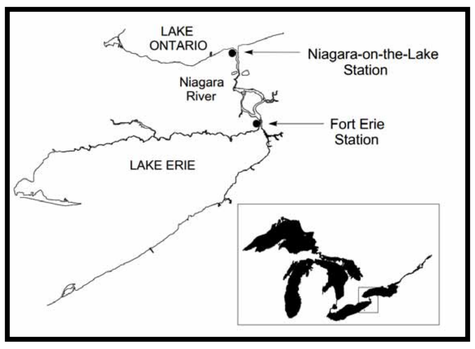
Characterization of Persistent Organic Pollutants in Suspended Sediments by Thermal Desorption Coupled to GC×GC-TOFMS

Jonathan D. Byer[1], Brad Hill[2], and Joe Binkley[1]
[1]LECO Corporation, St Joseph, MI, USA | [2]Water Quality Monitoring and Surveillance, Environment Canada, Burlington, ON, Canada

Background

- The Niagara River is the primary inflow to Lake Ontario, connecting the lower Great Lakes, and historically receives significant inputs of chemical contaminants from Niagara Falls, NY; i.e., the Love Canal dumpsite.
- Environment Canada has been monitoring the occurrence of persistent organic pollutants (POPs), such as polycyclic aromatic hydrocarbons (PAHs), entering Lake Ontario via the Niagara River since 1984, upstream at Fort Erie and downstream at Niagara-on-the-Lake.
- 21 PAHs are monitored routinely, including two alkyl PAHs, as well as several organochlorinated compounds, PCBs, and industrial byproducts.
- The objectives of this study were: (1) to screen for other POPs not monitored routinely, and (2) to minimize the need for wet chemistry clean-up prior to instrumental analysis.

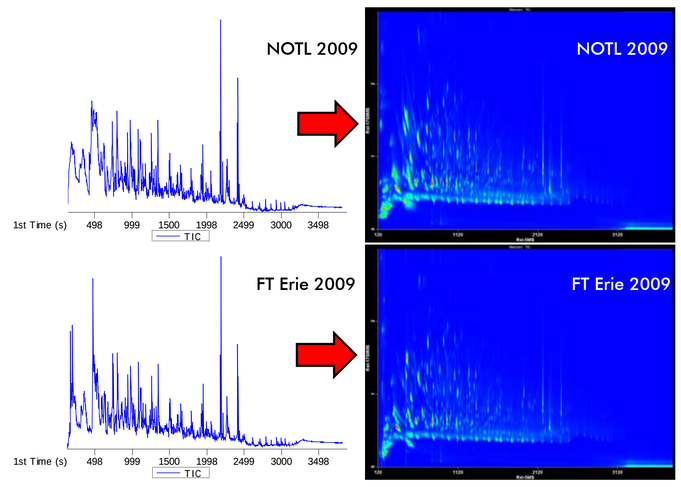


Methods

- About 20 mg of homogenized suspended sediment was thermally desorbed from 50°C to 300°C at 100°C, using a CDS Analytical pyroprobe 5200.
- Analytes were transferred directly to the GC inlet and held for 5 minutes at 35°C before ramping at 5°C to 320°C.
- Column configuration: Restek Rxi-5MS 30 m x 0.25 mm x 0.25 µm; Rxi-17SilMS 1.5 m x 0.25 mm x 0.25 µm; 3 s modulation period.
- Pegasus 4D: 45 to 1000 m/z at 200 spectra/s.

