BFR Emission Rates in Non-Residential Buildings

Stuart Batterman

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GLC Webinar

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University of Michigan
School of Public Health

Brief biography

Appointments:

Professor of Environmental Health Sciences. School of Public Health, University of Michigan, Ann Arbor, Michigan.

Professor of Civil & Environmental Engineering, College of Engineering, University of Michigan, Ann Arbor, Michigan.

Director, Center for Occupational Health and Safety Engineering, University of Michigan, Ann Arbor, Michigan.

Professor of Mechanical Engineering. Faculty of Science and Technology, Universidade de Coimbra, Coimbra, Portugal.

Honorary Professor, Department of Occupational and Environmental Health, Medical School, University of KwaZulu-Natal, Durban, South Africa.

Education:

Ph.D., Water Resources and Environmental Engineering, Civil Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

M.S., Civil Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

B.S., Environmental Science, Rutgers University, New Brunswick, New Jersey.

Research activities:

Exposure assessment in occupational, indoor and environmental settings, including biological monitoring; air quality monitoring; air pollution control engineering; diesel exhaust; volatile organic compounds; “emerging” contaminants.

Also, environmental epidemiology; impact and risk assessment, environmental statistics; sustainable systems; life cycle analysis; public health interventions.

Outline of Webinar

Brief introduction to problem

- Relevance to Great Lakes, e.g., trends in biota

Approach

- Characterize BFRs in a newly constructed commercial building (including vapor, PM and dust)
- Trend concentrations as the building is completed, furnished and occupied & provide a mass balance among key indoor compartments.

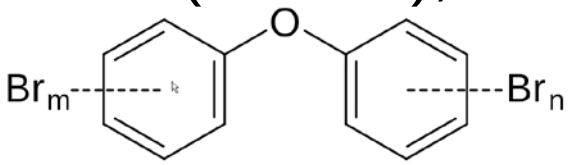
Extend approach to building surveys

- Other commercial buildings
- Examine residential buildings
- Estimate emission rates from buildings

Summary & conclusions

Introduction

- Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants (BFRs) that have been extensively used for decades in consumer, commercial and industrial products, e.g., polyurethane foam, thermoplastics, textiles and circuit boards.
- Commercial BDEs have been marketed in three mixtures with different congener profiles: pentaBDE (PeBDE); octaBDE (OBDE); and decaBDE (DBDE).



- Up to very recently, PBDE use in North America was unrestricted.
- BFRs, including PBDEs, are persistent, bioaccumulative and toxic chemicals. The lower brominated BDEs are more toxic to organisms. DecaDBE may debrominate under certain conditions. Human toxicity is suspected.
- Substantial, “exponential” increases in body burdens in humans, biota & environment.

PBDE monitoring in the Great Lakes

Lake Sturgeon

Rainbow Smelt

Native Clams

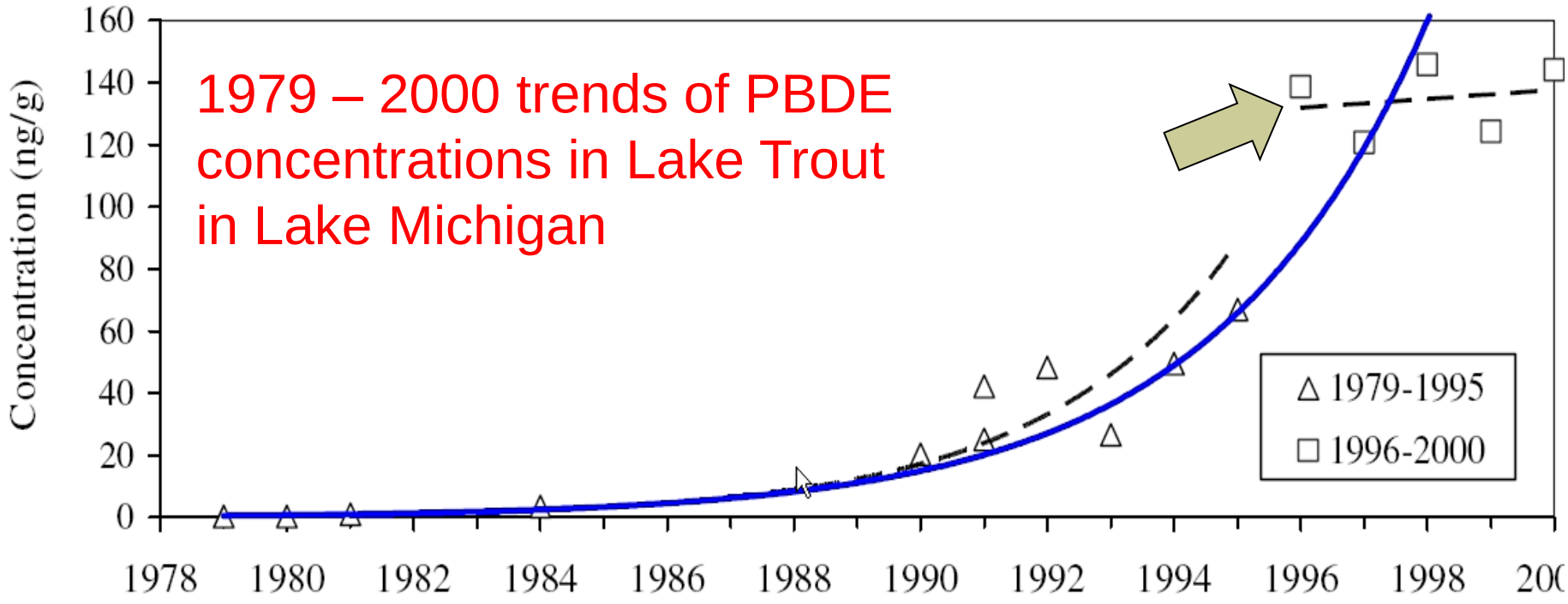
Common Carp

Lake Trout

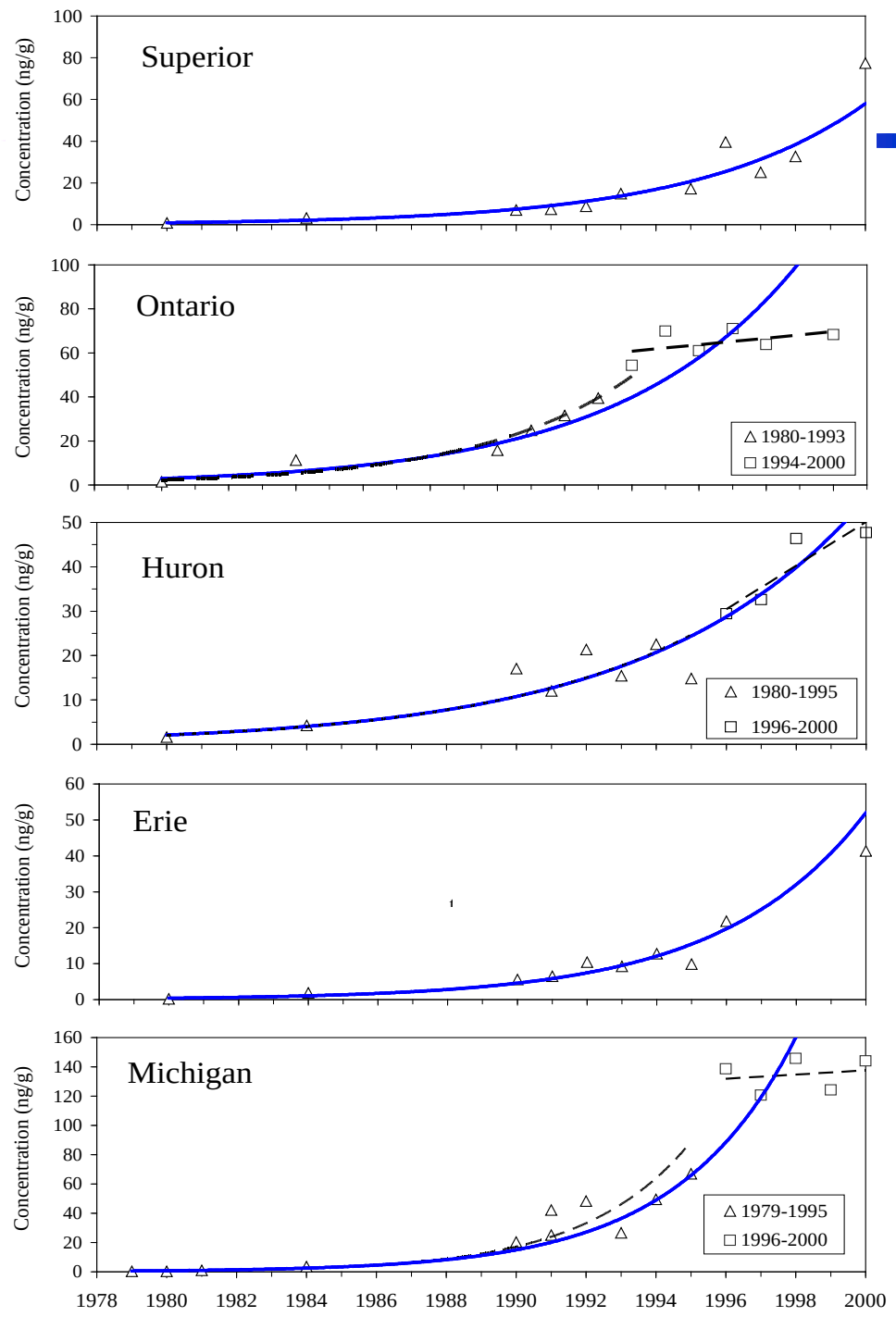
Available online at www.sciencedirect.com
ScienceDirect
Chemosphere 69 (2007) 444–457
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Trends of brominated diphenyl ethers in fresh and archived Great Lakes fish (1979–2005)

