Great Lakes Fish Monitoring and Surveillance Program (GLFMSP) Emerging Chemical Discovery

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Great Lakes Fish Monitoring Program

Open Lake Trends Monitoring – legacy

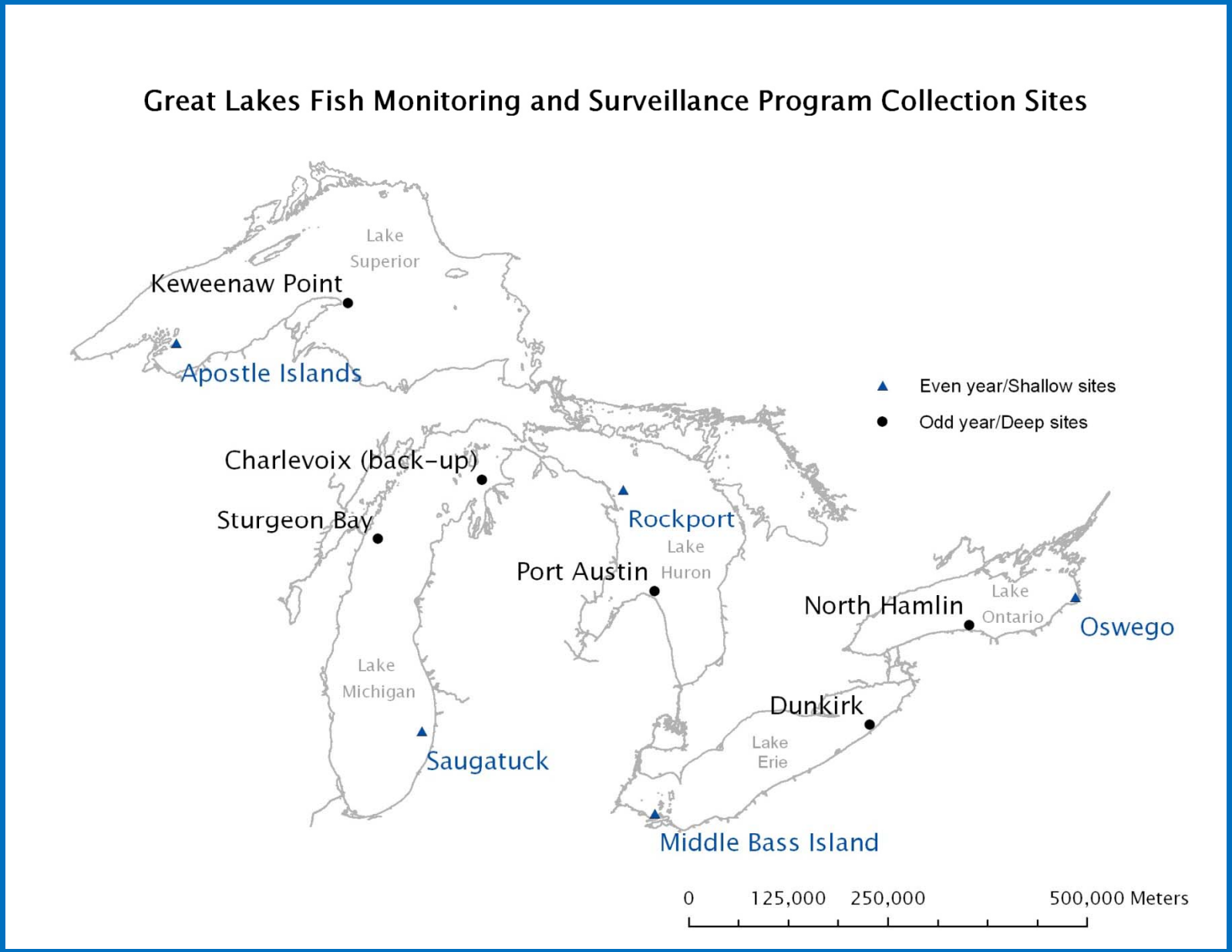
- Monitor contaminant trends in the open waters of the Great Lakes using whole fish (trout and walleye)
- 50 size-selected fish collected from each lake
- Alternate between near and offshore sites every year
- 10 composites containing 5 fish each.
- Yearly Mega-composites created after 2008 integrating all 50 fish collected for each lake

