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Qualitative analysis of halogenated organic contaminants in American eel by gas chromatography/time-of-flight mass spectrometry

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ABSTRACT

Target compound analysis with scanning mass spectrometers such as quadrupole or magnetic sector instruments is used extensively in environmental chemistry because of the selectivity, sensitivity, and robustness. Yet, target compound analysis selectively ignores the majority of compounds present in a sample, especially in complex matrices like fish. In this study, time-of-flight mass spectrometry was used to screen for and identify halogenated compounds in American eels (*Anguilla rostrata*). Individual and then pooled eel samples were analysed using electron ionization and electron capture negative ionization (ECNI) modes. Eels were differentiated by principal component analysis of chemical profiles and were grouped corresponding to their capture location, all with a single instrument injection per sample. Bromine containing compounds were further investigated by taking advantage of the selectivity of ECNI by utilizing the Br^- ion m/z 79 and 81. A total of 51 brominated compounds were detected and their identities were attempted by authentic standards, library searching, and/or chemical formula prediction based on accurate mass measurements. Several PBDEs were identified in the samples, and the majority of the non-PBDEs identified were bromophenols, bromoanisoles, and bromobenzenes. These classes of compounds are synthesized for use in flame retardant production either as intermediates or as final products. However, their occurrence in eels was most likely the result of metabolism or break-down products of high production volume flame retardants like polybrominated diphenyl ethers and bromophenoxy compounds.

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1. Introduction

American eel (*Anguilla rostrata*) is a catadromous, semelparous species that spawns in the Sargasso Sea. Offspring migrate up the Atlantic coast of North America and into continental waters where they often reside in less than pristine environments. In Canada, eels are native to rivers and lakes of Ontario, Quebec, and all of the Atlantic Provinces (COSEWIC, 2012). Eels are primarily benthic, long-lived, and fatty fish, and accumulate lipophilic persistent organic pollutants (POPs). As a result, they are an ideal species to investigate local sources of pollution like halogenated POPs (Hodson et al., 1994; Ashley et al., 2003, 2007).

A variety of targeted halogenated POPs were reported in eels captured at seven locations in eastern Canada (Byer et al., 2013a,b). Eels were differentiated using principal component analysis by their chemical profiles which related to local sources of pollution. The groupings corresponded to sampling location for the most part; however, migrating eels were also identified using specific chemical traces such as mirex. The groupings were also influenced largely by concentrations of legacy chlorinated POPs, and may have obscured possible groupings of less abundant brominated compounds.

Target analysis is excellent for providing sensitive and selective results for known compounds. Instruments that use chromatographic separation coupled to mass spectrometry (MS), such as gas chromatography–quadrupole MS (GC–MS) or high-resolution magnetic sector MS (GC–HRMS) and liquid chromatography–triple quadrupole MS (LC–MS/MS), are popular choices for target analysis of environmental samples. However, by design, target analysis

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filters out all ions not corresponding to the target analyte(s), making it inappropriate for new compound identification. Time-of-flight mass spectrometers (ToF-MS) have gained popularity over scanning instruments for screening applications (non-target and post-target analysis) because full mass range spectra are acquired, and high acquisition rates can be achieved (500 spectra/s) with minimal mass bias (Cervera et al., 2012; Mastovska and Lehotay, 2003). This provides a number of advantages, including the opportunity to deconvolve chromatographic interferences with modern software, which enhances the ability to isolate and identify a greater number of compounds. Screening approaches for halogenated POPs by GC–ToF-MS have proven effective at identifying non-target compounds in environmental samples (de Vos et al., 2011; Haglund et al., 2013). In the present study, two main research questions were addressed: Can we achieve a spatial resolution using qualitative comprehensive analysis by GC–ToF-MS similar to that reported previously with targeted analysis (Byer et al. 2013a,b)? Are there other local sources of halogenated organic contaminants in eels, specifically brominated compounds? The former was investigated by the principal component analysis of eel data acquired by GC–ToF-MS to differentiate sample location based on chemical profile. The latter was answered by non-target analysis with peak identification and mass spectral characterization, and post-target analysis by accurate mass searching for lipophilic brominated compounds known to be in commerce.

2. Experimental

2.1. Sample collection

A total of 60 eels were collected from seven locations in eastern Canada, from the Bay of Quinte, Lake Ontario to the Margaree River, Nova Scotia in 2007 and 2008 (Table 1). Sampling specifics were detailed elsewhere (Byer et al., 2013a). Whole fish homogenates were prepared according to standard laboratory practices outlined by Kiriluk et al. (1997), less 10% of the muscle for other analysis, the liver, and sagittal otoliths. Homogenates were stored at −80 °C in Environment Canada's National Aquatic Biological Specimen Bank and Database until chemical extraction.