Stuart Batterman [a,*], Sergei Chernyak [a], Erica Gwynn [a], David Cantonwine [a], Chunrong Jia [a], Linda Begnoche [b], James P. Hickey [b]



PBDE trends in lake trout

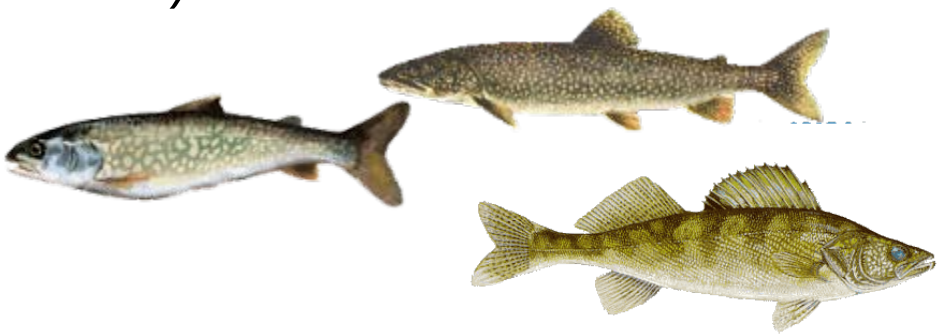


Trends of $\sum_4$BDE (PBDE congeners 47, 99, 100 and 153) in lake trout (walleye in Lake Erie).

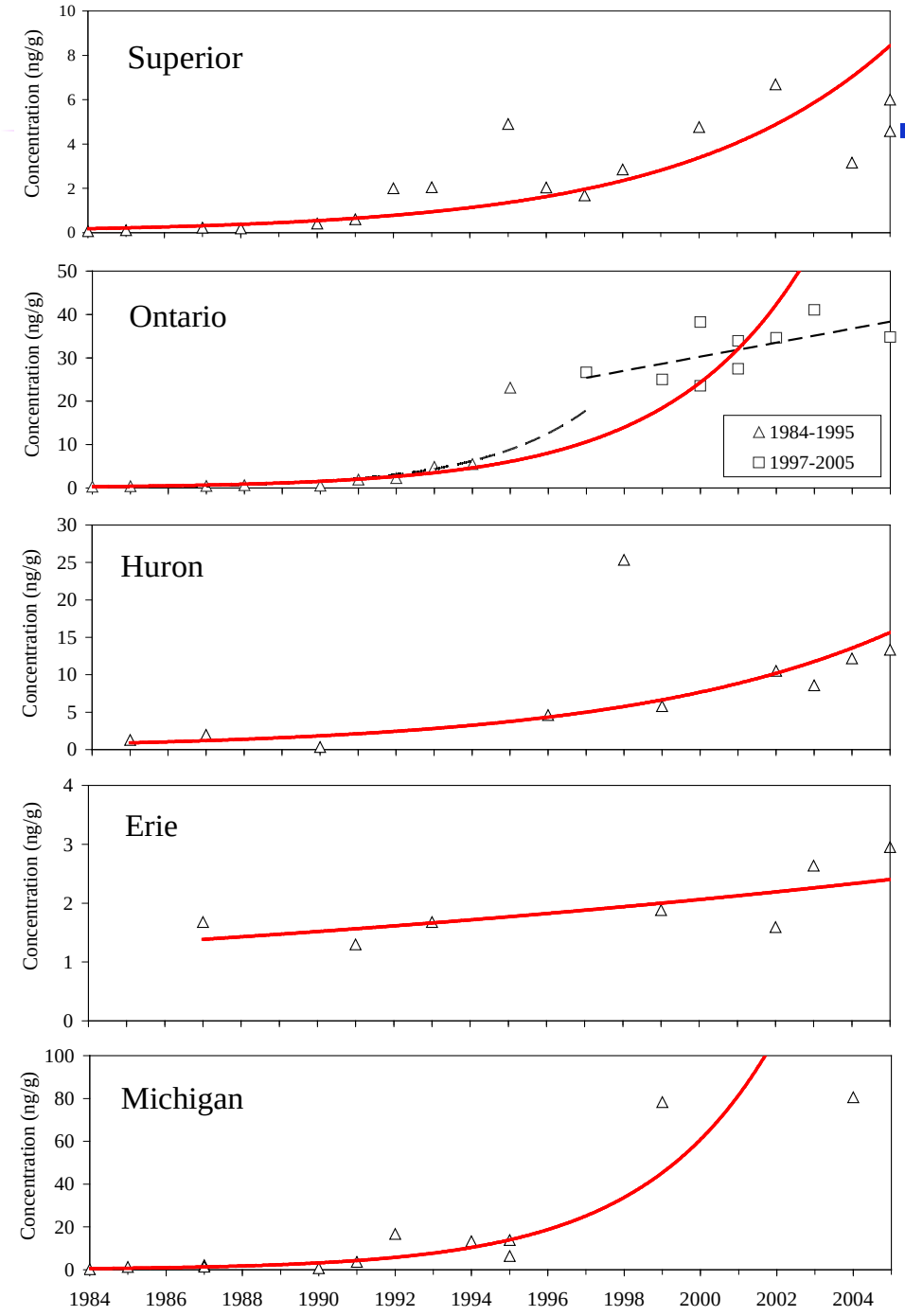
Solid line shows exponential model fit to entire record.

Dashed line shows bilinear models (exponential and linear) from change-point analysis.

For Lake Huron, the exponential portion of the bilinear model (1980-1995) is identical to the exponential model for the entire record (1980-2000).



PBDE trends in smelt



Trends of $\sum_4$BDE (PBDE congeners 47, 99, 100 and 153) in smelt.

Solid line shows exponential model fit to entire record.

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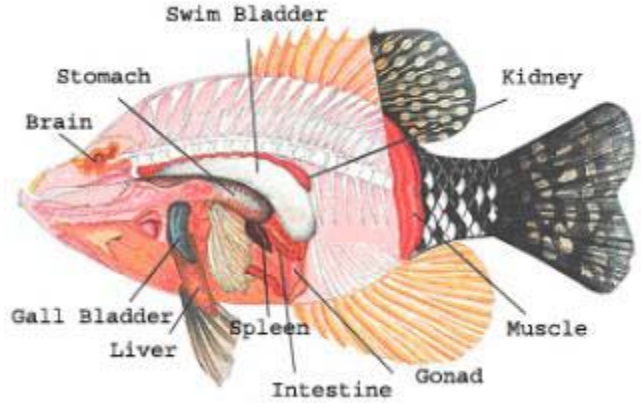
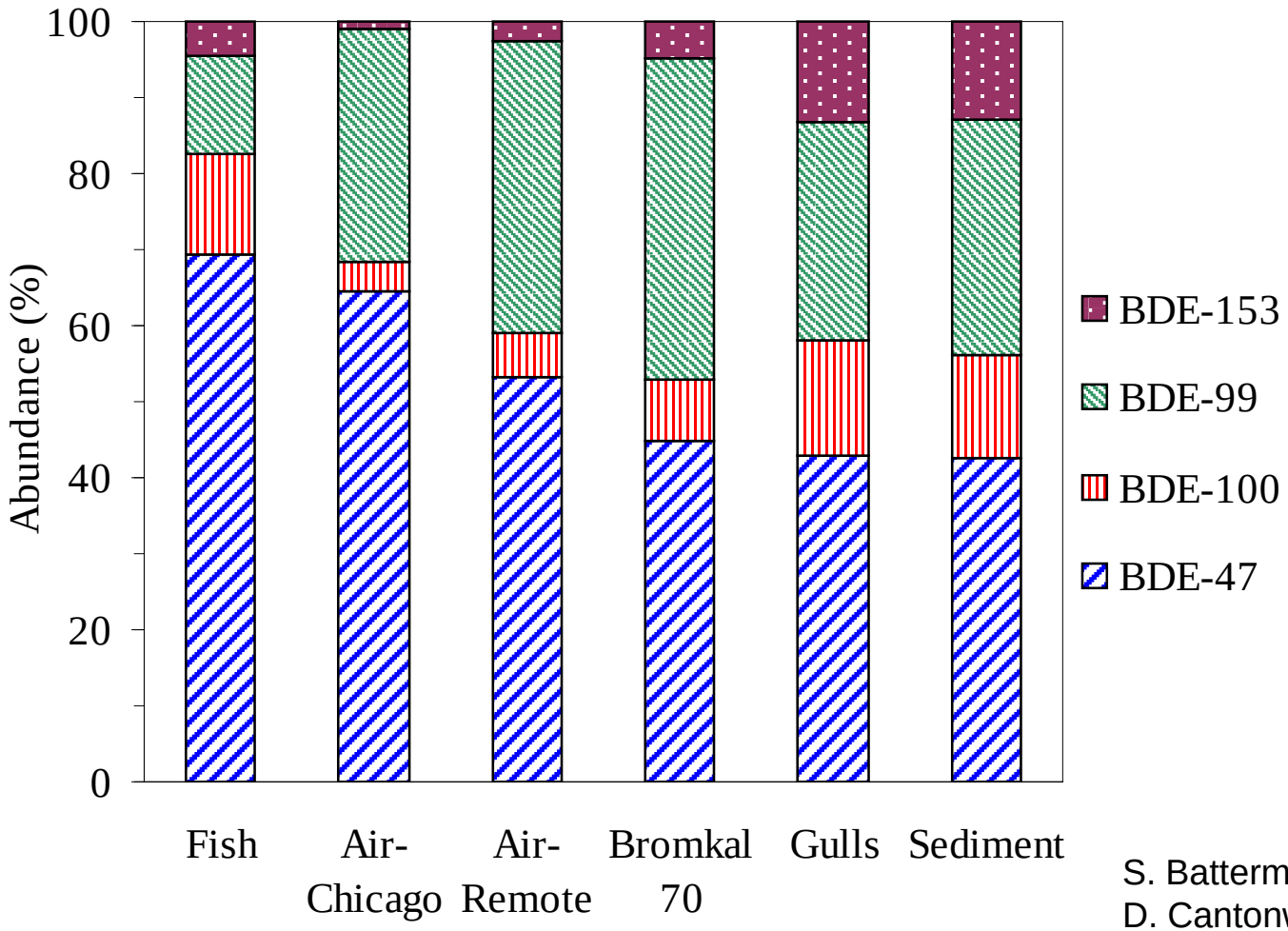