Sport Fish Fillet Program- discontinued 2008

Lake of the Year – Contemporary bioaccumulation and food web structure for each lake

Emerging Chemicals of Concern – Discovery of new PBTs

Monitoring Stations



Great Lakes Water Quality Agreement

- Addresses Annex 3 – Chemicals of Mutual Concern (CMC)
  - identify and assess the occurrence, sources, transport and impact of CMC, including spatial and temporal trends in aquatic biota;
  - maintain biological banks to support retrospective analysis and to establish background levels for use in assessing future management actions;
  - coordinating research, monitoring, and surveillance activities to provide early warning for chemicals that could become CMCs

Emerging Chemicals of Concern

Discovery of new (?) Persistent and Bioaccumulative Toxics (PBTs)

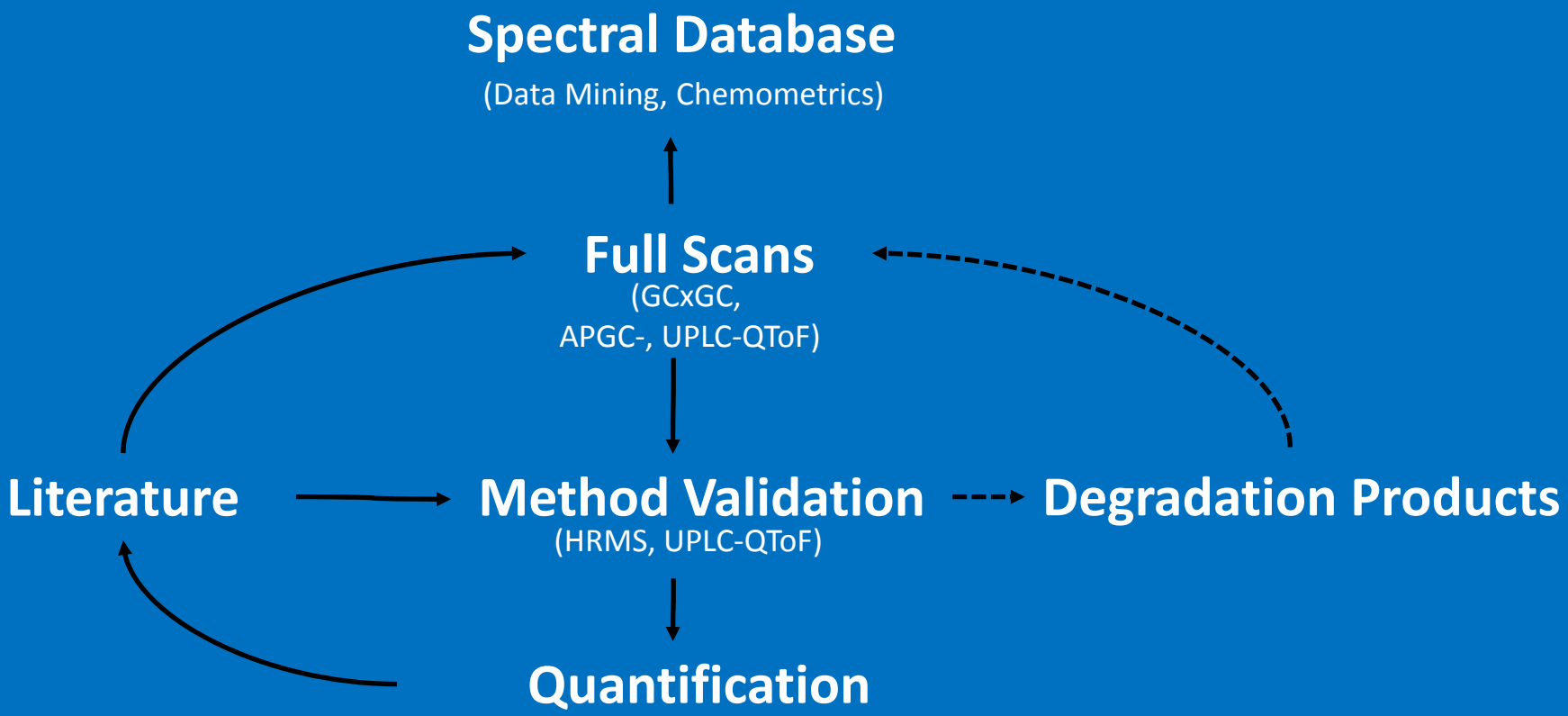
Evaluate the presence PBTs not widely monitored in the Great Lakes

