

Greening Analysis with Greater Efficiency: Greener Sample Preparation and Analysis Advancements for Complex Environmental Samples

**PAHs, Drinking Water Disinfection By-products
and other Persistent Organic Pollutants**

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Scientific Endeavors

- My roles: oversee and approve organic contaminant data for environmental samples
- New analytical method development
- Scientific consultation, external method review, court case samples

Environmental Sample Matrices

- soils & sediments, vegetation, biota tissue, air particulate, water

Target Analytes

- focus: polycyclic aromatic compounds (PAHs, alkyl-PAHs, thia-arenes); drinking water disinfection by-products.
- additional work: polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), chlorobenzenes (CBs), halogenated dioxins, furans, BDEs, PCNs...



Emergency Response in Ontario: Speed & Accuracy are Essential

Gogama Train Derailment 2015:
37 rail cars containing ~ 4 million L of oil left the track: 35 were involved in a fire, 2 landed in the Makami River. 995,000 L crude oil spilled to the ground and into the Makami River.



- Monitoring fires or spills for potential environmental contamination & public health impacts.
- Our data is vital for decisions: evacuations, damage control, drinking water quality, site remediation.
- Involves quantification of target analytes in complex samples.
- Requires specific identification of pollutants while removing complex matrix interferences.
- Rapid delivery of quality data.



Plastimet PVC Recycling Plant Fire 1997



Hagersville Tire Fire 1990: consumed 14 million tires, spewed toxic smoke for 17 days, drove 4,000 from their homes and cost the province > \$10 million for a year-long clean up



Environmental Samples: the Analytical Challenge

Separate and accurately quantify analytes in highly complex matrices (from pg/g (ppt) to % levels)

- soils & sediments, vegetation, biota tissue, air particulate
- drinking water, surface water, effluents
- challenges: analyte losses (volatility, lability)
- efficient extractions from complex matrices
- separation of analytes from interferences (humics, oils, fats)
- avoiding sample contamination/cross-contamination



Conventional Approach:

- Lengthy extractions requiring large volumes of toxic organic solvents (released to hazardous waste and to our air; digestions of biota tissues (strong acids = more hazardous waste).
- Time consuming separate extraction & sample cleanup procedures
- Multiple runs on several instruments required for various analytes

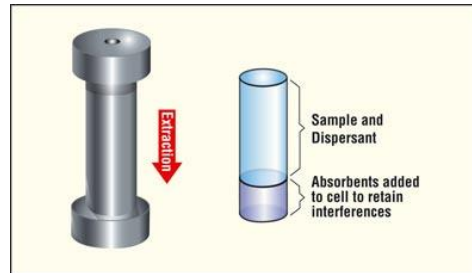
Greener Approach - developing new methods:

- Use less hazardous materials, smaller quantities & smaller scales
- Reducing steps provides savings in time/analyst effort/cost, maximizes efficiency/data quality
- Incorporate additional contaminant groups to minimize # of methods required.

New Method Development (PAH3124 Air, PAH3425 Soil sediment)

These methods provide “greener” procedures:

- a small-scale pressurized fluid extraction (PFE); 80% less organic solvent
- less sample required in less time (20 min. vs. 20 hr. soxhlet)
- silica cartridge cleanup (less solvent, 20 min. vs. 4 hr. open column)
- data corrected for sample preparation & analysis loss: isotope-dilution quantification (higher data quality/accuracy, lower detection limits)



- Method validation performance: soil/sediment (accuracy 88 – 119%, RSD 1-3%); air particulate (accuracy 89 – 116%, RSD 3-9%)
- Future enhancements: additional contaminant groups (e.g., pollution source tracing PACs, thia-arenes, higher molecular weight alkyl-PAHs.)

New Method Development: PAHs in Fish, Shellfish and Aquatic Animals

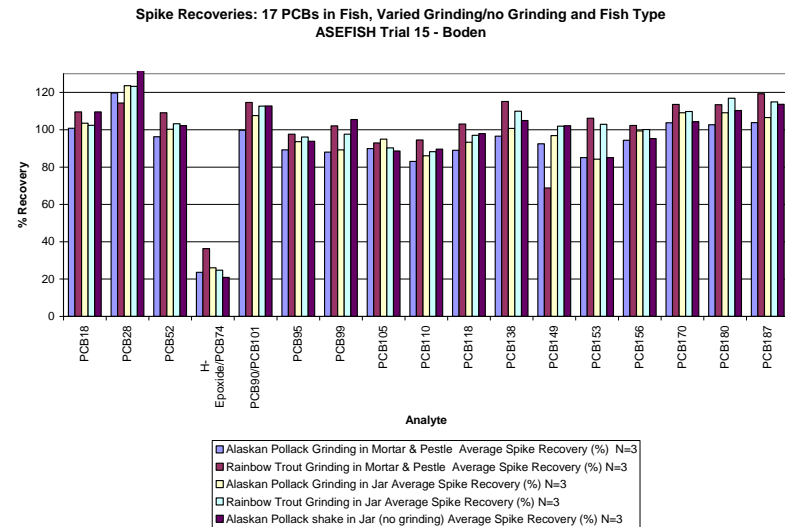


One-Step Extraction/Cleanup of PAHs in Biota Tissue: New Method (PAH3426)