Trends and change point analysis for PBDEs

Shows doubling time ($t_{1/2}$), percentage change over the period, and model fit (r^2) for sum of BDE congeners 47, 99, 100 and 153. (a) Denotes linear model, t1/2 not available

	Lake Trout (Walleye for Lake Erie)			Rainbow Smelt		
Lake	Year Range	$t_{1/2}$ (yr)	r^2	Year Range	$t_{1/2}$ (yr)	r^2
Ontario	1980-2000	3.7	0.89	1984-2005	2.5	0.91
	1980-1993	3.1	0.89	1984-1993	2.0	0.86
	1994-2000	(a)	0.25	1994-2005	(a)	0.36
Erie	1980-2000	2.9	0.94	1987-2005	22.6	0.52
Huron	1980-2000	4.2	0.93	1985-2005	4.9	0.63
	1980-1995	4.2	0.88			
	1996-2000	(a)	0.80			
Superior	1980-2000	3.4	0.96	1983-2005	3.8	0.80
Michigan	1979-2000	2.3	0.96	1984-2004	2.4	0.83
	1979-1994	2.1	0.96			
	1995-2000	(a)	0.04			

PBDEs in the Great Lakes



Comparison of relative abundances of four congeners in fish (average of all fish, lakes and years after 1996), air samples collected in air in Chicago and at three remote Lake Michigan sites (Strandberg et al. 2001); the commercial Bromkal 70 mixture (Sjodin et al. 1998); herring gull eggs (Norstrom et al. 2002); and Great Lake sediment cores (Song et al. 2005a; 2005b; 2005c).

S. Batterman, S. Chernyak, E. Gwynn, D. Cantonwine, C. Jia, L. Begnoche, J.P. Hickey, "Trends of Brominated Diphenyl Ethers in Fresh and Archived Great Lakes Fish (1979-2005)," *Chemosphere*, **69**, 444-457, 2007.

Trend analysis conclusions

Fish samples (archived lake trout, walleye and rainbow smelt samples collected between 1979 and 2005) showed:

- PBDEs in each Great Lake increased exponentially beginning in the early 1980s, and then leveled-off or decreased started in the mid 1990s for penta- and hexa-BDE congeners in Lakes Ontario and Michigan
- Concentrations among the lakes may be ranked as:

  Trout: Michigan > Superior = Ontario > Huron = Erie

  Smelt: Michigan > Ontario > Huron > Superior > Erie
- Differences among lakes, fish species & PBDE congeners, but overall rate of increase appears to be slowly diminishing (to 2005)

Emission sources of BFRs

BFRs can be released from many sources, e.g., building materials and furnishings, household/office products, chemical production, manufacturing (especially products that incorporate foams, plastics and textiles), waste water, product disposal, etc.

- Several studies (mostly in Europe & US) have shown that levels of BFRs are highly elevated in residences
- Information is starting to come out regarding levels in offices and other workplaces.
- Buildings contain a large reservoir of BFRs, and may represent an important environmental source of BFRs, but releases (and exposures) are highly uncertain.

Goal here is to investigate on BFR concentrations and in-use rates of BFR emission in residential and commercial buildings.

Commercial buildings

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Brominated flame retardants in offices in Michigan, U.S.A.

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[b] School of Public Health, University of Memphis, Memphis TN, USA
[c] Jiann-Ping Hsu College of Public Health, Georgia Southern University, Statesboro, GA, USA

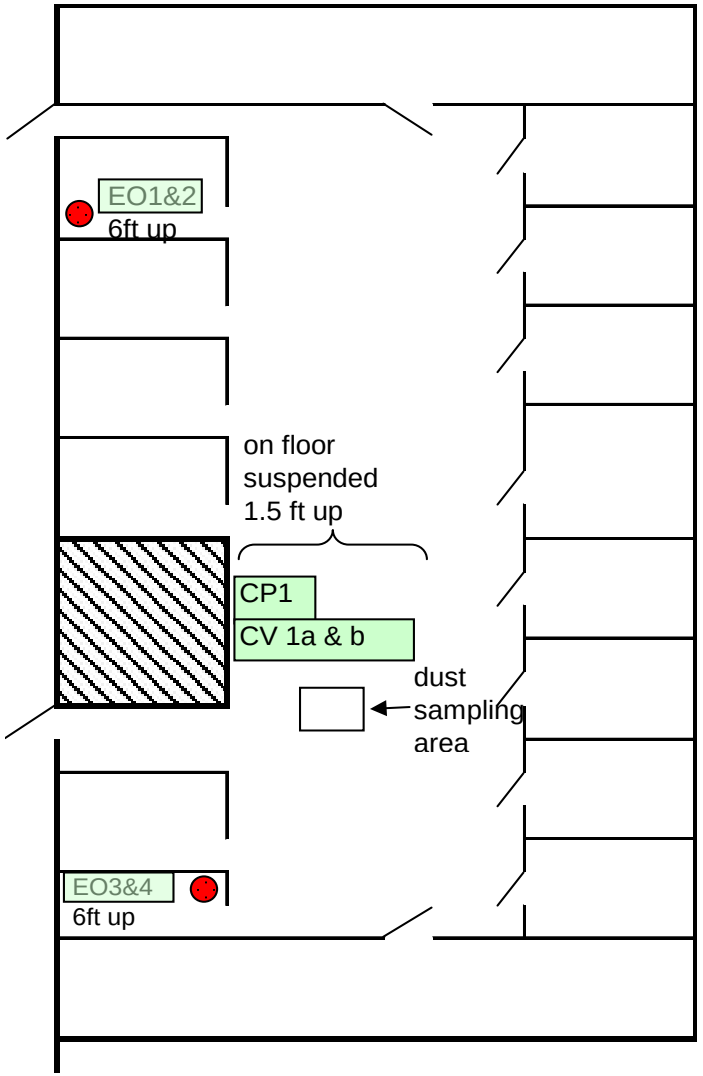
Objectives & study design

Objective: Quantify trends and explore mass balance of BFRs among air and dust in a newly-constructed building. Then expand to suite of 10 buildings.

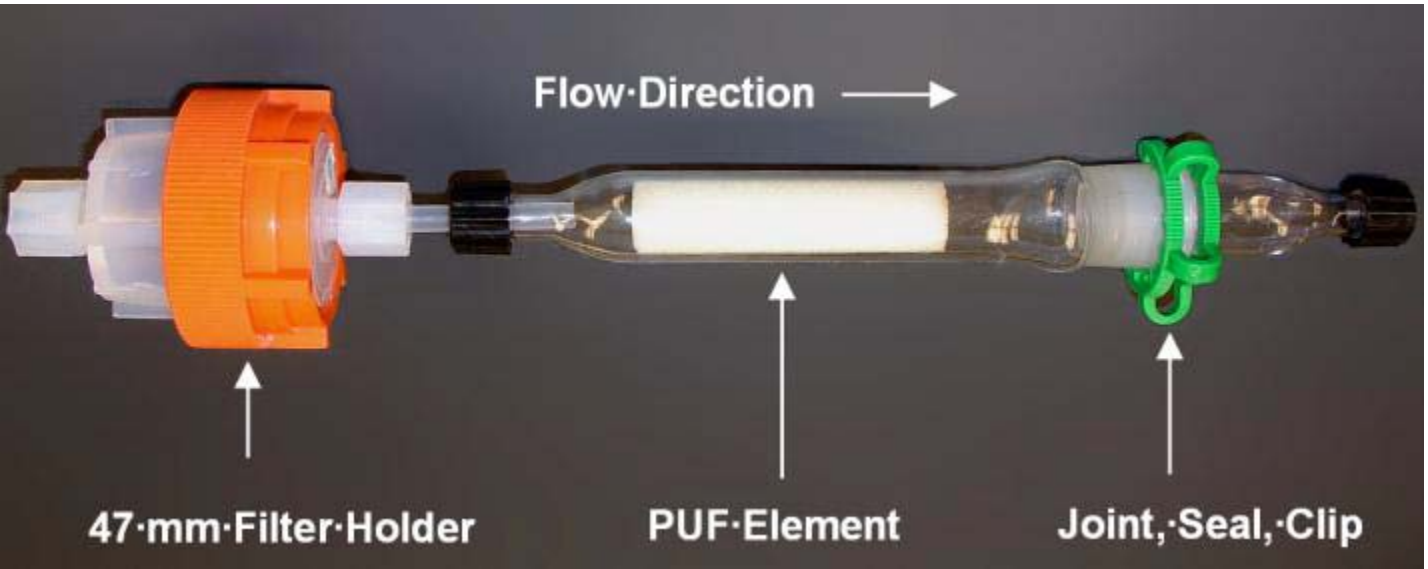
Sampling design: Case study: 7-floor mixed-use building containing offices, classrooms, cafeteria, computer rooms, and labs. Monitoring just prior to occupancy (August 2006); repeat seasonally (until November 2007), for total of 7 sampling events.