- **Flame retardants** – PBDE replacements (bromophthalates, bromobenzenes, organophosphorous, chlorinated "legacy" flame retardants)
- **Perfluorochemicals** – Perfluoroalkyl carboxylic (PFOA) and sulfonic acids (PFOS)
- **Synthetic Musks –** Prevalent use and sparse data
- **Polychlorinated Dioxins/Furans and Co-planar PCBs** – legacy, yet contemporary data is currently limited
- **Polychlorinated naphthalenes** – Legacy, dioxin-like, limited data
- **Howard Muir, 2010** - High Production Volume, *in silico* candidates

Full screens of mega-composites for chemicals with PBT properties.

- **GCxGC-ToF** – Multiple dimensional chromatographic separation of non-polar species paired with library search spectral matching
- **HRMS** – High resolution mass spectrometry for molecular formula confirmation of species not found in commercial libraries
- **UPLC-QToF –** Ultra High Performance liquid chromatography coupled with a high resolution mass spectrometer for identification and confirmation of PBTs containing polar functional groups

Emerging Contaminant Discovery



GCxGC Results: Targeted Approach

- Howard-Muir List of persistent and bioaccumulative in-use organic chemicals in commerce (2010)
  - 610 potential compounds, including a top 50 list

- Purchase neat compounds, prepare standards
  - Generate user-defined mass spectral library from standards
  - Process GCxGC-TOF data files – confirm hits based on MS and retention time

- Reverse MS library search for compounds where standards not available
  - NIST Mass Spectral Database: 213,000 chemicals

Howard-Muir (2010) PBTs in Commerce and PBT Suspects Observed: NIST Library Results

Halobenzenes
Hexachlorocyclopentadiene
Octachlorocyclopentene
Tetrachlorobenzene
Pentachlorobenzene
Hexachlorobenzene
Pentachlorobenzenethiol
Pentachloro-5,6-dimethoxy-benzene
1,4-dichloro-2-dichloromethyl-5-trichloromethylbenzene
Hexachloromethyl xylene
Nonachloromesitylene

Nitrobenzenes
Chlorodinitrobenzene
Dichloronitrobenzene

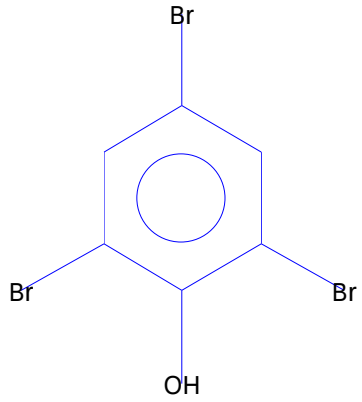
Brominated
Tribromophenol
Tetrabromobiphenyls
Dichlorobenzotrifluoride
Bromonaphthalenes (several isomers)
Bromomethoxybenzenes (several isomers)

OP Flame Retardants
Triphenyl phosphate
Tris (2-chloroethyl) phosphate
Tris (1,3-dichloroisopropyl) phosphate
Tris (3-chlorophenyl) phosphine
Di (2-methoxypropyl) ester

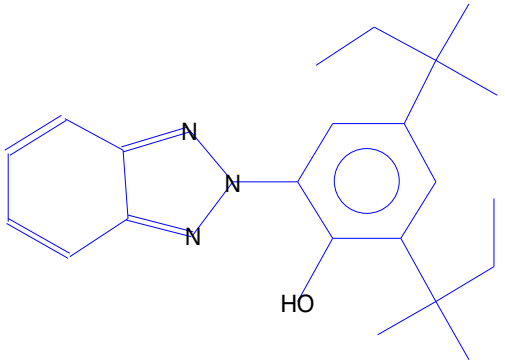
Misc
Tetrabromobisphenol S
Mitotane (DDD isomer, antineoplastic medication)
p-bis[trichlorovinyl] Benzene
Triclosan
Triphenyborane
2[p-Chloro-anilino]-4,6-bis[trchloromethyl]-S-triazine (& isomers)