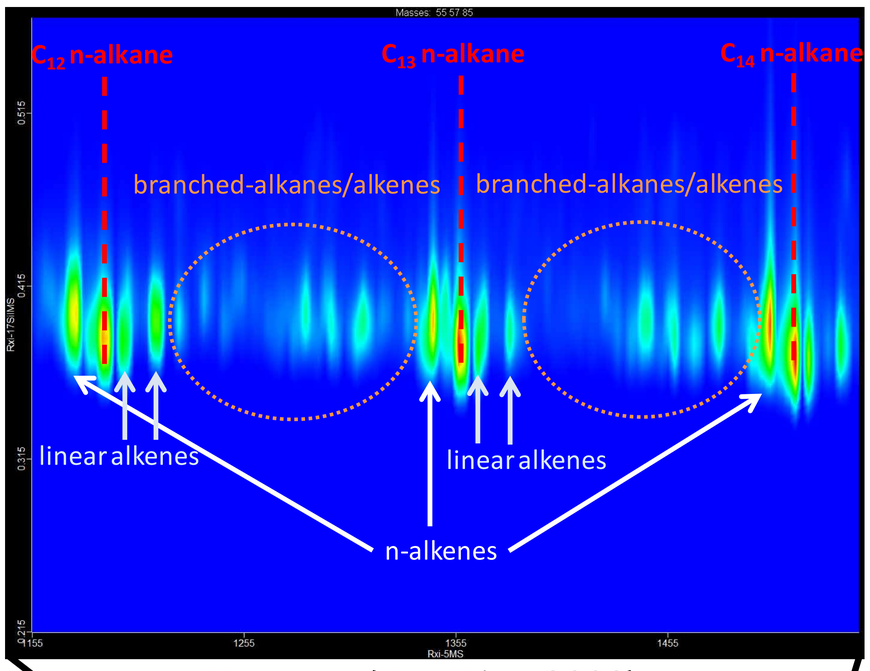
Summary

- Thermal desorption coupled to GC×GC-TOFMS was an effective tool for enhancing the number of compounds identifiable in suspended sediment without wet chemistry.
- Identified >100 additional PAHs and alkyl-PAHs than the list currently monitored.

