Emerging Contaminants in Fish & Water Samples from Both Sides of the Border

Beth Murphy, US EPA GLNPO

Sean Backus, Environment Canada

Chemical Screening

- Environmental Protection Agency
  - Muir / Howard List
  - Investigator Interest
  - State / Tribal Interest
- Environment Canada
  - CMP chemicals
  - Special Studies

Interlab Study

- EPA and EC have recently shared a set of fish tissue samples to be used in an inter laboratory comparison study.
  - Results are very positive
  - Plan to continue to share samples
  - Will allow division of labor between two labs with a great degree of confidence.

EPA Data Source

- All data is provided by the Clarkson University Research Team
  - Clarkson University: Dr. Tom Holsen, Dr. Phillip Hopke, & Dr. Bernard Crimmins
    SUNY Oswego: Dr. James Pagano
    SUNY Fredonia: Dr. Michael Milligan

EPA Screening Approaches

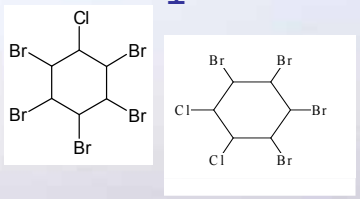
A. Perform detailed "Full Scan" analysis of Great Lakes Fish
   - Large composite sample ~30g extracted
   - Separate the extract prior to analysis using modified column chromatography based
   - Analyze extracts for previously unidentified peaks (non-legacy contaminants)

B. Utilize EPA Sponsored Potential Emerging Contaminant List (Muir and Howard, 2009) – http://www.epa.gov/grtlakes/p2/PBT_progress.pdf

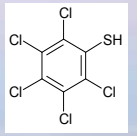
Full Scan Tentative Identifications by EPA

1. Halocyclohexanes
2. Pentachlorothiophenol
3. Chlorocyclopentane/ene
4. Hexabromocyclododecane
5. Polychlorinated diphenyl ethers

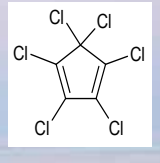
1



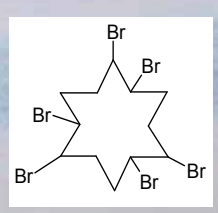
2



3



4



Limitations

- Spectra are complex
- Literature not available for most compounds

Utilize EPA Sponsored Potential Emerging Contaminant List (Muir and Howard, 2009)

- **Compile standards from "List" compounds and those tentatively identified during broad screen.**

Compounds Acquired

PentaBromoChlorocycloHexane
1,2-Dibromo-4-(1,2-dibromoethyl)-cyclohexane
Hexachlorocyclopentadiene
Cyanuric chloride
Pentachlorothiophenol
3,5-Dichloro-2,4,6-trifluoropyridine
Pentachloropyridine
2,4,6-Tribromophenol solution
Dibutyl chlorendate solution
SAYTEX® BT-93W
Hexabromocyclododecane
Chlorocyclopentane
Perbromophthalate/benzoate
Decabromodiphenyl Ethane
Tetradecabromo-1,4-diphenoxybenzene
Tetrabromophthalic anhydride
Decabromodiphenyl ethane

Emerging contaminants confirmed in Lakes Michigan and Superior Trout as part of GLFMP

Pentachlorothiophenol
2,4,6-Tribromophenol
Hexabromocyclododecane
Tetrabromoethylcyclohexane (TBECH)
PFC Analysis

- Also found in Lake Michigan Eggs (2006)
- BDE-209 Not found in trout but found in eggs!!!
- Musk / Fragarances currently being analyzed

Great Lakes Restoration Initiative

- The Great Lakes Fish Monitoring and Surveillance Program is included in the recently released RFP for the GLRI.

Contaminants of Concern

Contaminants of Concern

- Contaminants of Concern continue to be found with increasing frequency in the Great Lake's ecosystem.
- Persistent organic pollutants (POPs) are of particular concern because of their *toxicity*, their tendency to *accumulate* in human and animal tissue, and their *persistence* in the environment.

- **Legacy** contaminants such as PCBs and PAHs continue to be a source of concern as restoration of historic sites is undertaken.

- There is a growing body of science on the environmental occurrence, distribution, and mobility of **emerged** classes of contaminants such as polybrominated diphenyl ethers (PBDEs), and perfluorinated compounds, (PFCs).

Contaminants of Concern

- Recent awareness that many of the products and chemicals designed to offer improvements in industry, agriculture, medical treatment, and day-to-day life are causing contamination of air, water, and land resources and continues to lead to studies on **emerging** contaminants of concern.

- Chemicals such as organosiloxanes, pharmaceuticals and personal care products, current use pesticides, replacement flame retardants, and nanoparticles continue to stimulate new science in the Great Lakes Basin.

Contaminants of Concern

Legacy

Emerged

Emerging

Re-emerging

LEGACY- PCBs

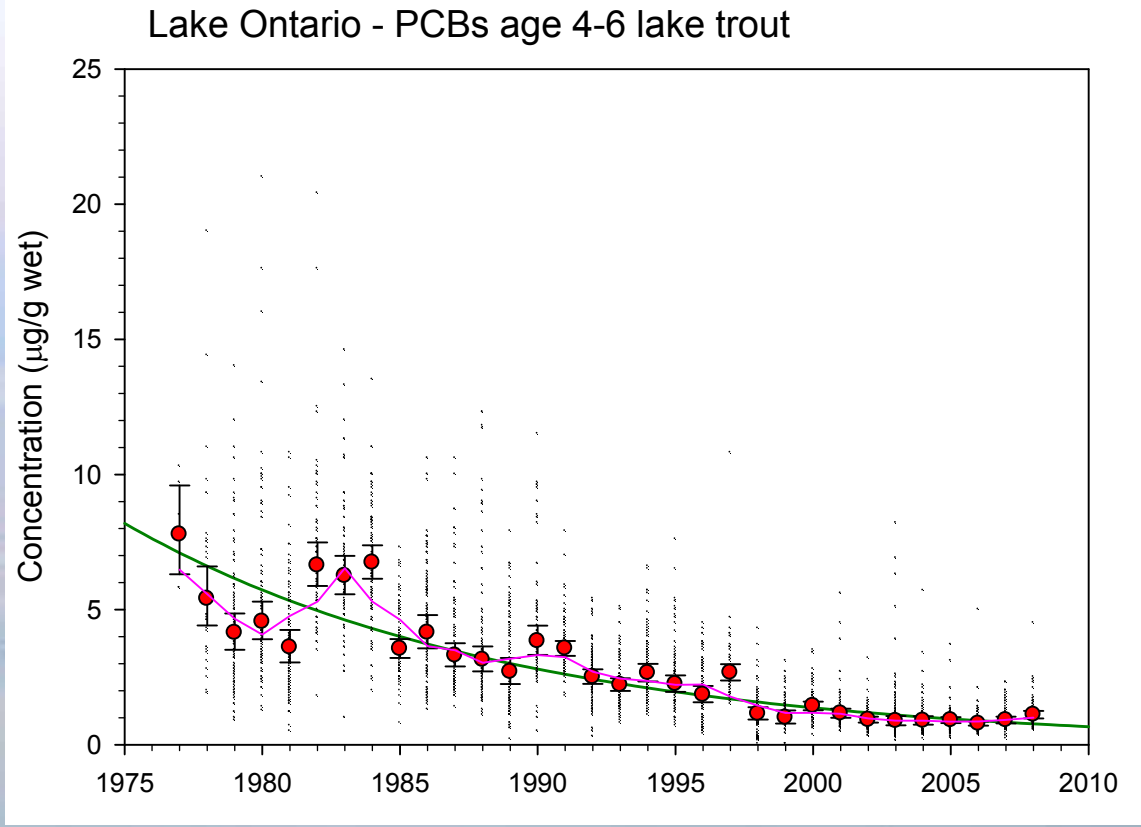
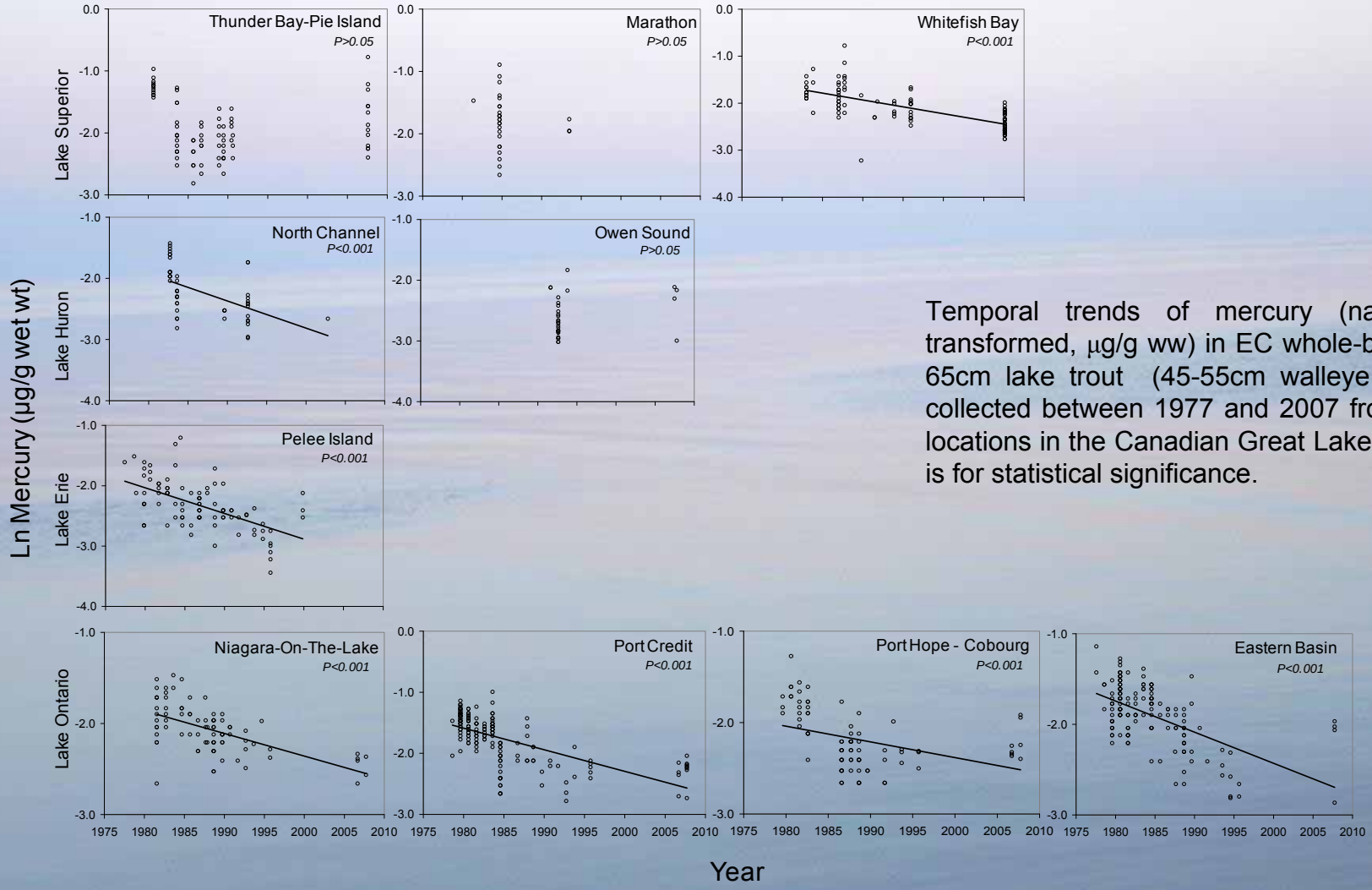


Figure 1. Trends of Total PCBs in Lake Trout (whole fish) collected from Lake Ontario

The mean concentration of total PCBs in whole body homogenates of lake trout in the latest year of monitoring (2008) in Lake Ontario was 1.10 ug/g wet (range = 0.54 – 4.5) which exceeds the target of 0.1 ug/g set in the GLWQA. Based on the mean annual decline calculated, the target concentration of 0.1 ug/g would be reached in the year 2037

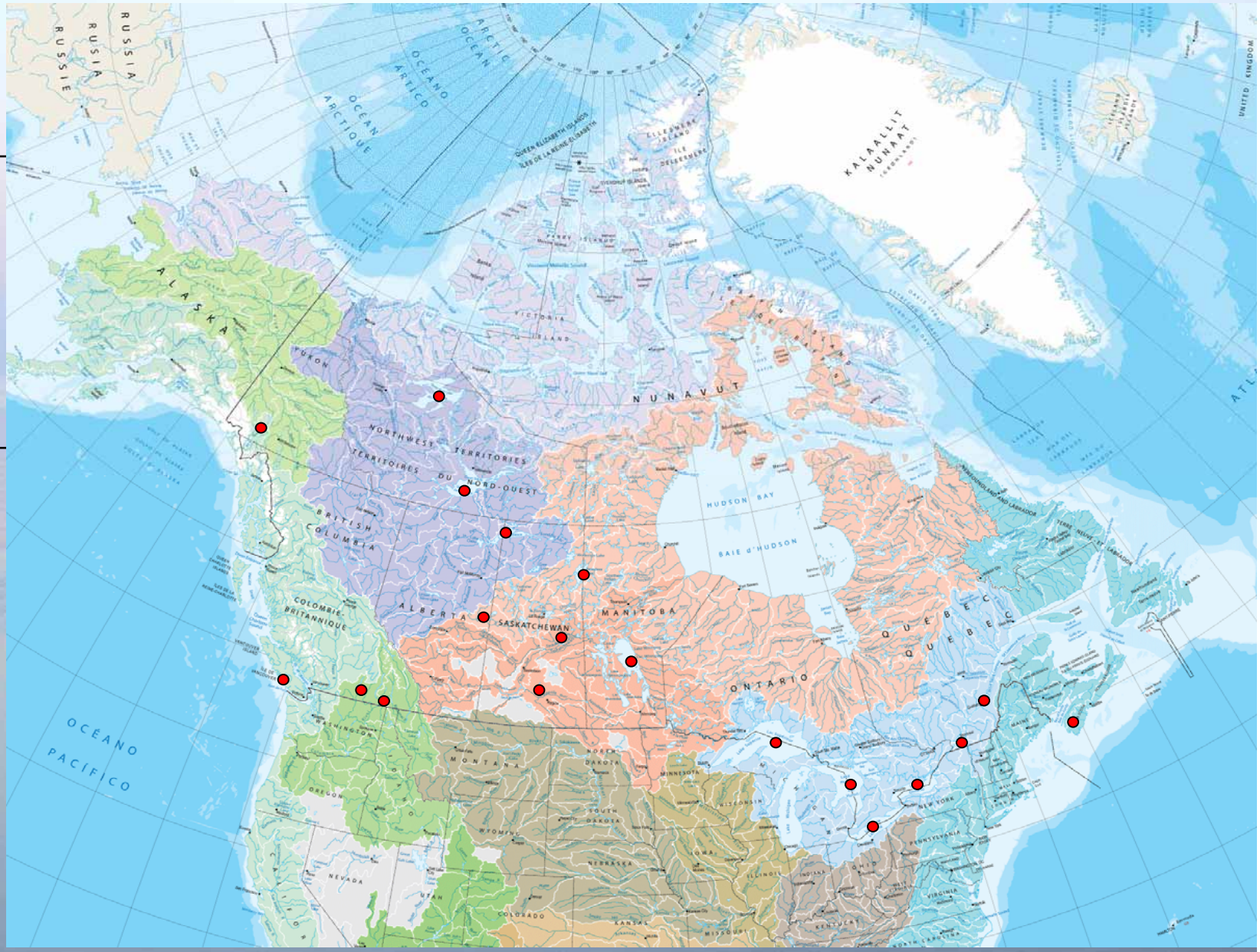
LEGACY-Hg



Temporal trends of mercury (natural log-transformed, µg/g ww) in EC whole-body of 55-65cm lake trout (45-55cm walleye for Erie) collected between 1977 and 2007 from various locations in the Canadian Great Lakes. *P*-value is for statistical significance.

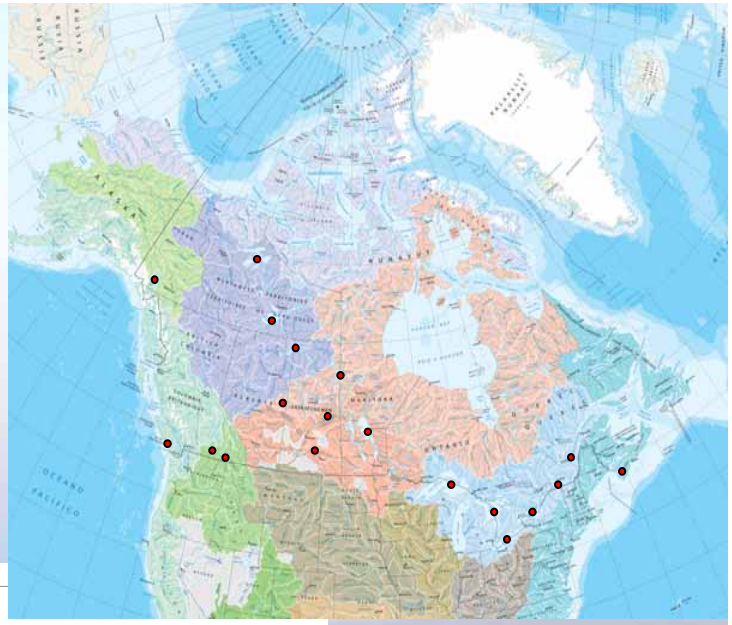
EMERGED

Drainage Basin
Pacific seaboard
Yukon
Columbia
Mackenzie
Hudson Bay
Nelson
St. Lawrence
St. Lawrence
Atlantic Seaboard



Spatial Distributions

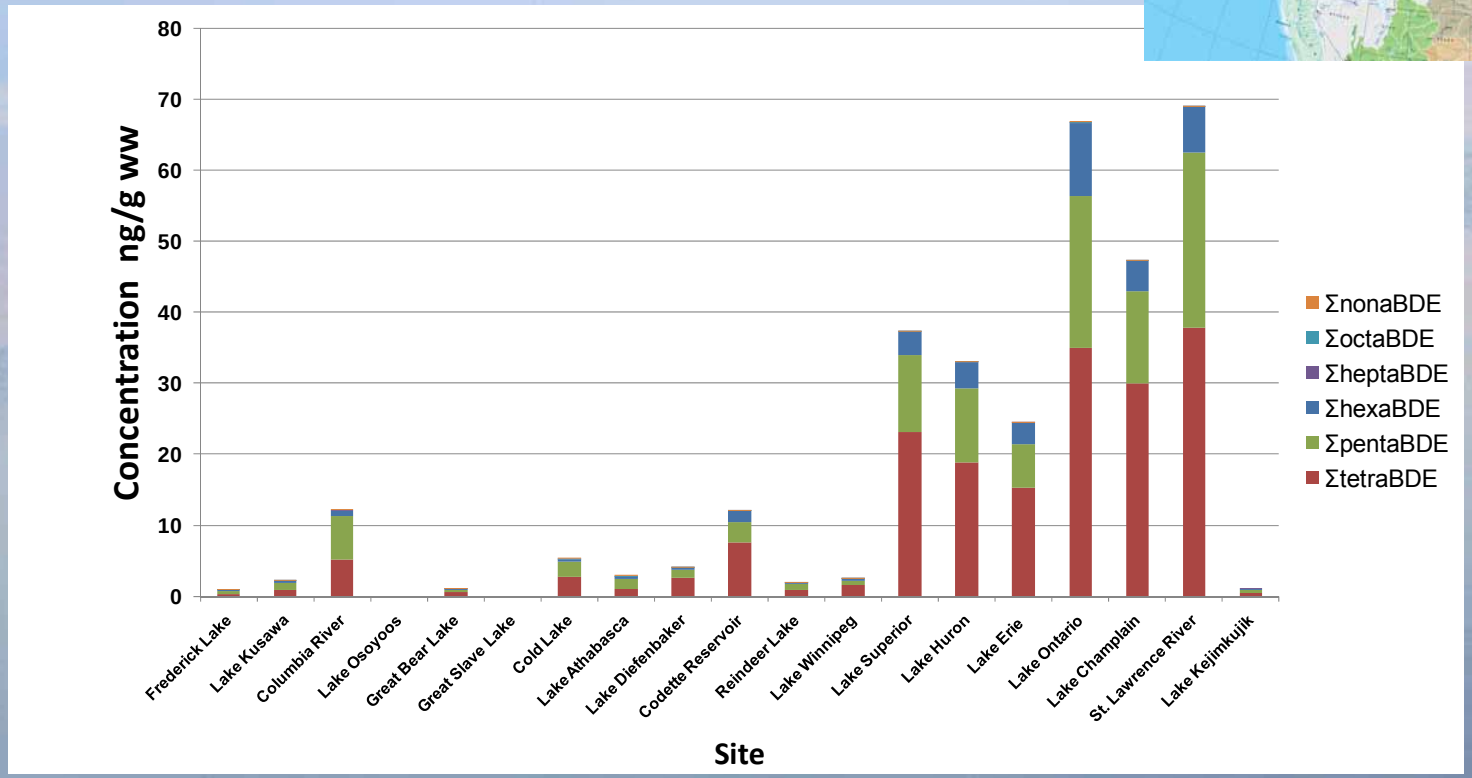
Sum_{46} BDE (-209)



Dominant species include:47,99,100,153,154

Ontario > Superior > Huron > Erie

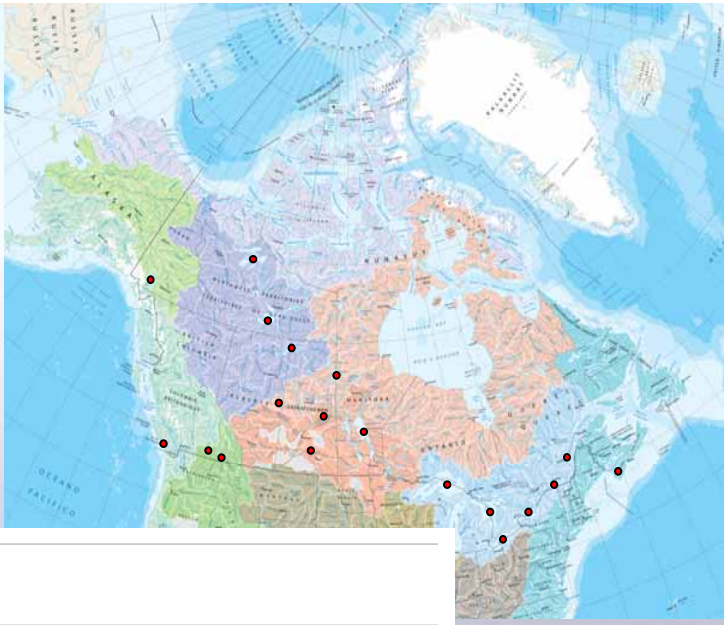
agrees with Luross *et al*. 2002 – 1997 samples

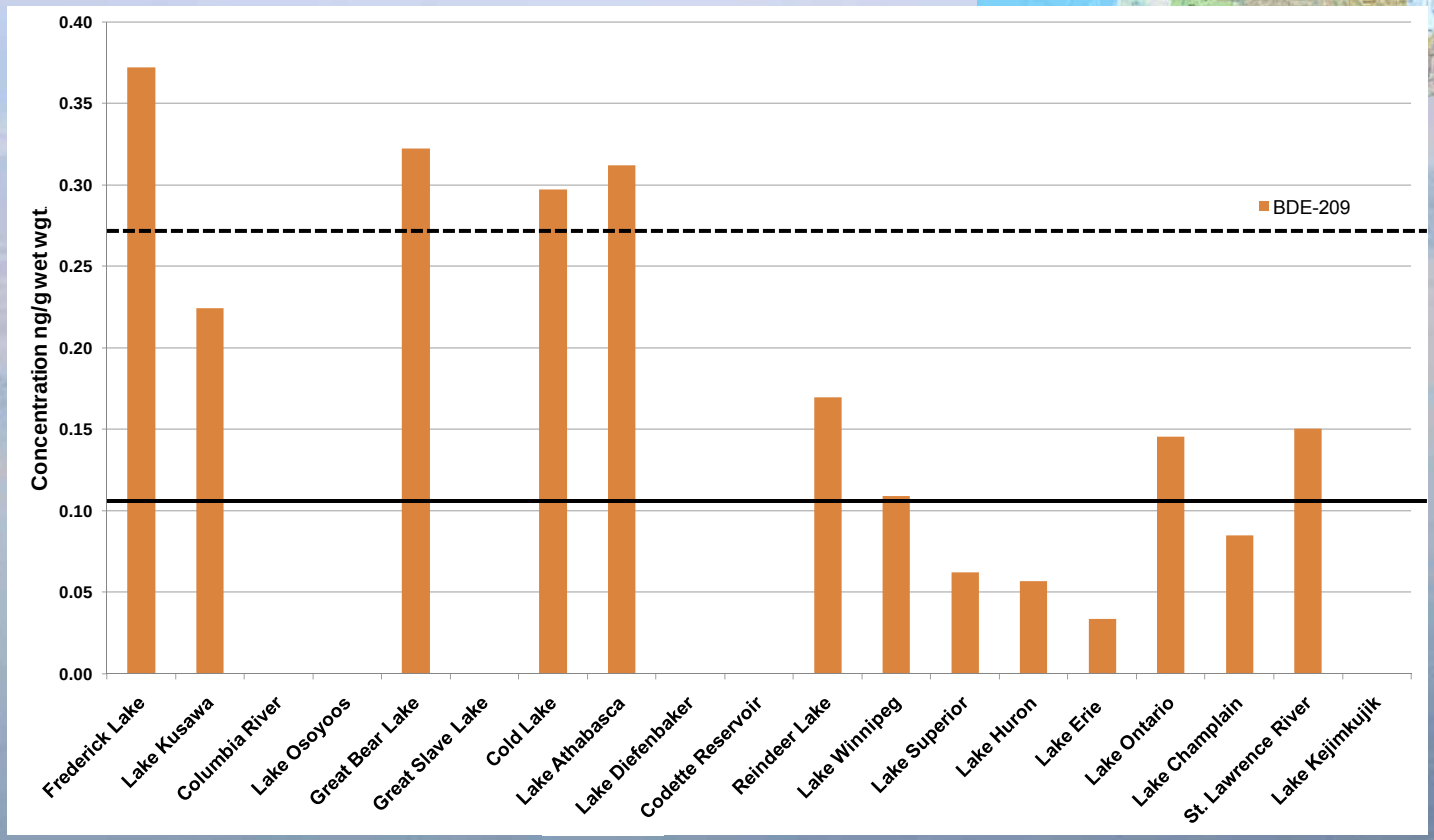


Concentrations of BDE homologues in fish collected from sites in 2007/2008.

Spatial Distributions

BDE-209





n=27

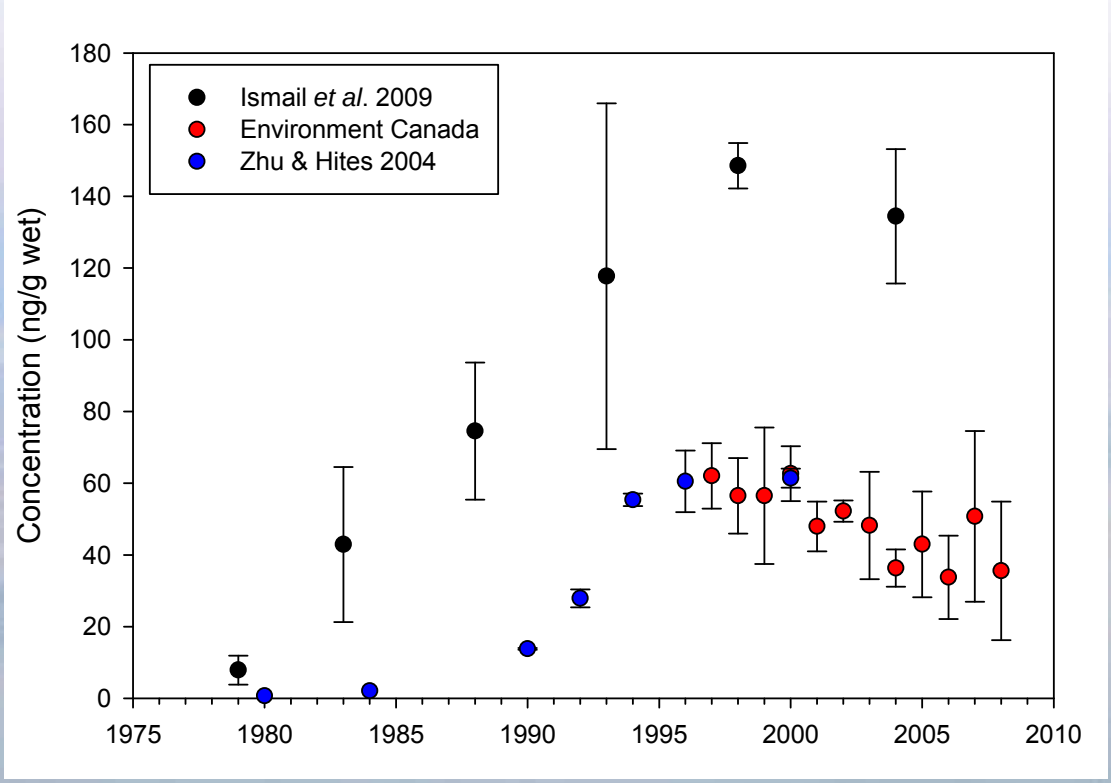
Zhu and Hites, 2004: Blanks 0.14 - 0.34 ng/g wet wgt.

Temporal Trends

- Luross *et al*. 2002
  - HRGC/HRMS
  - Individual fish (n = 10)
  - 1997 only
- Environment Canada
  - AXYS Analytical Services Ltd
  - HRGC/HRMS
  - Individual fish (n = 4-24)
  - 1997–2008 annually
- Ismail *et al*. 2009
  - GC/MS
  - Individual fish (n = 4-5)
  - 1979–2004 ~every 4 years
- Zhu & Hites 2004
  - Environ. Sci. Technol. 38(10): 2779-2784.
  - GC/MS
  - Composites of 5 fish (n = 1-3)
  - 1980–2000 ~every 4 years

Datasets – Lake Ontario

Temporal Trends: BDE-47



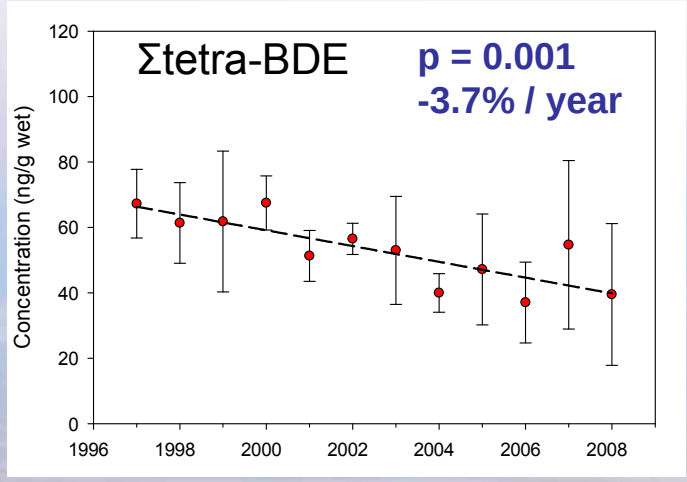
2008 (n = 24)

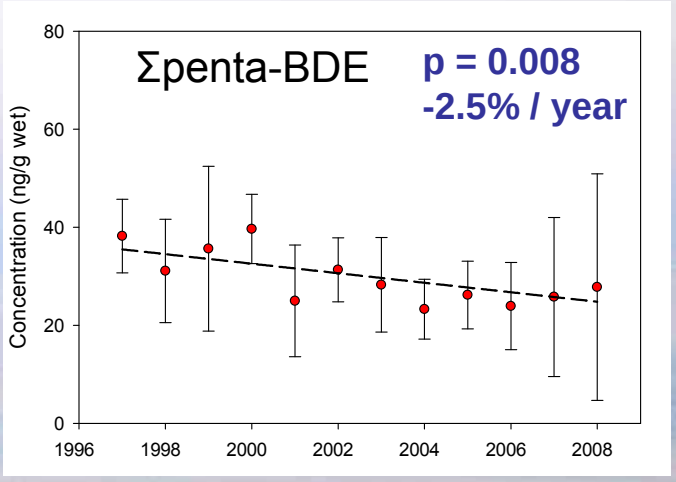
35.6 ± 19.3 ng/g wet

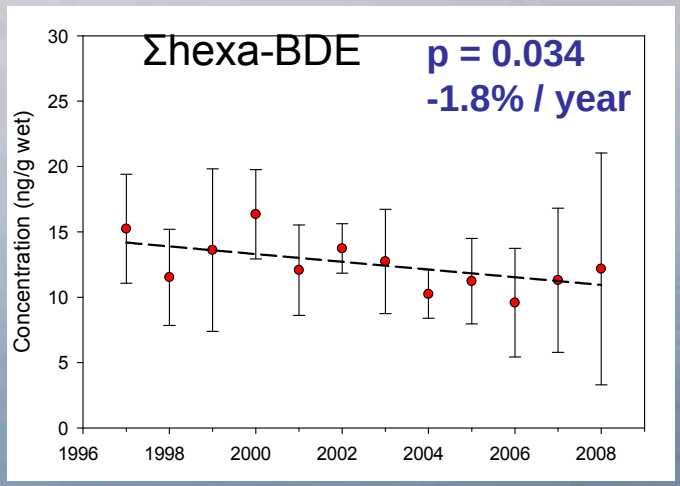
Luross *et al*. 2002: 58 ± 15 ng/g wet (1997)

Lake Ontario

Temporal Trends: Regulated BDEs







All significant declining trends

Lake Ontario

EMERGING

EMERGING


Photo: Fraunhofer IME


Photo: Tjelvar Odsjö

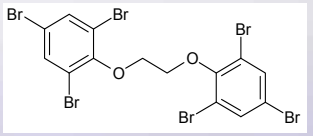
- Formal environmental specimen banks (ESBs) exist in several countries
  - Sweden, Japan, USA, Germany, Italy, others
- 2 within Environment Canada
  - NWRC: “Canadian Wildlife Service Specimen Bank”
  - CCIW: “National Aquatic Biological Specimen Bank (NABSB)”

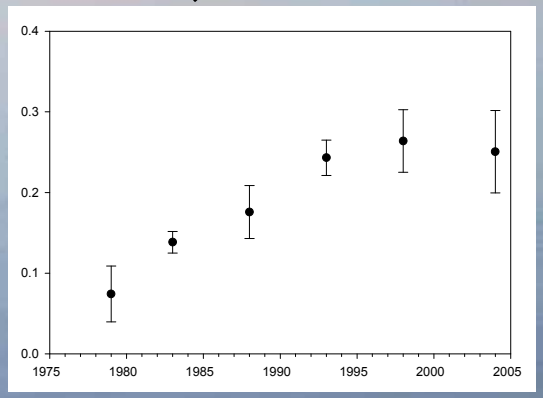
Environmental Specimen Banking

Frozen History

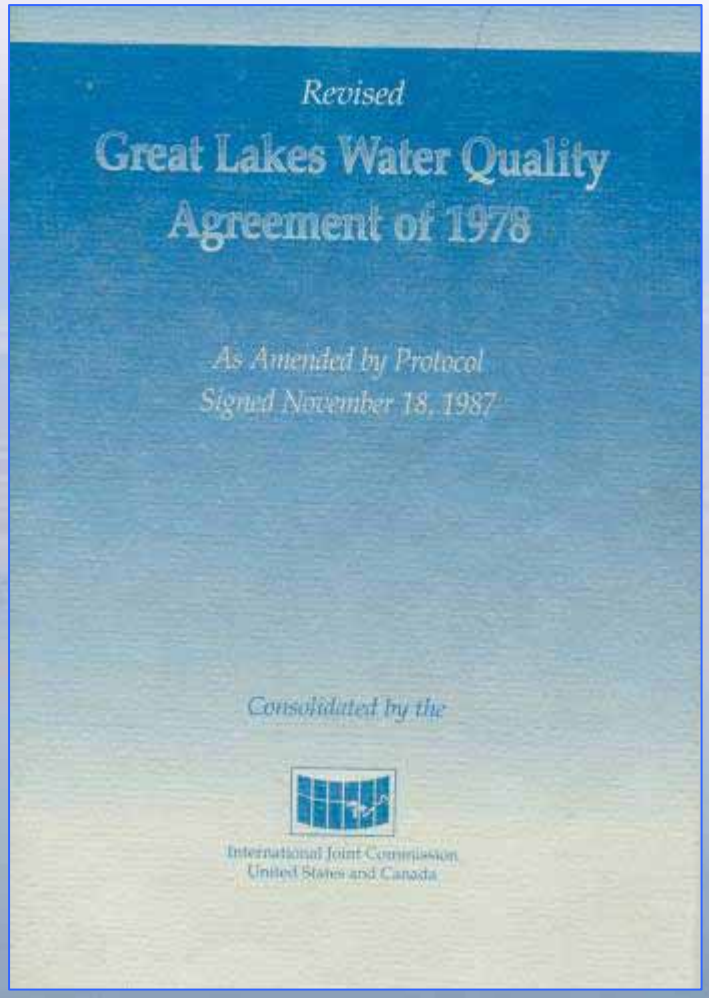
Environmental specimen banks have:

- Many important uses
  - retrospective analyses
    - emerging contaminants
    - food webs changes
- Received increased interest
  - genetic studies
  - deferred analysis of emerging contaminants until budgets improve





Brief History of the NABSB



- Banking of Great Lakes fishes began as a result of the Great Lakes Water Quality Agreement (GLWQA)
  - The Fish Contaminants Surveillance Program (FCSP) – 1977
  - Fish tissues from the FCSP not analyzed are archived - a requirement of GLWQA (Annex 12 Section 5(e)).
- Great Lakes Fisheries Specimen Bank (GLFSB)

Source of Specimens

Great Lakes Fish Contaminants Surveillance Program

Measuring trace metals and trace organics in top predator and forage fishes at approximately 10 locations annually since 1977

Primary target species:

- lake trout and walleye
- rainbow smelt, alewife

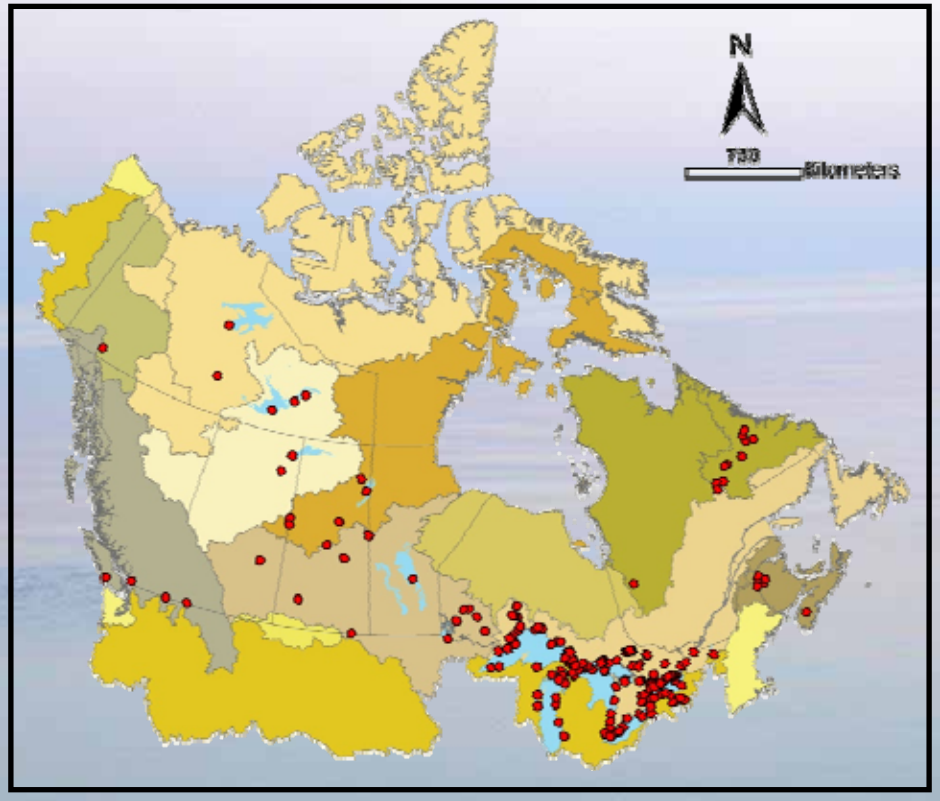
Also:

- *Mysis relicta*, *Diporeia hoyi,* and plankton

Recent additions:

- dreissenid mussels
- round goby

Source of Specimens



Map of Canada showing locations where specimens archived in the NABSB were collected

- Several focused, short term projects targeted on specific threats have contributed samples from across Canada

Examples:

- Toxic Substances Research Initiative (TSRI)
- Chemicals Management Plan (CMP)
- Clean Air Regulatory Agenda (CARA-Hg)

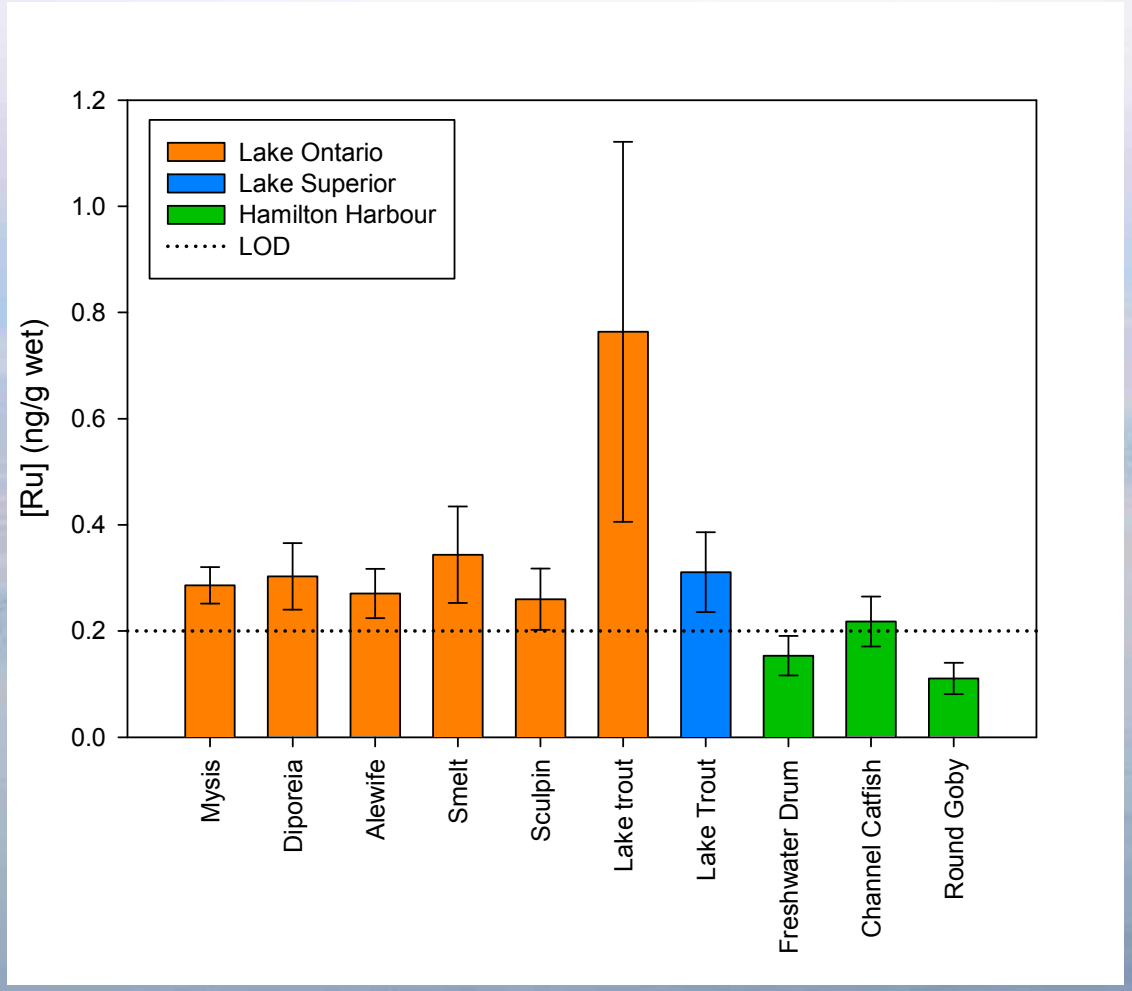
EMERGING

Platinum Group Elements

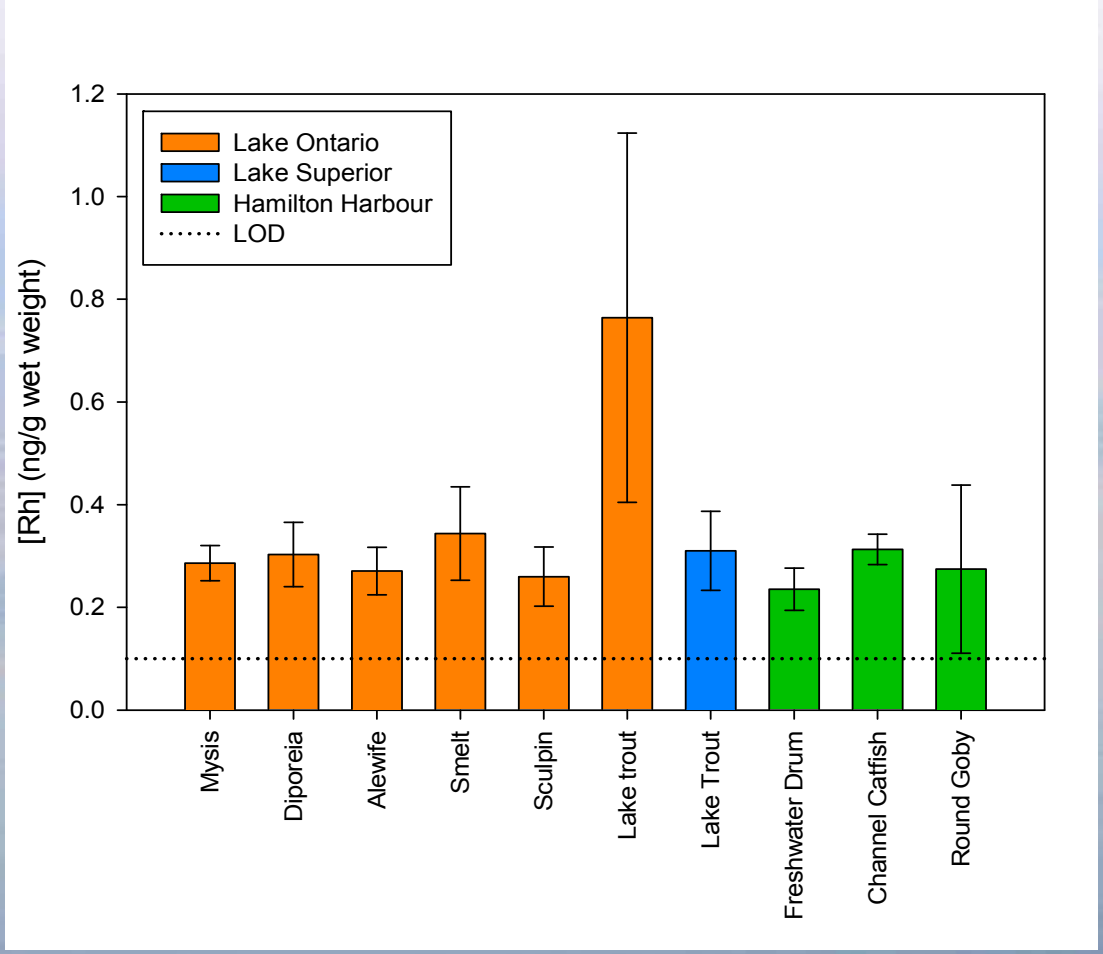
- The following slides present the preliminary results of analyses for platinum group elements (PGEs) in fish tissues from the Great Lakes.

- The graphs present the results of fish and forage species from Lake Ontario (2006), Lake Superior (2006), and Hamilton Harbour (2004).