Fluorinated
5,5-difluorohexanechloro-1,3-pentadiene

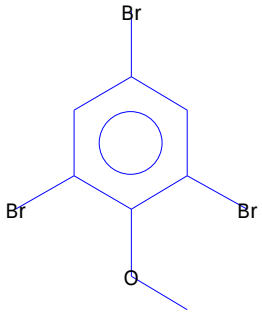
Compounds Confirmed by Mass Spectra and GCxGC Retention Time



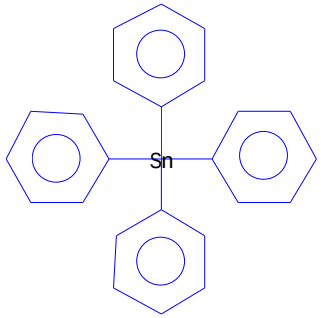
Tribromophenol
-Top 50 H-M list



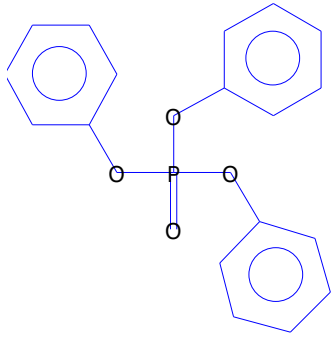
Phenol, 2-(2H-benzotriazol-2-yl)-4,6-bis(1,1-dimethylpropyl)-
- Top 50 H-M list



Tribromomethoxybenzene
- Degradation product of tribromophenol?



