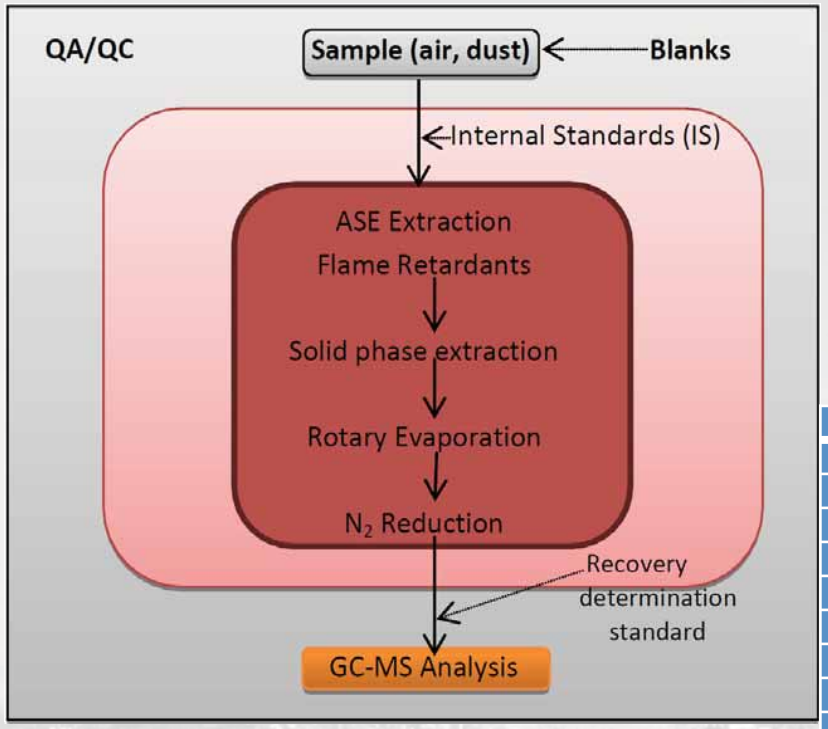
Chemicals of interest:

ATE - Tribromophenyl allyl ether
PBT – Pentabromotoluene
syn-DP & anti-DP – Dechlorane Plus
TBB - Ethylhexyl-tetrabromobenzene
TDCPP - Tri(2,3-dichloropropyl) phosphate
TBPH - Bis(2-ethlyhexyl)tetrabromophthalate
OBIND – Octabromo trimethylphenyl indane
DBDPE - Decabromodiphenylethane
PBBZ – Pentabromobenzene
PBEB - Pentabromoetheyl benzene
HBB – Hexabromobenzene

PBDE Congeners: 15, 17, 28, 49, 47, 66, 100, 99, 154, 153, 183, 209



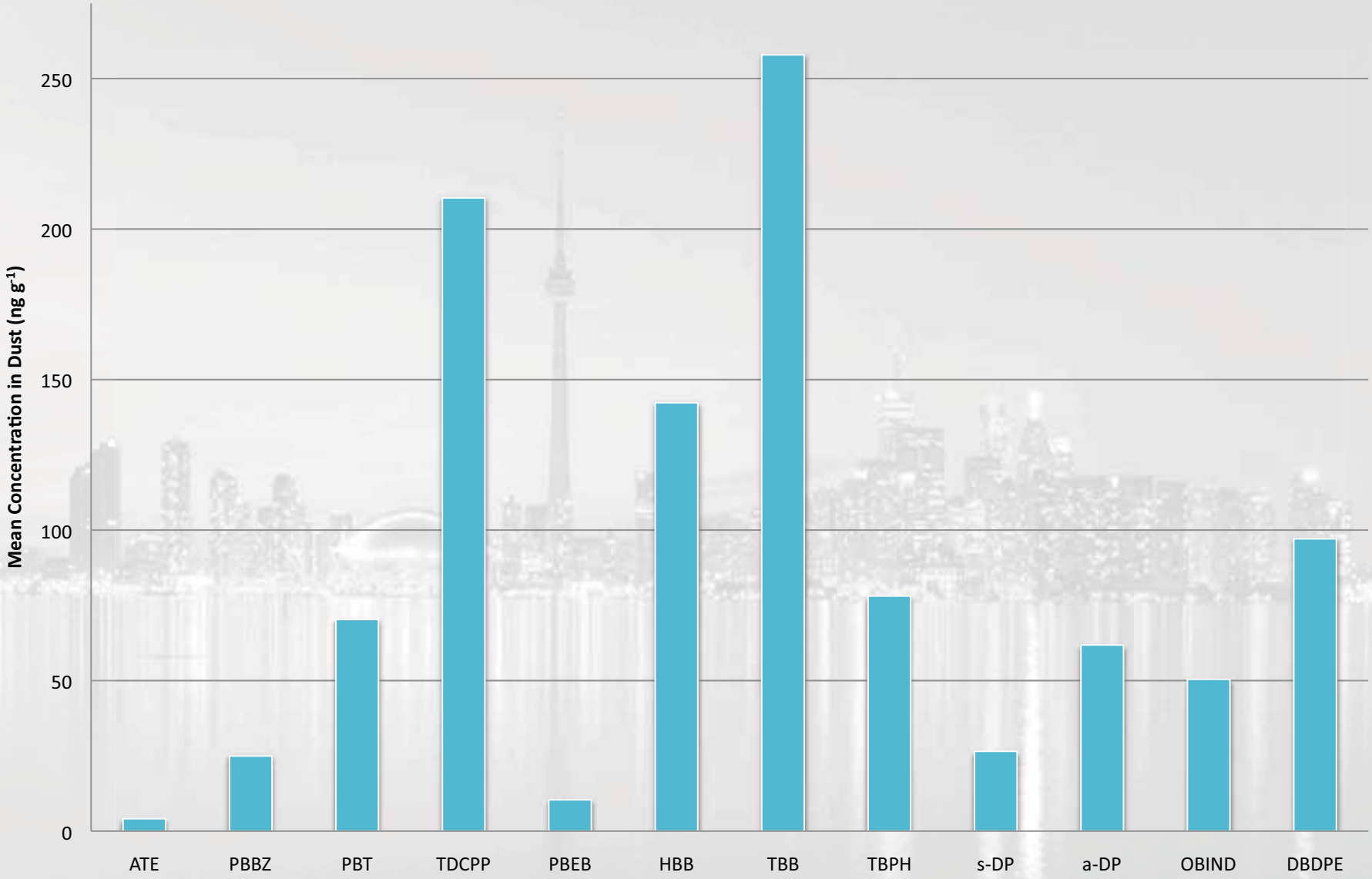
Samples & Analysis:



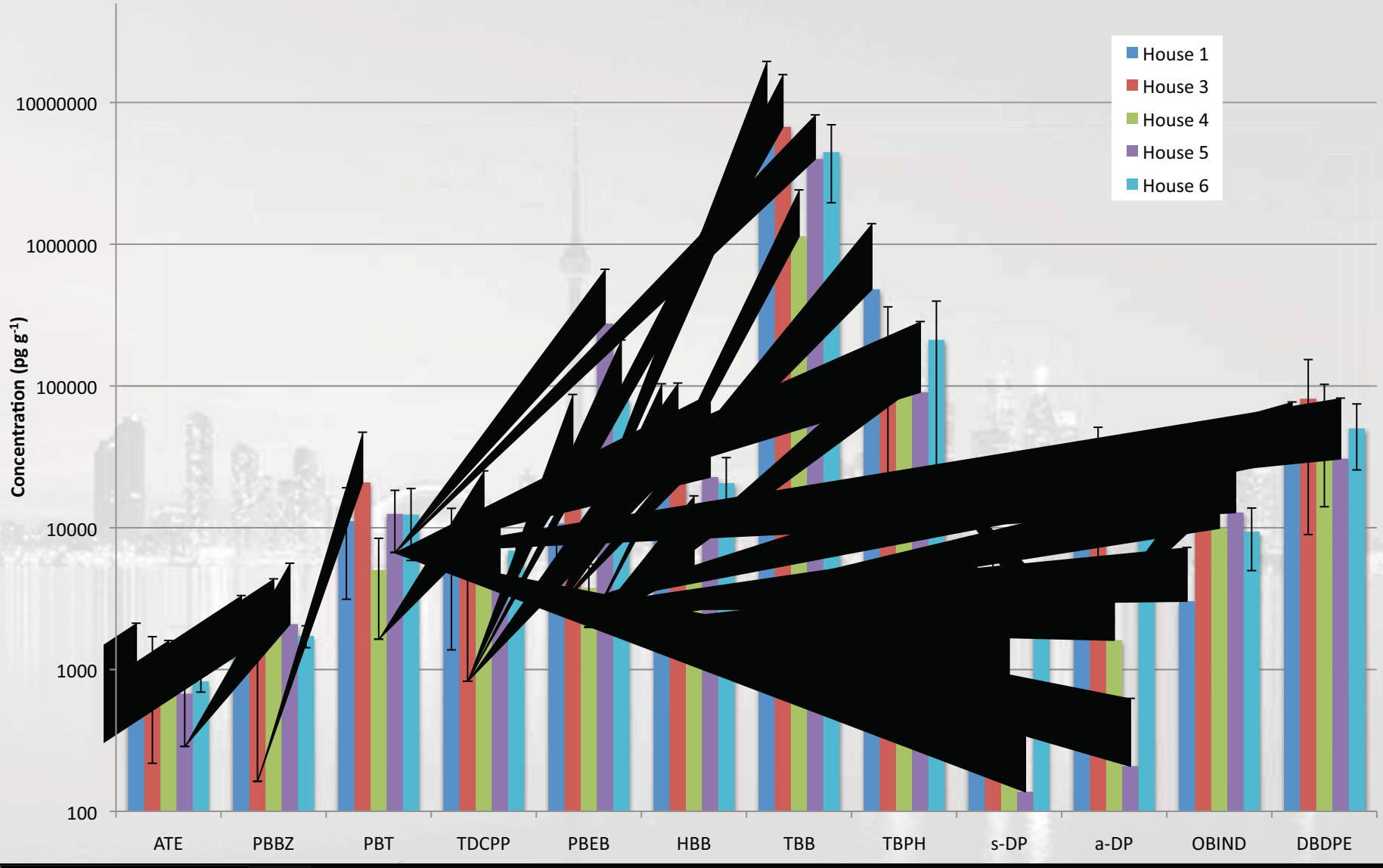
The operating system is an Agilent 6890-N GC coupled to a 5975-C mass spectrometer.

