Non-Target and Post-Target Analysis of Emerging Halogenated Contaminants in American and European Eels

Jonathan D. Byer[1], Grazina Pacepavicius[2], Peter V. Hodson[3], Claude Belpaire[4], David Alonso[1], Joe Binkley[1], Mehran Alaee[2]

[1]LECO Corporation, Saint Joseph, MI, USA | [2]Aquatic Contaminants Research Division, Environment Canada, Burlington, ON, Canada | [3]Queen's University, Kingston, ON, Canada | [4]Research Institute for Nature and Forest, Groenendaal-Hoeilaart, Belgium

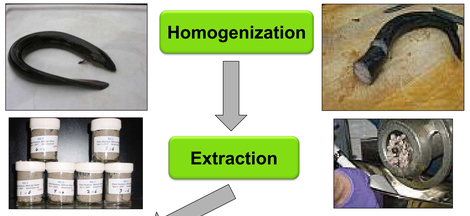
Introduction

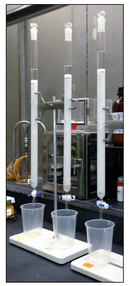
Time-of-flight mass spectrometers (TOFMS) have gained popularity over scanning instruments for non-target and post-target analysis because:

- Full mass range spectra are acquired
- High acquisition rates can be achieved (>200 spectra/s)
- Minimal mass bias
- Spectral deconvolution using modern software

In this study, we used non-target analysis to determine the occurrence of lipophilic halogenated contaminants in American and European eel (*Anguillid sp.*) not previously identified by traditional target analysis.

Methods



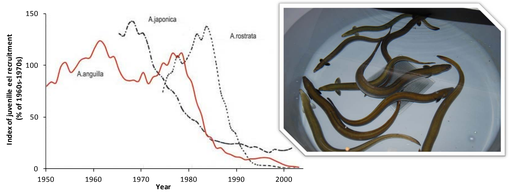


LECO Pegasus® GC-HRT

Mass spectra collected in EI mode with mass range m/z = 45-1000 and resolving power >25, 000 for m/z = 218.9856.

Background

- **American eel** are listed as a **threatened species** by the Committee on the Status of Endangered Wildlife in Canada.
- **European eel** are considered **critically endangered** by the IUCN Red List of Threatened Species.



Dekker, W., *Fisheries* **2003**, 28, (12), 28–30.

- Bioaccumulation of halogenated chemical contaminants has lead to a reduction in spawner quality and may be related to recruitment decline.

Objective: To identify halogenated contaminants in eels using high resolution TOFMS that are not routinely monitored.

Results

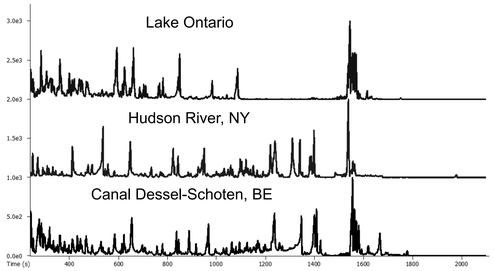
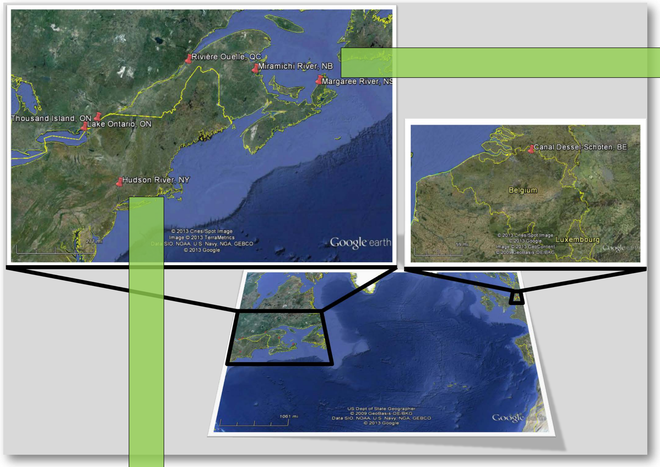


Figure 1. Analytical ion chromatograms for pooled eel extracts from Lake Ontario, Hudson River, and Canal Dessel-Schoten.

- Fish from these sample locations are historically contaminated with polychlorinated biphenyls (PCBs; RT 1000-1800s), and other legacy halogenated persistent organic pollutants .
- The AICs show that there are spatial differences in the chemical contamination profile of eels among these sampling sites, particularly between retention times 1200-1400 seconds.