Tetraphenyl tin
- Triphenyl tin hydroxide on H-M lilst



Triphenyl phosphate
- Many organophosphorous compounds on H-M list

Great Lakes Trout (2008) Exact Mass Screening via Literature

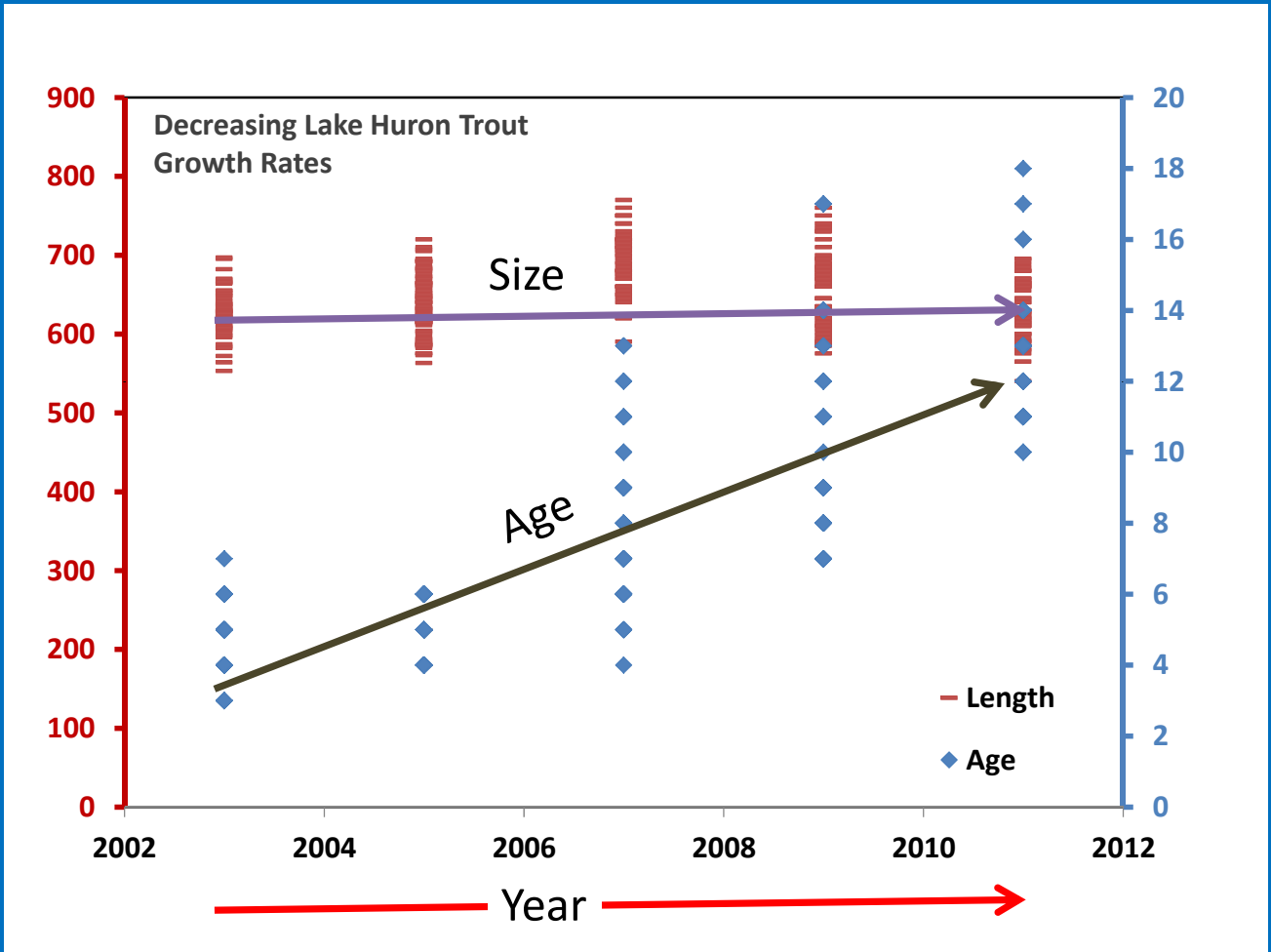
CODE	COMPOUND	LEWE	LELT	LHLT	LMLT	LOLT	LSLT	LOD
PCP	pentachloropyridine	M-RT	M-RT	M-RT	M-RT	M-RT	M-RT	0.3
PCBZ	pentachlorobenzene	133	542	225	242	541	216	0.8
2,4,6-TBP	2,4,6-tribromophenol	M-RT	M-RT	M-RT	M-RT	M-RT	ND	
ANISOLE	methylpentachlorophenyl sulfide	42	958	200	342	1233	108	1.1
PBBZ	1,2,3,4,5-pentabromobenzene	D-O	D-O	D-O	D-O	D-O	D-O	1.4
TBCT	tetrabromo-o-chlorotoluene	ND	ND	ND	ND	ND	ND	1.8
4-CPS	4-chlorophenyl sulfone	458	M-RT	42	66	433	58	8.1
PBBA	pentabromobenzyl acrylate	ND	ND	ND	ND	ND	ND	32.9
TBB	(2-ethylhexyl)-2,3,4,5-tetrabromobenzoate	150	M-RT	142	133	208	75	41.9
a Cl10DP	Cl10 Dechlorane Plus	ND	ND	ND	ND	ND	ND	9.9
BTBPE (TBE)	1,2-bis(2,4,6-tribromophenoxy)ethane	ND	ND	ND	ND	ND	ND	983
s-DP	syn-Dechlorane Plus	LOD	ND	LOD	LOD	LOD	ND	42.4
a Cl11DP	Cl11 Dechlorane Plus	D-O	M-RT	D-O	D-O	8	ND	5.6
a-DP	anti-Dechlorane Plus	25	M-RT	33	M-RT	M-RT	8	2.3
OBIND	octabromotrimethylphenylindane	ND	ND	ND	ND	ND	ND	542
DBDPE	decabromodiphenylethane	ND	ND	ND	ND	ND	ND	16008

pg/g wet wt.; M-RT = matrix - retention time shift; D-O = detected - optimize method; ND = not detected; LOD = limit of detection