Parameter	Conditions		
Source	NCI		
Ion source Temperature	180°C		
Quadrupol Temperature	150°C		
Injection Volume	2 µL		
Carrier Gas	Hydrogen		
Inlet Conditions	Pulsed splitless, He		
	1.3 mL min^{-1}		
	280°C		
	pump flow to vent:	50 mL min^{-1} - 0.5 min	
	pressure:	17.02 psi	
	Purge flow:	50 mL min^{-1}	
	Purge time:	0.5 min	
Column	DB-5MS (15 m, ID 0.25 mm, film 0.25 µm)		
	Flow:	1.2 mL min^{-1}	
	°C min^{-1}	Target Temperature	Hold (min)
Oven Profile		90°C	0.5 min
	10°C min^{-1}	280°C	0 min
	15°C min^{-1}	300°C	0 min
	30°C min^{-1}	310°C	20 min
Interface (AUX) Temperature	280°C		

NFR Results (*n*= 35):



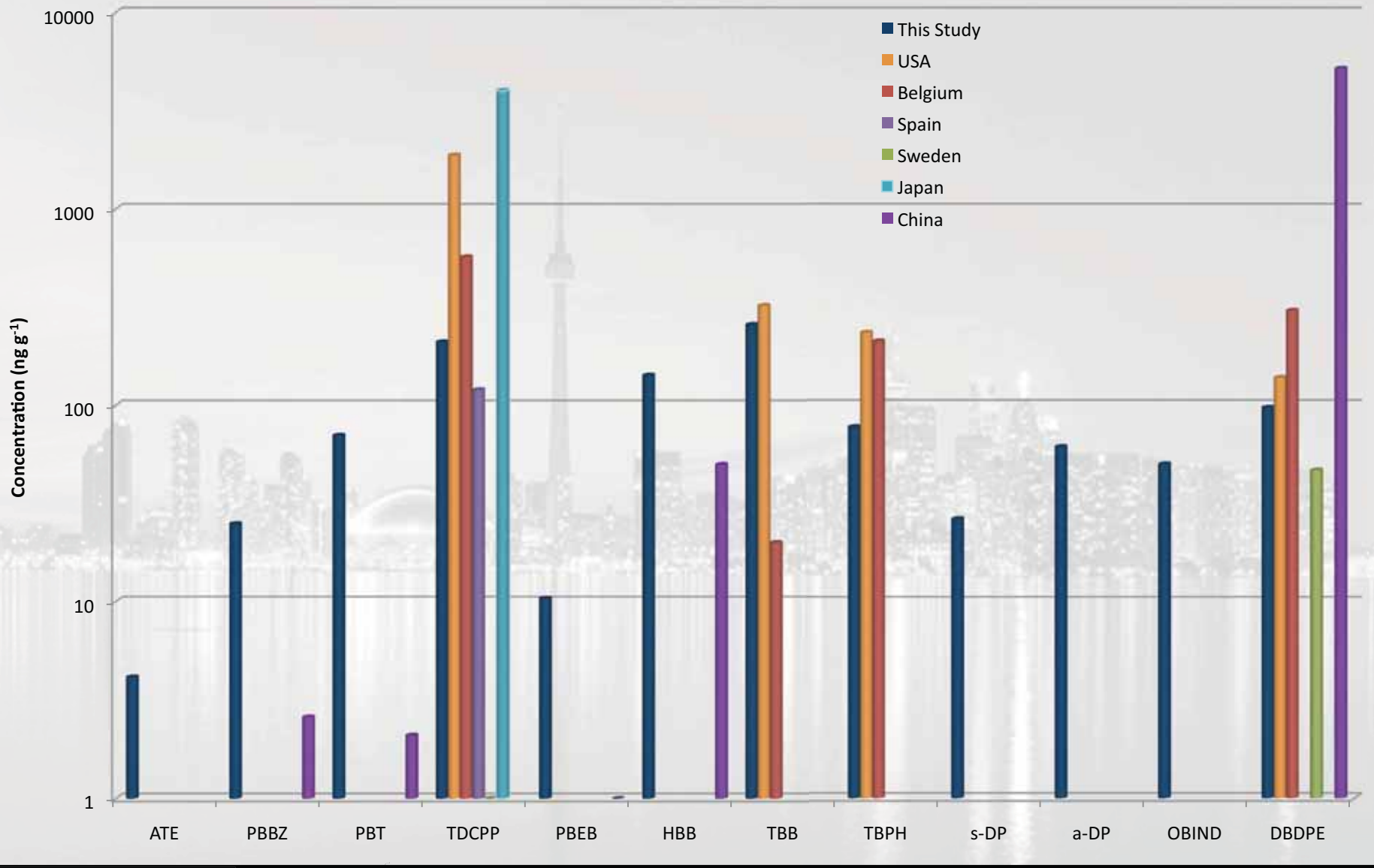
Homes (*n* = 35):


