Non-Target and Post-Target Analysis of Organic Environmental Contaminants in Suspended River Sediments

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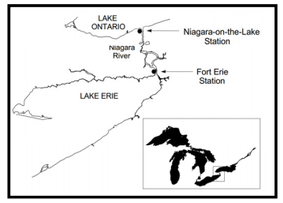
Background

- 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.



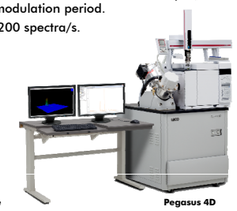
Methods

- About 20 mg of homogenized suspended sediment was thermally desorbed from 50°C to 300°C at 100°C/min, 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/min to 320°C.

GC×GC-TOFMS Instrument Configuration

- 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.


Pyroprobe

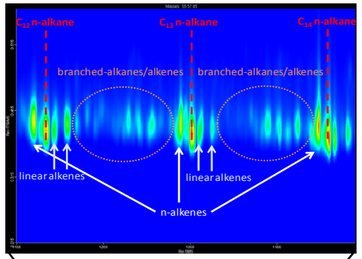

Pegasus 4D

High Resolution GC-TOFMS Instrument Configuration

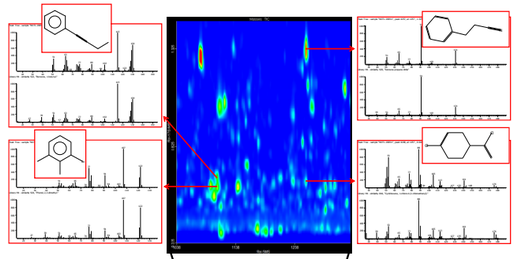
- Column Configuration: Restek Rxi-5MS 30 m x 0.25 mm x 0.25 µm.
- Pegasus GC-HRT: 33 to 650 m/z at 5 spectra/s and 25K resolution at FWHH.

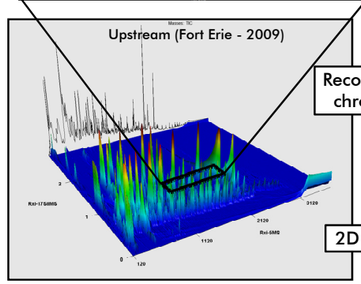
GC×GC-TOFMS: Nominal Mass Resolution

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



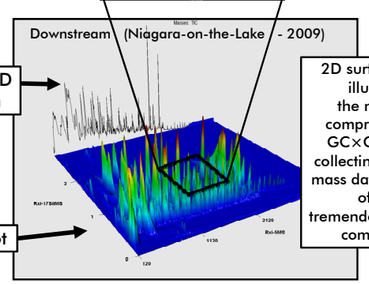
Coelutions in 1D show superior separation in the 2nd dimension, with excellent mass spectral deconvolution and library database searching.



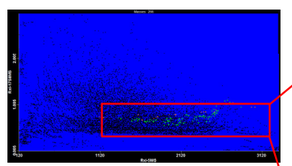


Reconstructed 1D chromatogram

2D surface plot

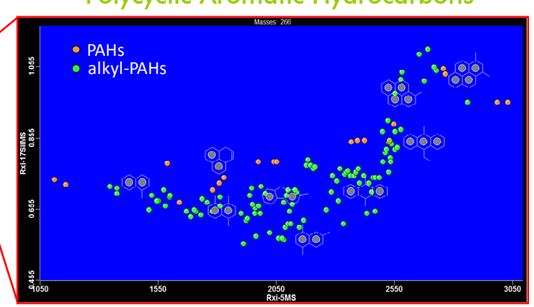


2D surface plots illustrate the need for comprehensive GC×GC when collecting nominal mass data because of the tremendous sample complexity



Area %							
	Parent	C1	C2	C3	C4	C5	C6
Naphthalene	6.96%	9.07%	17.50%	16.53%	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	0.42%	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[c]pyrene	0.15%						
Perylene	0.06%						
Total	18.34%	20.07%	25.80%	20.29%	10.96%	3.95%	0.69%