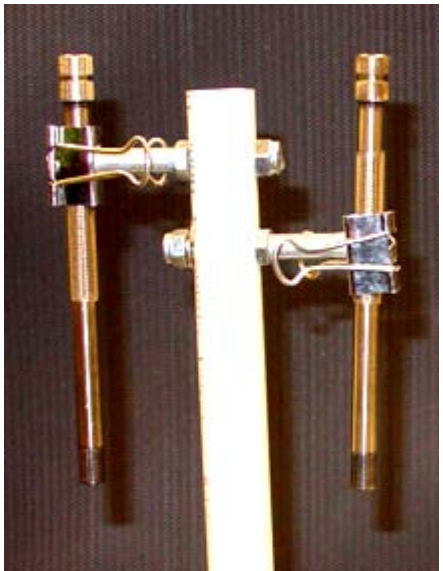
- BFRs measured in office suites on 6th floor.
  - Air (vapor and particulate fractions)
  - Floor dust (and new carpets)
  - Heating, ventilating and air conditioning (HVAC) filters, including unused (new) and used (after 1 year) filters.
- Outdoor sampling was conducted simultaneously.
- Additional measurements at same sites included VOC samples and air exchange rates (AERs) using tracer gases.

Building layout



BFR and VOC Sampling Systems





Sample Analysis & MDLs

Sample analysis

- Samples were analyzed for 20 BDE congeners and tetrabromobisphenol-a by GC/MS.
- VOC and PFT samples were analyzed using a short-path thermal desorption/cryofocusing system, and GC/MS operating in EI mode for 90 compounds.

Method detection limits (MDLs)

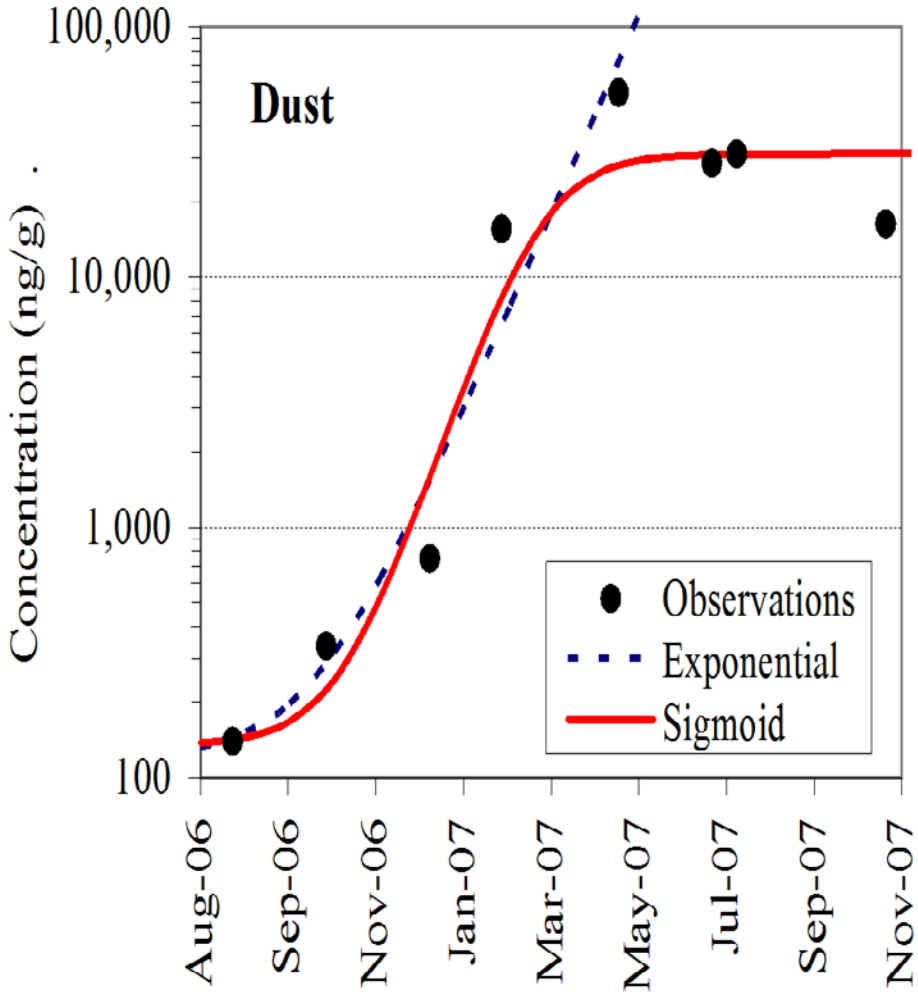
- Air samples: 0.01-0.02 ng/m^3 for tetra- and octa-BDEs, 0.2 ng/m^3 for nona-BDEs, 0.6 ng/m^3 for deca-BDE, 0.1 ng/m^3 for TBBPa.
- Dust samples: 0.005–0.02 ng/g for tetra- and octa-BDEs, 0.4 ng/g for nona-BDE, 2.5 ng/g for deca-BDE, 0.2 ng/g for TBBPa.

S. Batterman, Chen TC, Chernyak SC, Godwin CC, “Performance evaluation of a medium flow sampler for airborne brominated flame retardants (BFRs),” *Journal of Environmental Monitoring*, 11, 858-866, 2009. http://xlink.rsc.org/?doi=B817298F.