Lake Erie 2009
BDE-47 13,000 pg/g

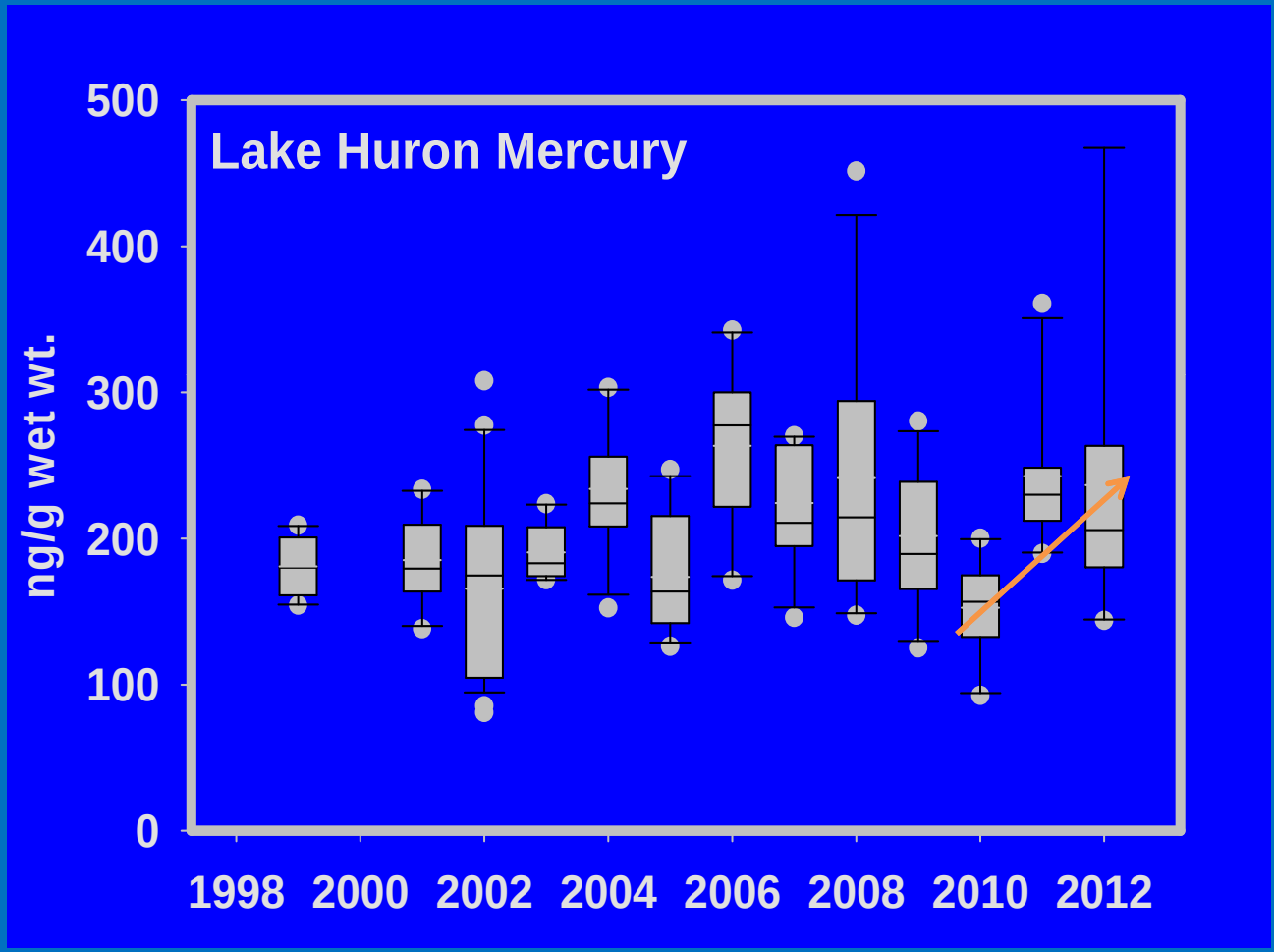
Lake Ontario 2009
BDE-47 74,000 pg/g

Legacy Contaminants of Emerging Concern
System Change Effect



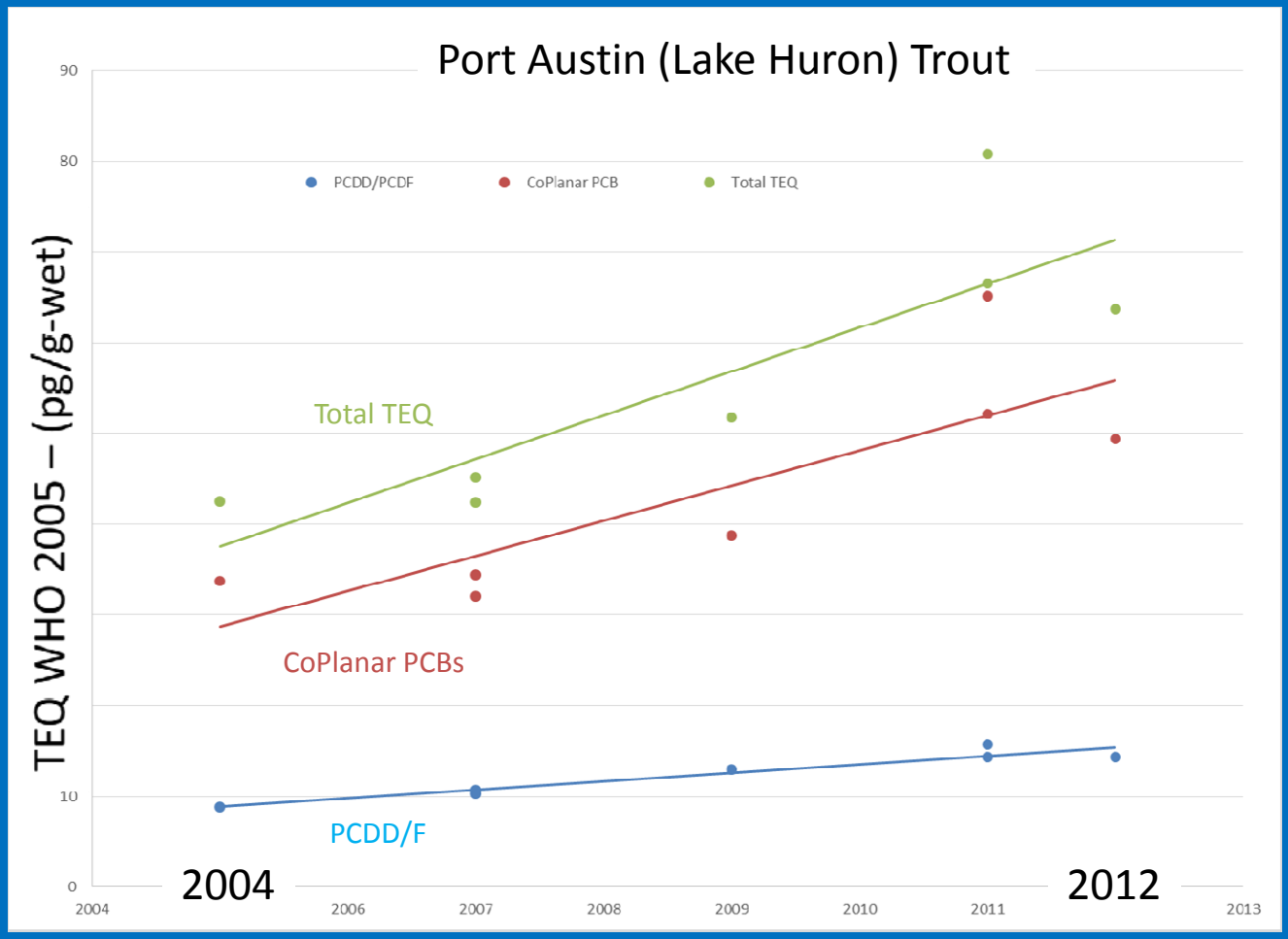
Decreased Growth rates Lake Huron trout – older fish are currently being analyzed

