

New contaminants in Lake Ontario: siloxanes, perfluoros, organophosphates, and halogenated phenolics

Derek Muir, Mehran Alaei, Bill Lee and Brian Scott

Aquatic Ecosystem Research Protection Division,
Water Science and Technology Directorate,
Environment Canada, Burlington ON L7R 4A6

Outline

- **Some thoughts on selecting “new” chemicals for environmental measurements in Lake Ontario**
- **Recent “new” chemical measurements in the Great Lakes**
 - **siloxanes, perfluoros, organophosphates, and halogenated phenolics**
- **Conclusions and recommendations**

Screening of *existing chemical* lists is widening the data available for identifying potential contaminants

- TSCA Inventory Update Rule (IUR) screening (US EPA)
 - EPA Screening of 8511 chemicals with production >4.5 t/yr for P & B using the EPIWIN suite of QSARs (Walker and Carlsen 2002)
- Environment Canada's Domestic Substances List categorization
 - screening of 11,300 chemical substances with QSAR predicted properties
 - biodegradation, toxicity (production/use >100 kg/yr)
 - Completed September 2006; 4500 chemicals categorized for further assessment
- USEPA GLNPO funded project (2006-07) by Muir and Howard is selecting persistent and bioaccumulative chemicals from a combined IUR and DSL list for organic chemicals

Combining the Canadian DSL and EPA HPV Lists

DSL – 11,317 organic compounds

TSCA IUR HPV Chemicals – 3549 substances

UVCB Substances – 3059 substances

Total =15164

Persistence and Bioaccumulation Characteristics of the 15164 Chemicals

“POP” Characteristics*	#	%	Notes
log Kow > 5	3389	22%	Indicates tendency to adsorb to sediments and to bioaccumulate
BCF > 2000	779	5%	BCF is an estimate of bioaccumulation potential
BCF > 5000	497	3%	
BCF > 50000	17	0.1%	
AO* half-life > 2 day	1571	10%	AO half-life indicates stability to atmospheric oxidation
AO half-life > 10 day	572	4%	
log Kaw > -5 <u>and</u> log Kaw < -1	4815	32%	Kaw describes air-water partitioning. Compounds with Kaw > -5 are “hoppers”

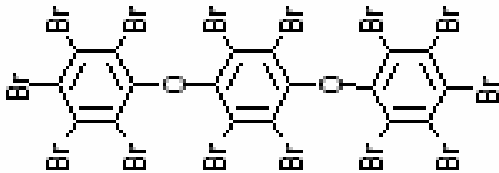
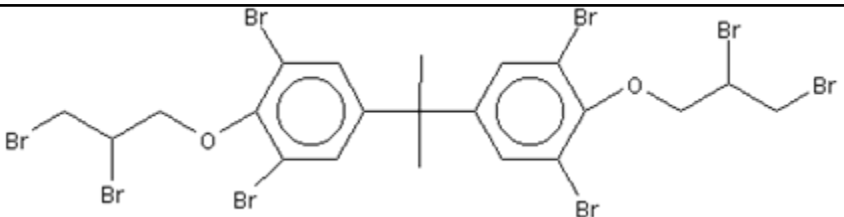
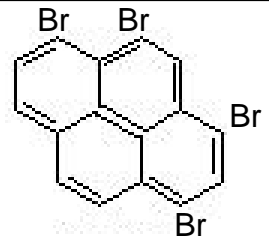
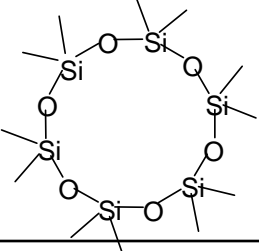
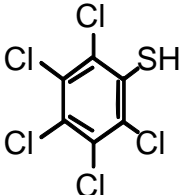
*Kow = octanol water partition coefficient

BCF = bioconcentration factor predicted with EPIWIN software

AO= atmospheric oxidation half-life

Kaw = air-water partition coefficient

Some halogenated compounds of potential interest in the Great Lakes due to high predicted persistence and bioaccumulation