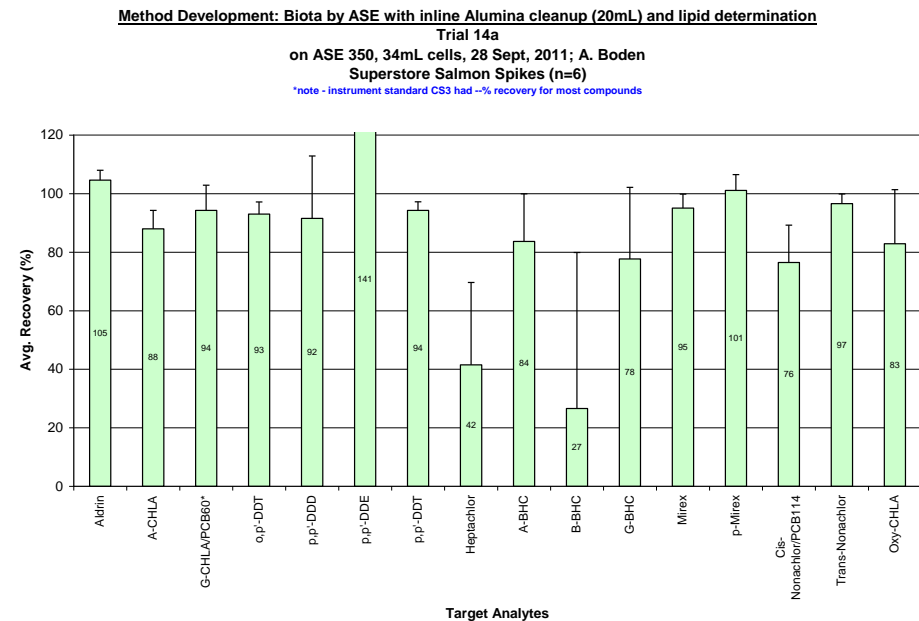
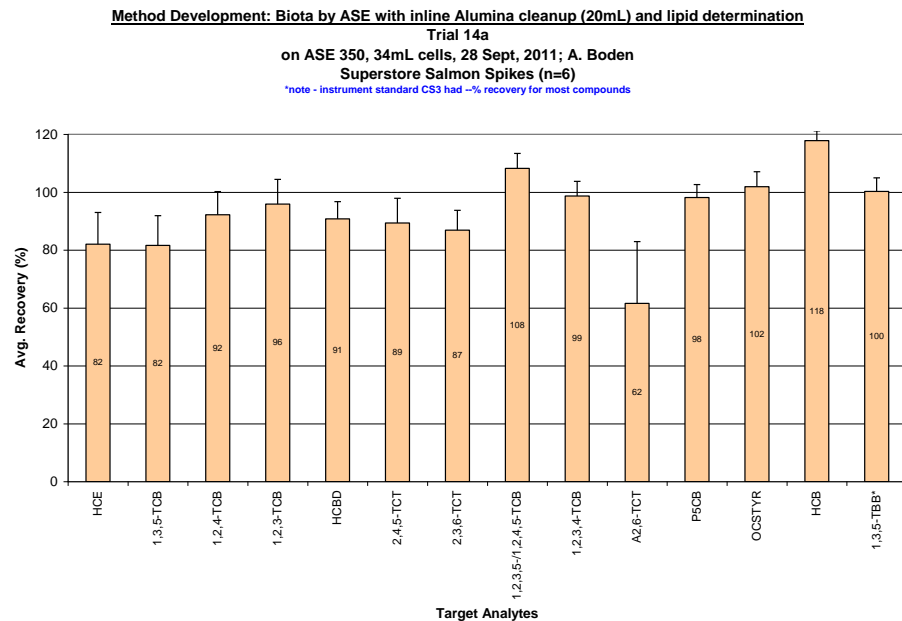
- Developed a new sample preparation method and faster analytical method for the determination of PAHs in biota tissue (fish, mussels, worms).
- This method provides a simpler, faster & “greener” procedure:
 - a small-scale accelerated solvent extraction (24 samples, 20 min. each, unattended)
 - 80% less organic solvent consumption (waste/air)
 - removal of the use of 20 mL concentrated acid per sample (no digestion), & removal of 1 evaporation.
 - incorporation of the sample cleanup into the extraction step (alumina in-cell cleanup)
 - Lipid removal and % lipid content determination in one shot; 1 sample aliquot/1 procedure
 - reduces sample preparation time by ~2 days.
- Use of recyclable labwares where possible (i.e., recyclable glass jars, vials and pipettes, recyclable plastic caps and weighing boats); reuse of metal labwares & tools (washed).