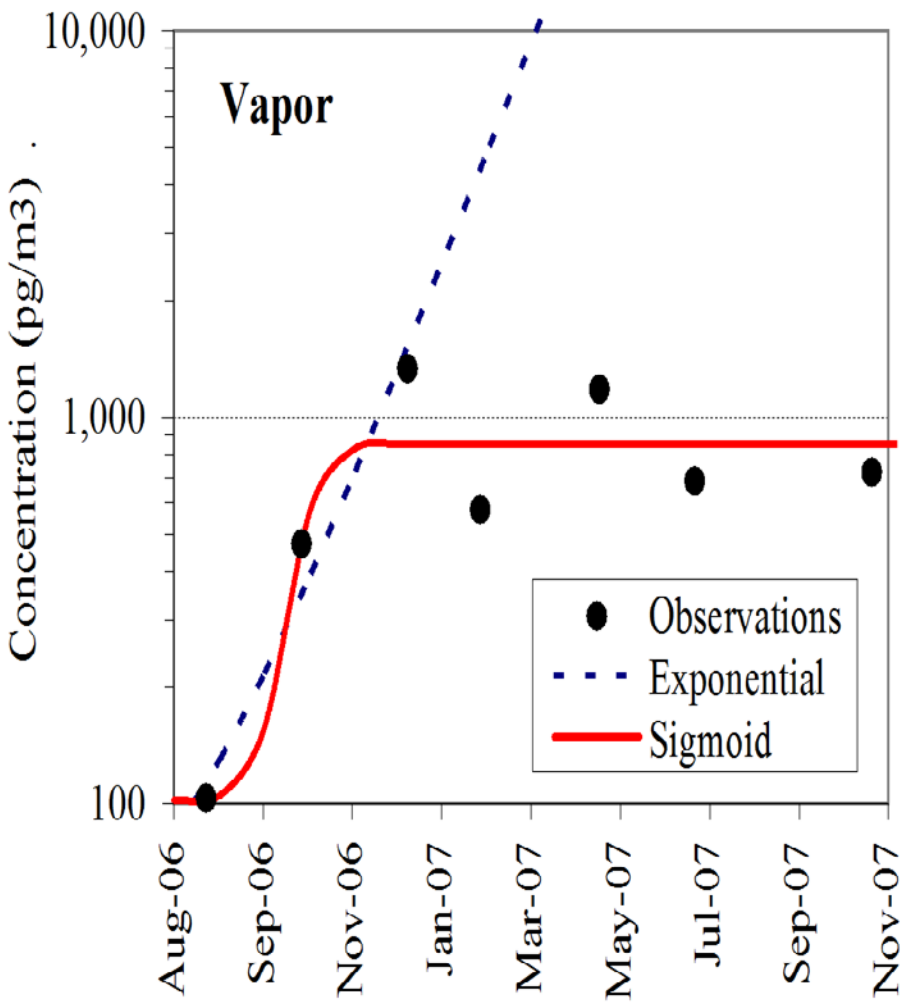
Evolution of BFR Concentrations

Σ_{21}BDE observations and fit to logistic and exponential models

Dust

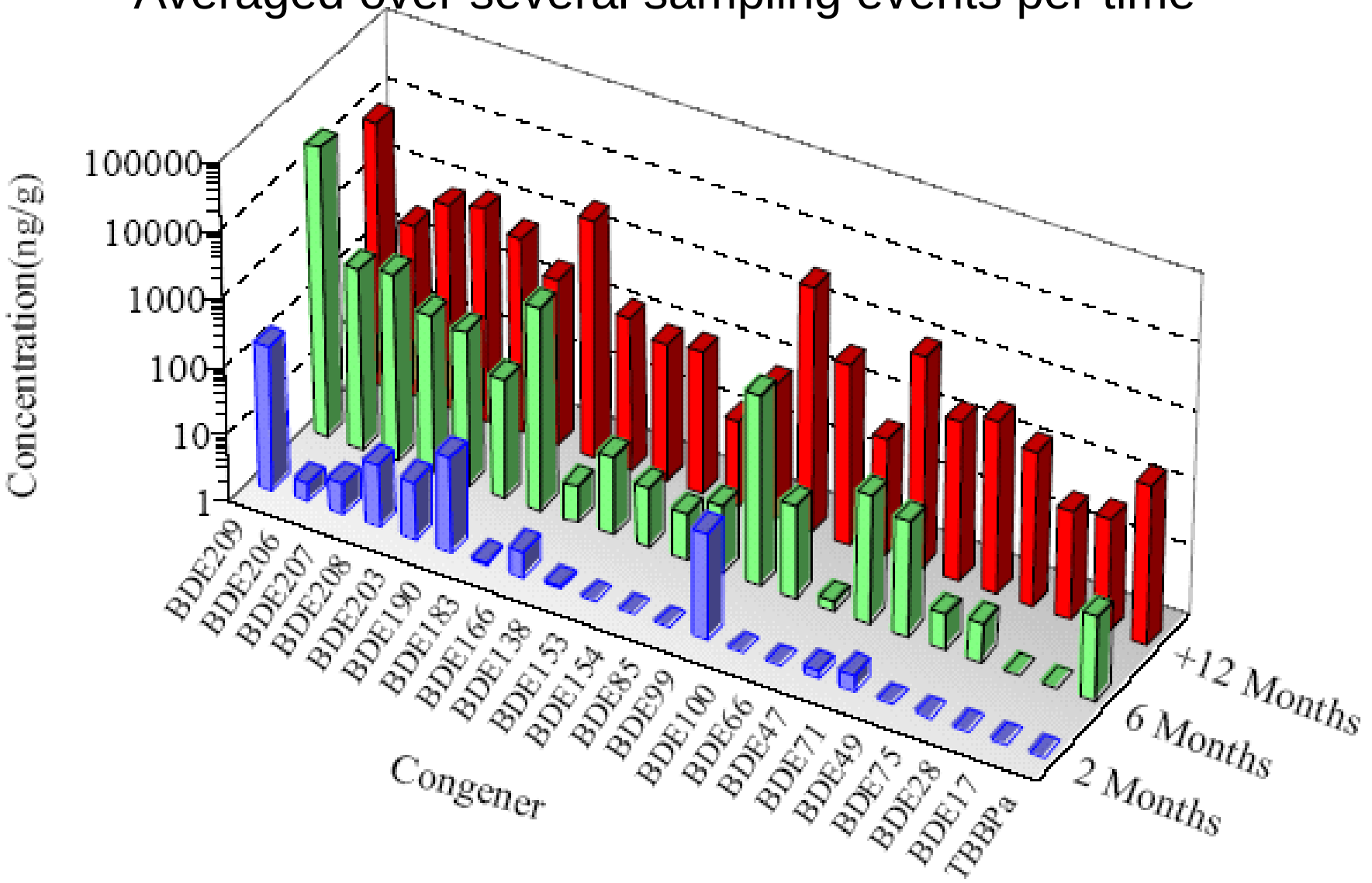


Vapor



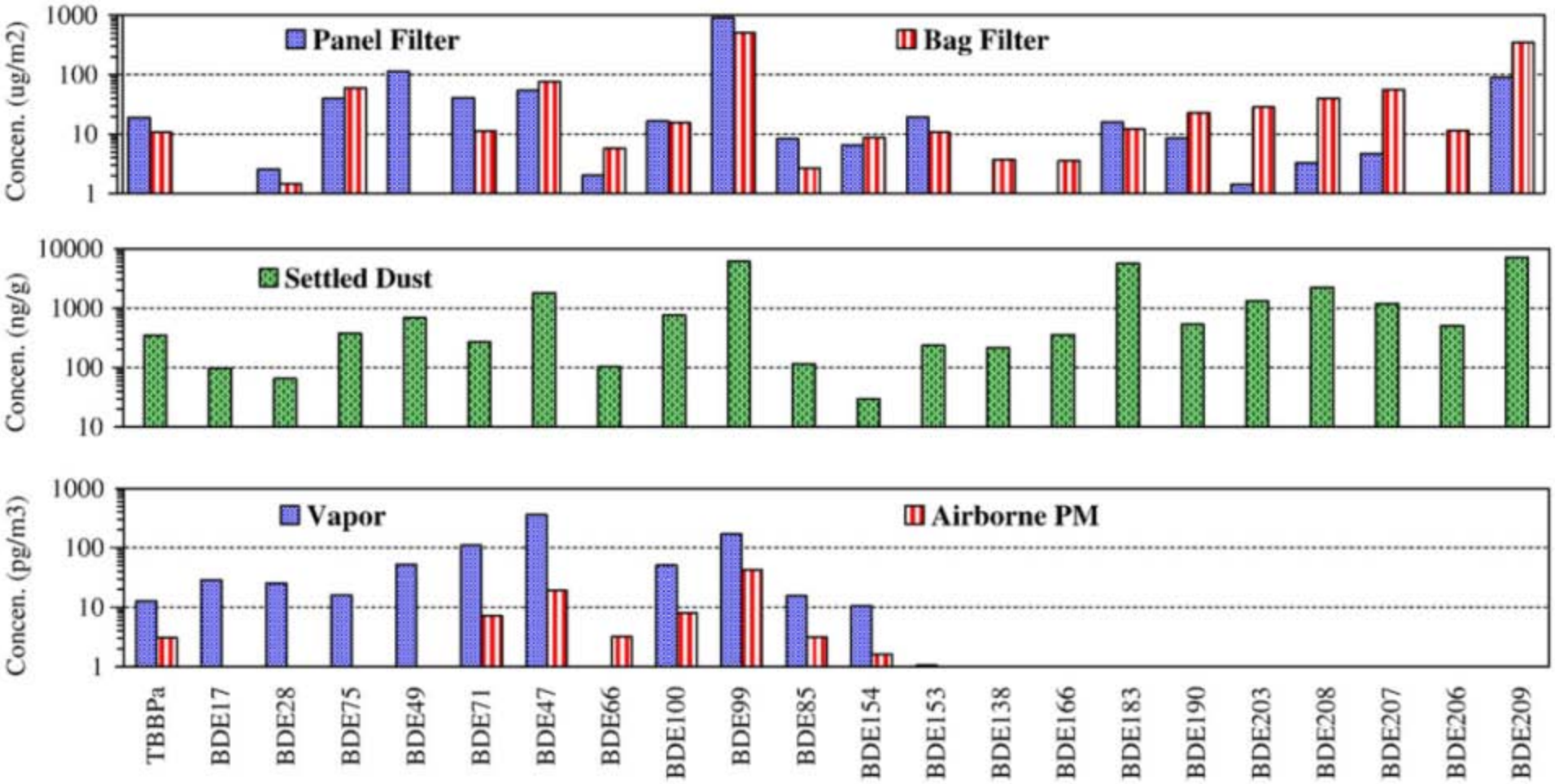
BFR Composition in Dust Over Time

Averaged over several sampling events per time



BFR Composition

Comparison of BFR composition in HVAC filters, settled dust, and airborne vapor and PM. Dust (n=4), vapor (n=6), and PM (n=6) samples from May–Nov. 2007. Panel (n=2 composite) and bag (n=2 composite) filter samples (from HVAC system) are corrected for levels in new filters.