House 1
House 3
House 4
House 5
House 6
Concentration (pg g-1)
10000000
1000000
100000
10000
1000
100
ATE
PBBZ
PBT
TDCPP
PBEB
HBB
TBB
TBPH
s-DP
a-DP
OBIND
DBDPE

NFR Discussion:

- Concentrations present in the domestic indoor environment within Toronto, suggests that a number of commercial products containing these alternate compounds are available, and there is potentially a growing inventory of sources.
- The presence of OBIND and DBDPE, which are known to be decaBDE replacements were present in >80 % of the samples. Considering the restrictions on deca-BDE use are not due to be implemented until 2013, suggests that manufacturers are already switching formulations.
- Concentrations measured in houses across Toronto indicate little variability between the houses (15%< RSD < 50%) for ATE, PBBZ, PBT, TDCPP, HBB, OBIND and DBDPE, indicating that similar sources may be present in these homes. Whilst PBEB, TBB, and TBPH indicate a much larger variability (70% < RSD < 160%)

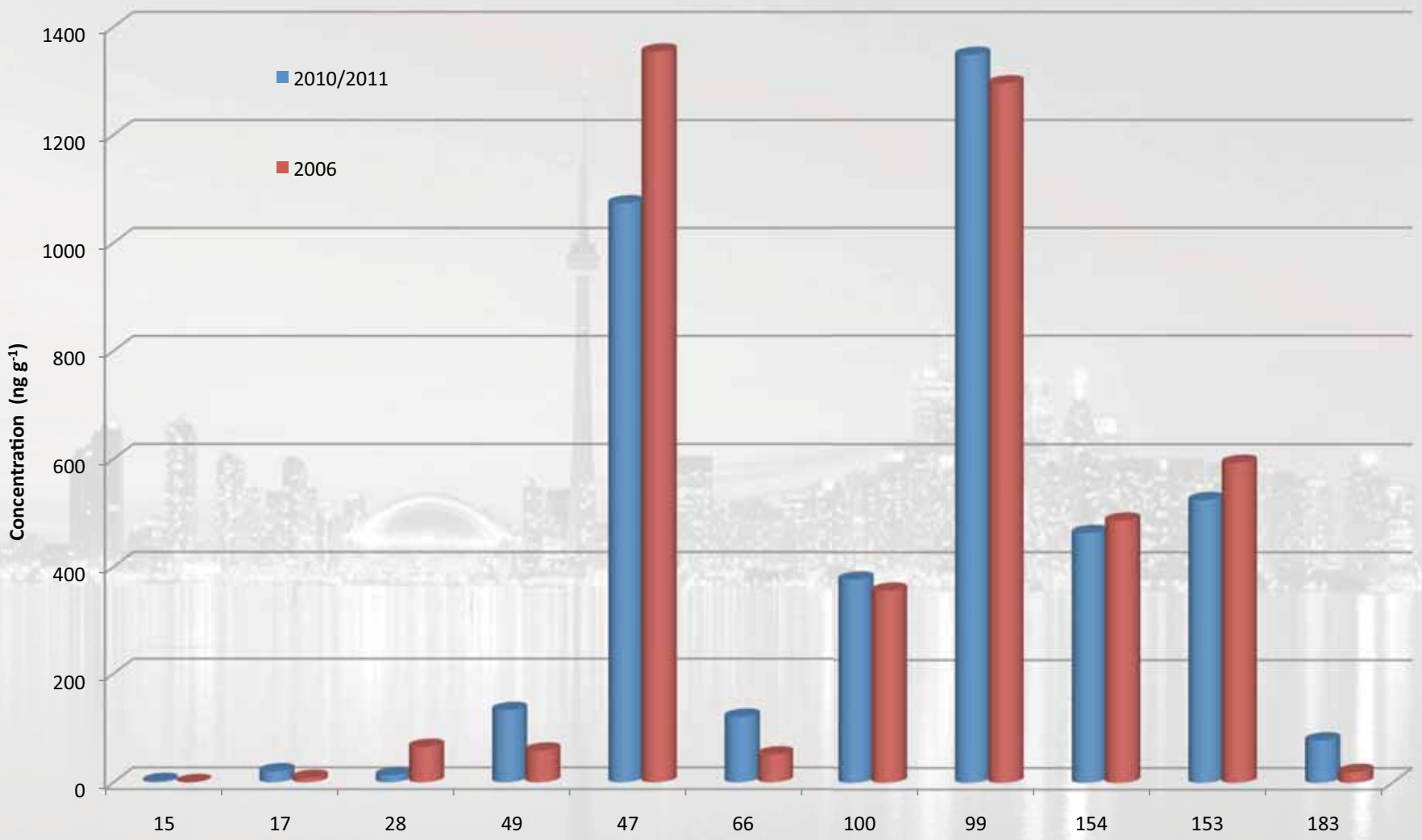
NFR Comparisons:



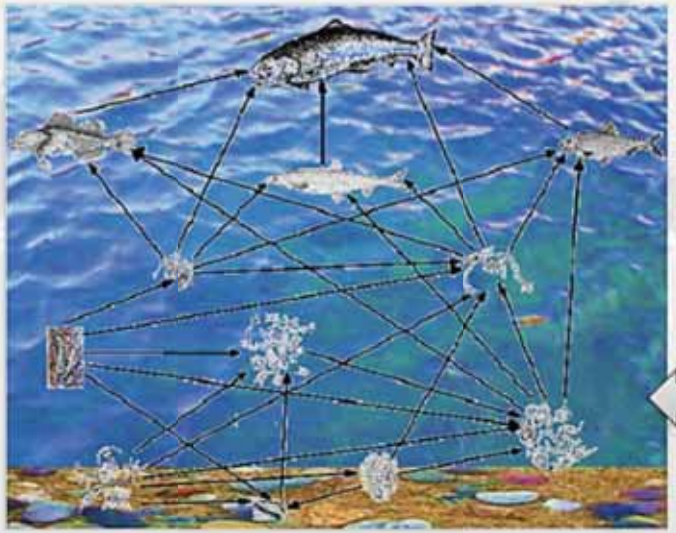
Discussion:

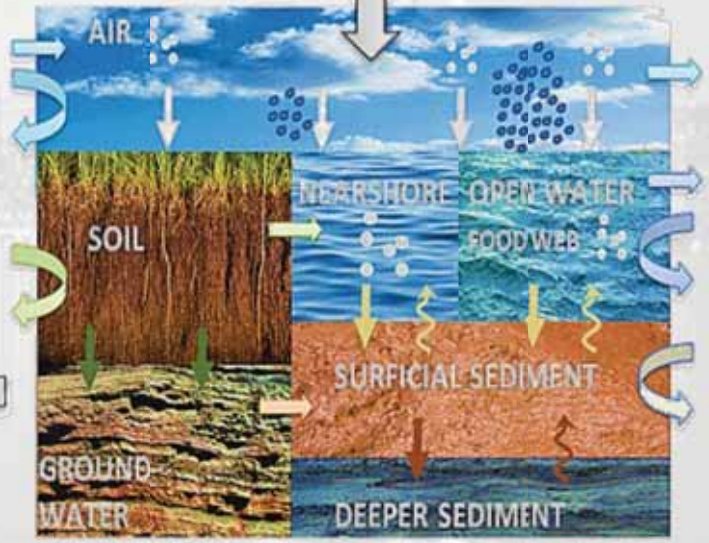
- Concentrations of NFRs in dust from a variety of countries present a comparison between continents. A high detection frequency of TBB was noted in the Canadian dust samples from this study, whereas TBB indicated a presence in only around a third of samples from Belgium. The discrepancy between detection frequencies may be an artifact of differences in industry preferences for flame retardant mixtures differing between the contents. In particular the popularity of Firemaster 550 for foams in North America may be an important source of TBB, TBPH and TDCPP in the indoor environment.
- Concentrations of TBB and TBPH are on a similar range to those measured by Stapleton et al. (2008), who noted the ratio of TBPH:TBB has been noted to be 1:4. However ratios of these two compounds in the samples from this study are lower.
- The higher concentrations and presence of TBB in these samples is the opposite to what is noted in Belgium, where Ali et al. (2010) hypothesised additional sources of TBPH. It is hypothesised that the North American flame retardancy requirements is the driving force for the higher presence of these compounds measured in Canadian dust.
- Concentrations measured in Canadian dust are on a comparable concentration to dust from homes in other countries for compounds PBBZ, PBT, TDCPP, HBB, and DBDPE. Sources of these chemicals to dust in homes, is likely to derive from similar sources, such as electronics, plastic casings, and wiring.