Original Work: PCBs, Organochlorine Pesticides and Chlorobenzenes in Biota Tissue: New Method Development PFE w/ In-cell Cleanup



- Previously evaluated in-cell cleanup for PCBs, OC pesticides and chlorobenzenes.
- Yielded promising results: most PCB/OC/CB >80% recovery (except H-epoxide/PCB74, A2,6-TCT, B-BHC).

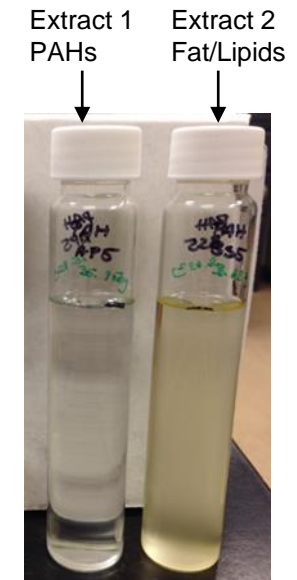
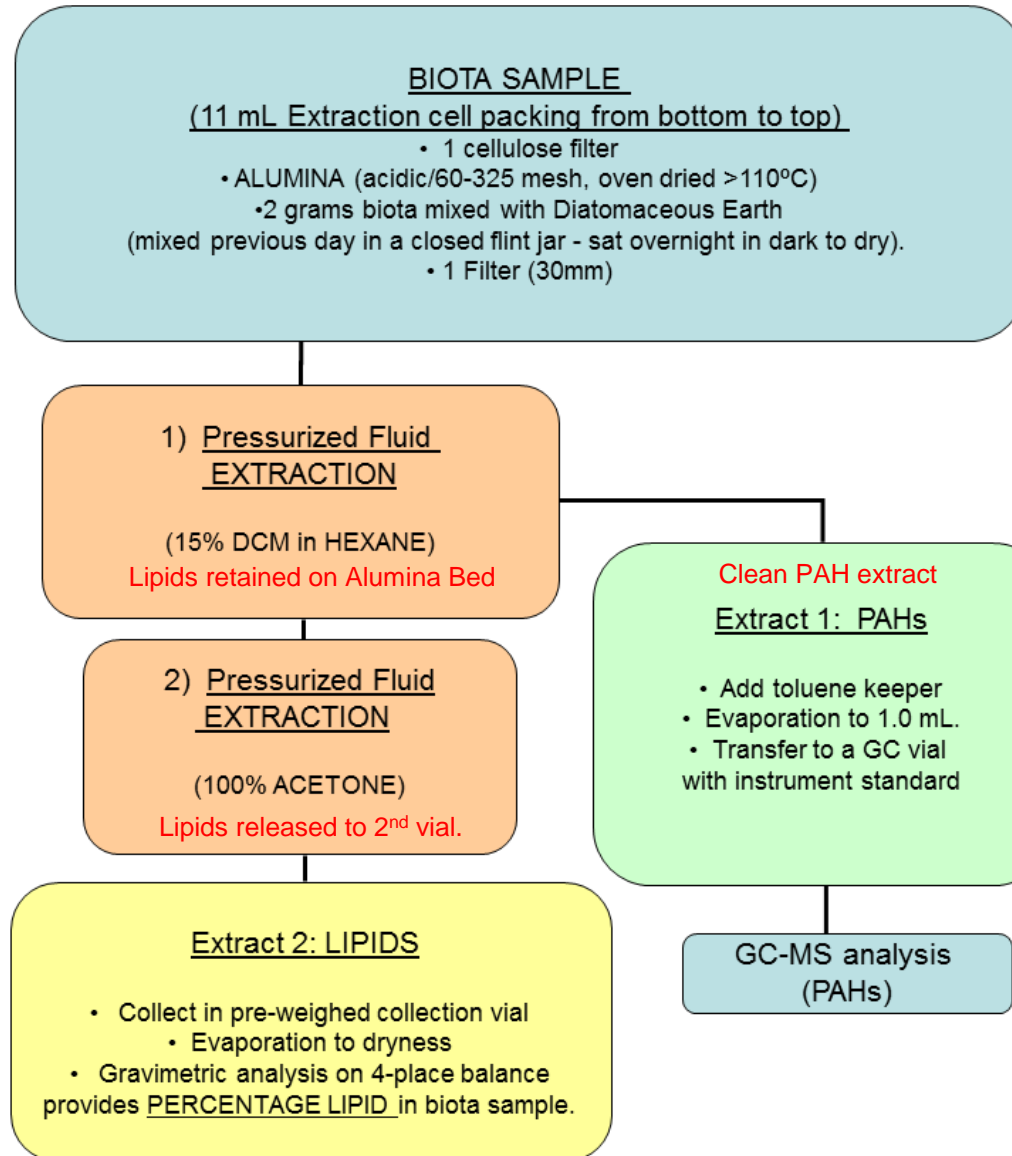