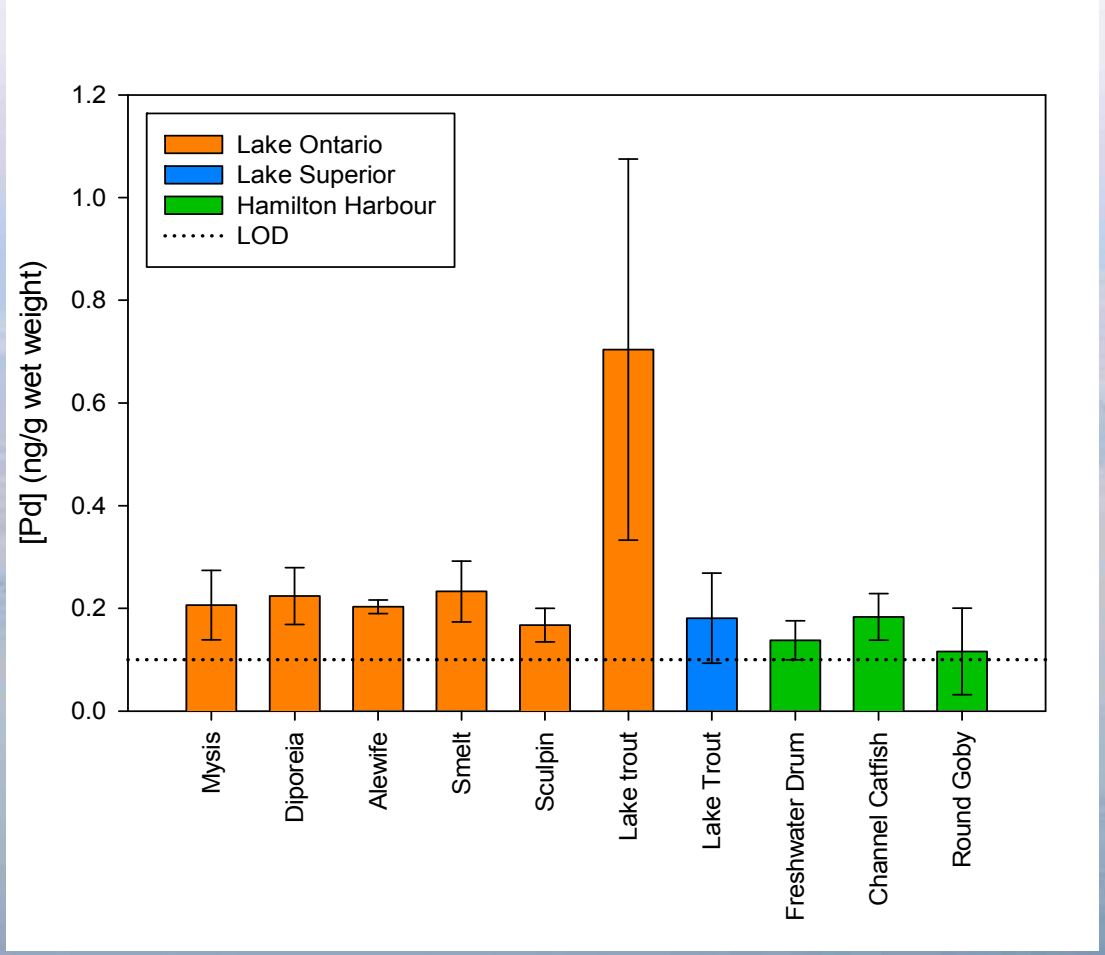
Ruthenium



Rhodium



Palladium



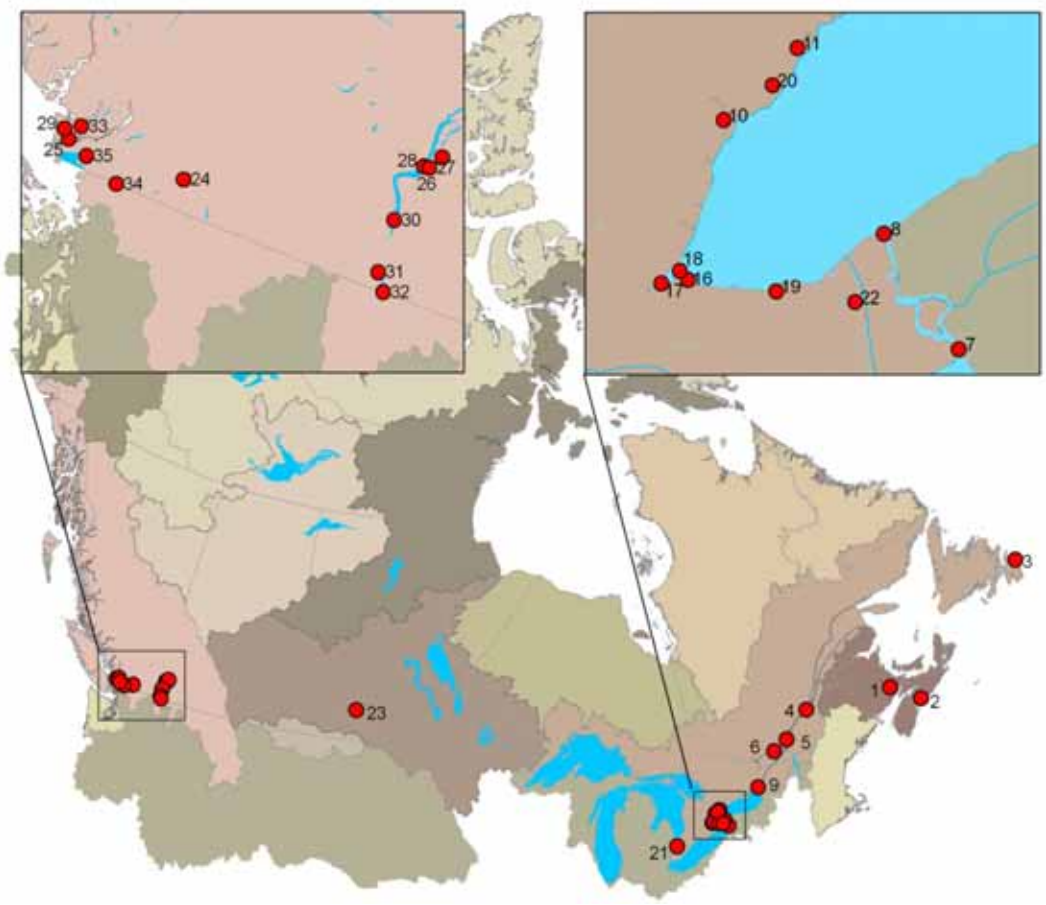
Initial Discussion

- PGE levels in fish are low and close to the detection limit of the analysis – could be due to the analysis of high moisture content samples
- Ir were not detected in any samples
- Pt detected only in lake trout from Lake Ontario and Superior
- Highest concentrations in lake trout from Lake Ontario – Niagara-On-The-Lake
- Lake trout from Lake Ontario are ~ 3-4 times higher than in the forage species.

EMERGING

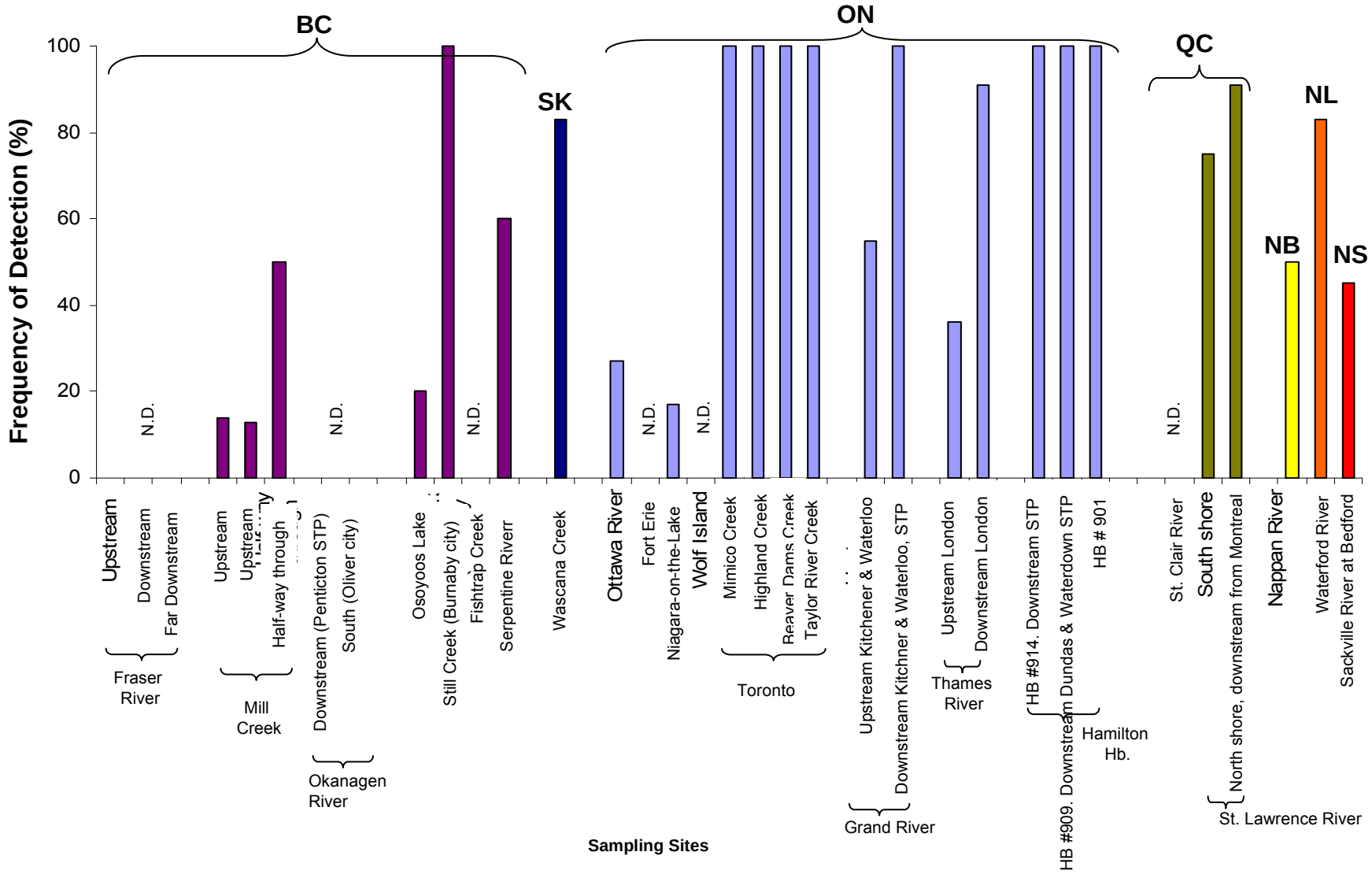
Water

Emerging: BPA Sampling Sites Across Canada

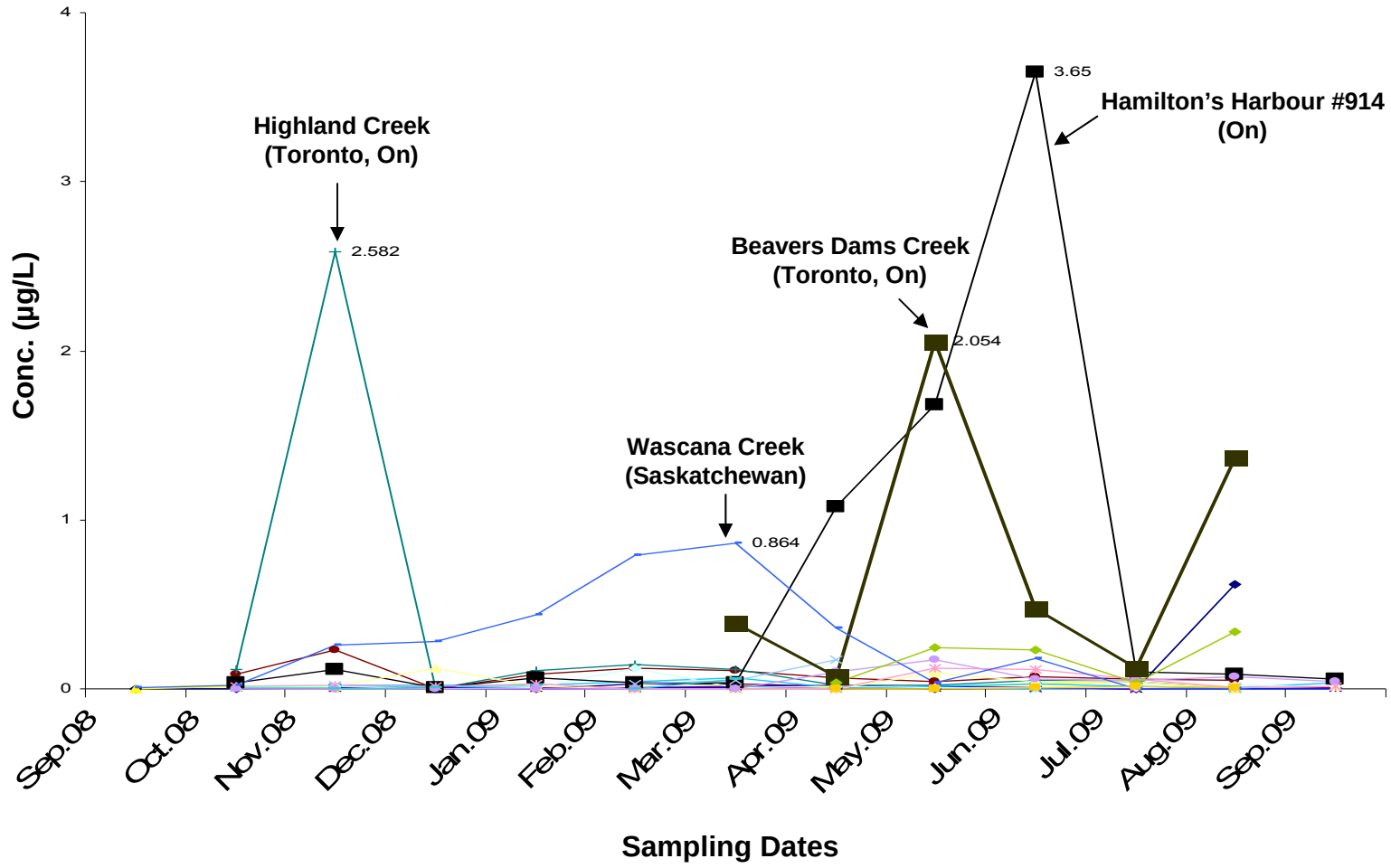


- 35 sampling sites across Canada.
- 290 water samples collected monthly during 2008-2009.
- BPA was detected above detection limit (0.005 µg/L) in 57% of the samples (164 samples).
- The concentration levels were in the low µg/L range.

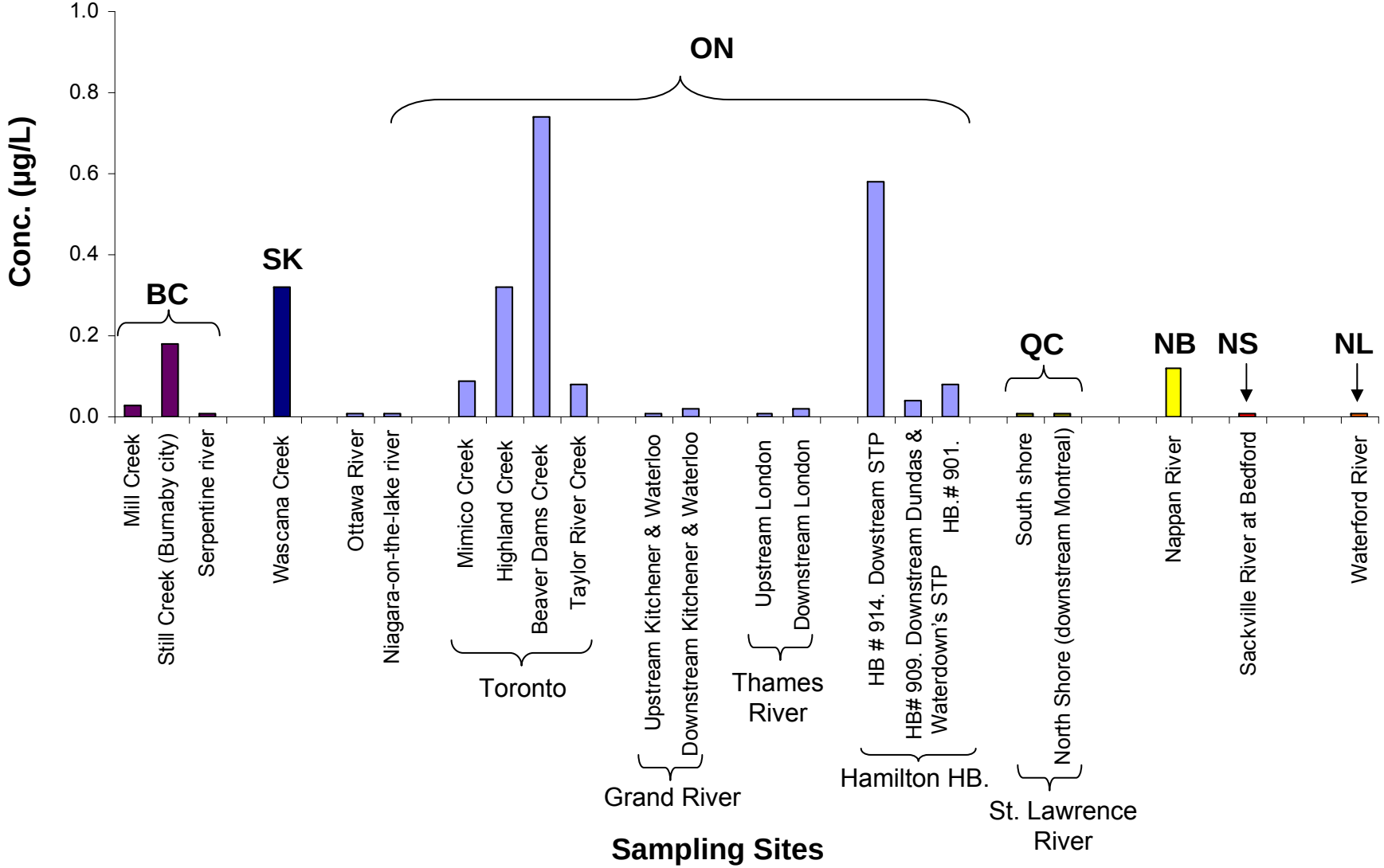
Frequency of Detection of BPA in Freshwater Samples Per Sampling Site During 2008-2009



Monthly Concentrations of BPA in Freshwater Samples Collected Across Canada



Average Monthly Concentrations of BPA in Freshwater Samples Across Canada (2008-2009)



RE-EMERGING

Long Term Trends of Chloride in the Great Lakes

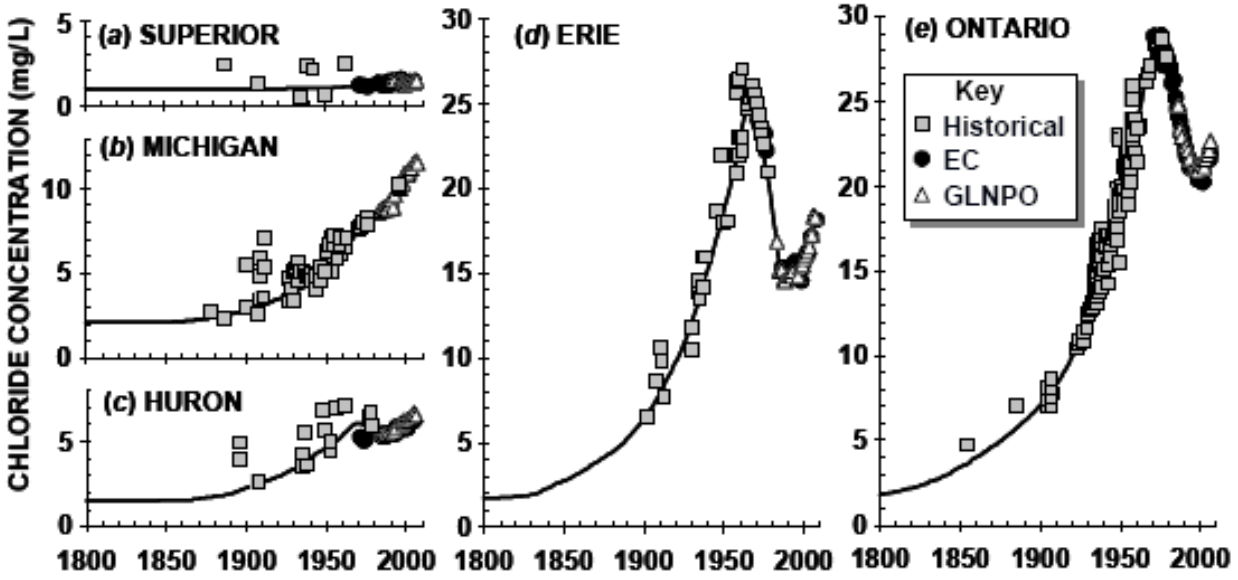


Figure 3 Great Lakes chloride concentration data (mg/L) along with trend lines.

Great Lakes Chloride: Long-Term Mass Balance and Loading Analysis. Steve Chapra, Alice Dove, and David Rockwell. Journal of Great Lakes Research. Volume 35, Issue 2, June 2009, Pages 272-284

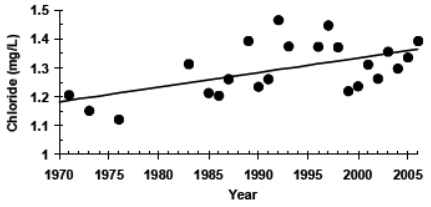


Figure 4 Average annual chloride concentrations for Lake Superior versus year along with a best-fit line determined by linear regression.

Contaminants of Concern

Legacy

Emerged

Emerging

Re-emerging

Thank you!

Beth Murphy
US EPA GLNPO
773-835-0853
murphy.elizabeth@epa.gov

Sean Backus
Environment Canada
905-336-4646
sean.backus@ec.gc.ca