Mercury – Legacy, emerged or emerging?



Increasing concentrations in Lake Huron?

Legacy Contaminants of Emerging Concern – Polychlorinated dioxins, furans and Co-Planar PCBs

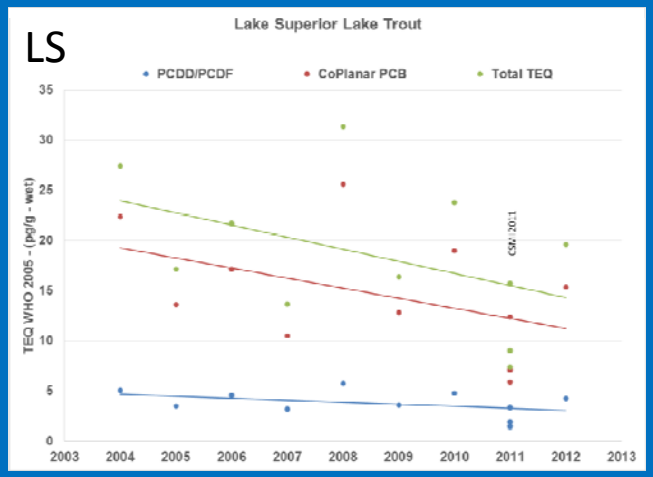


Increasing concentrations in Lake Huron too?

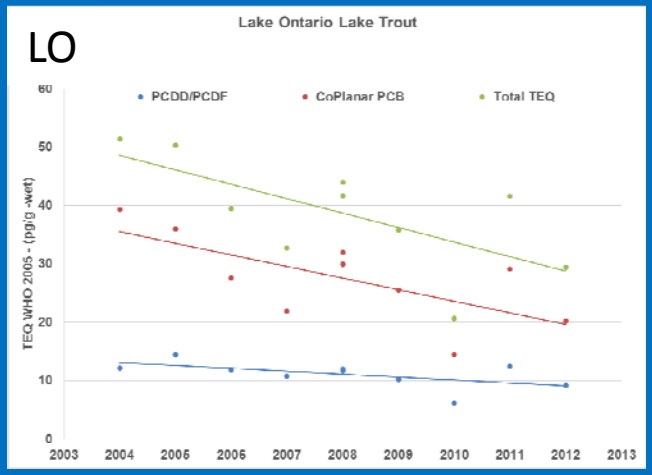
Total PCDD/F and CoPlanar Summary

> 1.2 ppt-TEQ should not be consumed by anyone (EPA)

LS



LO



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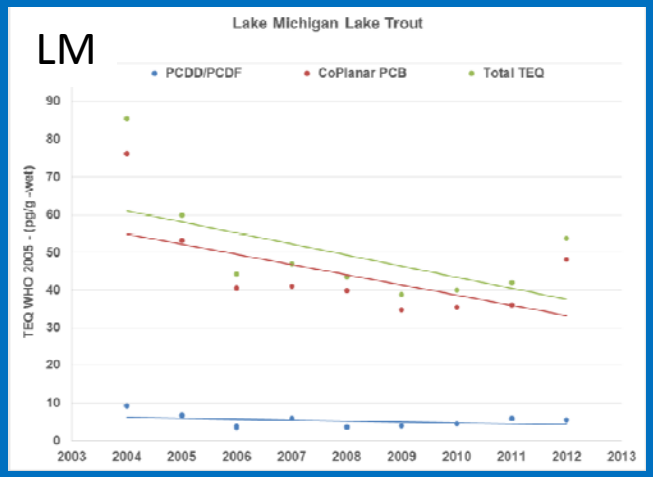
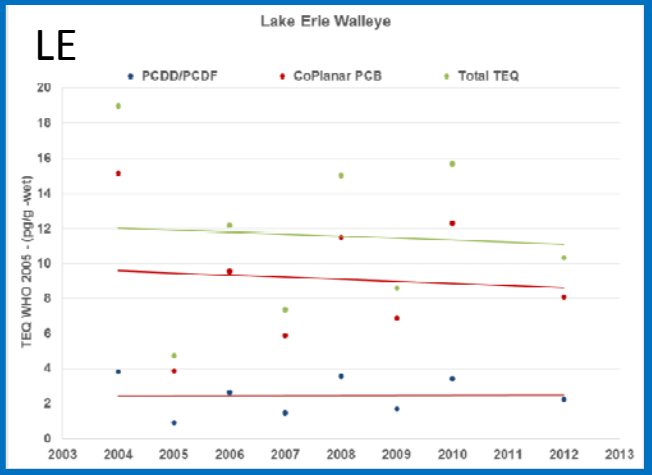


LE



Status and Recommendations

1. We must be cautious to not to overlook “legacy” chemicals:
   a) Likely drive the consumption advisories (higher levels)
   b) Provide evidence of system-wide changes (growth rate depression)

2. New chemicals are out there and we are slowly combing through the thousands of compounds,

3. The *in silico* work based on physical chemical properties has yielded detectable chemicals of concern in Great Lakes biota (Howard and Muir, 2010),

4. Current compound analogues, metabolites, replacements are helpful in the discovery of new chemicals,

5. We are not at a point to provide concentration data or an all-inclusive list of emerging chemicals in the various Great Lakes (standard availability, data quantity),

6. States should consider archiving extracts for future high resolution screens when contaminants are confirmed as significant PBTs