PAHs in Biota Method E3426 Overview

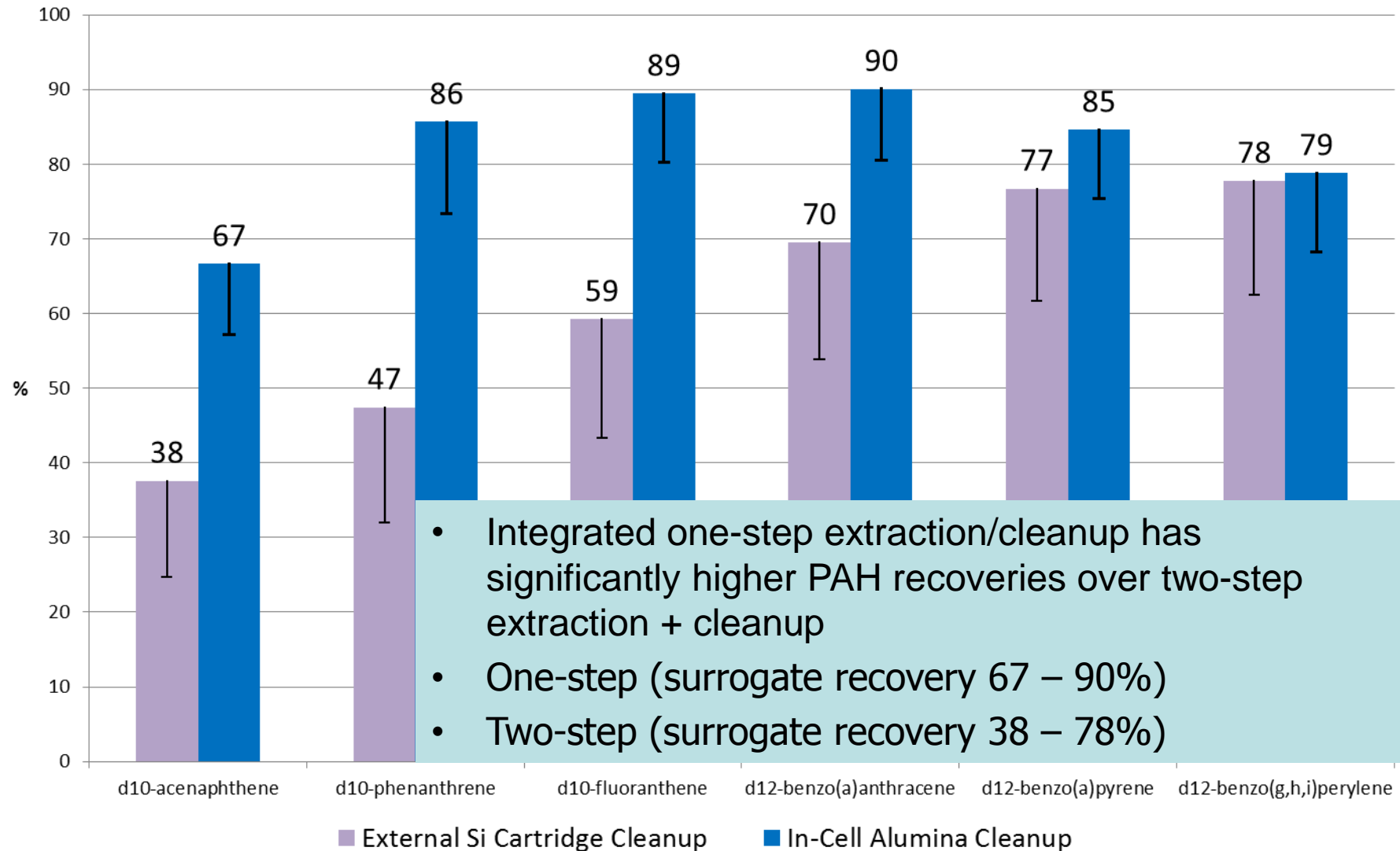
New ASE extraction method with in-cell cleanup and lipid determination for PAH in Biota samples.