PBDEs:


1400
1200
1000
800
600
400
200
0
Concentration (ng g-1)
2010/2011
2006
15
17
28
49
47
66
100
99
154
153
183

Model Framework:





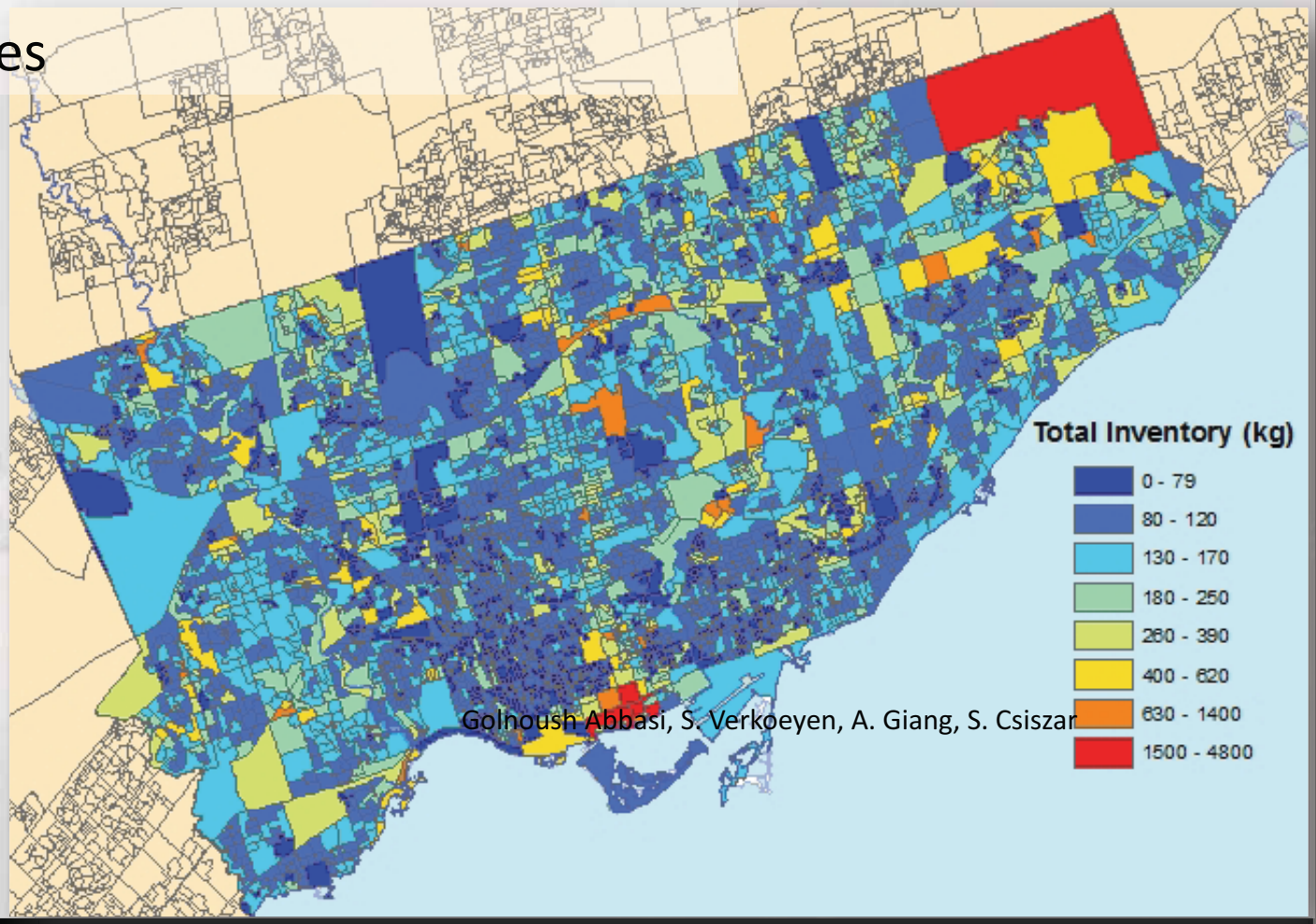
Model Framework:

Mass of PBDEs in Toronto (2008)