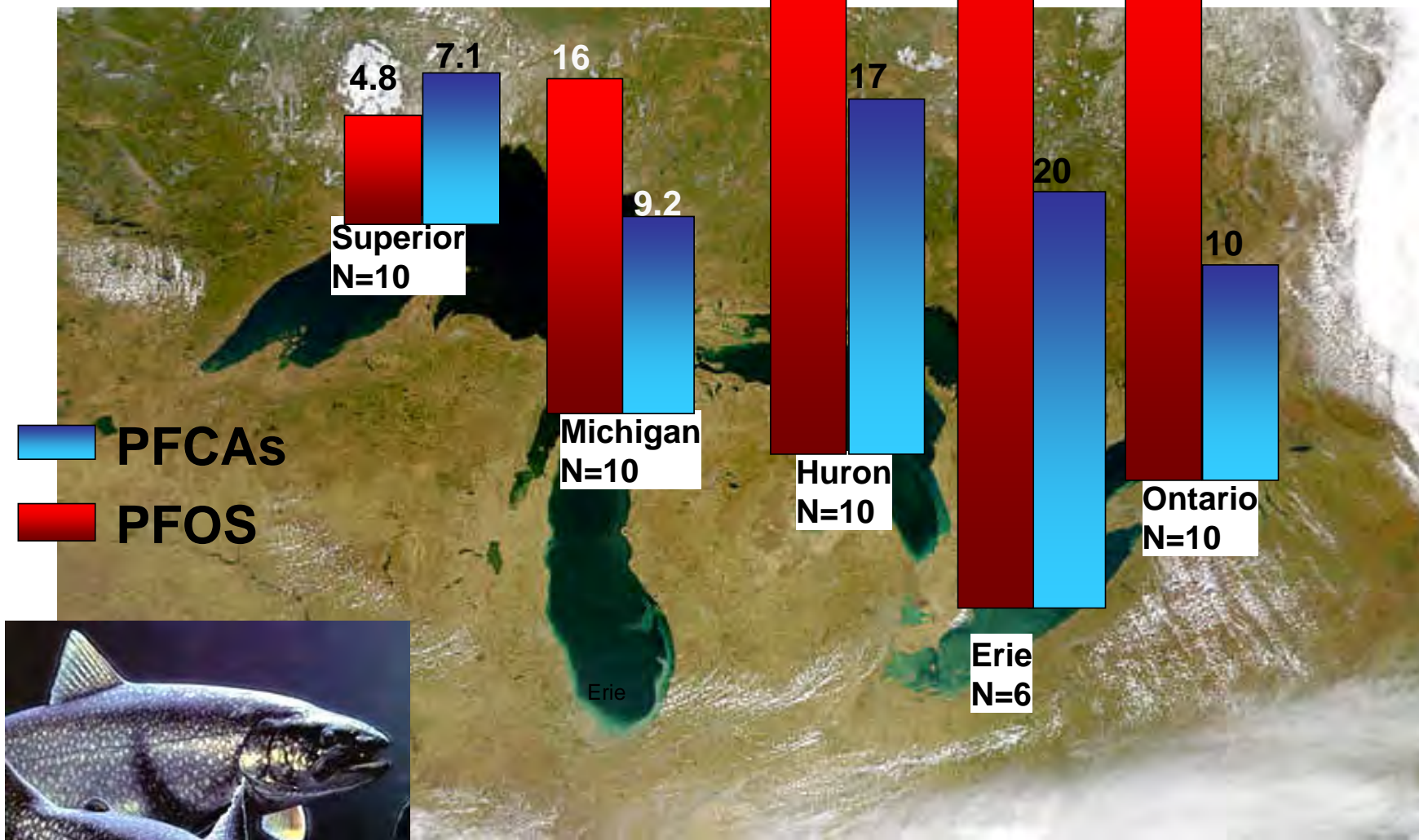
Substances	Predicted properties	Prod'n/yr (USA, lbs)	Structure
Benzene, 1,2,4,5 tetrabromo 3,6 bis(Br ₅ -phenoxy)	Log Kow= \sim 16 Persistent May not be B	>1M	
Benzene, 1,1' (1 methylethylidene)bis[3,5 dibromo 4 (2,3 dibromopropoxy)]	Log Kow= \sim 11 Persistent May not be B	>10K	
1,3,6,8 tetrabromo pyrene	Log Kow=8.5 Persistent May not be B	>500K	
Cyclohexasiloxane, dodecamethyl (D6)	Log Kow=8.5 P and B	>1M	
Pentachloro-benzene-thiol	Log Kow=5.9 P and B	10-500K	