Figure 2. Map of American and European eel sampling locations in 2008.



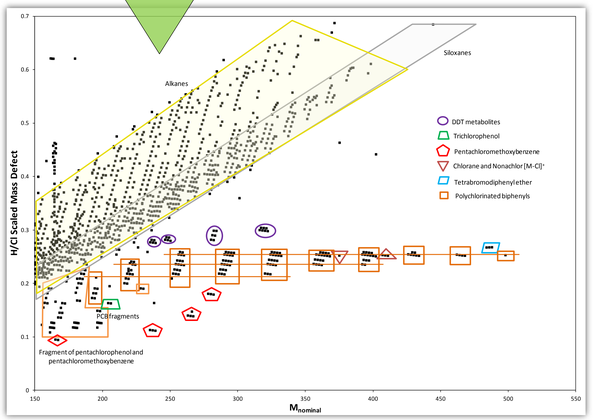


Figure 3. H/Cl Scaled Mass Defect Plot for Hudson River eels showing typical legacy halogenated contaminants and their breakdown products.

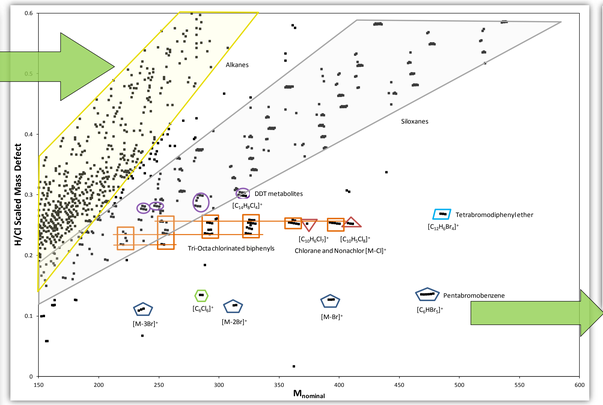


Figure 4. H/Cl Scaled Mass Defect Plot for Miramichi, NB eels shows unique features corresponding to pentabromobenzene.

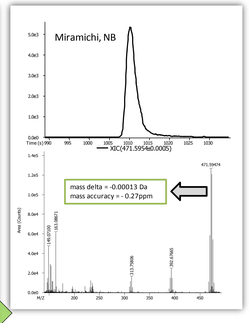


Figure 5. XIC and mass spectrum of pentabromobenzene with mean mass accuracy of base peak ion cluster; not in the NIST 11 mass spectral library.

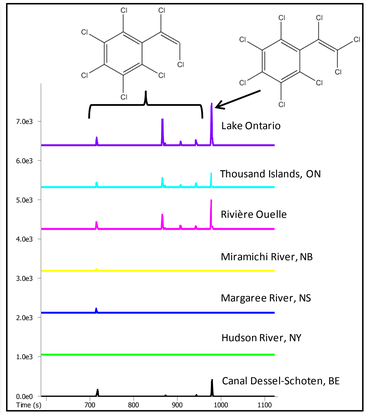


Figure 6. XICs for octa- and heptachlorostyrenes (379.7449+343.7868, respectively) for all seven sampling sites.

Table 1. Mass measurements for base peak of molecular ion clusters show good mass accuracy values.

Name	Formula	Expected	Observed	Mass Delta (Da)	Mass Accuracy (ppm)
Pentabromobenzene	C_6HBr_5	471.5949	471.5948	-0.0001	-0.27
Octachlorostyrene	C_8Cl_8	379.7444	379.7441	-0.0003	-0.80
Heptachlorostyrene	C_8HCl_7	343.7863	343.7859	-0.0004	-1.18
Pentachloroanisole	$C_7H_3Cl_5O$	279.8592	279.8591	-0.0001	-0.24
Trichlorophenol	$C_6H_3Cl_3O$	195.9244	195.9245	-0.0001	-0.08

Conclusions

- H/Cl scaled mass defect plots were an effective tool for identifying halogenated compounds in these eel samples.
- A series of non-legacy chlorinated styrenes, as well as brominated aromatics that were formerly unknown were identified in these samples.
- The LECO Pegasus GC-HRT demonstrated mass accuracy of ~1 ppm or better for a number of halogenated compounds.

Thank you to contributors from Queen's University and Environment Canada for their support.

Environment Canada Environnement Canada

Canada