Emerging Contaminant Monitoring and Surveillance in the Great Lakes

Binational Toxic Strategy
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Strategic Surveillance Plan

• Identify chemicals of concern
  – Chemicals Management Plan – National in scope
  – Pesticides Management Regulatory Agency (PMRA) – National in scope
  – Syracuse Research Corporation/Environment Canada North American Chemical Inventory Screening Project - Great Lakes in scope
  – External Expert Consultation (SETAC NA & Europe)
  – Etc.

• Develop Screening protocols
  – Physical / Chemical Properties
  – Production rates
  – Analyzability
  – Etc.

• General Categories of Emerging Chemicals
  – Siloxanes
  – Non Halogenated compounds (Musks, fragrances, etc.)
  – Halogenated compounds (BR, F, Cl, etc.)
  – Other
Pilot and National CEC Projects

• Pharmaceuticals and Personal Care Products (PPCPs), Hormones, and Alkylphenol Ethoxylates (APEs) in the North Shore Channel of the Chicago River
  – Supplement to NFTS – EPA OW
  – Tissue, effluent, & Stream collections
  – Legacy and CECs

• National River and Stream Assessment
  – EPA OW Sponsored
  – 1200 Urban and rural boatable streams
  – Whole and fillet tissue
  – Legacy and CECs
Great Lakes Monitoring Programs

- Air (Binational IADN)
- Water (EC open lake & Connecting Channels; MOE nearshore)
- Sediment (EC with EPA collaboration)
- Fish (EPA and EC/MOE)
- Wildlife (EC herring gull, mink)
- Cooperative Monitoring & Science
Information exchange through collaboration & binational programs

EC & CMP
- Fish – (EC) Routine + emerging contaminants
- Air – (EC) Routine + emerging contaminants
- Sediment – (EC) Routine + emerging contaminants
- Water – (EC) Routine + emerging contaminants
- Wildlife – (EC) Routine + emerging contaminants

EPA & Syracuse Research Corporation Screening
- Fish – (GLNPO & Clarkson) Routine + emerging contaminants
- Air – (GLNPO & IU) Routine + emerging contaminants
- Sediment – (GLNPO & UIC) Emerging contaminants

BTS Monitoring & Surveillance Project
- Identify potential threats in the Great Lakes
- Priority Setting
- Collaborate with & Inform other agencies and programs

Other Sources: DSL, HPV, TSCA, ToxCast etc.
Emerging Chemicals - Air

- Analyte selection by Environment Canada is driven by CMP priorities
- Analyte selection in US determined by results of peer review and driven by grantee

\[ \text{IADN (air)} \]
- Siloxanes
- PFCs
- PFSAs
- FHETs
- Flame Retardants (PBDE and non-PBDE)

\[ \text{IADN (precipitation)} \]
- PBDEs
- New Flame Retardants
- PFCs
Emerging Chemicals - Water

• Emerging chemicals are measured in the water (dissolved and/or suspended sediment) by Environment Canada as part of their open lake surveillance program (spatial distribution) and the connecting channels monitoring (temporal trends).

• Priorities determined by CMP and needs of Pesticides Management Regulatory Agency

• Ontario Ministry of the Environment Nearshore Monitoring Program

  • Endocrine disruptors
  • In-use pesticides
  • Pharmaceuticals
  • PFOS/PFOA
  • PBDEs
Emerging Chemicals - Sediment

- Emerging chemicals are measured in bottom sediments (spatial distribution) and cores (temporal trends) by Environment Canada: Priorities are determined by CMP.

- In 2008, GLNPO augmented an existing grant to the University of Illinois at Chicago for identification of select emerging chemicals in Great Lakes Sediment Cores. Chemicals are being chosen based upon the SRC work and best professional judgment.

- Dechlorane plus
- BFRs
- PFOS/PFOA
- Chlorinated paraffins
Emerging Chemicals – Fish & Herring Gull Eggs (EC)

- Priorities determined by CMP (PBDEs & other BFRs, PFOS/PFOA, BPA, chlorinated paraffins, PGEs)
- Utilize archived tissue for confirmation and temporal trends
- Collect foodweb samples for bioconcentration/bioaccumulation studies
- Develop method to move emerging contaminants onto routine list
Summary Highlights #1 – PBDEs / BDE-209

43 congeners monitored, 39 quantifiable with frequency bioaccumulation in mothers and in ovo transfer to egg

Spatial trends:
- detectable in egg from all sites in the early to mid-1990s
- reflect site-specific diet, e.g., aquatic vs. terrestrial?
- northern Great Lakes sites highest concentrations, Agawa Rocks and Gull Is. (L. Michigan) - post-breeding migrations/overwintering in south L. Michigan

Temporal trends:
- dramatic changes in levels and patterns
- conc. doubling times: BDE-209 > Br₉ > Br₈ > lesser brominated BDEs
- pattern shift to Br₅, Br₉ and BDE-209

Slide provide by Dr. Rob Letcher, Dr. Craig Hebert, & Dr. Chip Weseloh
Summary Highlights #2 – non-PBDE BFRs

- HBB, BTBPE, DBDPE, β-TBEC; low ppb w.w. regardless of site or collection year
- HBCD and for some sites and years DBDPE, at levels comparable/surpassing BDE-209
- bioaccumulation in mother and in ovo transfer to egg
- numerous BFR (and degradation products) unidentified
- BFR exposure underestimated; thermally liable (and thus non-GC) substances in eggs?

Temporal and spatial trends:
- detectable in egg from all sites going back 25 years
- site-dependent trends – reflect diet and food web shifts, e.g., aquatic vs. terrestrial diet?
- northern Great Lakes sites highest concentrations, Agawa Rocks (L. Superior) and Gull Is. (L. Michigan) - post-breeding migrations/over-wintering in south L. Michigan
- recent exposures, e.g., DBDPE, increasing trends?
- fate: degradation of higher brominated BFRs

Overall: BFR and degradation products and DP exposure and/or accumulation in Great lakes food web and ultimately in herring gulls is becoming increasingly more complex and of growing concern

Letcher, et. Al
Emerging Chemicals – Fish (U.S.)

• Use GLFMP steering committee to help identify emerging contaminants for analysis in whole fish
  – Develop an integrated approach to screening emerging chemicals
• Utilize archived tissue for confirmation
• Collect sport fish if necessary
• Develop method to move emerging contaminants onto routine list
• Inform and collaborate with other Federal and State programs
Preliminary Results for
GLFMP Chemical Screening

- GC/MS scan for chemicals in a large Lake Trout Sample from Lake Michigan:
  - PCBs, DDE
  - Other organochlorine pesticides (chlordane, nonachlor, dieldrin, etc.)
  - Toxaphene, polychlorinated diphenyl ethers (PCDEs)
  - PBDEs
  - Chlorinated tertphenyls

Data provided by Clarkson et. Al
Program Collaboration & Integration

- Harmonizing binational programs based upon similar criteria in an effort to avoid duplication and to provide effective and efficient programs.

- Bisphenol A
- Chlorinated paraffins
- Siloxanes
- PFCs
- PFSA & Sulfonamides
- Non PBDE BFRs

- Non BR flame retardants (Dechlorane plus)
- PBDE BFRs
- Linear saturated fluorotelomer alcohols (FHETs)
- Linear fluorotelomer unsaturated acids (FTUCAs)

- HHCB (Galaxolide)
- AHTN (Tonalide)
- ADBI (Celestolide)
- AHMI (Phantolide)
- ATII (Traseolide)
- Musk Xylene
- Musk Ketone
- methyl triclosan
Challenges

• Access to analytical standards
• Access and Quality of archived tissue
• Method development
• $$$
• Changing political climate
• Pioneering in the field
Thank you

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