OCS Biota & Sediments Unit – Adrienne Boden

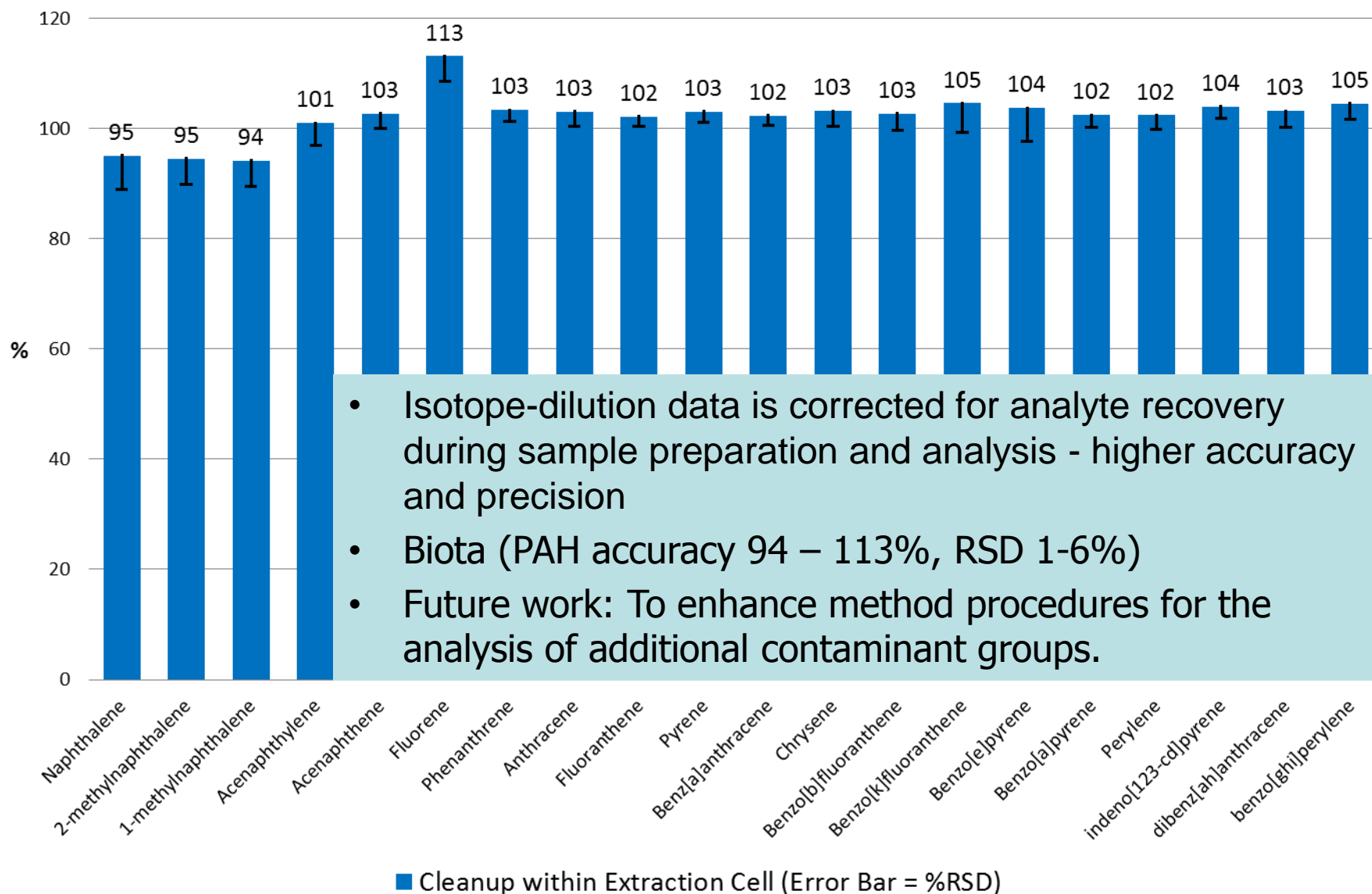
“Catch & Release my lipids!”



Method Recoveries of Labelled PAH Surrogates
External Si Cartridge Cleanup vs. Cleanup within Extraction Cell
Method PAH3426 (N = 12)



PAH Recoveries: Method PAH3426 **One Step Sample Prep. - Cleanup within Extraction Cell (N = 12)**



PAHs in Biota Tissue: New Method Development (PAH3426)

- This method provides a simpler, faster more accurate procedure:



- Pressurized solvent extraction (24 samples overnight)
- One-step Extraction/Cleanup
- 1) Lipid retention on Alumina bed → clean PAH extract
- 2) Lipid release from Alumina bed → % Lipid determination
- Isotope-dilution data is corrected for analyte recovery during sample preparation and analysis.
- Higher accuracy and precision
- Biota (PAH accuracy 94 – 113%, RSD 1-6%)

Future work:

To enhance method procedures for the analysis of additional contaminant groups, such as PCBs, pesticides, thia-arenes and other aromatics.