PFOS and PFCAs (ng/g wet wt) in Great Lakes lake trout

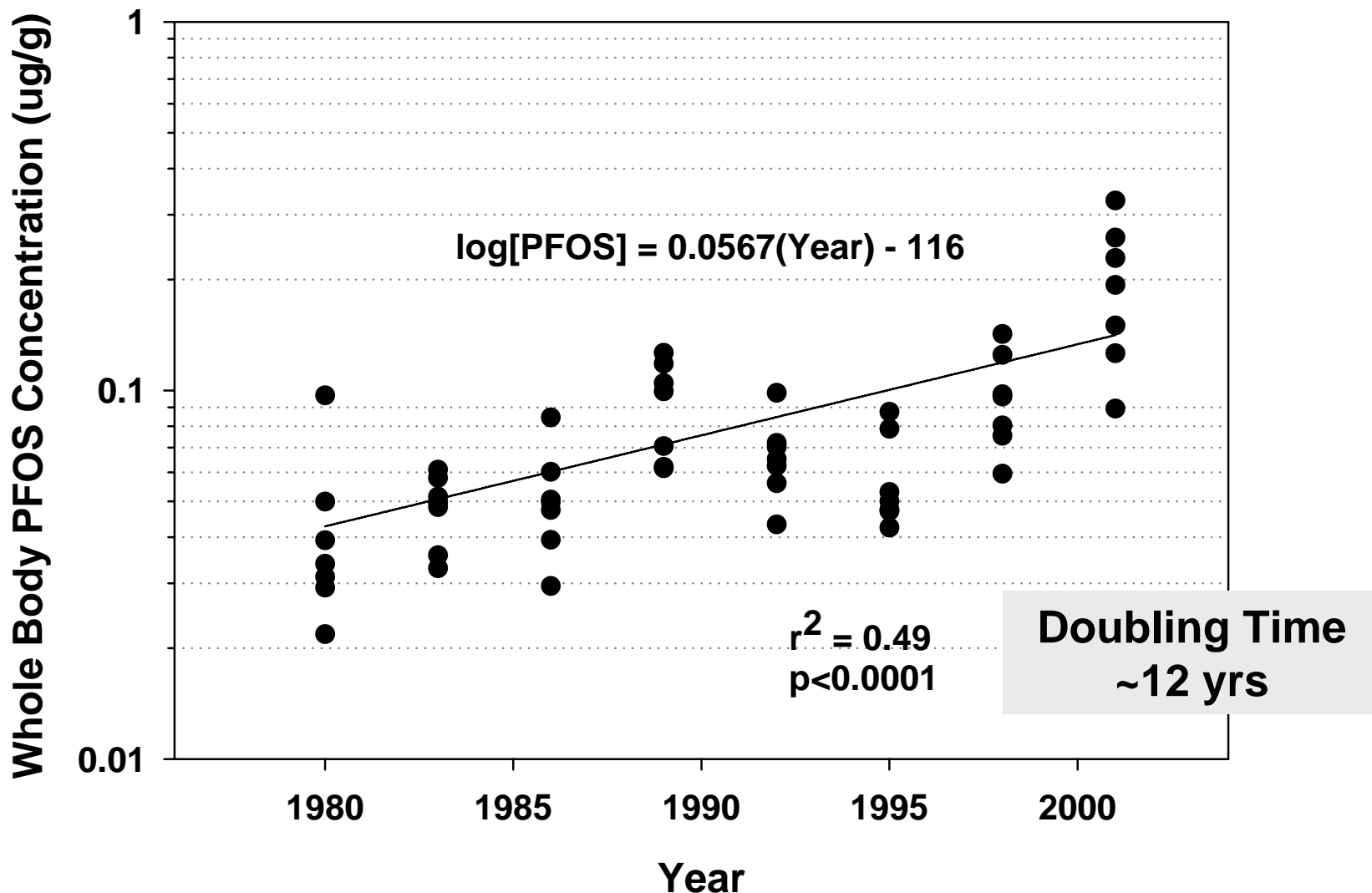
(whole fish; age = 4 yrs)

Furdui et al. ES&T 2007

 PFCAs
 PFOS



PFOS concentrations are increasing in Great Lakes fishes: Trend in Archived Lake Trout (whole fish) from Lake Ontario (1980-2001) (Martin et al ES&T 2004)



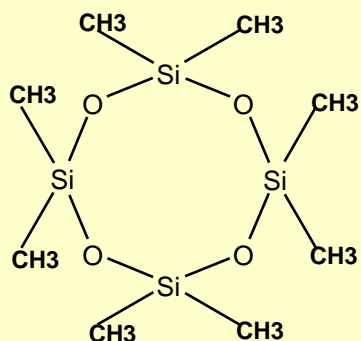
Volatile cyclic methyl siloxanes

- Carrier in antiperspirants/deodorants
- Shampoo and conditioners
- VOC exempt cleaning solvents
- Estimated 1993 U.S. releases – 20 kT/yr not including industrial use for PDMS production
- No published global estimates

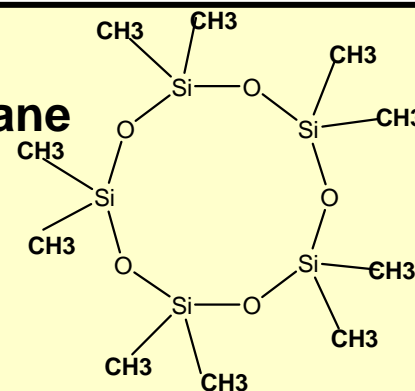
Cyclic siloxanes (D4, D5)

