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

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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

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
Tetrabromophthalic anhydride
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 / Fragrances 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
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.
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
<table>
<thead>
<tr>
<th>Drainage Basin</th>
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<tr>
<td>Pacific seaboard</td>
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<td>Yukon</td>
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<td>Mackenzie</td>
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<td>St. Lawrence</td>
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<td>St. Lawrence</td>
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<td>Atlantic Seaboard</td>
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Spatial Distributions

$\text{Sum}_{46} \text{BDE} \ (-209)$

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

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

n=27
Temporal Trends

- Luross *et al.* 2002
  - HRGC/HRMS
  - Individual fish (n = 10)
  - 1997 only

- Ismail *et al.* 2009
  - GC/MS
  - Individual fish (n = 4-5)
  - 1979–2004 ~every 4 years

- Environment Canada
  - AXYS Analytical Services Ltd
  - HRGC/HRMS
  - Individual fish (n = 4-24)
  - 1997–2008 annually

- Zhu & Hites 2004
  - GC/MS
  - Composites of 5 fish (n = 1-3)
  - 1980–2000 ~every 4 years

Datasets – Lake Ontario
Temporal Trends: BDE-47

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

2008 (n = 24)
35.6 ± 19.3 ng/g wet
Temporal Trends: Regulated BDEs

\[ \Sigma \text{tetra-BDE} \quad p = 0.001 \quad -3.7\% / \text{year} \]

\[ \Sigma \text{penta-BDE} \quad p = 0.008 \quad -2.5\% / \text{year} \]

\[ \Sigma \text{hexa-BDE} \quad p = 0.034 \quad -1.8\% / \text{year} \]

All significant declining trends

Lake Ontario
EMERGING
EMERGING

• 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)”
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)
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

- 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)
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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

![Graph showing ruthenium levels in various organisms from different locations.]

- **Lake Ontario**
- **Lake Superior**
- **Hamilton Harbour**

**Organisms:**
- Mysis
- Diporeia
- Alewife
- Smelt
- Sculpin
- Lake trout
- Lake Trout
- Freshwater Drum
- Channel Catfish
- Round Goby

**Units:** [Ru] (ng/g wet)

**Levels:**
- 0.0
- 0.2
- 0.4
- 0.6
- 0.8
- 1.0
- 1.2

**Legend:**
- Orange: Lake Ontario
- Blue: Lake Superior
- Green: Hamilton Harbour
- Dotted line: LOD (Limit of Detection)
Rhodium

[Diagram showing concentrations of Rhodium in different species and locations.]

- Lake Ontario
- Lake Superior
- Hamilton Harbour
- LOD
Palladium

![Pd] (ng/g wet weight)

- Lake Ontario
- Lake Superior
- Hamilton Harbour
- LOD

Species:
- Mysis
- Diporeia
- Alewife
- Smelt
- Sculpin
- Lake trout
- Lake Trout
- Freshwater Drum
- Channel Catfish
- Round Goby
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

- Highland Creek (Toronto, On) - Concentration: 2.582 µg/L
- Wascana Creek (Saskatchewan) - Concentration: 0.864 µg/L
- Beavers Dams Creek (Toronto, On) - Concentration: 2.054 µg/L
- Hamilton’s Harbour #914 (On) - Concentration: 3.65 µg/L

Sampling Dates:
- Sep 08
- Oct 08
- Nov 08
- Dec 08
- Jan 09
- Feb 09
- Mar 09
- Apr 09
- May 09
- Jun 09
- Jul 09
- Aug 09
- Sep 09
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.


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!

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