New Method Development: Drinking Water Disinfection Byproducts



Analytical Method Development: Disinfection Byproducts in Drinking Water



- There are a large number of organochlorine and organobromine disinfection by-products (DBPs) formed during the drinking water treatment process.
- Haloacetaldehydes (HAs): are more toxic than trihalomethanes (THMs) and haloacetic acids (HAAs) and are the most cytotoxic in the emerging disinfection by-product classes.
- Haloacetonitriles (HANs), are the most genotoxic DBPs; cited by the U.S. EPA as having relatively high potential impacts on public health in drinking water.
- Challenges: trace-levels, labile analytes, few ions to choose from, separating analytes from solvent front. Difficulty finding an extraction and instrumentation platform capable of reaching the sensitivity requirements. Previous scientists evaluations (rotating liquid-liquid extraction, GC-ECD, GCxGC-ECD, GC-MS, GC-MS/MS).
- Developed a new analytical method for the determination of disinfection byproducts in drinking water (haloacetaldehydes & haloacetonitriles).

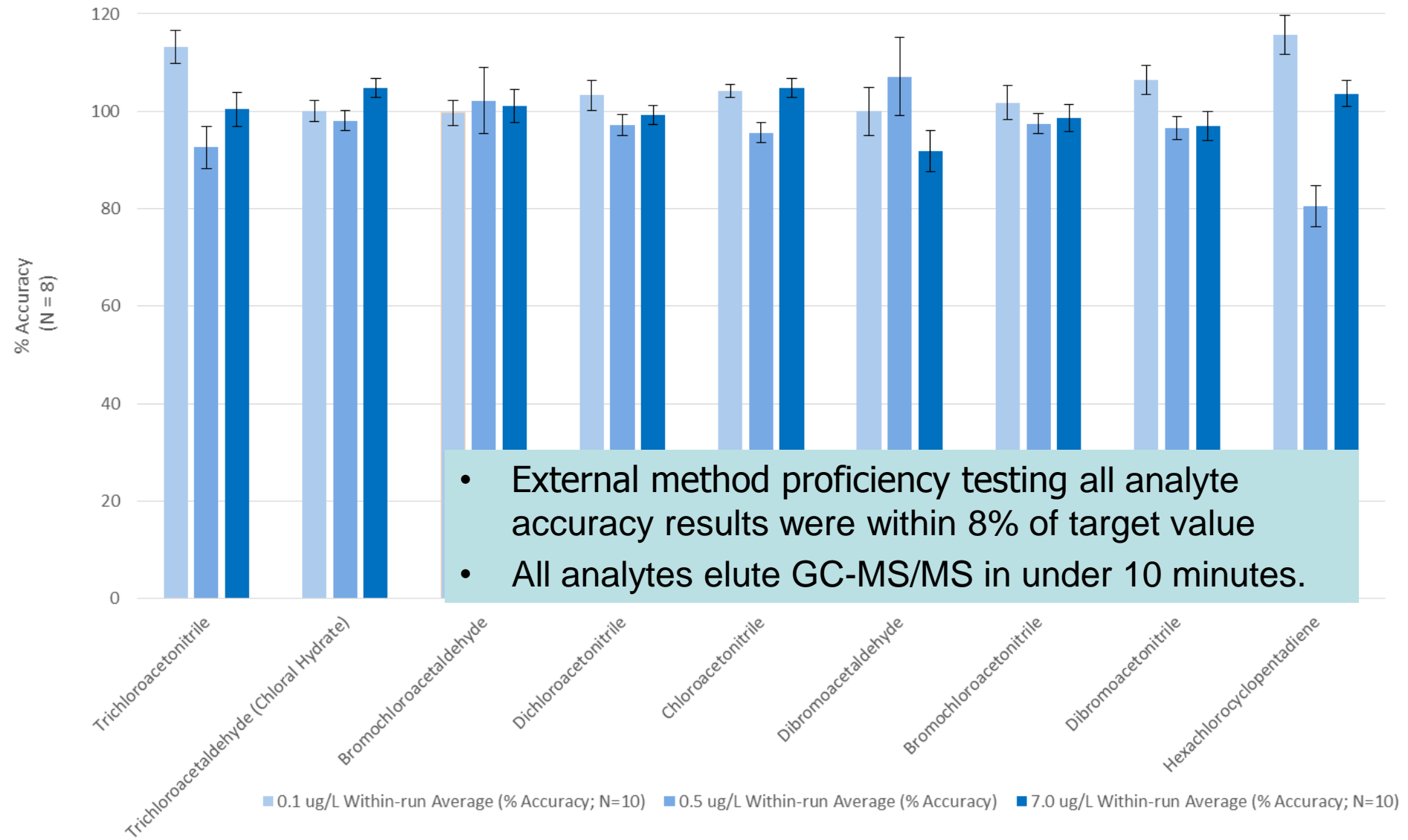
Analytical Method Development: Disinfection Byproducts in Water (HAHAN3528)