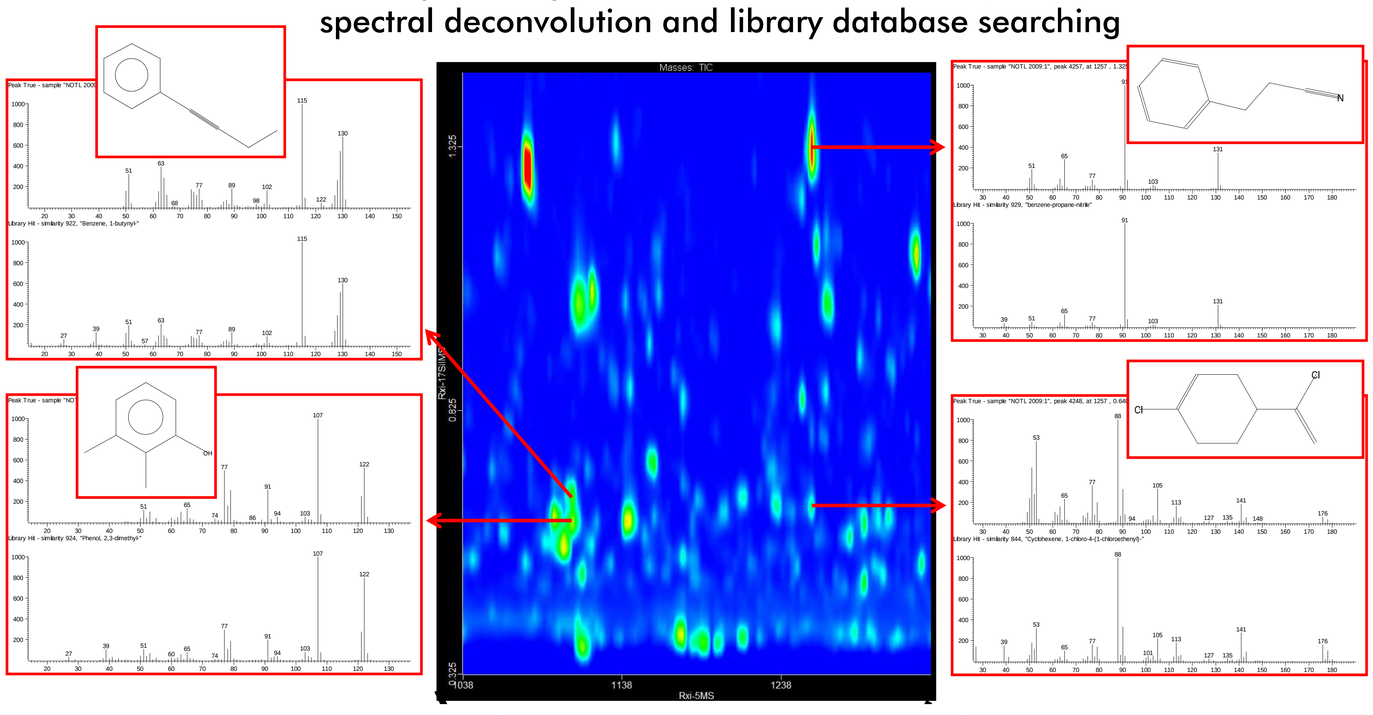


Results

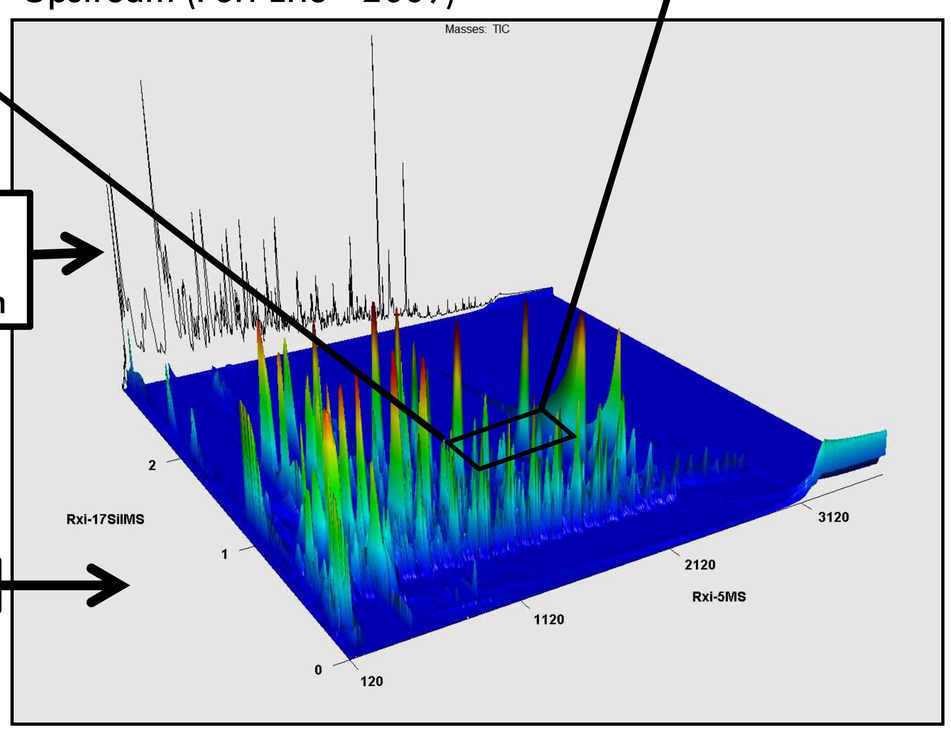
Linear and branched alkanes/alkenes demonstrate that the 1st dimension separation was maintained