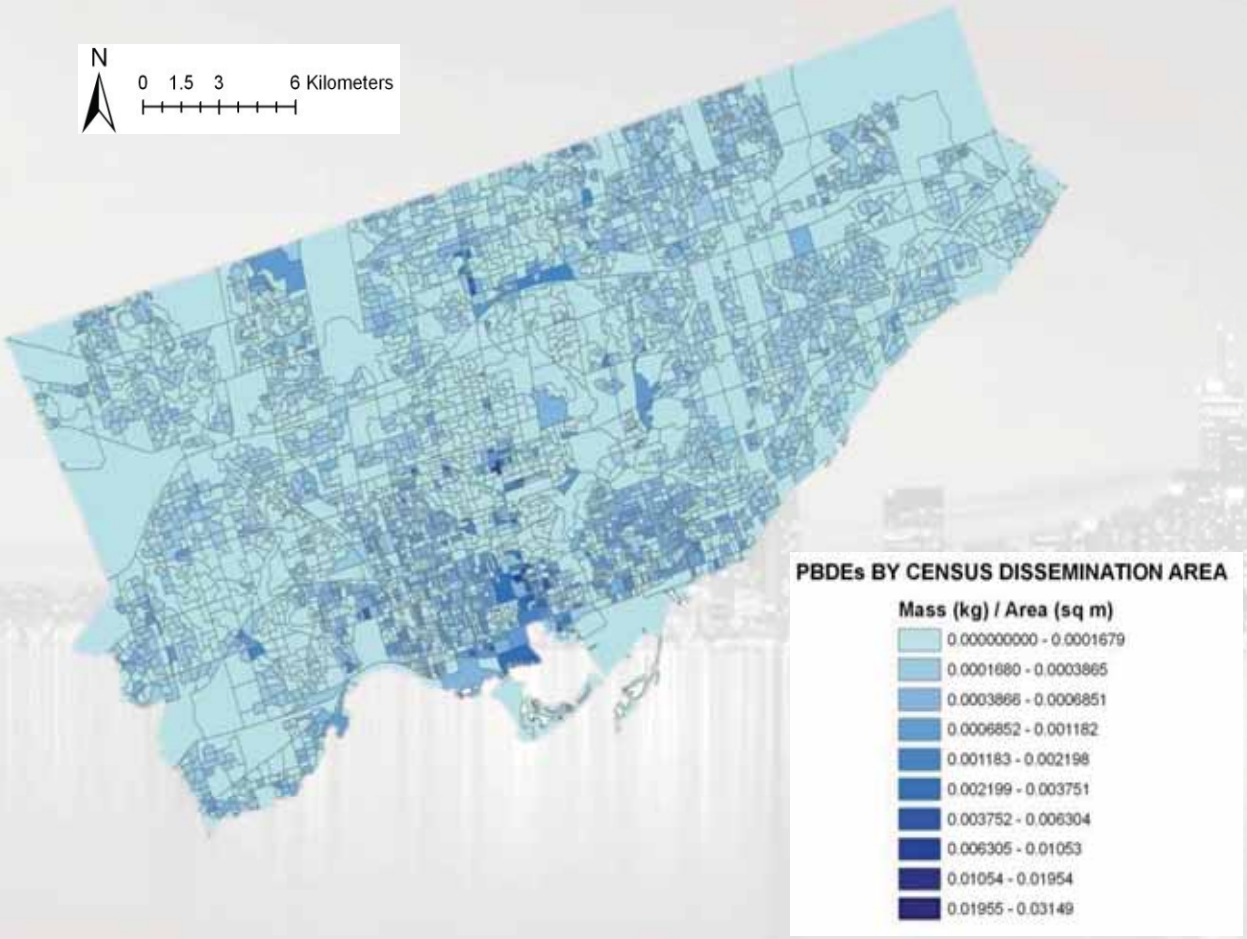
~235 tonnes indoor stuff +

~260 tonnes vehicles

TVs 65%
Computers 15%
Furniture 11%
Printers 9%



PBDE Inventory:



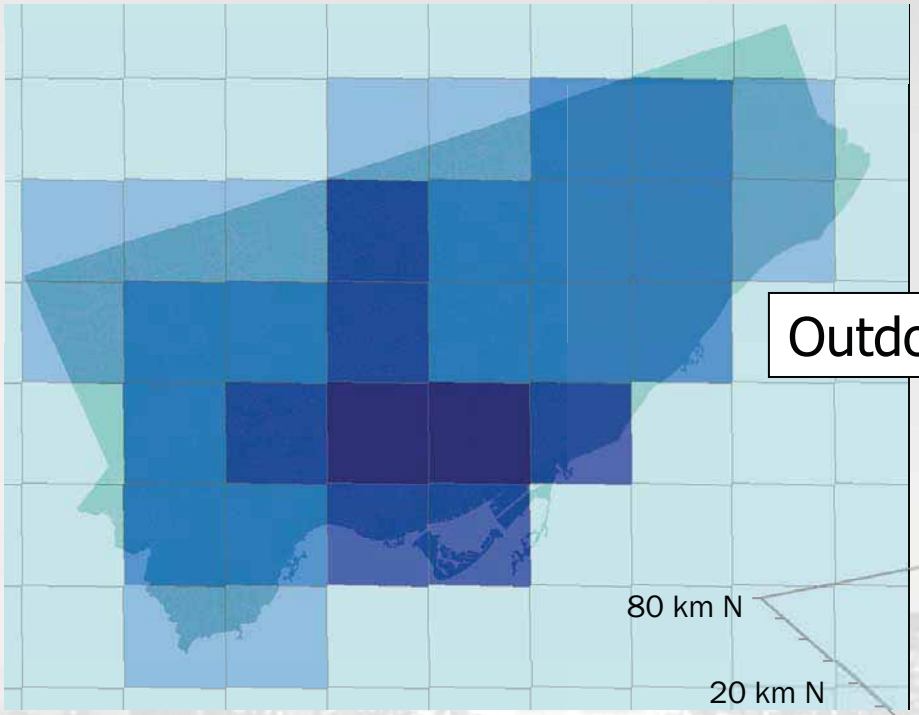
- CDAs which have a high mass/area are found in downtown core, along main transit corridor, and flanking other subway lines