2.2. Extraction and fractionation procedure

About 20 g of whole fish homogenate for each fish was dried chemically with anhydrous sodium sulfate, spiked with $^{13}C_{12}$-2,2′,3,3′,4,4′,5-heptachlorobiphenyl (CB-170) and 2,3,7,8-[$^{37}Cl_4$]-tetrachlorodibenzo-*p*-dioxin, and extracted with dichloromethane. About 2 g wet weight equivalent (ww eq) was used for gravimetric lipid determination, 5 g ww eq was used for legacy contaminant analysis (Byer et al., 2013a), another 5 g ww eq was used for dioxin-like compounds analysis (Byer et al., 2013b), leaving about 8 g ww eq for other analyses. To screen for emerging halogenated hydrophobic contaminants, bulk lipids were removed from about 40% (3.2 g ww eq) of the back-up fraction by gel permeation chromatography. No other clean-up was done on these fractions before they were concentrated to a 100 μL final volume. Individual samples were considered first ($n = 60$), then pooled by capture location for instrumental analysis ($n = 7$).

2.3. Instrumental analysis

Sample extracts were introduced into a GC/ToF-MS using a CTC Combi Pal autosampler through a Gerstel CIS-4 PTV injection port (Linthicum, MD). Gas chromatographic separation was performed using an Agilent 7890 GC equipped with a 30 m Restek Rxi-XLB column, 0.25 mm i.d., 0.25 μm film thickness (Bellefonte, PA). Oven temperature program was: initial temperature 100 °C, held for 2 min, raised to 325 °C at 10 °C min^{-1} and held for 19.5 min with a transfer line temperature of 280 °C. The accurate mass GC/ToF (Waters GCT Premier) was operated in both electron capture-negative ionization (ECNI) and electron ionization (EI) modes with an electron energy of 70 eV. For ECNI, a rhodium filament was used with a source temperature of 150 °C, and for EI, a tungsten filament was selected with a source temperature of 200 °C for library searching. Mass spectra were acquired between $m/z = 45$ and 800 Da, with a resolution >7000 at full width at half maximum using continuum and dynamic range enhancement (centroid). The acquisition rate was 0.30 s per scan with an interscan delay time of 0.05 s, which enabled the recording of about 7–10 data points per chromatographic peak.

2.4. Data processing

Mass spectral data were accurate mass corrected using perfluorotributylamine (PFTBA) ions as references. The processing software used was Waters MassLynx 4.1, which included ChromaLynx and MarkerLynx (Milford, MA). ChromaLynx identified unique peaks in the acquired data based on m/z and retention time called features, and where possible the National Institute of Standards and Technology (NIST) AMDIS_32 software was used for deconvolution. MarkerLynx facilitated comparative data analysis among samples based on features with unique retention times and exact masses that were peak aligned and normalized called markers. These markers were subject to principal component analysis to differentiate samples. Markers were defined over the mass range $m/z = 45$–800 Da and chromatographic run time from 7 to 45 min, with a minimum peak height more than 10% of the base peak. Markers identified in the loadings plot that had a significant degree of variance from the origin ($p > 0.05$), and thus, contributed to the differentiation among samples, were subsequently subjected to compound identification.

2.5. Method for compound identification

The retention time and exact mass information for the differentiated markers from MarkerLynx were used to generate a list of potential compounds for identification. Identities of these compounds were first compared against a list of previously targeted contaminants. Accurate mass data of the remaining unknown compounds were used to calculate possibly elemental compositions,

Table 1
Summary of American eel sample collection in eastern Canada.

Capture location	Acronym	Number	Coordinates
Margaree River, NS	NS	10	46°25.20′N 61°05.27′E
Miramichi River, NB	NB	10	47°02.44′N 65°27.04′E
Rivière du Sud-Ouest, QC	RSO	4	48°20.40′N 68°46.27′E
St. Lawrence estuary, Kamouraska, QC	KAM	5	47°34.00′N 69°51.58′E
St. Lawrence estuary, Rivière Ouelle, QC	RO	11	47°25.48′N 70°01.11′E
St. Lawrence River, Thousand Island, ON	SLR	10	44°26.98′N 75°49.24′E
Prince Edward Bay, Lake Ontario, ON	LO	10	43°57.01′N 76°58.01′E

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