AO $t_{1/2}$	10 days
BCF	5300-12400
Toxicity	D5 – suspect carcinogen

D4 octamethyl-
cyclotetrasiloxane



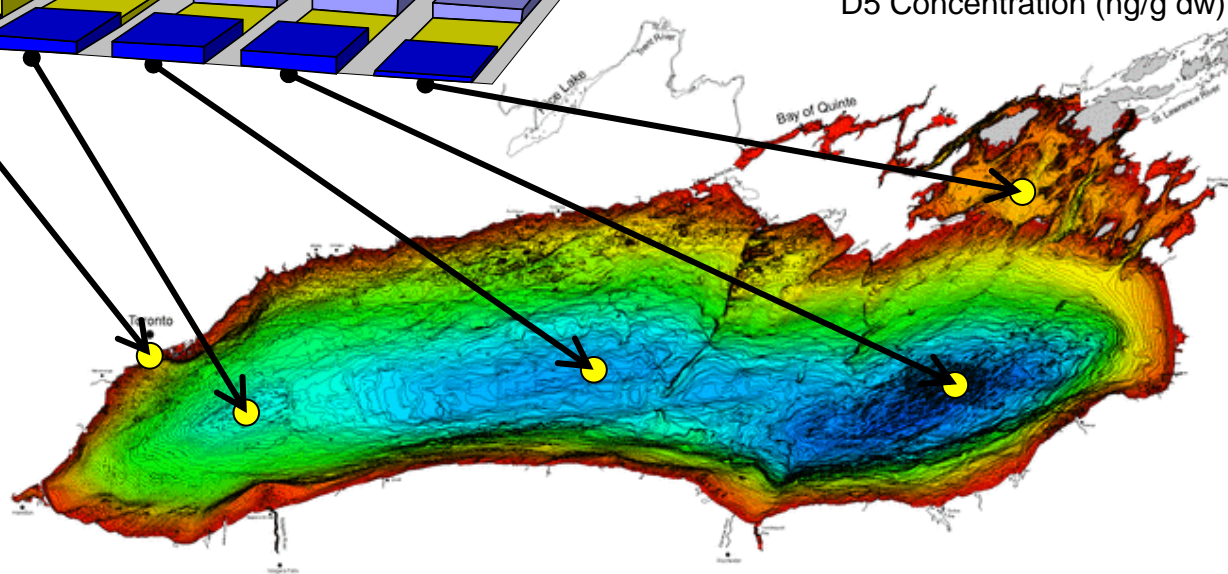
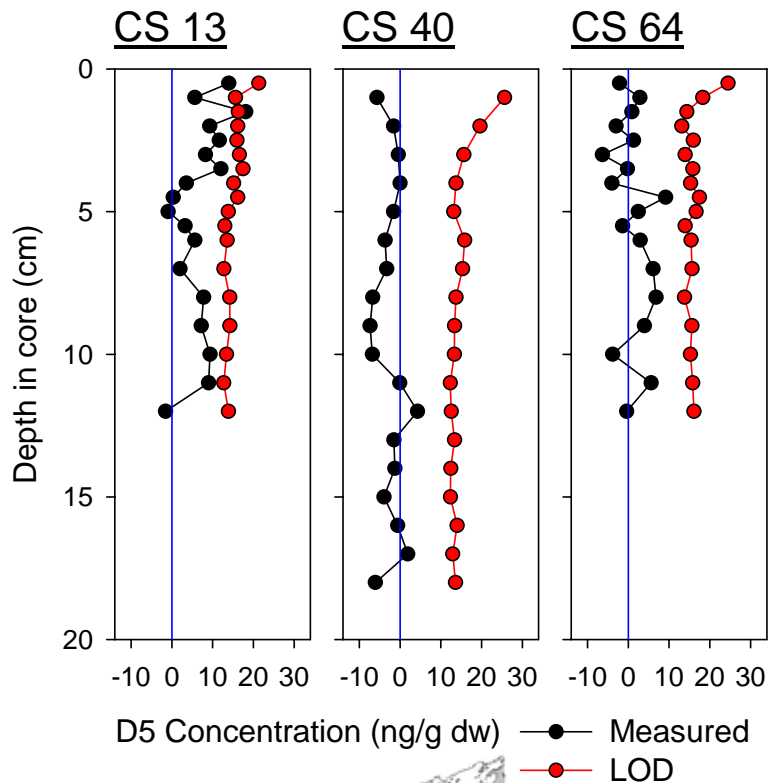
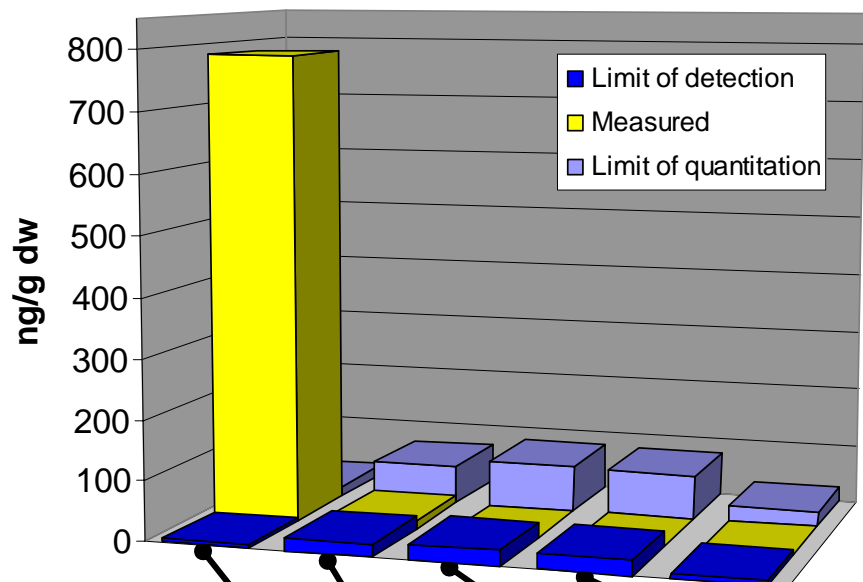
D5 decamethyl-
cyclopentasiloxane