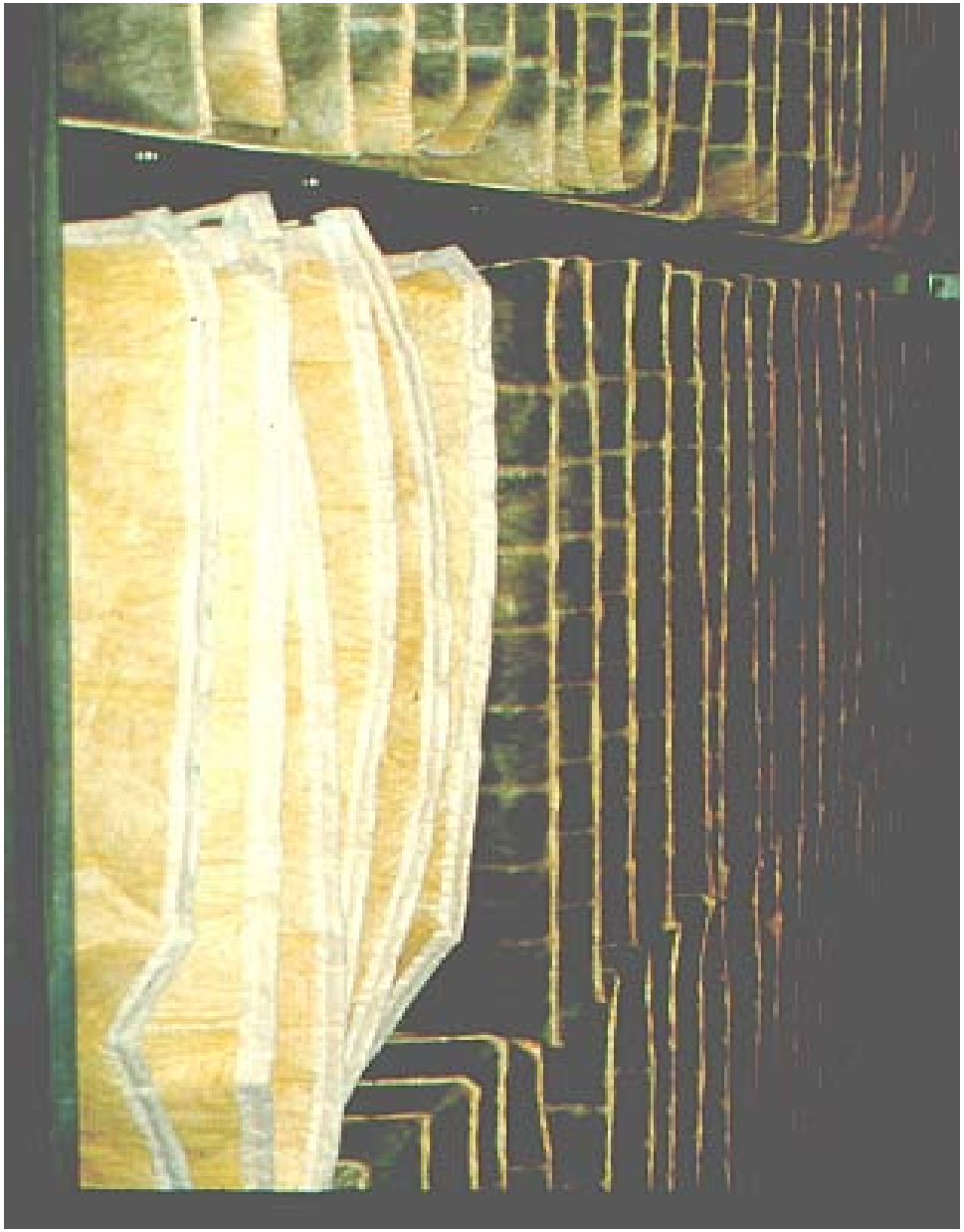
Trends in settled dust

- BDEs-47, 99, 100, 209 and TBBP-A were detected in most dust samples.
- Traces of BDEs-28, 49, 66, 85, 153, 154, 206, 207 and 208 were found in several samples.
- Prior to building opening (August 2006), BFRs in floor dust were at very low levels.
- For the next eight months, concentrations increased with a doubling time $t_{1/2}$ = 23 days (based on the exponential model fitting for Σ_{21}BDE).
- TBBPa also increased from trace levels at the study start (0.4 ± 0.1 ng g^{-1}) to 270 ± 250 ng g^{-1}.

Trends in indoor air

- Vapor-phase Σ_{21}BDE concentrations increased from about 100 pg m^{-3} at the beginning of the study (a typical urban outdoor air concentration) to about 930 pg m^{-3} at the end of the study, a striking change.
- Indoor airborne concentrations of BFRs also fit a logistic trend, but compared to dust, more rapidly approached a steady level (5 months).
- Rate of increase was slightly slower than dust with $t_{1/2}$ = 31 days.
- Indoor air was dominated by tetra- and penta-congeners, mostly BDE-47& 99.

HVAC filters



BFRs on HVAC filters

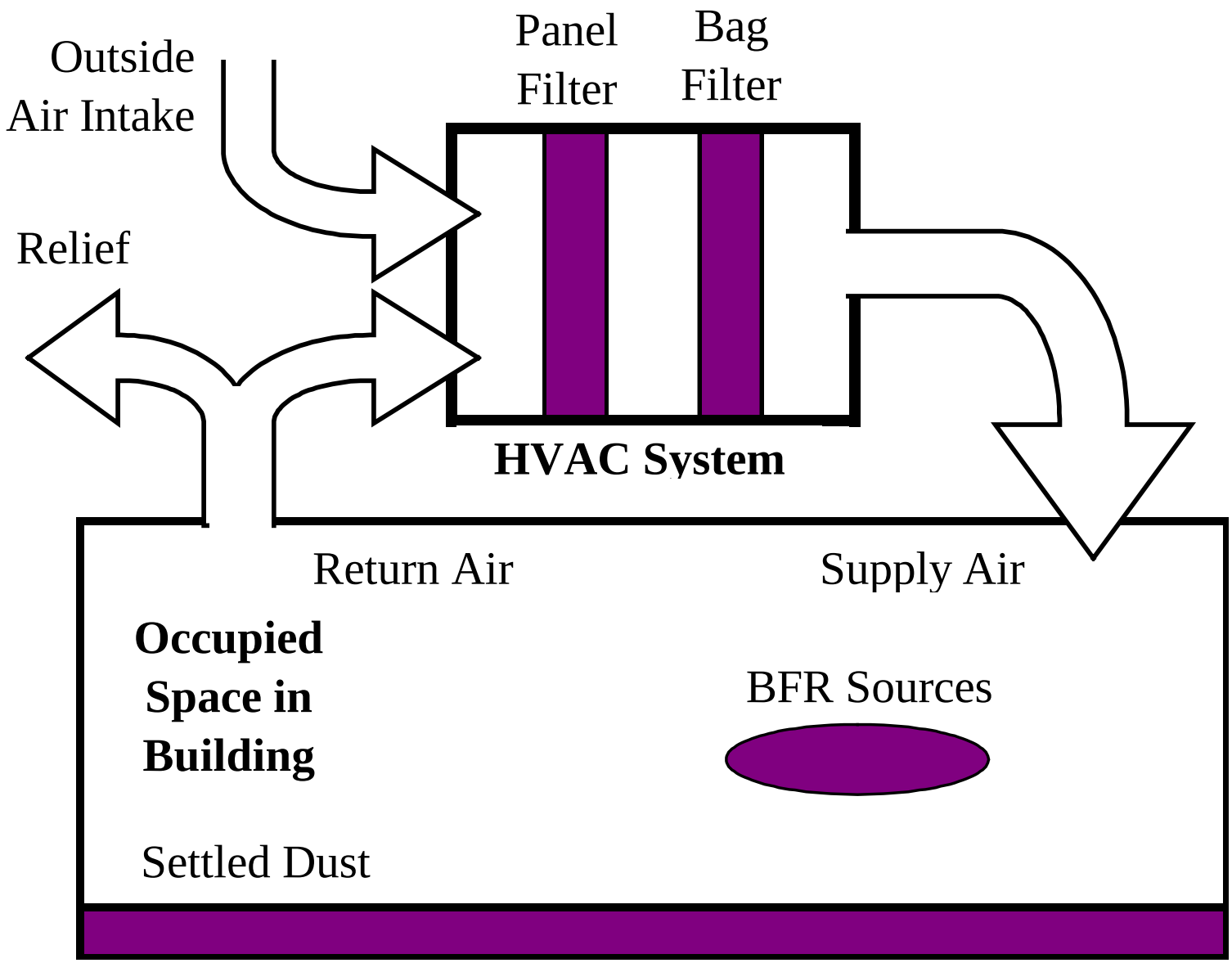
Panel filters (pleated paper, changed quarterly)

- New filters had trace levels (Σ_{21}BDE = 162 ng g^{-1}).
- Used filters (used 3 months, taken at 1 year) showed dramatic increases (Σ_{21}BDE = 10,600 ng g^{-1}). Equal to loading of 1.37 mg m^{-2} or 39 mg in the filter bank.

Bag filters (fibrous multilayer, changed yearly)

- New filters had trace levels (Σ_{21}BDE = 25 ng g^{-1}).
- Used filters (1 year of use) also showed large increases (Σ_{21}BDE = 6,600 ng g^{-1}), equal to 1.23 mg m^{-2} or 201 mg of BDEs in the filter bank.
- Panel and bag filters collected different congeners, e.g., BDE-99 on panel, BDE-209 and octa- and nona-congeners on the bag filter.

Mass Balance – Pathways & Compartments



Mass balance - details

BFR and PM mass balance based on following:

- HVAC filters exposed to an PM_{10} level of 13 µg m^{-3}
- 30% outside air (70% re-circulated), HVAC duty cycle = 70%, HVAC flow rate average = 22 m^3 s^{-1} (based on operation)
- Typical filter PM removal efficiencies, size specific, and different for panel and bag filter
- Dust accumulations estimated as 600 g of PM_{10} in the panel filters per 3 months, and 4,460 g PM_{10} in the bag filters per 1 year
- Samples assumed to be representative, etc.