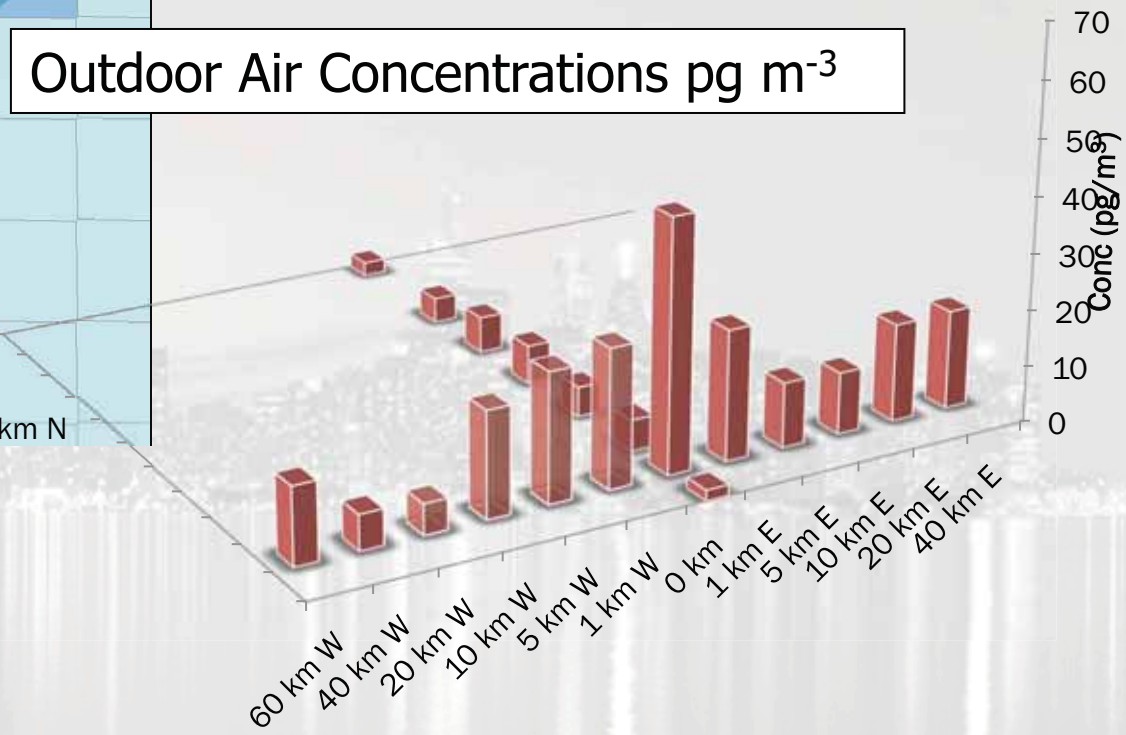
Factors which may contribute to this are:

- commercial zones
- high-density living
- post-secondary institutes

*Slide by Golnoush Abbasi

PBDE Inputs:





Melymuk L, M Robson, PA Helm, ML Diamond. PCBs, PBDEs and PAHs in Toronto air: spatial and seasonal trends and implications for contaminant transport. *Science of the Total Environment* In final revision.

Conclusions:

- Concentrations at measurable levels in the domestic indoor Canadian environment, suggesting the use of these NFRs has been underway for some time.
- Chemical alternatives for PBDEs and decaBDE such as OBIND and DBDPE are seen to be present in over 60% of the samples to a varying degree.
- Concentrations in Canadian dust remain within the range seen in other countries for all compounds. The presence of these compounds at similar concentrations are likely to derive from widely available consumables, such as electronics, wiring etc.
- Dust samples indicated a high detection frequency of TBB and TBPH, which are constituents of FM 550, a common and preferred flame retardant commercial mixture.
- The large difference in concentrations between the Canadian samples and those in Europe is likely to be the source, where foam and materials coated with FM 550 being the predominant sources in North America.
- The restriction of PBDE use in Canada is opening the market for alternate flame retardant compounds, both chlorinated and brominated products. The chemical structures and halogenation suggests potential persistent, bioaccumulative and toxic to the environment, and accumulation within the indoor environment already beginning.
- The presence of these compounds should be noted for human health effects, in particular for young children and uptake via dermal, inhalation and dust ingestion occurring from their indoor environments.

Future Work:

Products **Pulverized Samples**

LCD panel

Printed Circuit Board

Printed Circuit Board (power supply unit)

GC/MS analysis

Questions?

I would like to acknowledge:
Miriam Diamond and the Diamond Environmental Research Group, in particular:

Amandeep Saini	**Lisa Melymuk**
Susan Csiszar	**Golnoush Abbasi**

Model Framework: