Legacy and new POPs: What the North American Great Lakes can tell us.

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6th Network Conference on
Persistent Organic Pollutants
17–18 April, 2012

UNIVERSITY OF BIRMINGHAM

Why the Great Lakes?

- Their total surface is ~250,000 km^2 (94,000 m^2), and the total volume is 23,000 km^3 (5,500 mi^3)
- The lakes are sometimes referred to as the North Coast or "Third Coast“ of the US.
- The Great Lakes hold 21%of the world's surface fresh water

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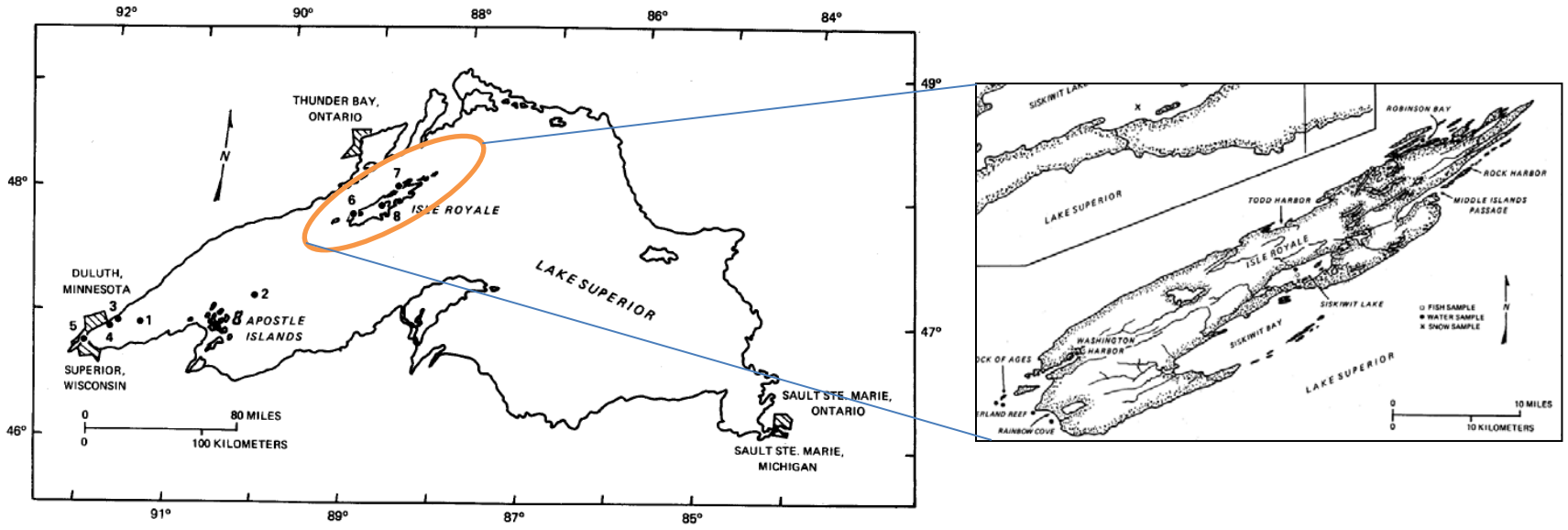
It all started with the Great Lakes: first evidence of long range transport

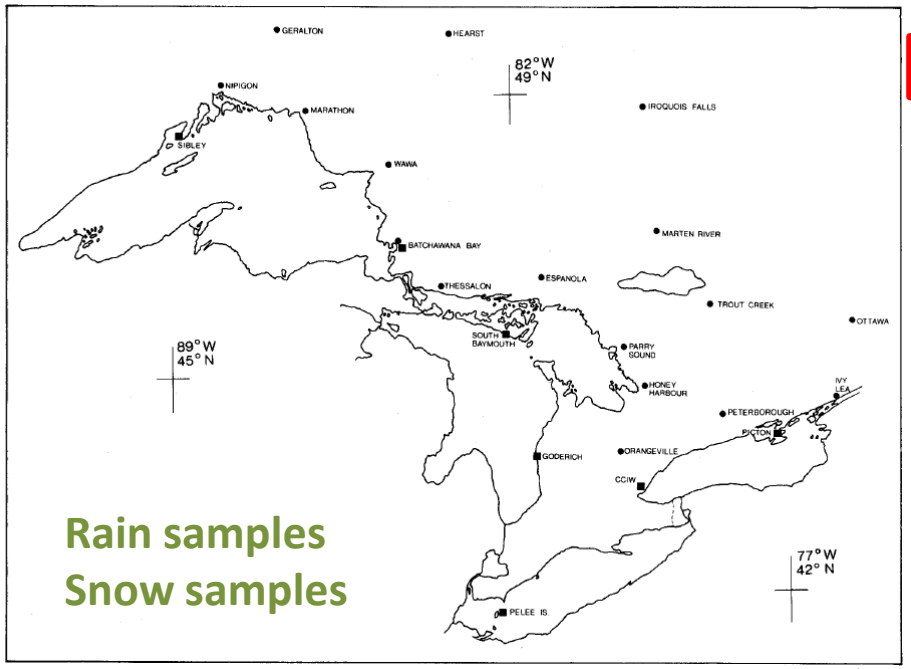


PCBs and chlorinated pesticides were measured in fish, water and precipitation.

These findings were the first to suggest that **atmospheric transport** to Lake Superior was important.

Swain, *J Great Lakes Res*, 1978

Evidence was piling up

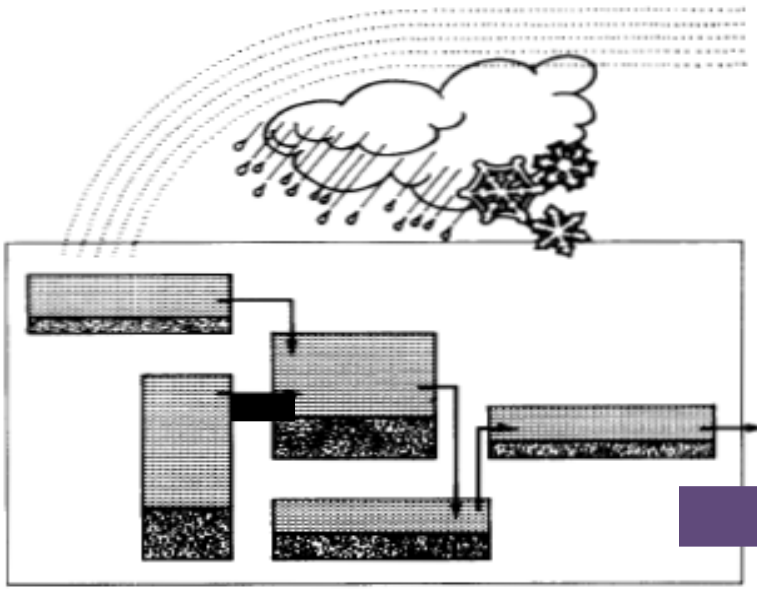


CONCLUSIONS

PCBs and organochlorines are present in rain in the Great Lakes region in such levels as to give rise to great concern. It is apparent that atmospheric deposition is a major route for the introduction of the persistent substances among these materials into biological tissue, either through aquatic food chains or through deposition in the terrestrial com-

Strachan & Huneault, J Great Lakes Res, 1979

From science to policy: Annex 15 of the Great Lakes Water Quality Agreement



Summary Report of the Workshop on Great Lakes Atmospheric Deposition

Held October 29 – 31, 1986

The Guild Inn, Scarborough, Ontario

Sponsored by
the International Joint Commission's
Great Lakes Science Advisory Board
Water Quality Board, and
International Air Quality Advisory Board

If you use the water, it matters

GREAT LAKES WATER QUALITY AGREEMENT
UNITED STATES AND CANADA

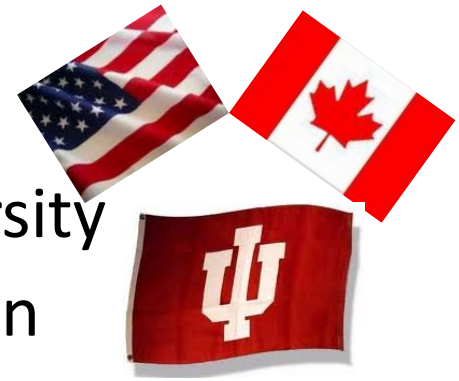
ANNEX 15 - AIRBORNE TOXIC SUBSTANCES

Called for the Integrated Atmospheric Deposition Network

Why Great Lakes air now?

- Atmospheric transport is now the primary transport pathway for the input of toxic and persistent organic pollutants (POPs) into the Great Lakes.
- Air concentrations respond rapidly to changes in emissions, but it is not known how rapidly the lakes and the fishes in them will respond
- Increasing number of fish consumption advisories

Integrated Atmospheric Deposition Network (IADN)



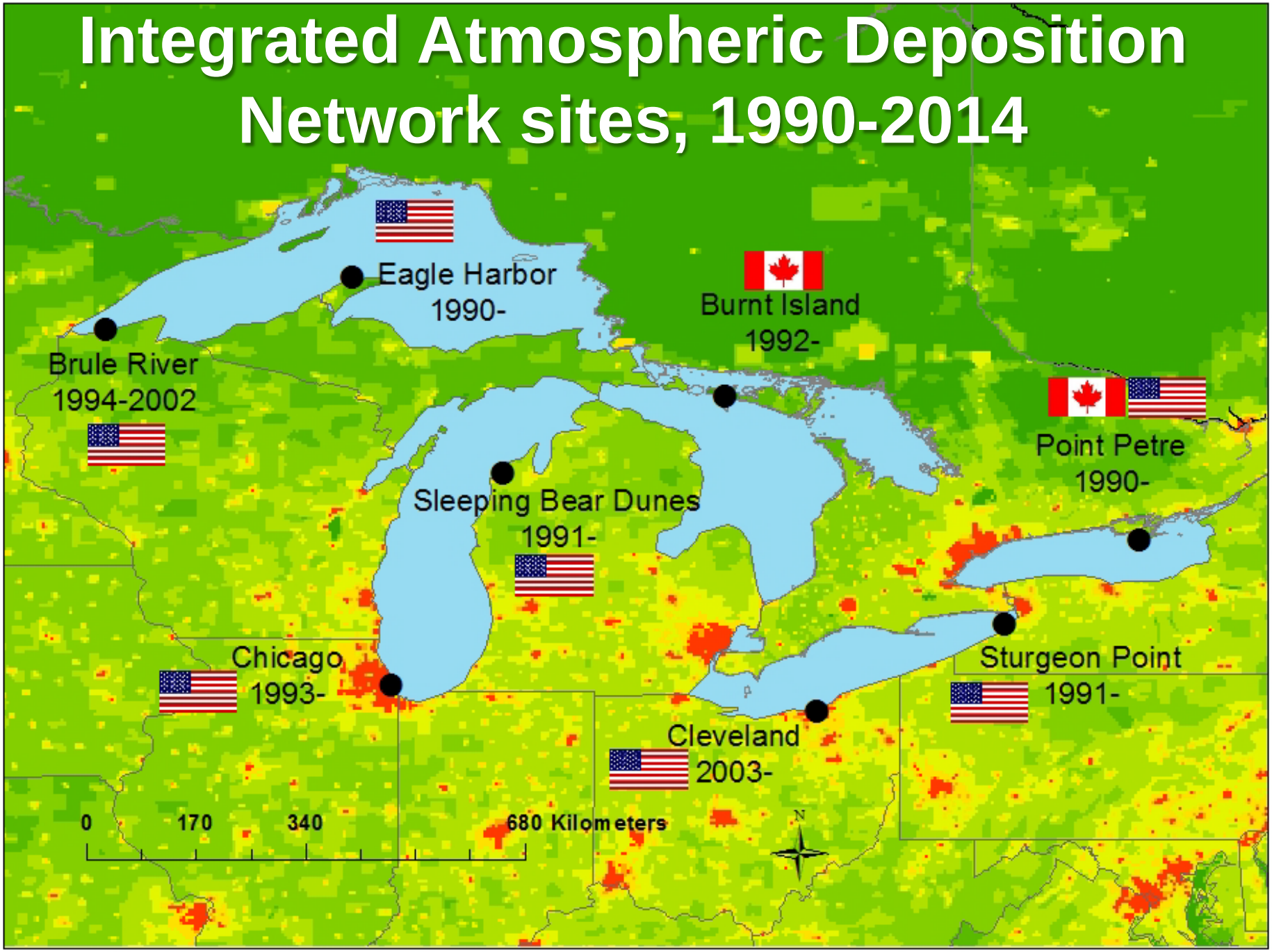
- Joint EPA-Environment Canada project
  - Grantee is Prof. Hites at Indiana University
- Measure pollutants in air and precipitation around the Great Lakes (U.S. runs five sites)
- Goals:
  - Determine atmospheric loadings to the lakes
  - Look at trends in levels (spatial and temporal)
- Strengths:
  - Long term (running continuously since 1990)
  - Good spatial coverage
  - Legacy and emerging compounds

Comparison of long term air programs

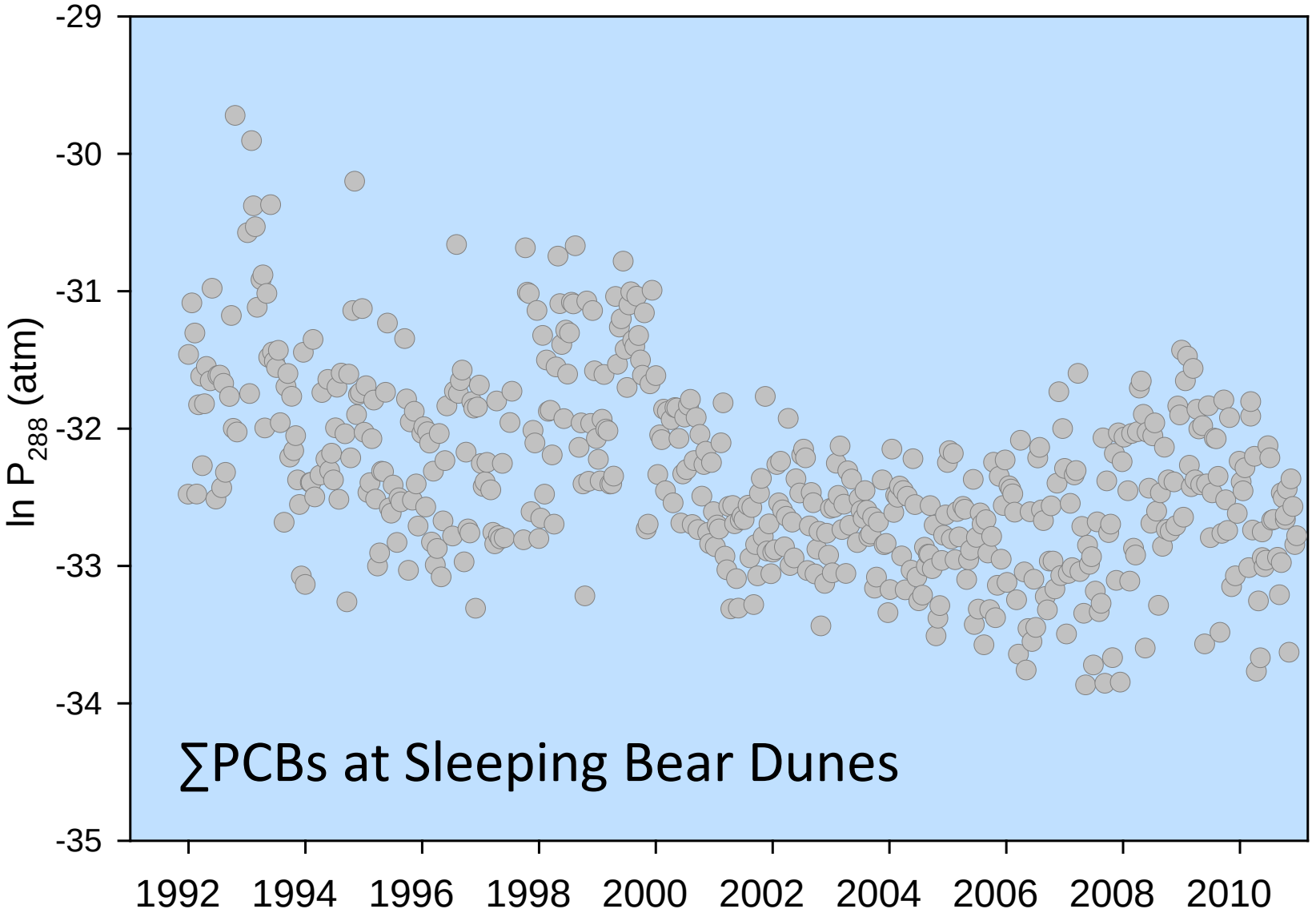
	TOMPS	EMEP	IADN	AMAP
Location	UK	EU (NILU)	USA	Arctic
Starting date	1990	1991*	1990	1992+
N. sites	6	22*	6	4+8
Analytes	PCDD/Fs, PCBs, PAHs	PCBs, PAHs, OCPs, PBDEs	PCBs, PAHs, OCPs, PBDEs	PCBs, OCPs, PBDEs

* 1991: 1; 1995:5; 2000:8; 2005:11; 2009:22

\+ 1992: Alert; 1993: Zeppelin


Integrated Atmospheric Deposition Network sites, 1990-2014
Eagle Harbor
1990-
Burnt Island
1992-
Brule River
1994-2002
Point Petre
1990-
Sleeping Bear Dunes
1991-
Chicago
1993-
Sturgeon Point
1991-
Cleveland
2003-
0
170
340
680 Kilometers
N

The need for long term data



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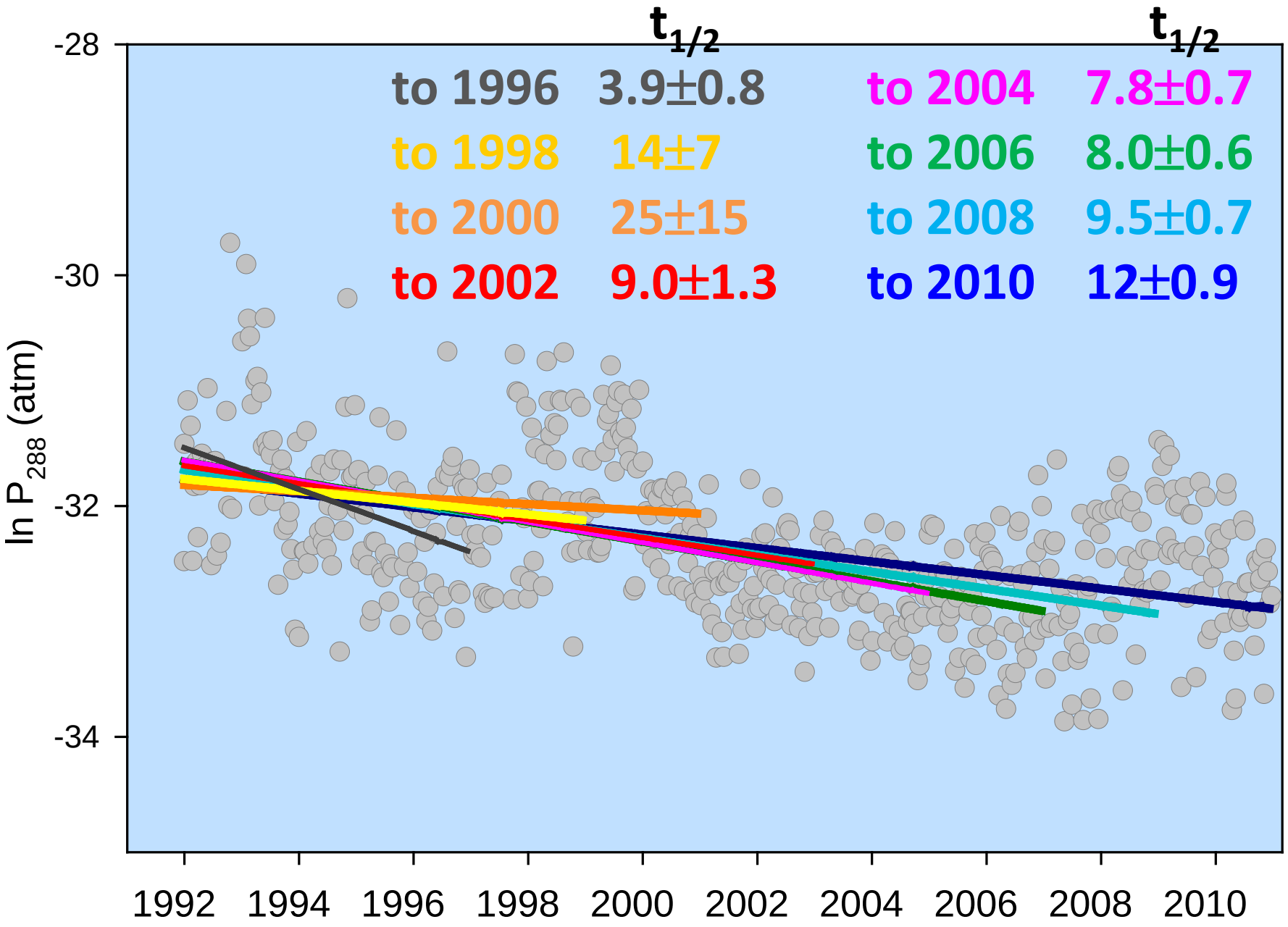
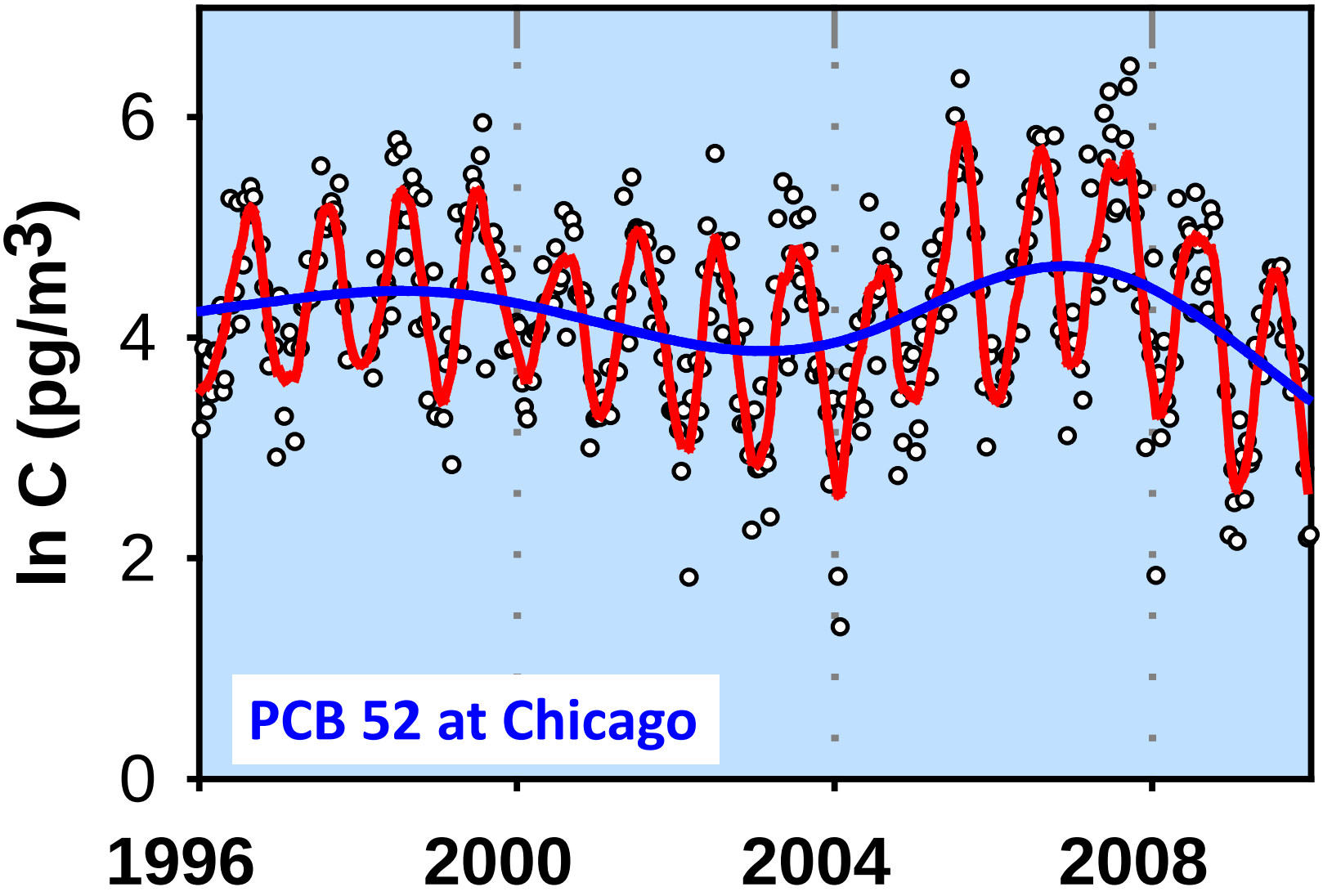
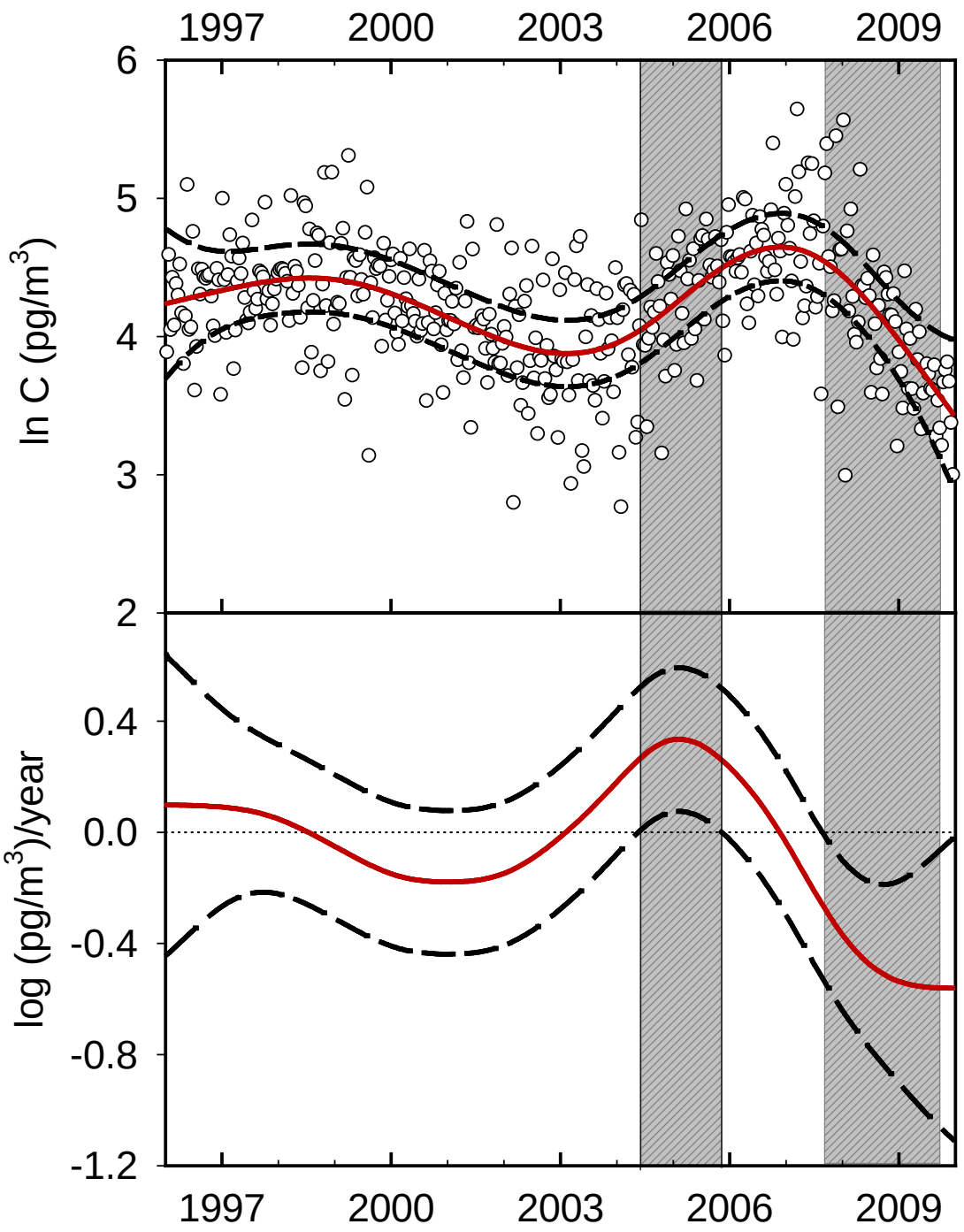


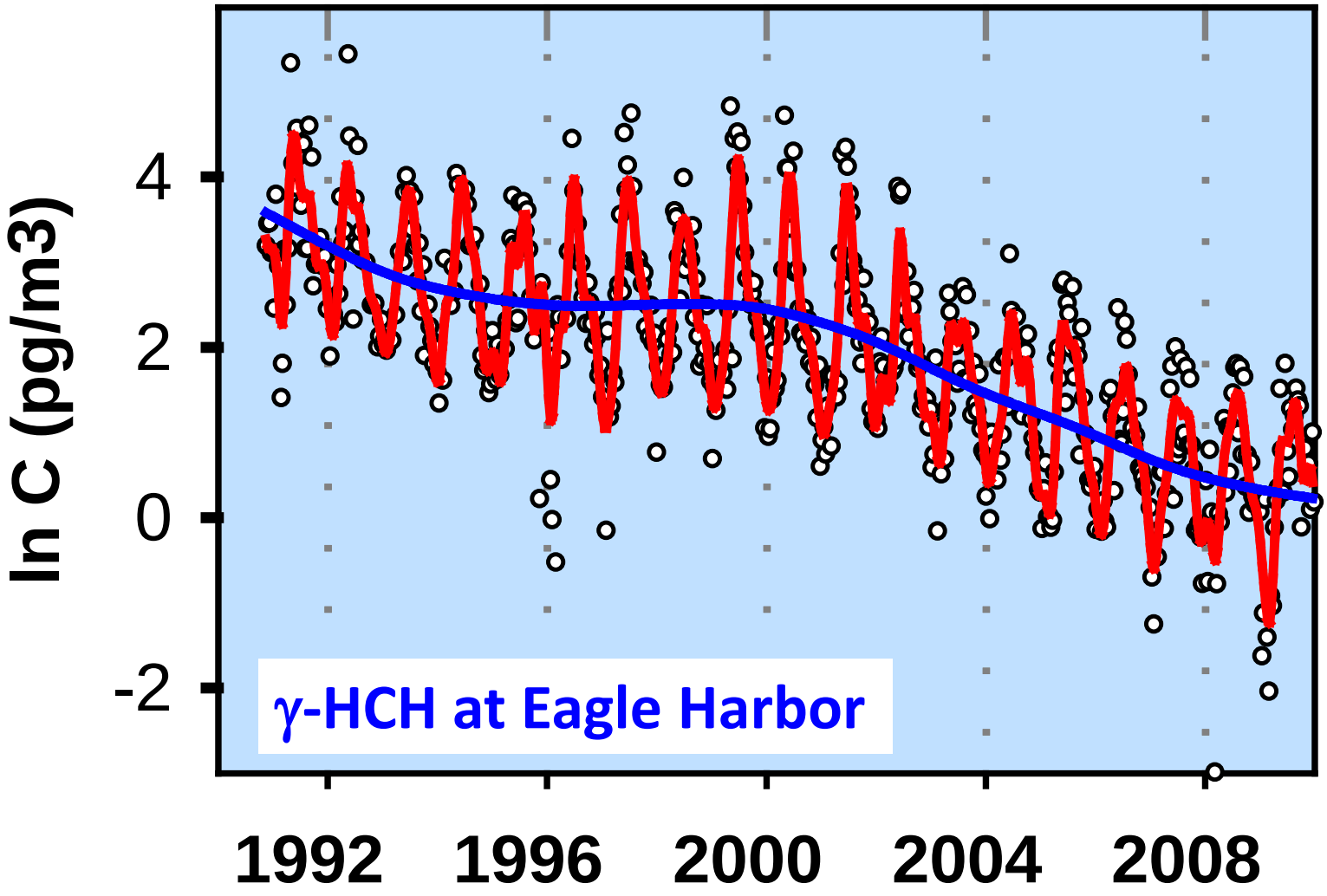
The need for long term data



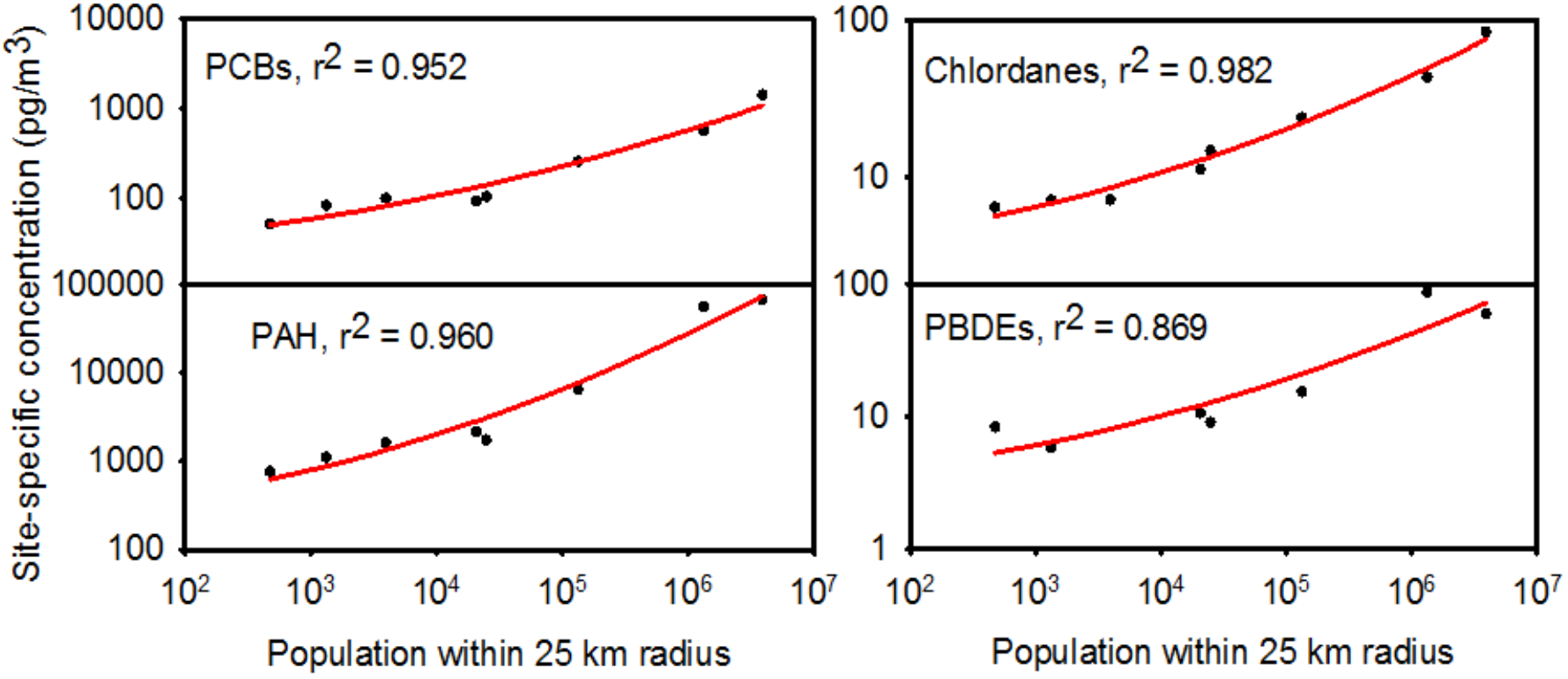


PCB 52 at Chicago: what happened around 2005?

The atmosphere shows rapid declines for banned chemicals



Atmospheric concentrations track population density



Other r^2 values: DDTs=0.774; Endosulfans=0.314; α-HCH=0.128; lindane=0.098

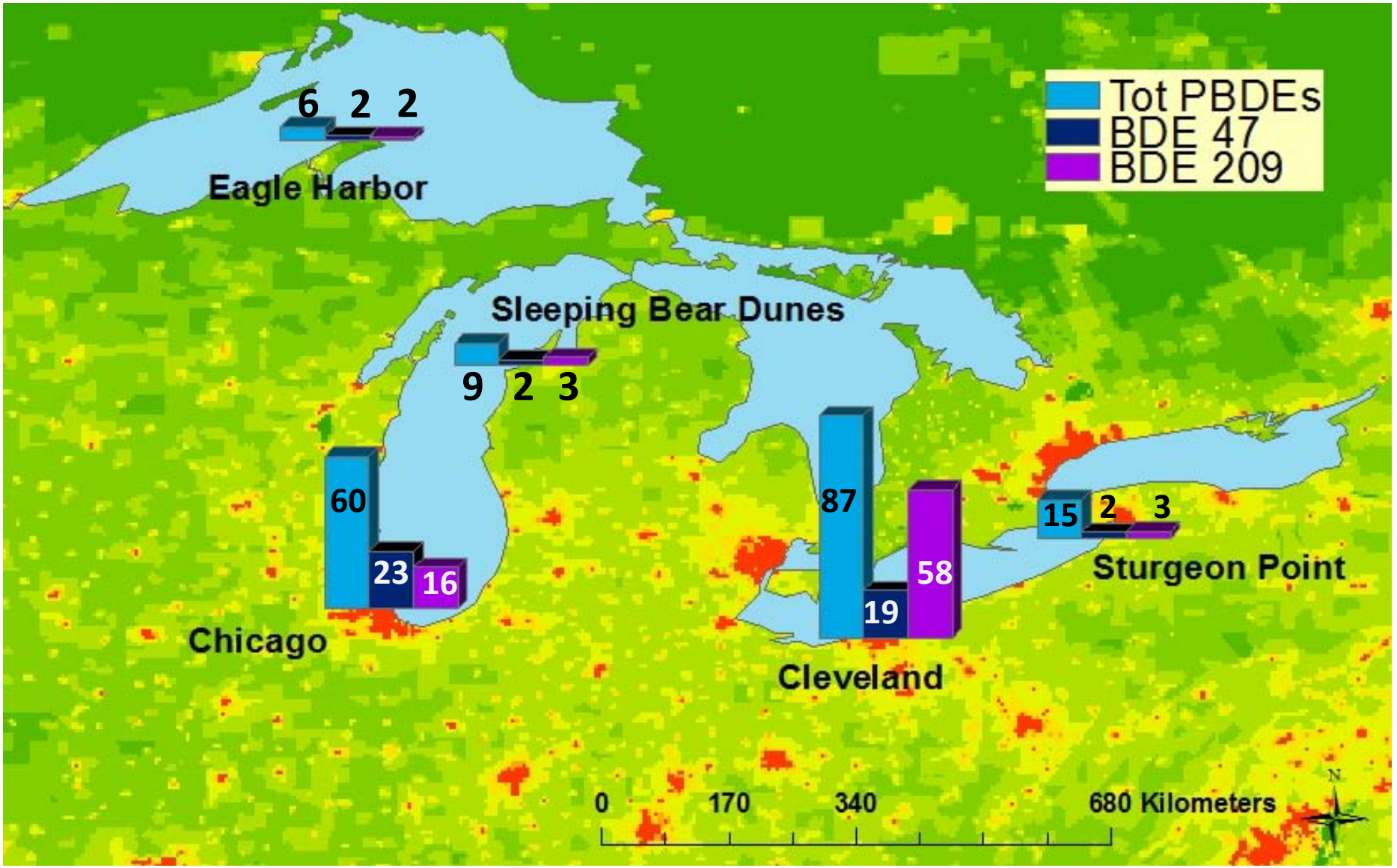
What's Going On?

	Half-life (years)	Primary Control	Secondary Control	Date Banned
ΣPCB	20^{+}	Urbanization	Seasonality	1977
ΣPAH	20	Urbanization	--	In use
α-HCH	4	Time	--	1980
γ-HCH	5	Seasonality	Time	2004/2009
ΣDDT	8	Urbanization	Seasonality	1972
ΣEndosulfans	10	Seasonality	--	2016
ΣChlordanes	13	Urbanization	Seasonality	1980

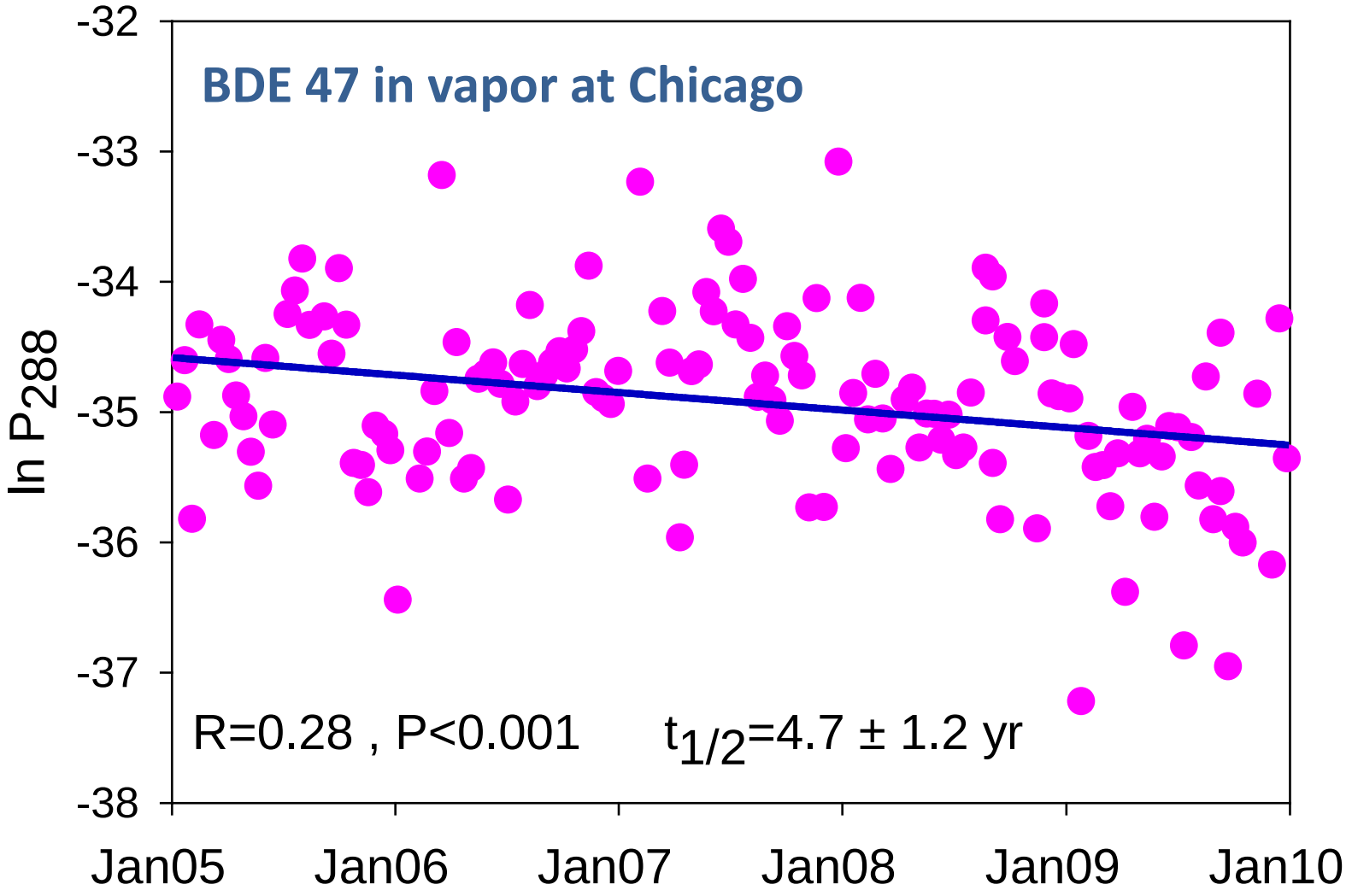
What about emerging compounds?

- Starting from 2004, PBDEs were added to the list of target compounds.
- They were officially included in IADN in 2009.
- The list of brominated flame retardants (BFR) is ever expanding.

Levels of PBDEs in air (pg/m^3)



PBDEs levels in the air are going down (only the abandoned ones)



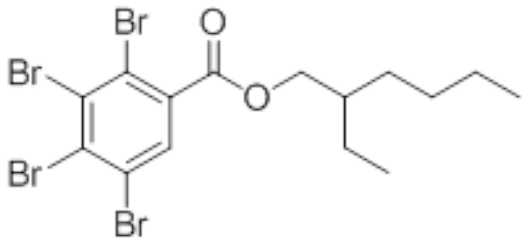
IADN data

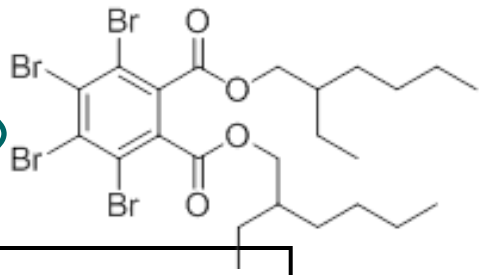
It’s like a whack-a-mole game (with chemicals)

Replacements for penta BDEs: Firemaster 550

Components:

1. Triphenyl **Phosphate**
2. Triaryl **phosphate** isopropylated
3. Bis(2-ethylhexyl) tetra**bromo**phthalate
4. 2-ethyl hexyl 2,3, 4, 5-tetra**bromo**benzoate





Chemtura

Technical Information
www.Chemtura.com
Effective: 11.01.2007

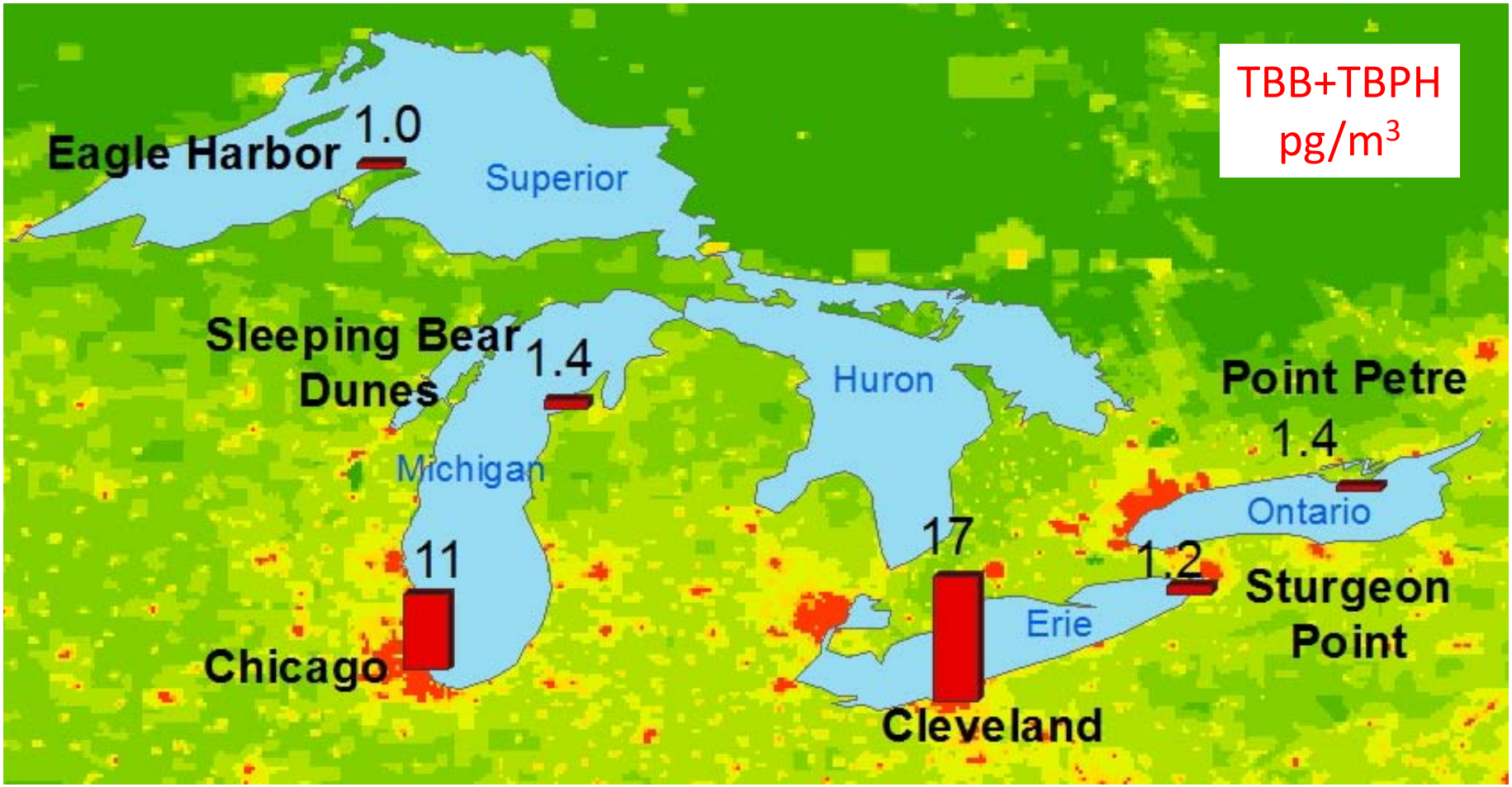
Firemaster® 550

Phosphorus-Bromine Flame Retardant

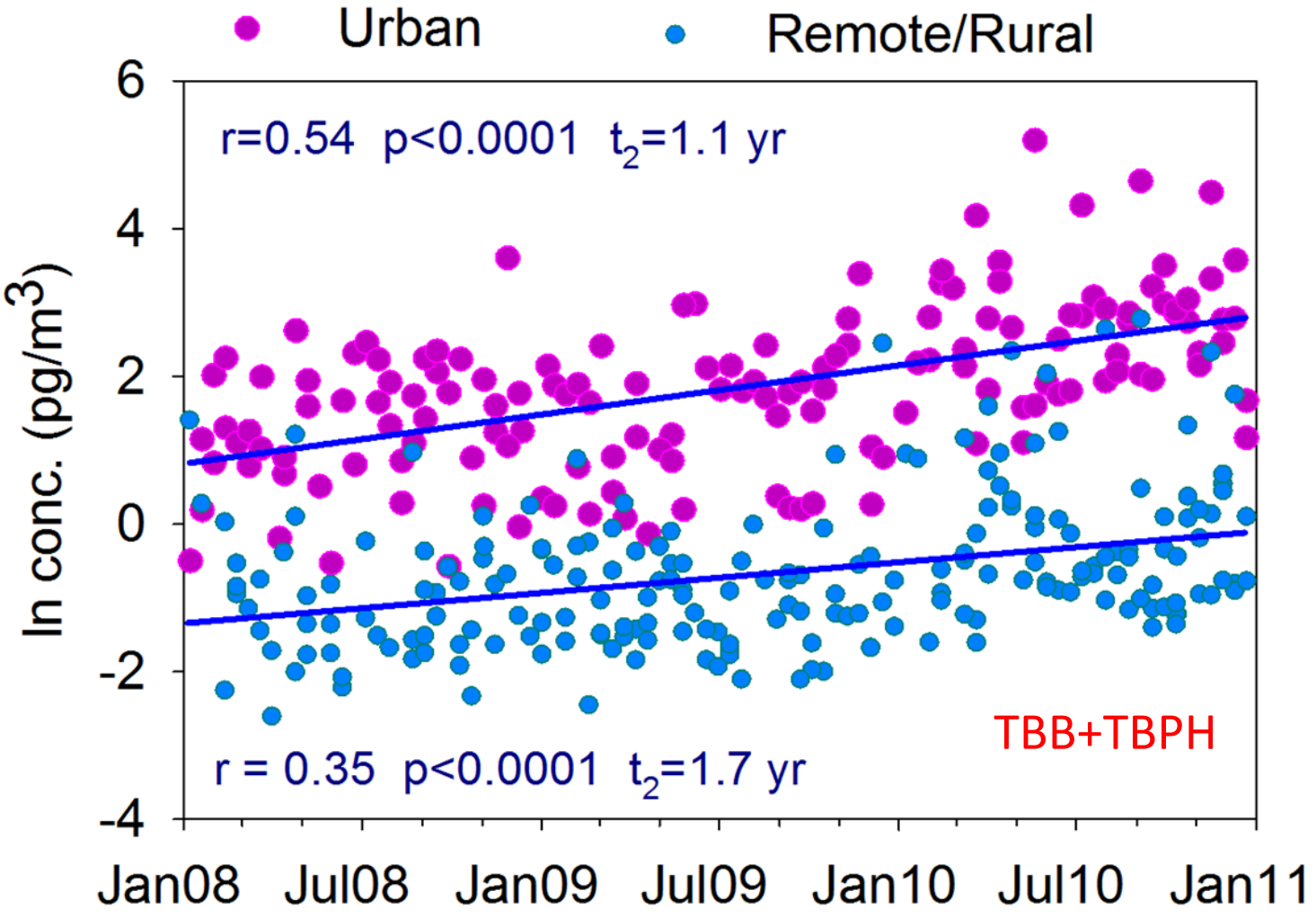
Firemaster 550 is a low viscosity liquid flame retardant for polyurethane foams and other applications, which require a liquid product. Firemaster 550's high efficiency as a flame retardant is a result of phosphorus-bromine synergy. It is based on proprietary Chemtura technology and does not contain brominated diphenyl ethers.

Phosphorus-Bromine Flame Retardant
CAS Reg. Number Proprietary

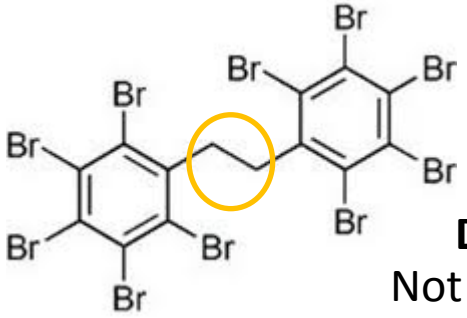
Levels of tetrabromo esters in air are close to those of PBDEs



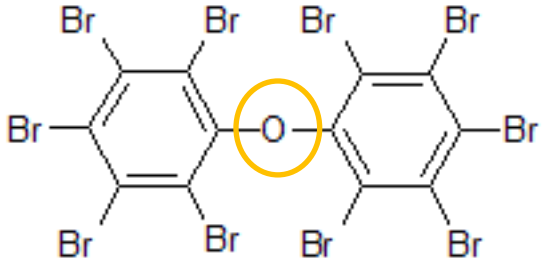
Levels of tetrabromo esters are increasing in the Great Lakes' air



Alternative FR: Decabromodiphenylethane (DBDPE)



DBDPE
Not regulated

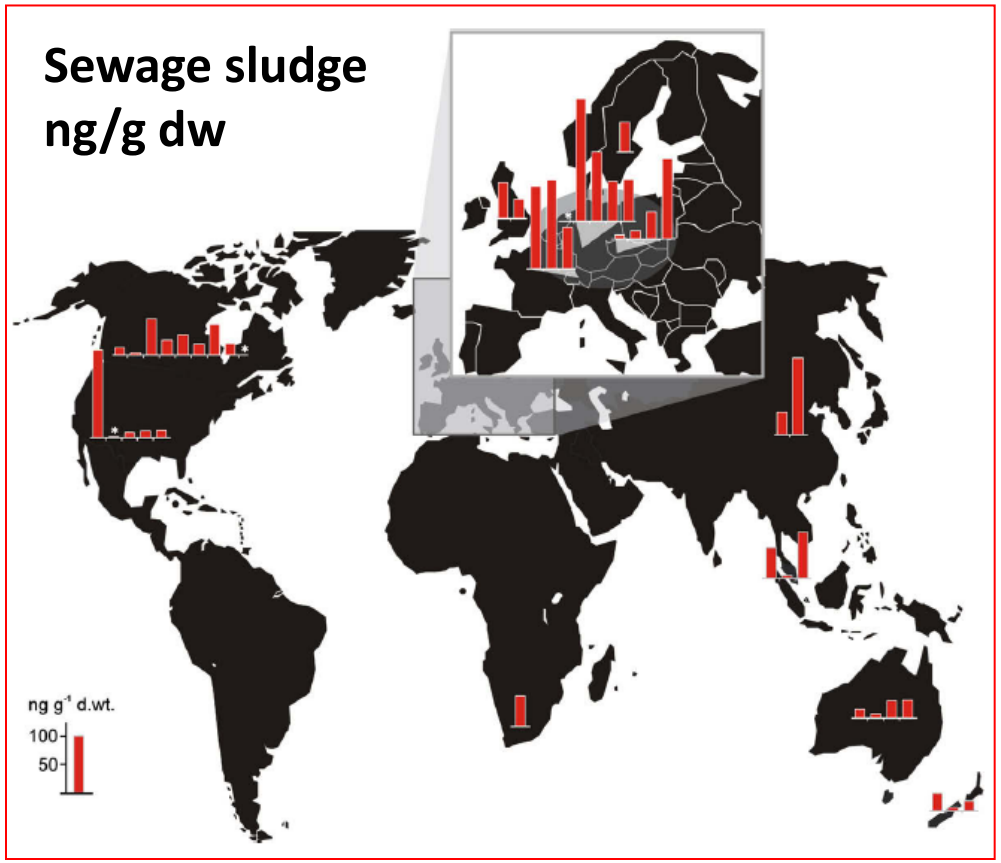


BDE-209
Phasing out from 2012

- DBDPE has been marketed as general purpose substitute for BDE-209. Produced since the 1990s as SAYTEX 8010.
- It is an additive flame retardant with similar applications to those of BDE209: acrylonitrile-butadiene-styrene (ABS), high impact polystyrene (HIPS) plastics, and textile backcoating)
- Not much data on toxicology, especially from independent sources (several published papers are from sources related to Albemarle)

http://oehha.ca.gov/multimedia/biomon/pdf/120408flamedoc.pdf

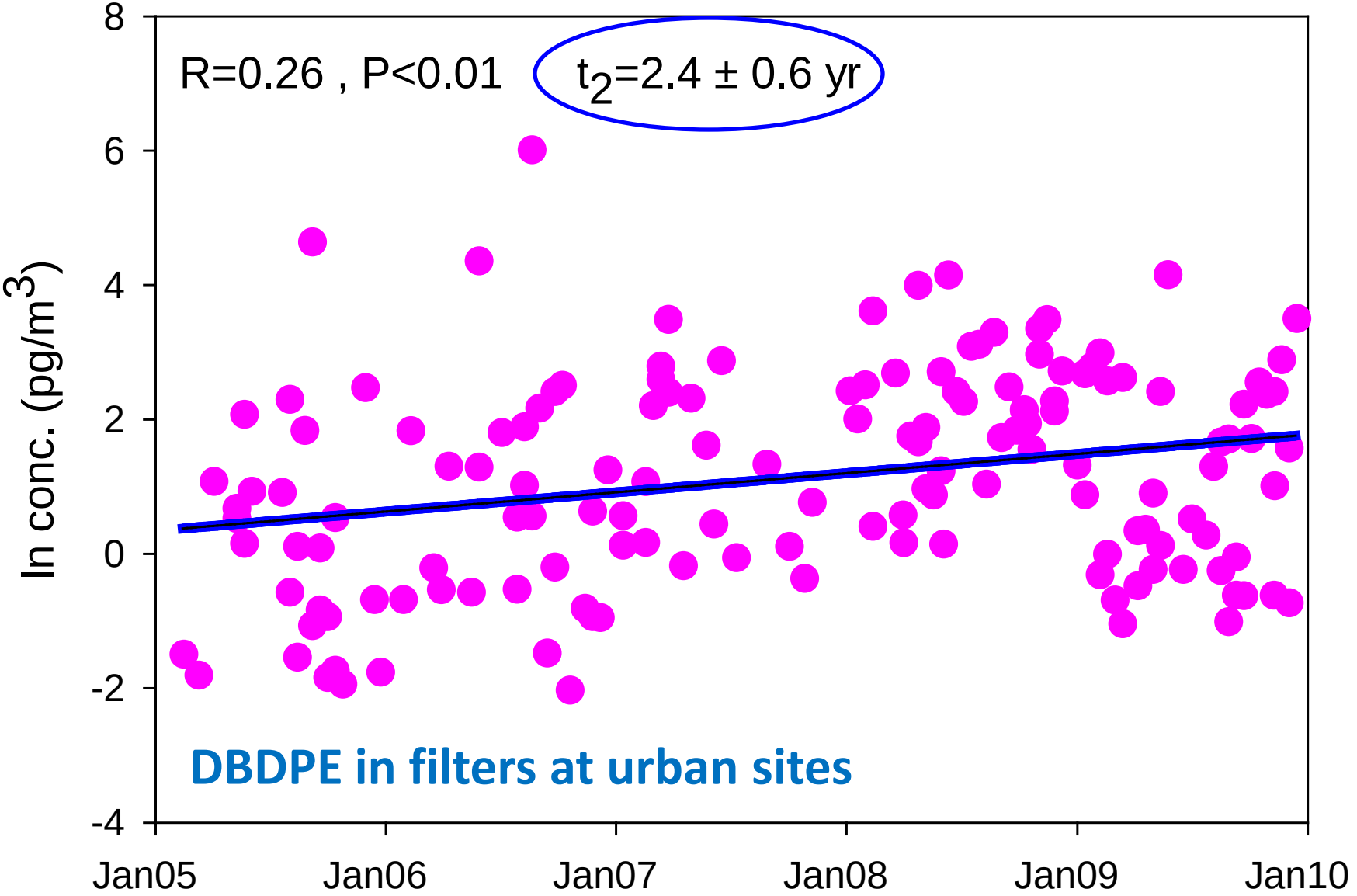
Decabromodiphenylethane (DBDPE)



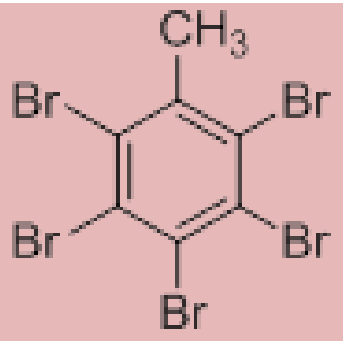
Ubiquitous and worldwide pollutant!

Rickund, 2008; Hu, 2008; Gauthier, 2009; Harrad, 2008

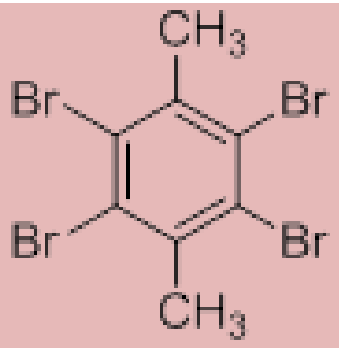
Decabromodiphenylethane (DBDPE) levels increasing in the Great Lakes' air



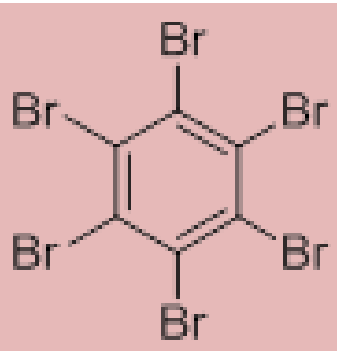
Bromobenzenes: a puzzling group of compounds



PBT 87-83-2



pTBX 23488-38-2



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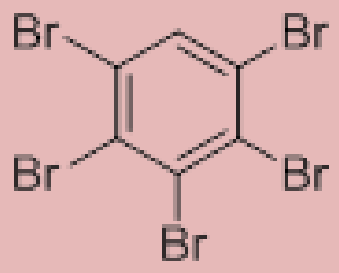
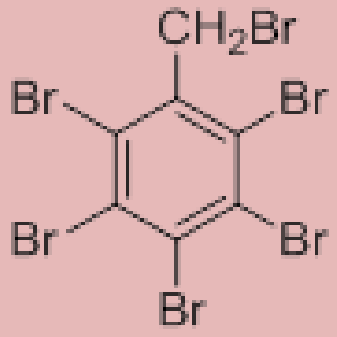


PBBz 608-90-2



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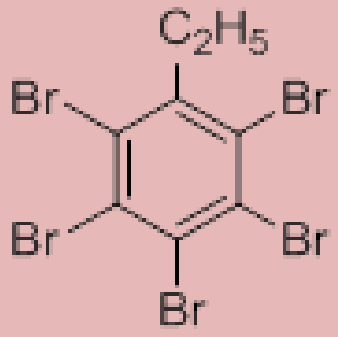
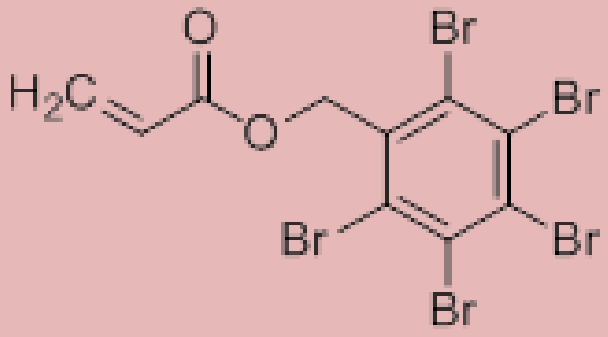
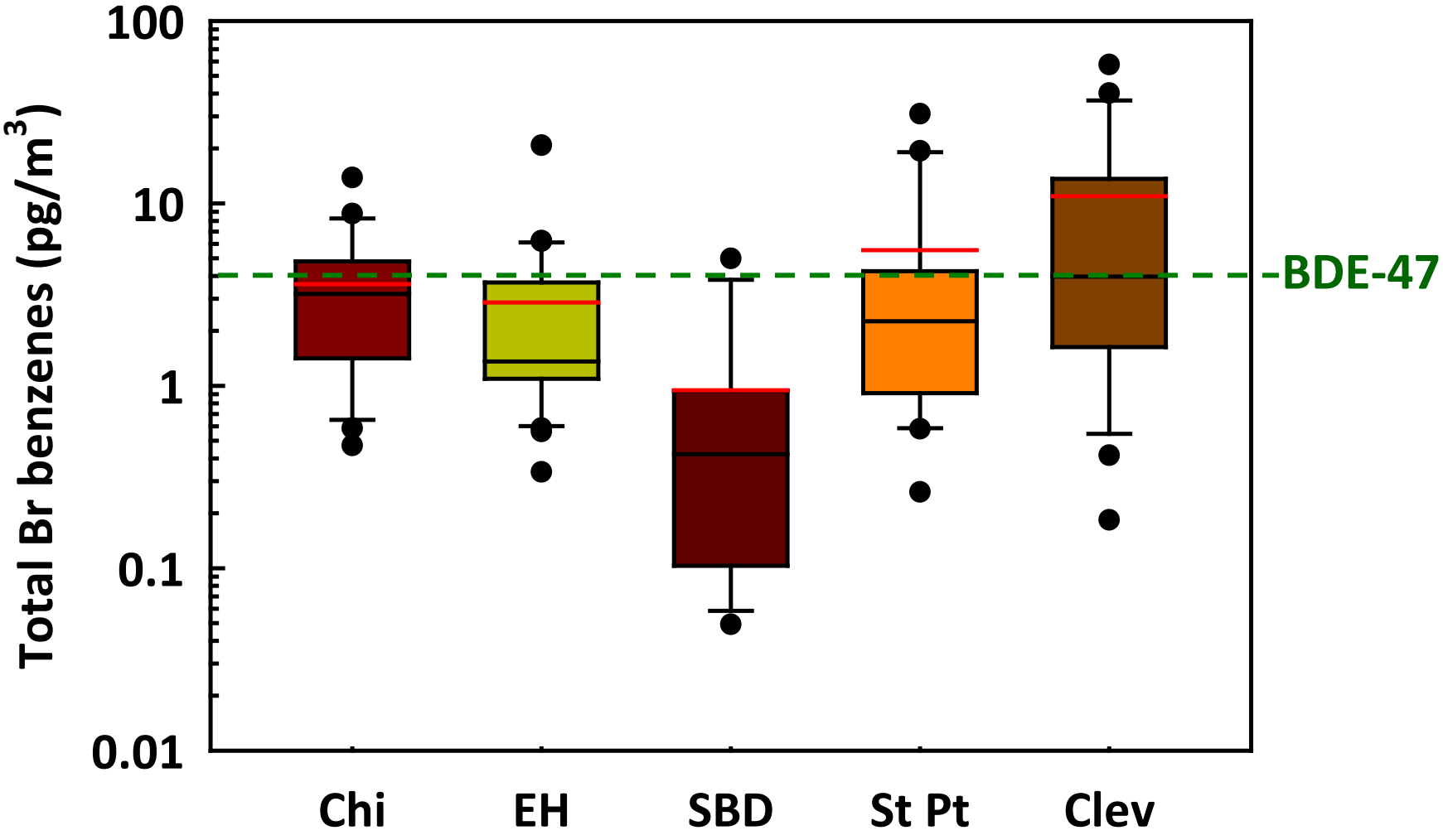


PBEB 85-22-1

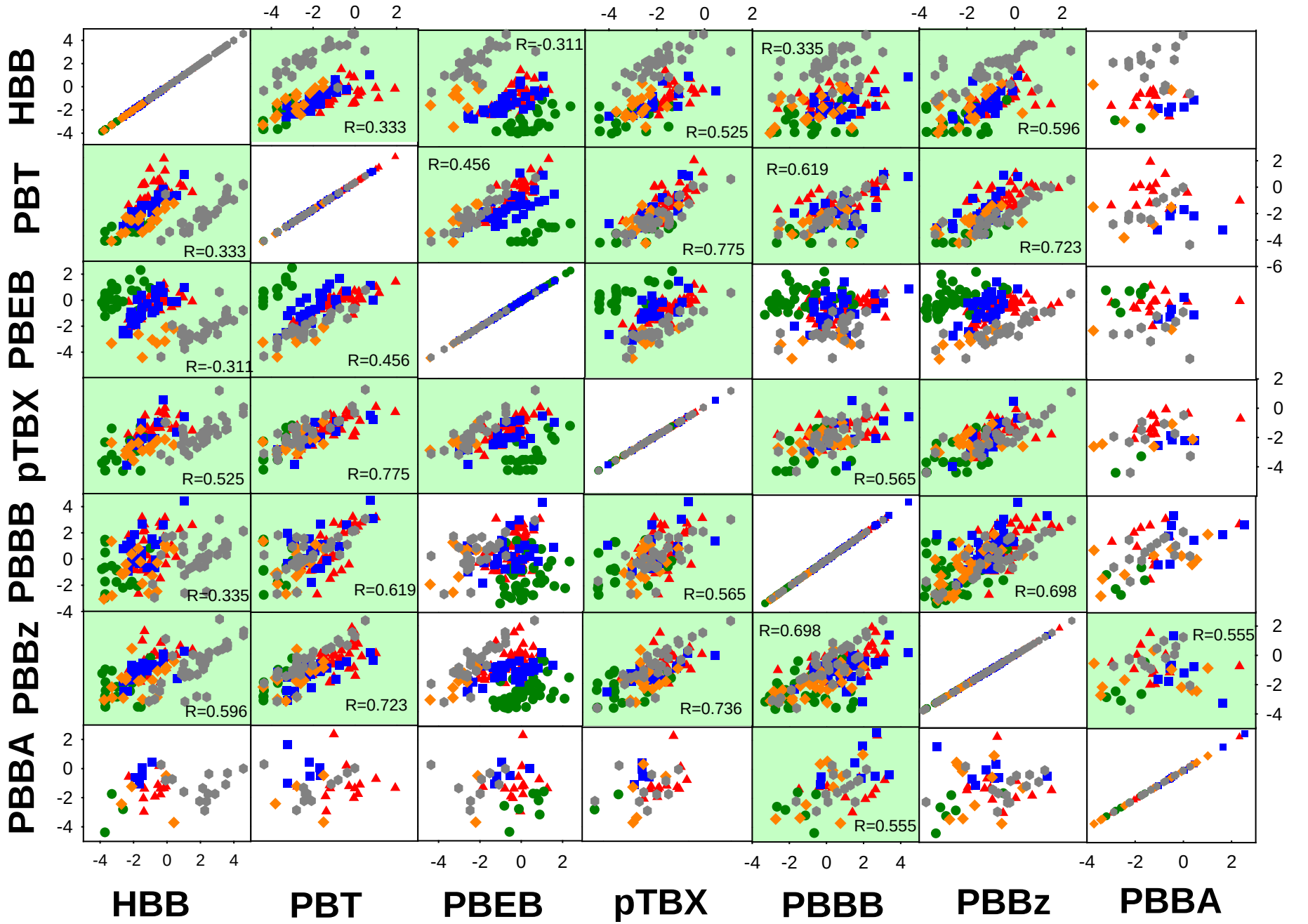


PBBA 59447-55-1

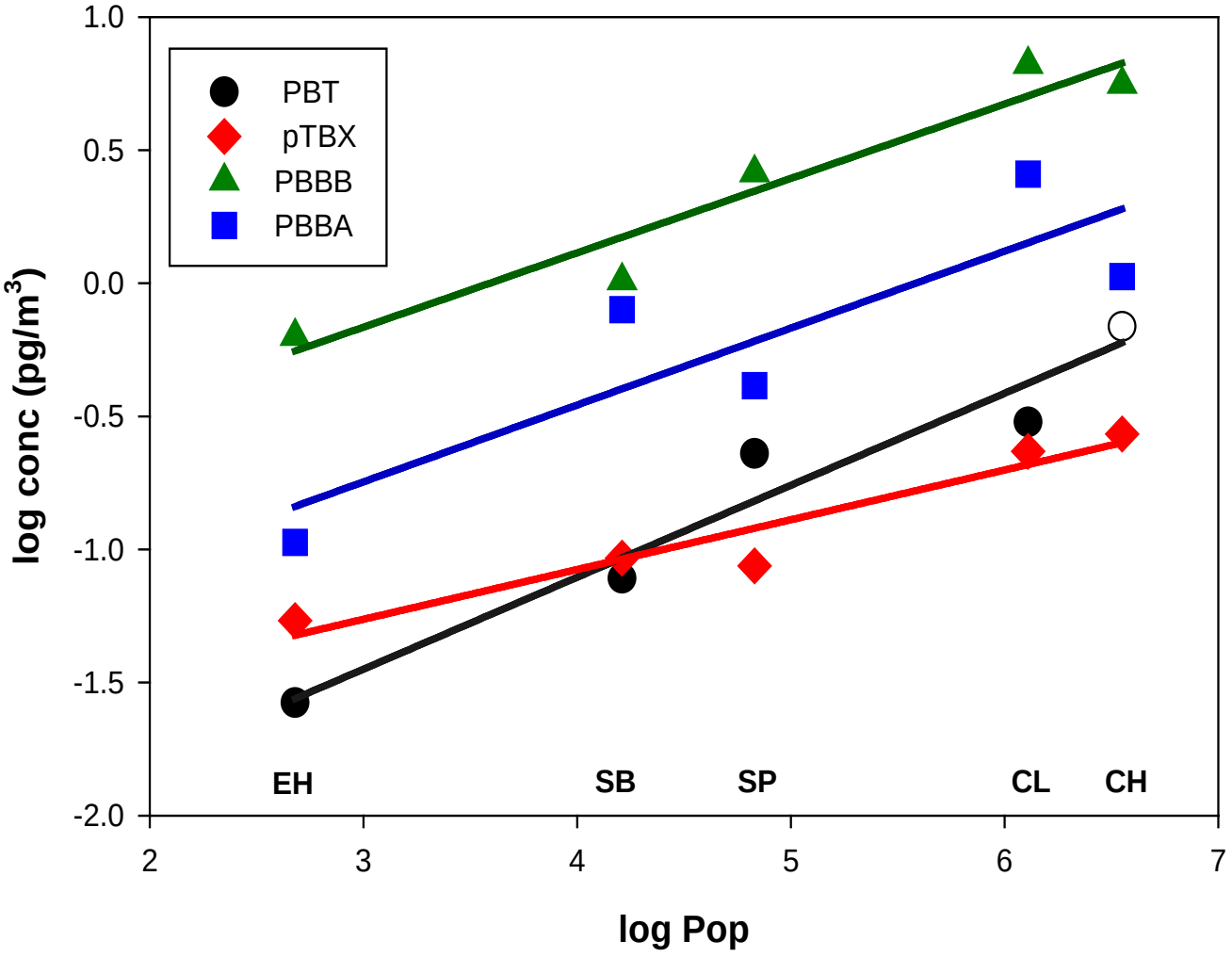
Total concentrations of the 6 brominated benzenes in Great Lakes air (vapor phase)

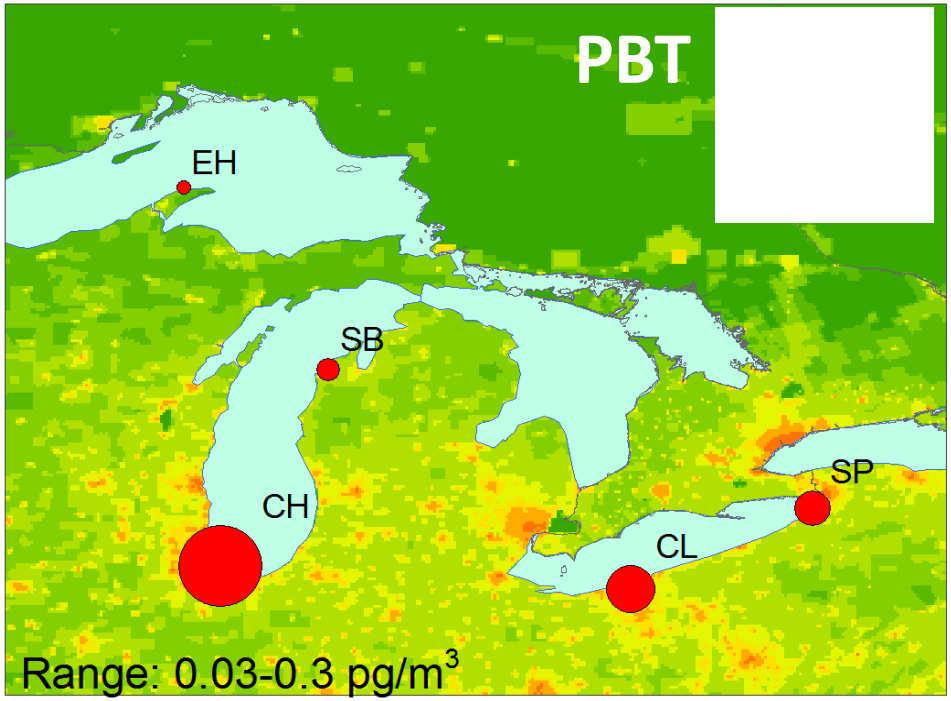


High correlation



Relationship with population

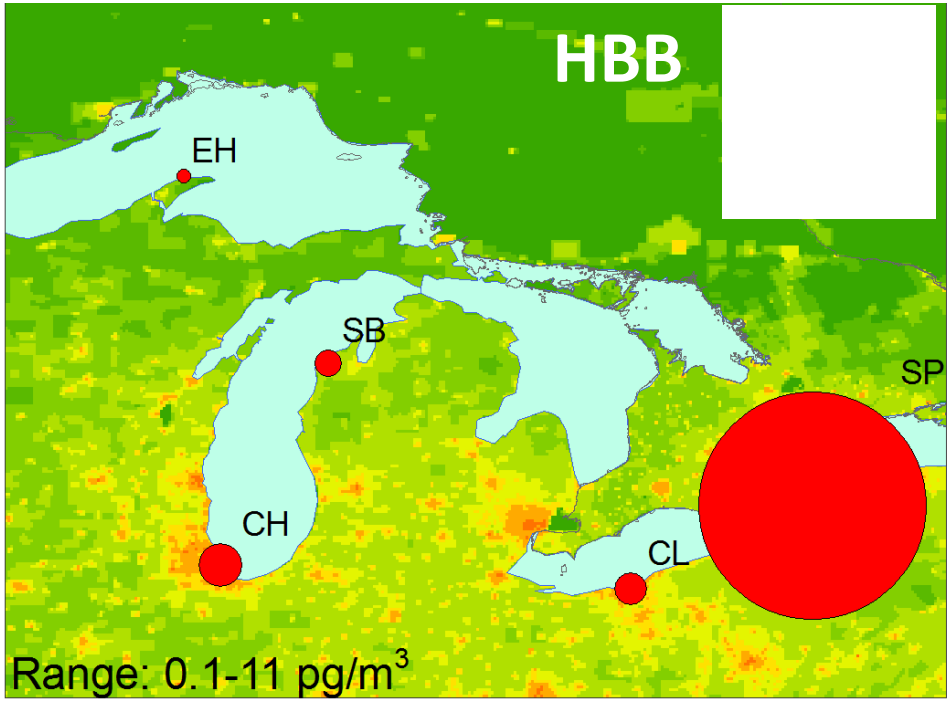


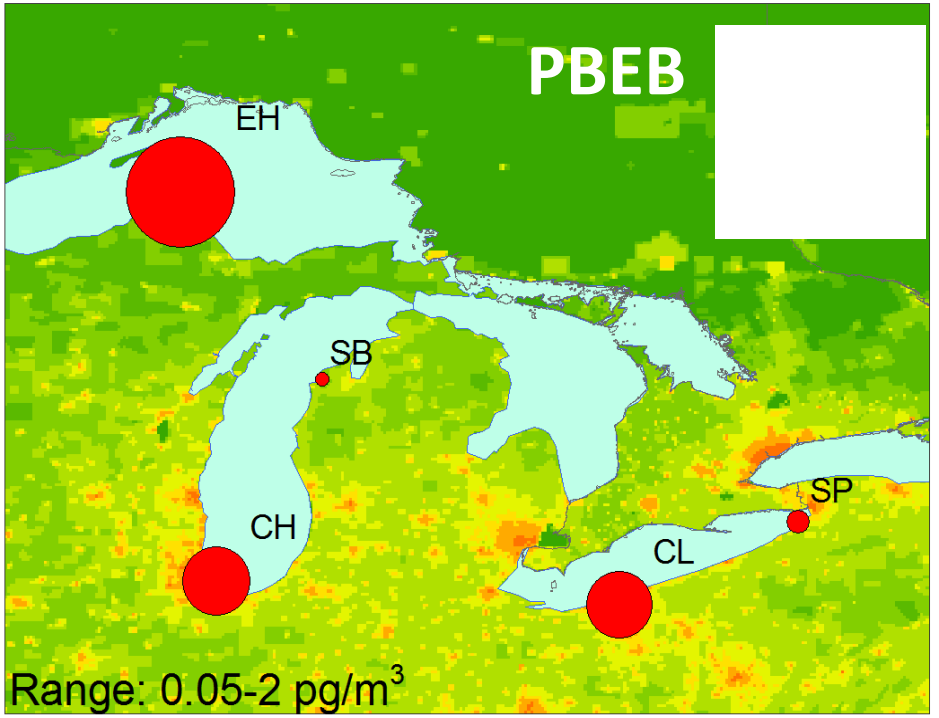


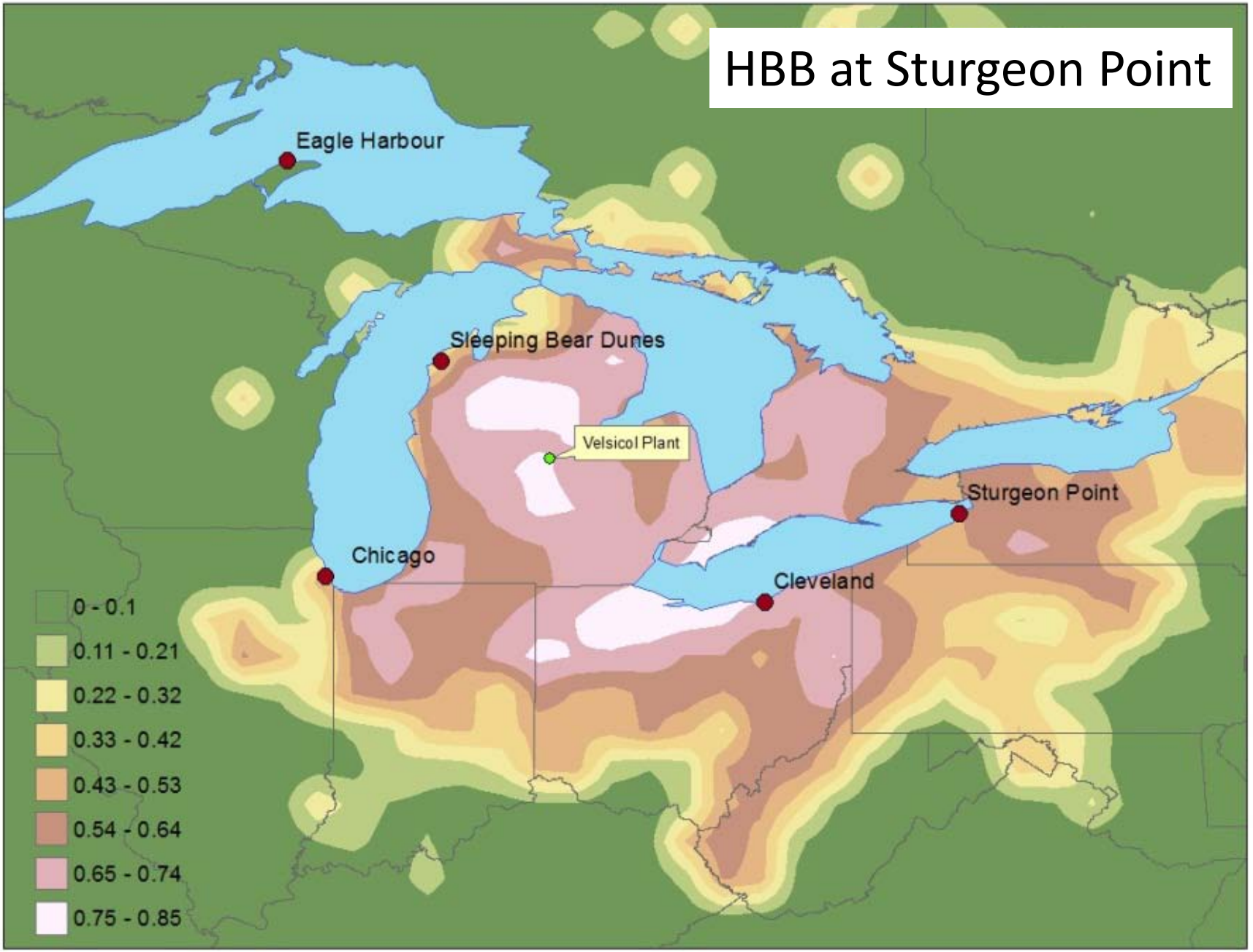
High urban effect

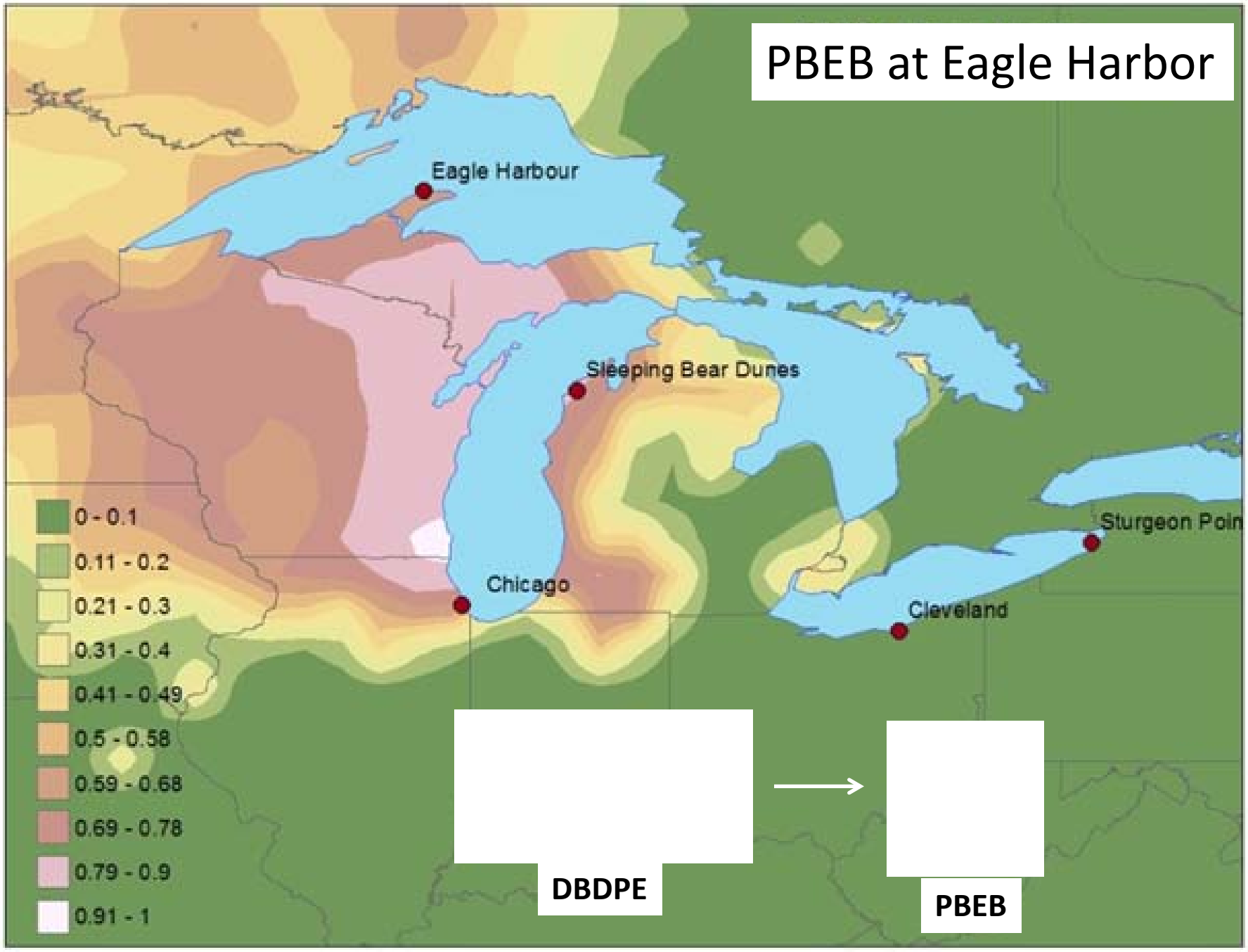
vs

Localized sources





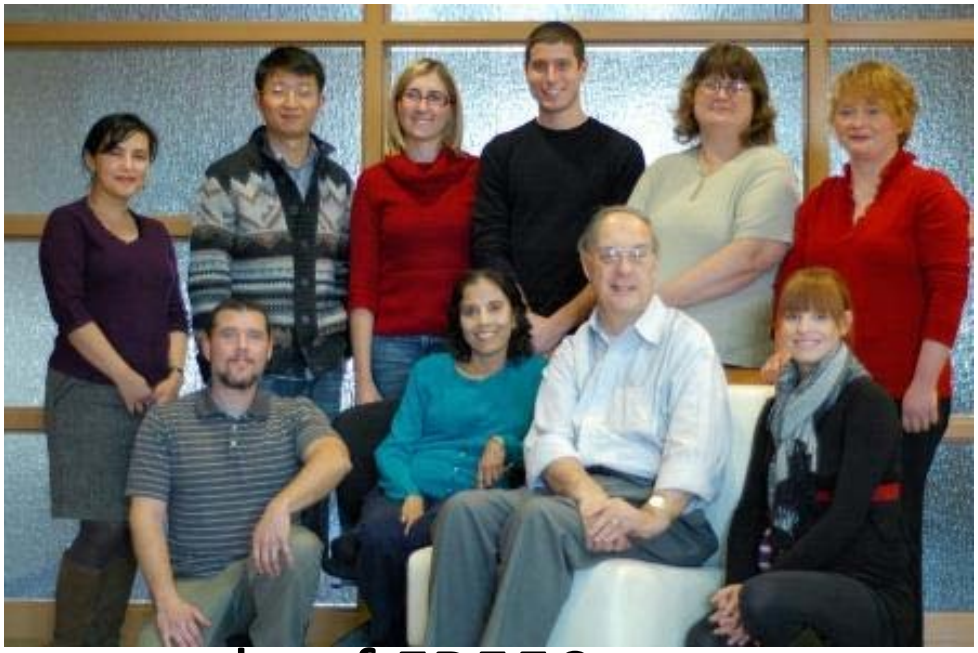

HBB at Sturgeon Point
Eagle Harbour
Sleeping Bear Dunes
Velsicol Plant
Sturgeon Point
Chicago
Cleveland
0 - 0.1
0.11 - 0.21
0.22 - 0.32
0.33 - 0.42
0.43 - 0.53
0.54 - 0.64
0.65 - 0.74
0.75 - 0.85


PBEB at Eagle Harbor
Eagle Harbour
Sleeping Bear Dunes
Chicago
Cleveland
Sturgeon Poin
0 - 0.1
0.11 - 0.2
0.21 - 0.3
0.31 - 0.4
0.41 - 0.49
0.5 - 0.58
0.59 - 0.68
0.69 - 0.78
0.79 - 0.9
0.91 - 1
DBDPE
PBEB

Conclusions

- We should use the lessons learned from legacy compounds to predict the behavior of emerging compounds, especially for temporal trends.
- Air responds quickly to changes in emissions
- Urban locations are generally sources of POPs
- We need good spatial coverage to obtain an exhaustive picture

Acknowledgements



- Stuart Harrad
- Ron Hites
- Team IADN
- Heather Stapleton for a sample of FR550
- United States EPA for funding (Todd Nettesheim, Program Officer)