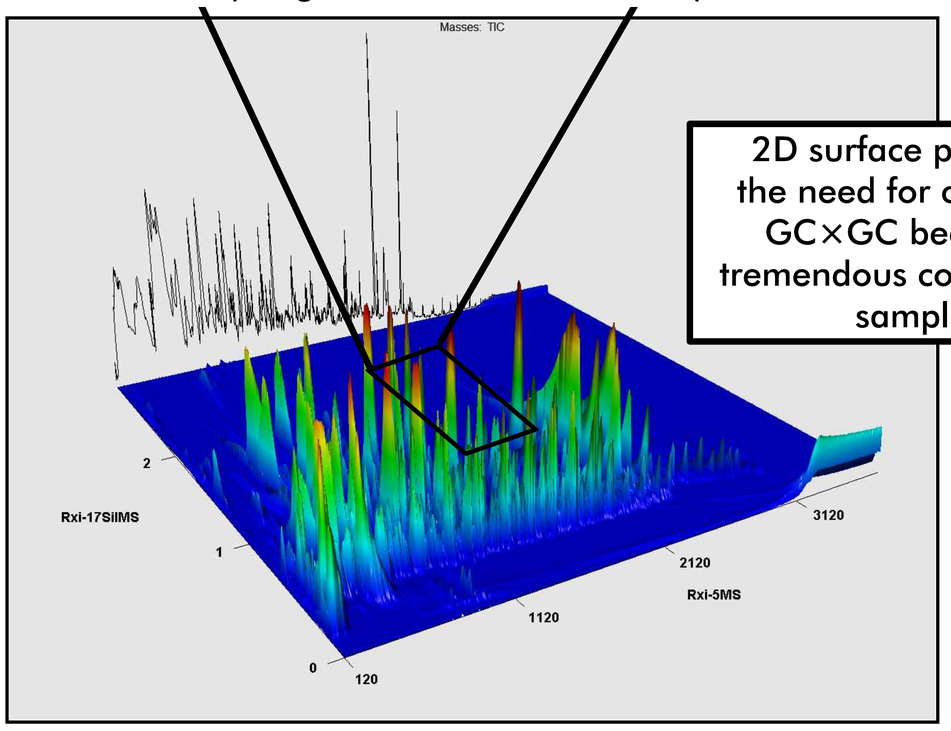
Coelutions in 1D show superior separation in the 2nd dimension, with excellent mass spectral deconvolution and library database searching



Upstream (Fort Erie - 2009)

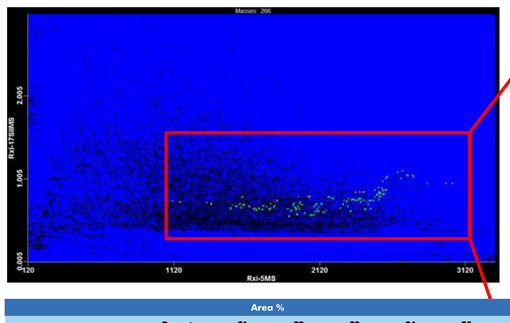


Downstream (Niagara-on-the-Lake - 2009)