Mass balance results

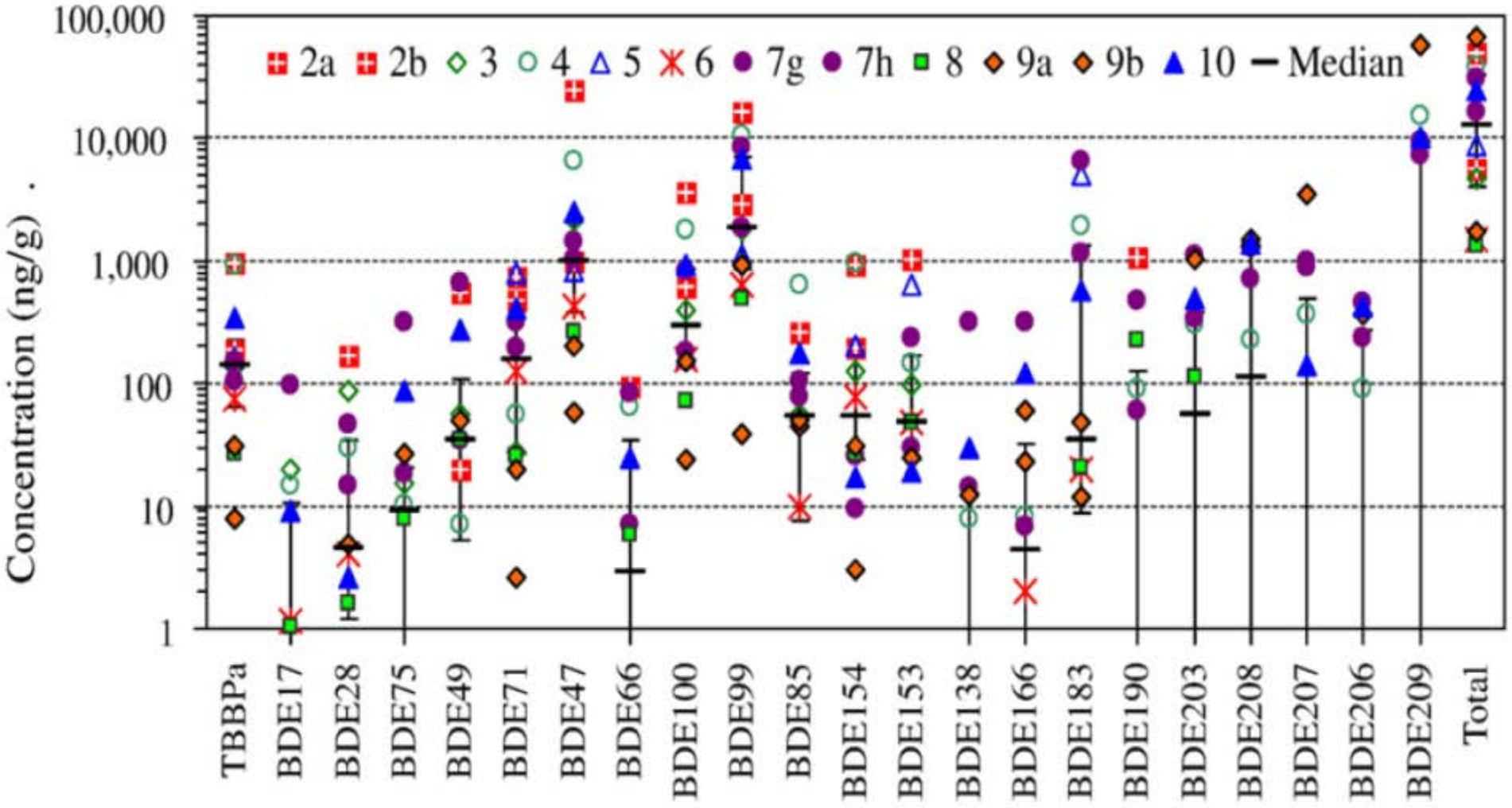
- Panel filters: Σ_{21}BDE = 64 μg g^{-1} in collected PM.
- Bag filter: Σ_{21}BDE = 45 μg g^{-1} in collected PM.
- Levels are somewhat higher (1.5 to 2 times) than floor dust, reasonable since HVAC filter PM excludes sand, soil & other low sorption-capacity materials.
- At steady-state, HVAC filters collected 420 mg y^{-1} of Σ_{21}BDE. This is a filter-based estimate.
- For floor dust, measured concentration (Σ_{21}BDE = 33 μg g^{-1}), dust loading (1 g/m^2 per 2 months), office area (3,690 m^2), gives 730 mg y^{-1}.
- *Loadings of BDEs in floor dust are not quite twice that to the air … Airborne and deposited BDEs are roughly comparable.*

Mass balance – independent check

- Use measured indoor (930 ± 290 pg m^{-3}) and outdoor (320 ± 270 pg m^{-3}) Σ_{21}BDE concentrations
- Air passing over filter (blended together) with Σ_{21}BDE = 750 ± 220 pg m^{-3} (30% outside air).
- With complete capture of vapor and PM BDEs on the HVAC filter dust, then 370 mg y^{-1} of Σ_{21}BDE would be collected by HVAC filters
- Estimate is within 12% of that estimated using HVAC filter measurements.
- Remarkable agreement between airborne and HVAC filter measurements!
- *Implies that the HVAC filters capture essentially all airborne BDE.*

PBDEs in dust in 10 commercial buildings

Levels of 20 PBDE congeners & TBBPa in dust in offices in 10 commercial buildings, all located in SE Michigan



Residential buildings

10.1021/es8029957 CCC: $40.75
Published on Web 03/19/2009

Research

Concentrations and Emissions of Polybrominated Diphenyl Ethers from U.S. Houses and Garages

STUART A. BATTERMAN,*,† SERGEI CHERNYAK,† CHUNRONG JIA,† CHRISTOPHER GODWIN,† AND SIMONE CHARLES‡

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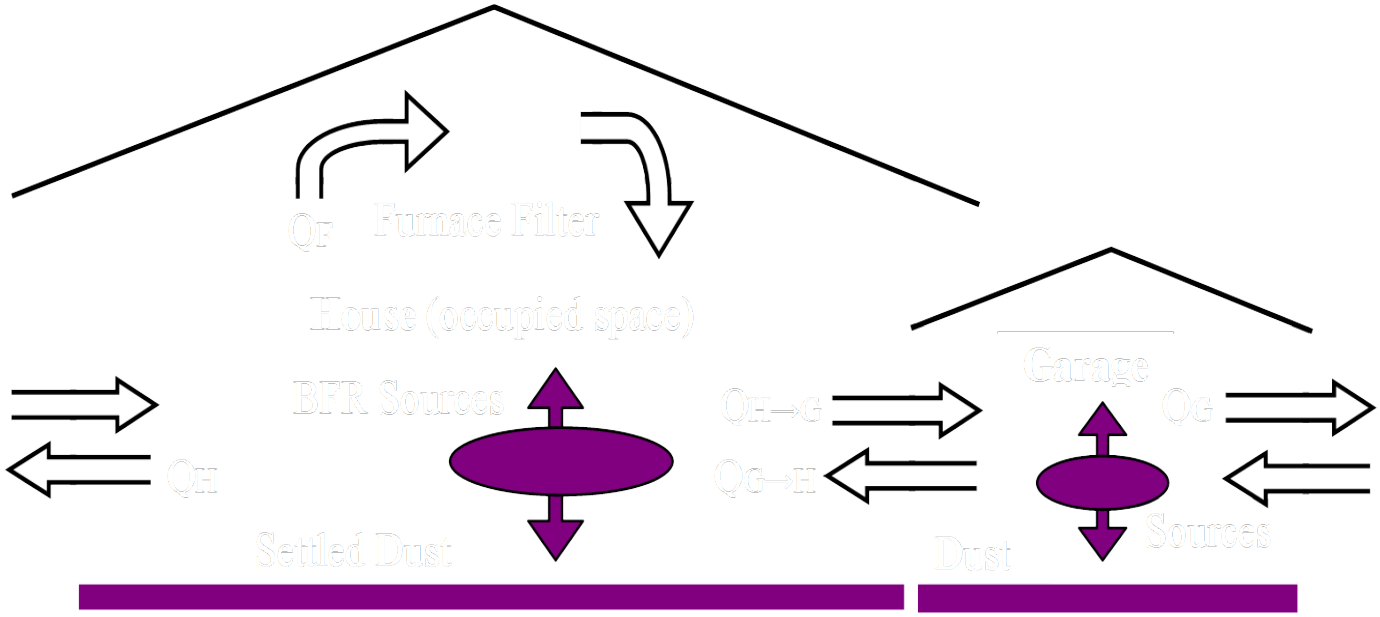
Approach



Schematic of BFR reservoirs in houses, garages and furnace filters, and air flows between these compartments and outside air

Potential pathways for PBDE releases from houses include:

(1) House → outside air: house materials/furnishings → airborne BFRs in house

(2) Garage → outside air: garage materials/contents → airborne BFRs in garage

(3) House → dust: house materials/furnishings → settled dust in house

(4) Garage → dust: garage materials/contents → settled dust in garage

(5) House → filter: house materials/furnishings → airborne BFRs in house → capture on furnace filter

Study design

We examined 12 houses with attached garages in two seasons, all located in southeast Michigan.

We collected samples of building air and settled dust which were analyzed for 20 PBDE congeners by GC/MS analysis. Also sampled dust in cars in garages.