Cyclic siloxanes in Lake Ontario Sediment

(D. Powell, Dow Corning unpublished data)

D5 Concentrations

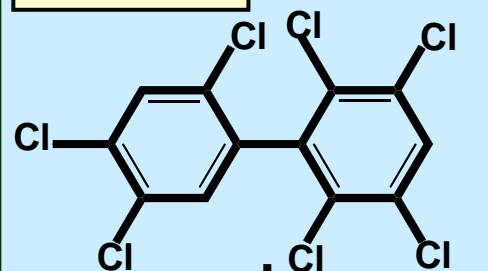


OH-PCB and OH-PBDE Formation

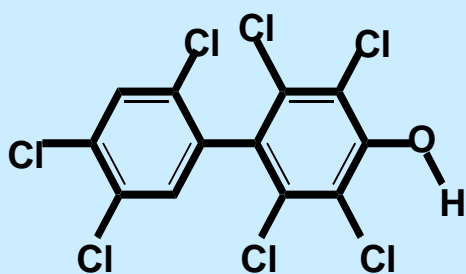
Metabolic

Atmospheric

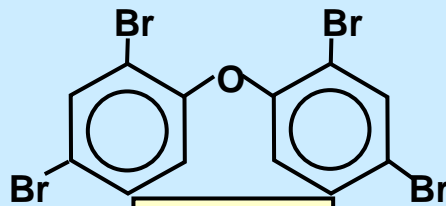
PCB 187



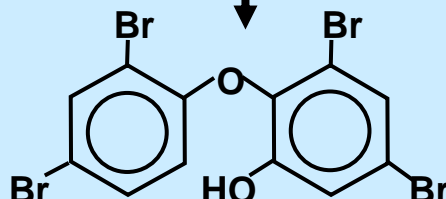
Cytochrome P450
Liver enzymes



4-OH-PCB 187

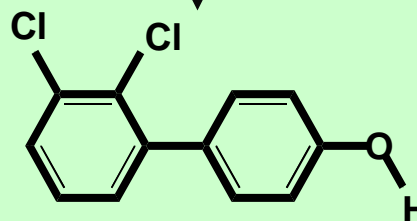
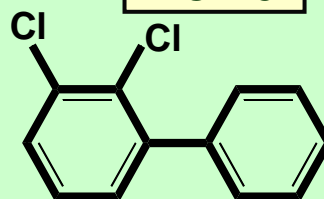