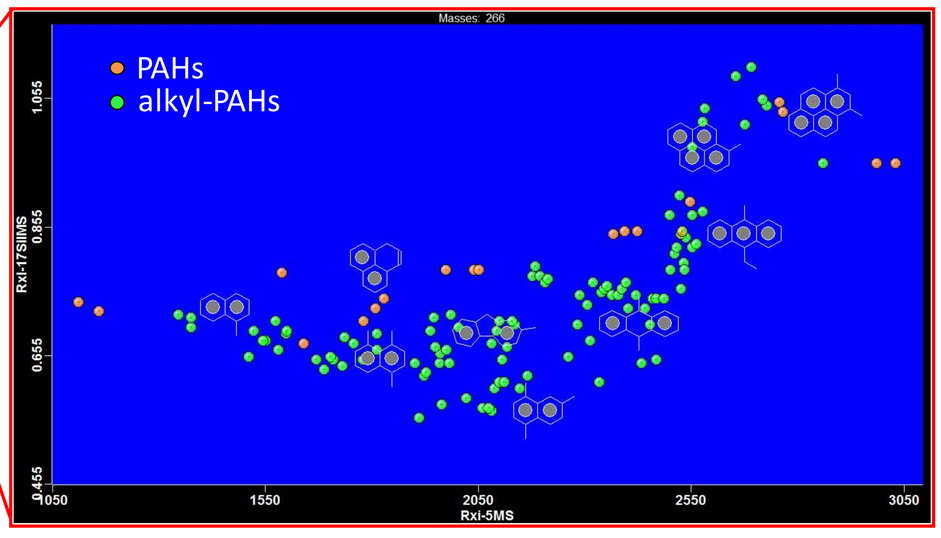


2D surface plots illustrate the need for comprehensive GC×GC because of the tremendous complexity of the sample data

Polycyclic Aromatic Hydrocarbons

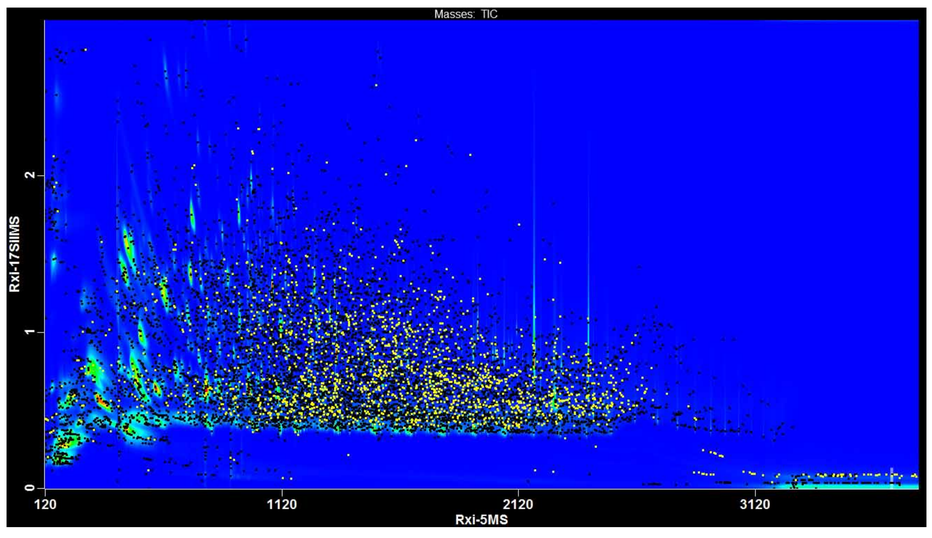


	Area %						
	Parent	C1	C2	C3	C4	C5	C6
Naphthalene	6.96%	9.07%	17.50%	16.55%	9.62%	3.95%	0.69%
Azulene	0.70%						
Acenaphthene	0.64%						
Biphenylene	0.36%						
Fluorene	1.80%	2.86%	2.14%				
Phenalene	0.13%						
Phenanthrene	1.92%	4.74%	2.78%	2.62%	1.34%		
Anthracene	0.43%	0.39%	1.55%	0.54%			
Anthracene, 9,10-dihydro	2.27%	2.52%	1.49%	0.58%			
Benz[a]azulene	0.10%						
Fluoranthene	1.30%						
Pyrene	0.63%	0.42%	0.34%				
Benzo[a]fluorene	0.23%						
Benzo[b]fluorene	0.13%						
Triphenylene	0.32%						
Benz[a]anthracene	0.09%	0.07%					
Benzo[a]pyrene	0.15%						
Perylene	0.06%						
Total	18.24%	20.07%	25.80%	20.29%	10.96%	3.95%	0.69%



The abundance of alkyl-substituted PAHs (green) detected far outweigh the parent PAHs (orange). More than 120 PAHs and alkyl homologs of PAHs were detected in the sediment samples.

Future Work



The black peak markers indicate peaks that were identifiable by library database searching. The yellow markers indicate unknowns; candidates for high resolution mass spectrometry.