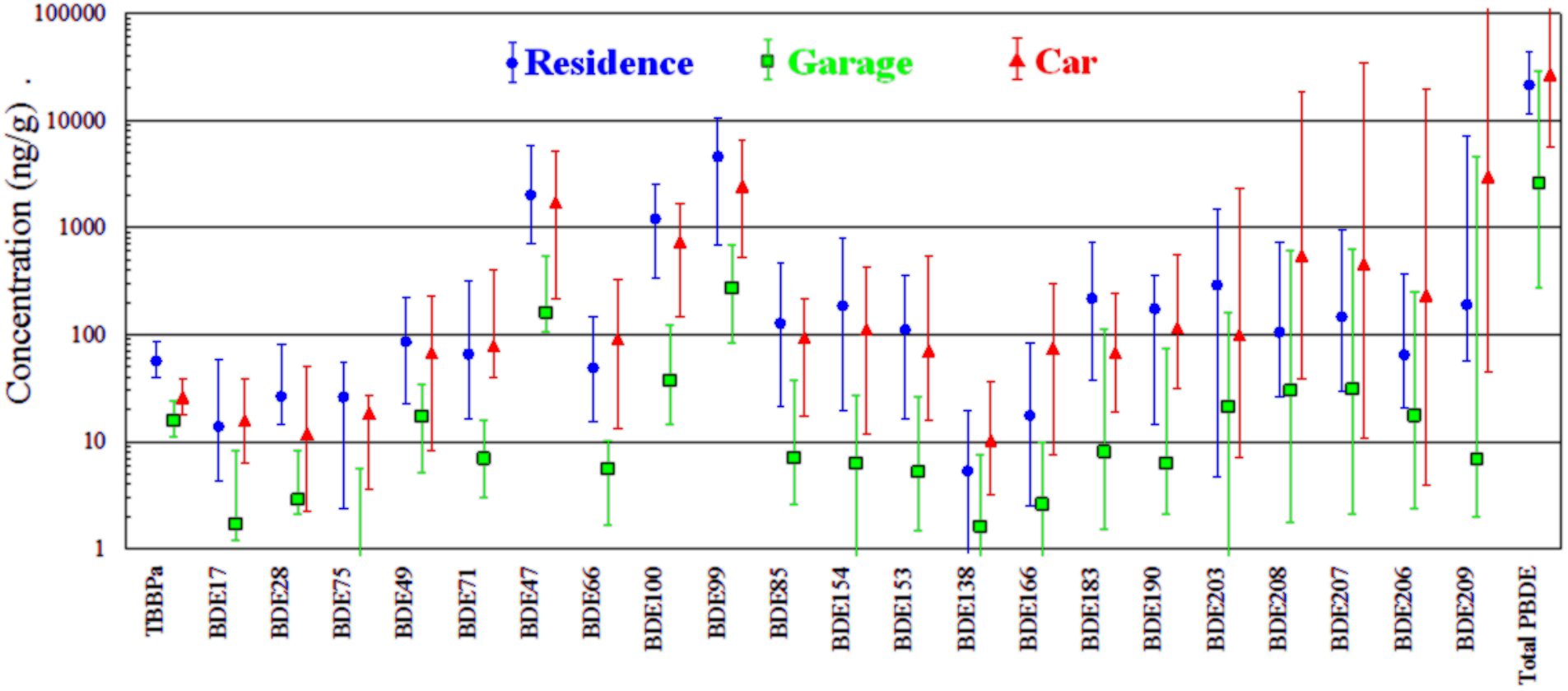
Building and zonal air exchange rates were measured using the constant injection perfluorocarbon tracer technique.

Data were integrated to estimate emissions in an mass-balance approach utilizing the building as a ‘natural’ test chamber.

Results were scaled to provide a first estimate of aggregate emission rates from U.S. buildings.

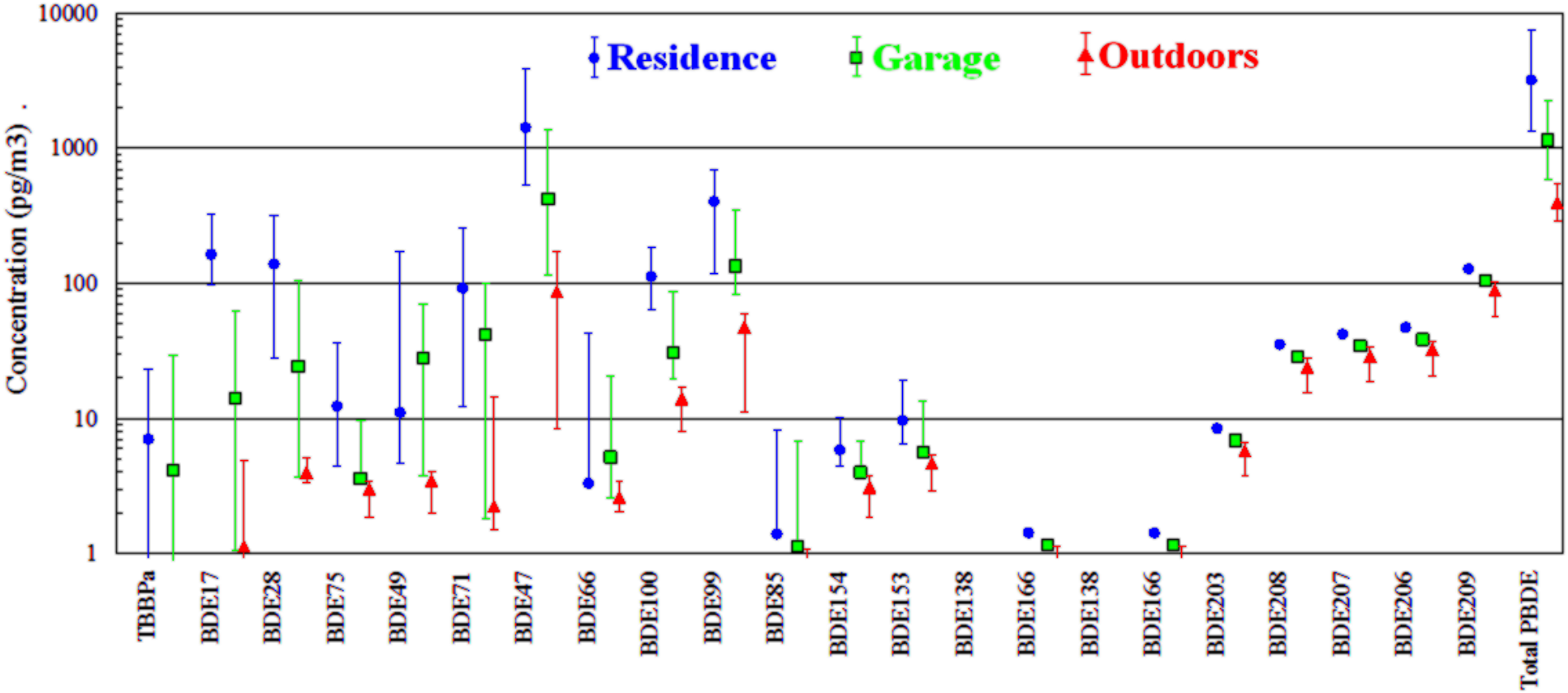
Concentrations in dust

BFR concentrations in dust from 12 houses, garages, and car cabins. Median and interquartile range shown. Note elevated nona- and deca-BDEs found in vehicles.



Concentrations in vapor

Airborne (vapor) BFR concentrations in 12 houses, garages and outdoors. Median and interquartile range shown. Note outdoor levels were low, and only tetra- and penta-congeners BDE-47, 100, and 99 exceeded MDLs. Concentrations decreased from indoor to garage to outdoor microenvironments for TBBPa and most tri- through penta-BDEs. Variation in concentrations, especially in garages, was large.



Derivation of emission estimates

Some key assumptions in estimating emissions:

- Estimated cleaning schedule
- Observed dust loading (similar to national average)
- Air flows from study: AERs averaged 0.34 ± 0.18 h^{-1} in houses and 1.56 h^{-1} in garages.
- Small house-to-garage flows (averaged 7.7 ± 18.7 m^3 h^{-1})
- Modest garage-to-house air flow (averaged 10.4 ± 8.9 m^3 h^{-1})
- 128 million households in U.S.
- 70.4 million garages in the U.S.

Emission estimates

Building Type	Test Buildings (mg/y-building)				National Estimate (kg/y)			
Type	Air	Dust	Filters	Total	Air	Dust	Filters	Total
House	4.6	21.2	3.0	28.8	585	2,715	382	3,682
Garage	1.9	4.1	-	6.1	137	292	-	429
Total	6.5	25.4	3.0	34.9	722	3,007	382	4,111

- House → outside air pathway is dominant pathway, mostly due emissions to dust; garage sources are small by comparison.
- House → filter pathway considers BFRs trapped on ventilation system filters.
- Interzonal transfers, e.g., house→garage and vice-versa, were small.
- ΣBDE emissions along all five pathways total 35 mg y^{-1} $house^{-1}$ or about 4 μg h^{-1} per house or 20 ng m^{-2} h^{-1}.
- About 20% are released directly to the ambient environment via airborne vapor and particulate matter; 80% to dust (filter and floor)

Summary (1)

Trends in new mixed-use building

- Dramatic increases in BFR levels in dust, vapor and PM after building commissioning; levels stabilized after about 1 year.
- After a year or so, BDE levels in dust and indoor air reached upper range of levels previously reported, quite similar to levels in U.S. residences.
- Such levels were unexpected since this building was constructed and furnished after the voluntary ban in the USA of the penta- and octa-mixtures.

Summary (2)

The mass balance worked out well

- The mass balance indicates that HVAC filters, if suitably sampled, extracted, and analyzed, can be used to estimate airborne BDE levels
- Requires representative filter samples (e.g., composites)
- Known or high filtration efficiency
- Possible corrections for background levels
- Sophisticated techniques to extract and analyze BDEs from the filter matrix.

Summary (3)

Emissions of PBDEs from residences

- First estimates of in-use residential emissions of BFRs, and also the first comparison of accumulations in vehicles, garages and houses.
- In ways, more realistic than emission chamber estimates.
- PBDE emission estimates range from 0.01 to 0.7% annually of the current stock *(Prevedouros et al. 2004).* No consistent estimates of the current stock. Assuming the N American stock of penta-, octa- and deca-mixtures is 320,000 (metric) tons, this yields 32 to 22,000 tons y^{-1}.
- On this basis, 4 ton y^{-1} of releases from houses and garages appear to be a small fraction of nationwide emissions. However, contribute a disproportionate amount of exposure since they occur in inhabited and confined environments.

Summary (4)

In terms of sources, exposure and risks:

- Commercial buildings are extremely diverse, e.g., very high levels found in computer server rooms
- Did not estimate contributions from these buildings due to this diversity, but rates may be similar.
- Could confirm emission factor estimates with in-use estimates, then scale to urban/national level.
- Exposures occurring in offices may be more important than previously recognized.
- Important transfers of BDEs from primary sources can occur via floor dust, air, and HVAC filters.
- Building ventilation filters and vacuum cleaner dust may need special handling to minimize releases.

Acknowledgements

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