BDE47

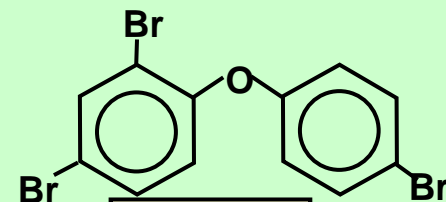


6'-OH-BDE47

PCB 5



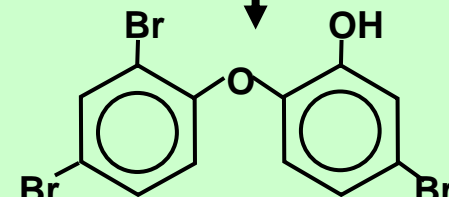
4-OH-PCB 5



BDE-28

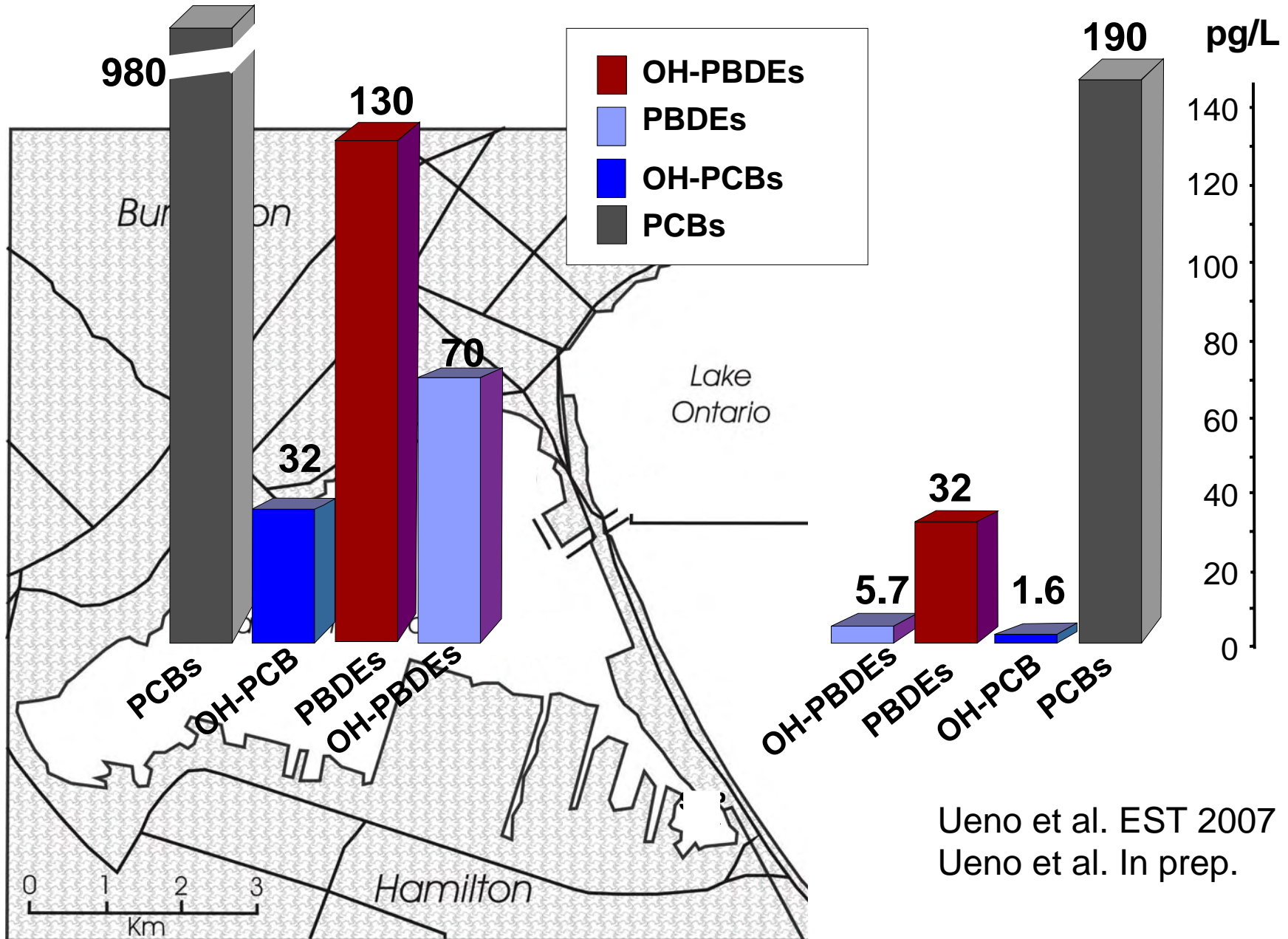
Sunlight

\cdot OH radical



2'-OH-BDE-28

Concentrations of OH-PBDEs and OH-PCBs in Lake Ontario and Hamilton harbour



Ueno et al. EST 2007
 Ueno et al. In prep.