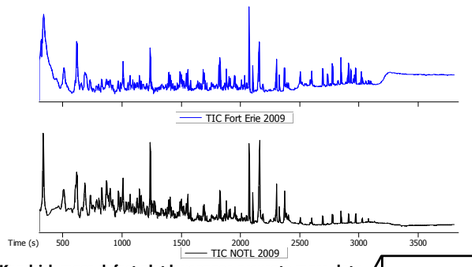
Polycyclic Aromatic Hydrocarbons



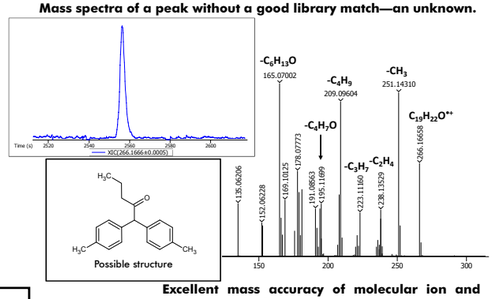
The abundance of alkyl-substituted PAHs (green) detected far outweigh the parent PAHs (orange). More than 120 PAHs and alkyl homologs of PAHs were detected in the sediment samples by GC×GC-TOFMS.

High Resolution GC-TOFMS

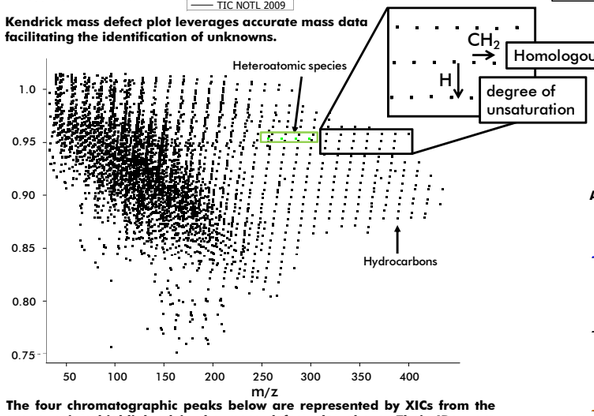
The 1D chromatograms of the upstream and downstream sampling locations are extremely complex with multiple coelutions.



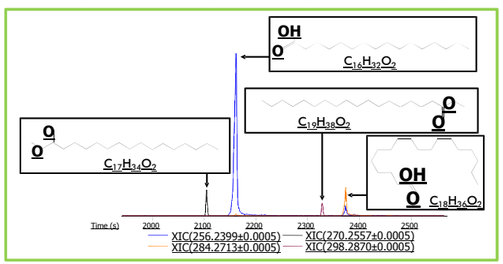
Mass spectra of a peak without a good library match—an unknown.



Kendrick mass defect plot leverages accurate mass data facilitating the identification of unknowns.



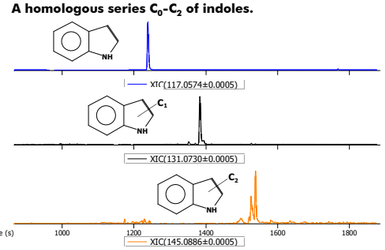
The four chromatographic peaks below are represented by XICs from the green points highlighted in the mass defect plot above. Their IDs were confirmed by accurate mass <1 ppm and library database searching.



Excellent mass accuracy of molecular ion and fragments may be used to propose a structure.

Mass	Formula	Mass Delta (mDa)	Mass Accuracy (ppm)	RDBE
266.1666	C19H22O	0.064	0.241	9
251.1431	C18H19O	0.059	0.235	9.5
238.1353	C17H18O	0.076	0.319	9
223.1116	C16H15O	-0.146	-0.656	9.5
209.0960	C15H13O	-0.054	-0.258	9.5
195.1170	C15H15	0.164	0.840	8.5
165.0700	C13H9	0.140	0.848	9.5

A homologous series C_0-C_2 of indoles.



Conclusion

- Thermal desorption coupled to GC×GC-TOFMS and GC-HRT were effective tools 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, as well as many heteroatomic classes of compounds.
- Mass defect plots are a useful tool for filtering through complex data, while leveraging accurate mass for chemical formulae determination—extremely valuable for tentative unknown identification.
- GC×GC-TOFMS provides high chromatographic resolution for unknown identification with 2D deconvolution and mass spectral library database searching.
- GC-HRT provides high mass resolution and selectivity for unknown identification with High Resolution Deconvolution™.

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