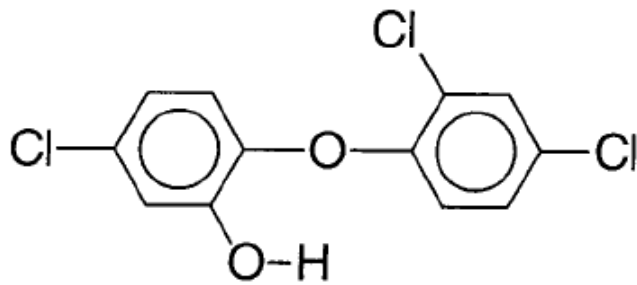
Triclosan and its methylated metabolite

Widely used bactericide

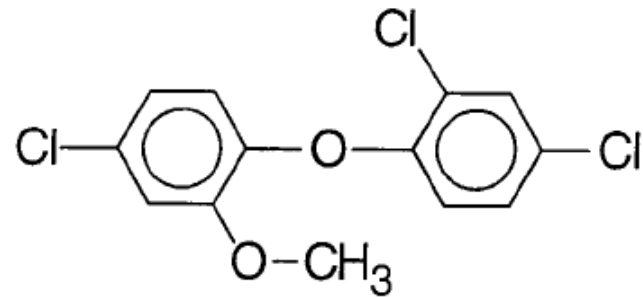
Toothpaste, mouthwash

Sports shoes

Sports underwear

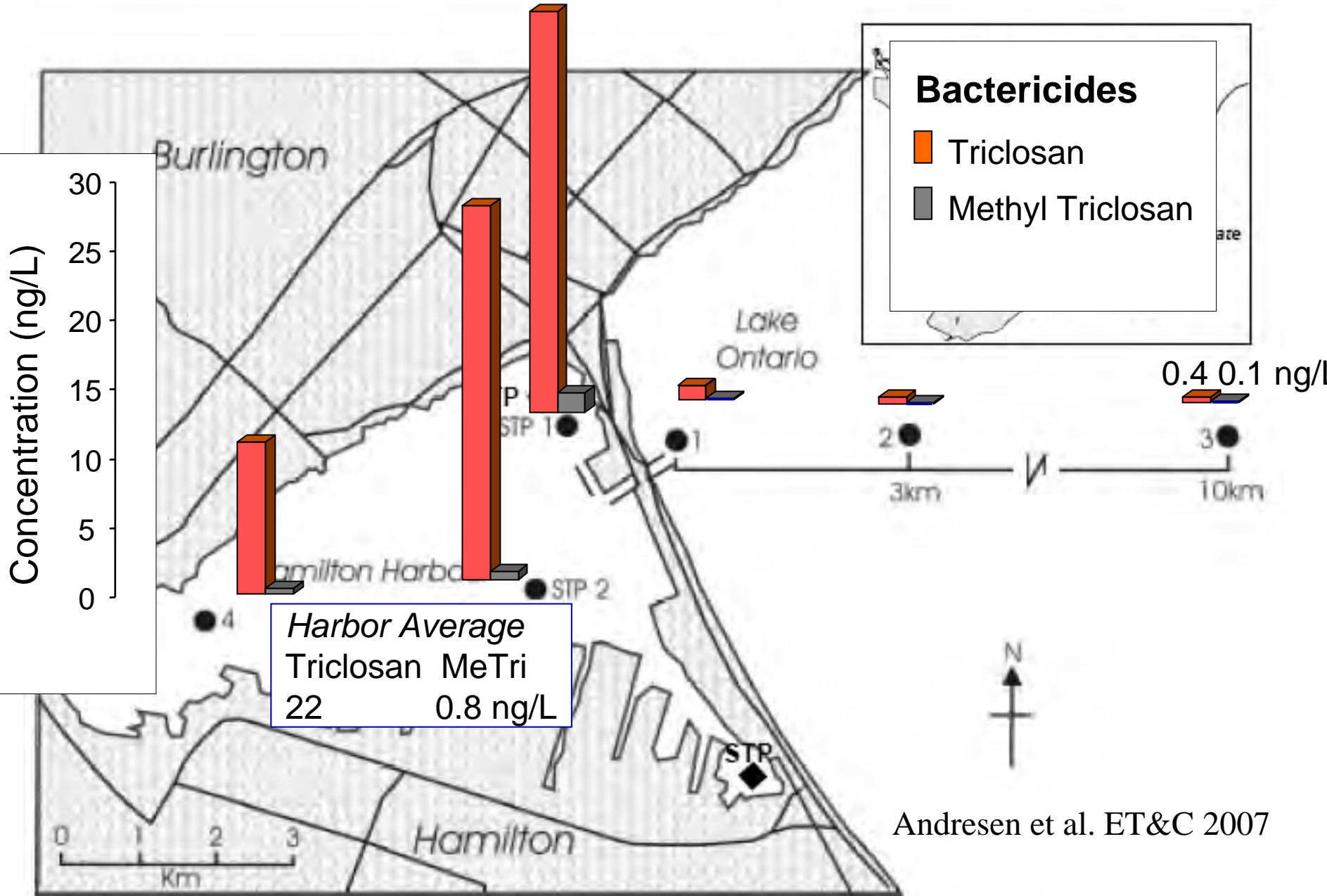


triclosan



methyl-triclosan

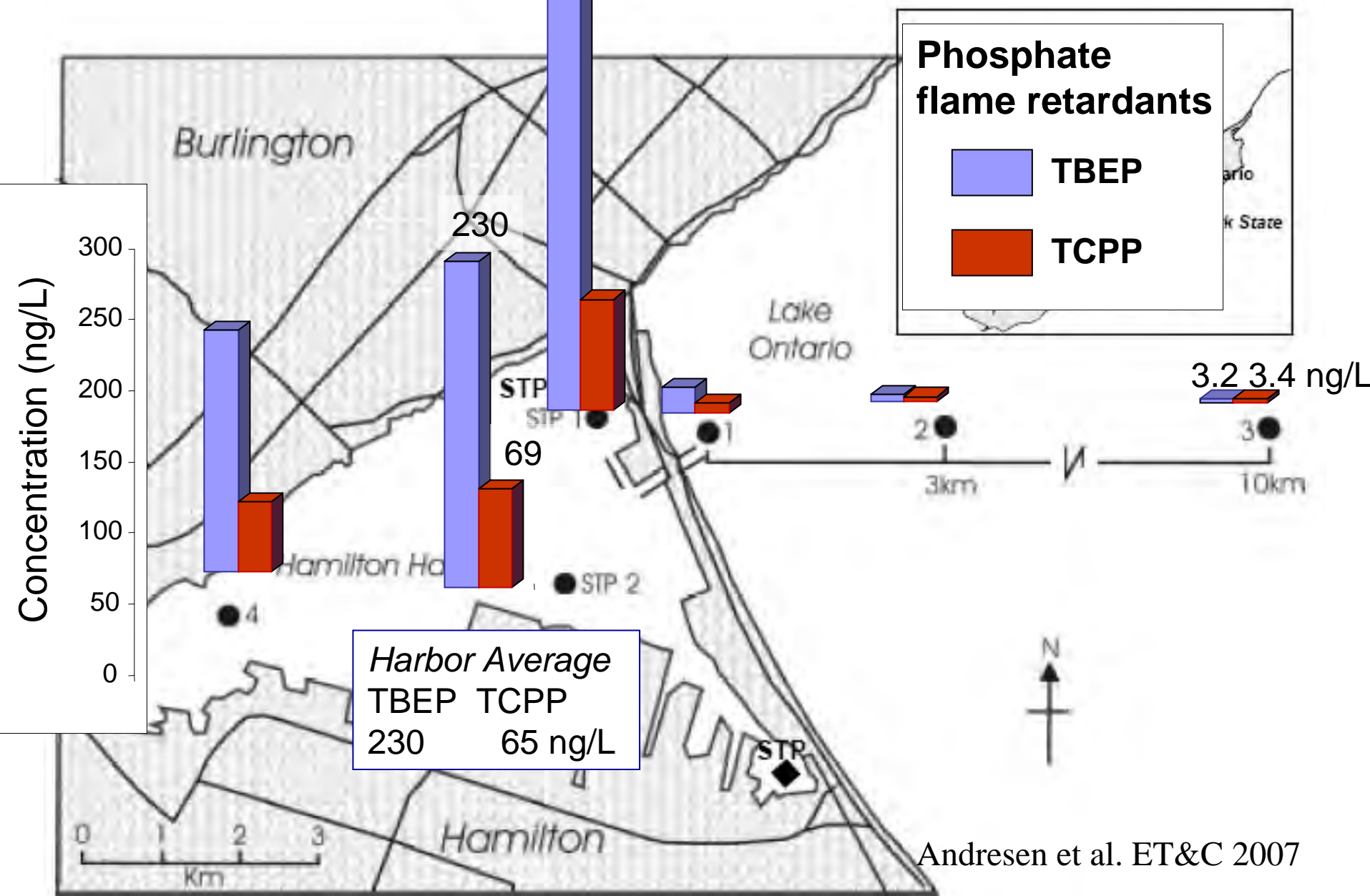
A harbour to open water gradient study: bactericides



Phosphate ester flame retardants – possible BFR substitutes

Chemical	Abbrev	Remarks
Tri- <i>n</i> -butylphosphate	T <i>n</i> BP	HPVC
Tris-(2-chloroethyl)-phosphate	TCEP	Phased out due to toxicity issue
Tris (chloropropyl)-phosphate	TCPP	Replacement for TCEP
Tris-(dichloro-propyl)-phosphate	TDCP	Phased out due to toxicity issues, only speciality applications still exist
Tri-phenylphosphate	TPP	HPVC
Tris-(butoxyethyl)-phosphate	TBEP	HPVC
Brominated aromatic phosphate ester (Grt Lakes Chemical)	Firemaster 550	PBDE replacement; Structure is proprietary business info. Firemaster 550 includes TPP

A harbor to open water gradient study: flame retardants,



Factors to be considered re New Chemicals

- **P, B & T characteristics and priority info from screening e.g. with QSARs or other assessments**
 - chemicals that biomagnify versus those that are less bioaccumulative but are constantly emitted?
- **Use in the region; Release/emissions, e.g. TRI and NPRI**
 - Modelled exposure by generic and realistic environmental fate models
 - evidence for increasing emissions
- **Environmental levels – approaching thresholds for effects?**
 - Temporal trends from biota, sediment cores or other archives
 - concentrations in open lake versus in shore or harbour waters