Sample Preparation & Analysis in 1 day:

- Drinking water sample (50 mL) is extracted with 3 mL of methyl tert-butyl ether by liquid-liquid extraction on a mechanical agitation apparatus (paint shaker).
- Due to the high volatility and lability of the target analytes, the sample extract is isolated (salted out in methyl tert-butyl ether, MTBE), dried, then analysed without further concentration/clean up steps.
- Analysis using gas chromatography with tandem mass spectrometric detection (GC-MS/MS).
- Successfully validated a new Agilent GC-MS/MS for all requested analytes.
 - MDL 0.1 – 0.2 µg/L water
 - 1 microliter injection, optimized MS/MS detection
 - extensive testing on Ontario drinking waters.
 - OCS's 1st routine GC-MS/MS method.



2016 DPB E3528 HA/HAN Method Development Trial Summary
Low/Mid/High level water spikes (0.1 ug/L, 0.5 ug/L, 7.0 ug/L; N=10)
Agilent GC-MS/MS data (A. Boden, H. Doai; 2016)



Drinking Water Disinfection Byproduct

Analytical Method Development: Disinfection Byproducts in Water by GC-MS/MS (HAHAN3528)



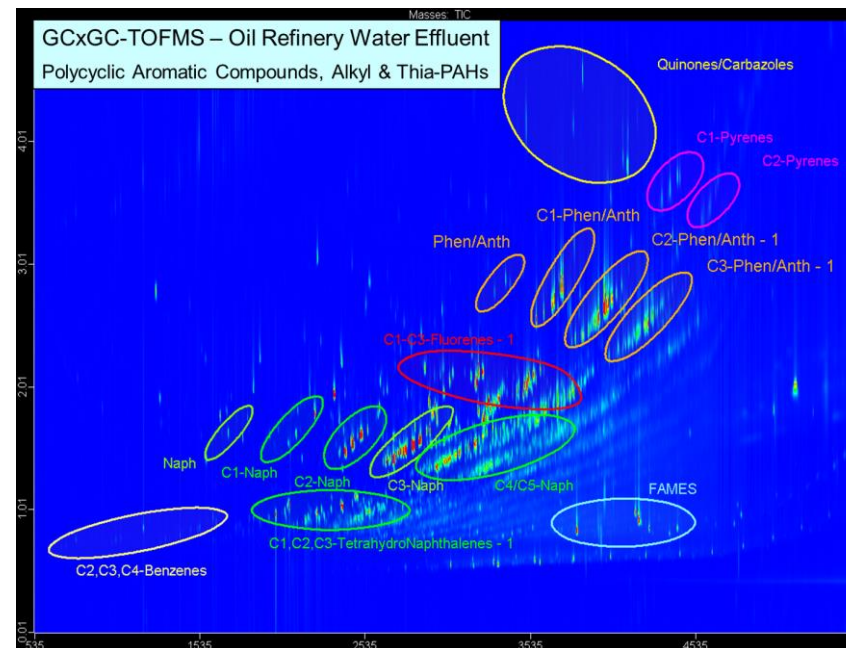
This method provides a “greener,” procedure by using:

- A small-scale extraction procedure which uses a minimal amount of extraction solvent per sample as compared to conventional liquid-liquid extractions. Reduced organic solvent consumption lowers hazards and reduces VOC emissions to indoor and outdoor air.
- Use of recyclable lab wares where possible (i.e., recyclable glass vials and pipettes, recyclable plastic caps and weighing boats). Reuse of metal lab wares (washed).
- Minimal waste management requirements and improved Health and Safety profile due to reduction of hazardous chemical usage.

Greater efficiency:

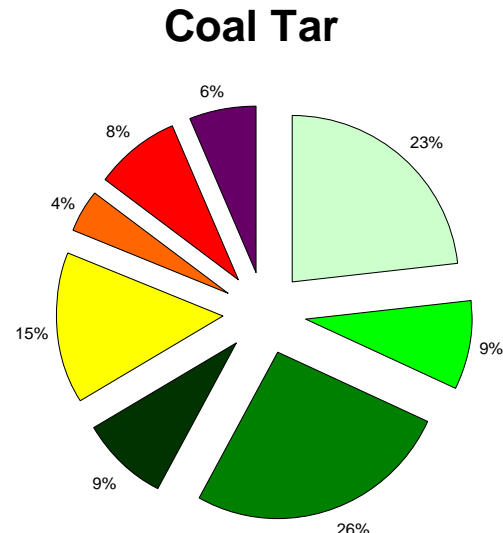
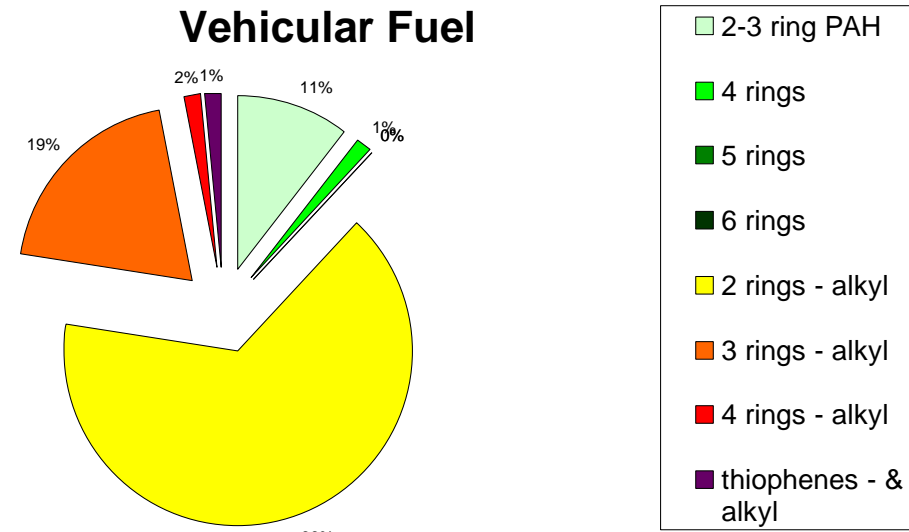
- removal of a sample clean-up step, reduces reagent consumption and restricts sample preparation and analysis time to 1 day total.
- Small scale MAE is also very effective for PAHs in water.

Separating Multiple Compound Classes of Pollutants using a Single sample preparation and Analysis

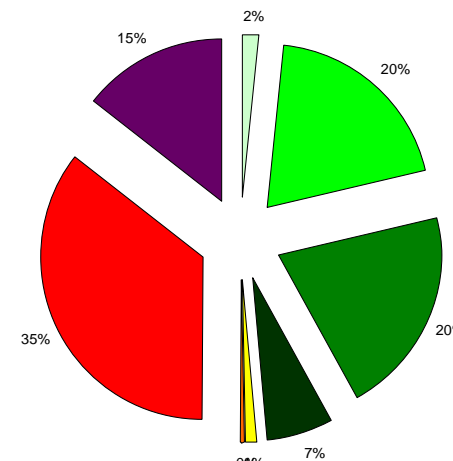


Pollution Sources have Different Proportions: PAH, alkyl-PAH, thiophenes

- Vehicular fuels – alkyl-PAHs dominant relative to parent PAHs; lower 4- to 6-ring PAHs
- Pyrogenic/Industrial – Parent-PAHs dominant relative to alkyl-PAHs; Elevated 4 - 6 ring PAHs (also in urban runoff)
- Coal tar - lighter PAHs present; Parent-PAH dominant relative to alkyl-PAH



Industrial Effluents



GCxGC-TOFMS benefits

Ordered chromatograms

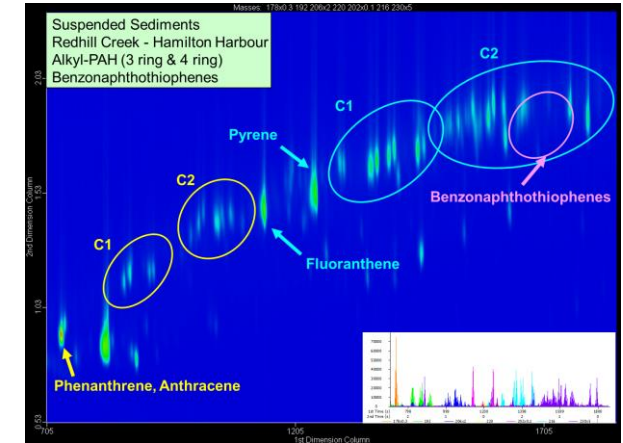
- Good for aliphatic, aromatic and organohalogen separations
- Ordering within compound classes
- Separation of target analytes from matrix interferences

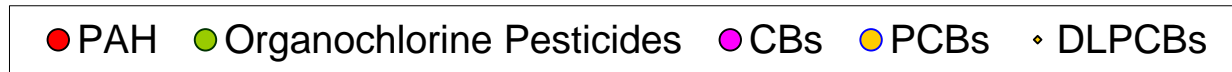
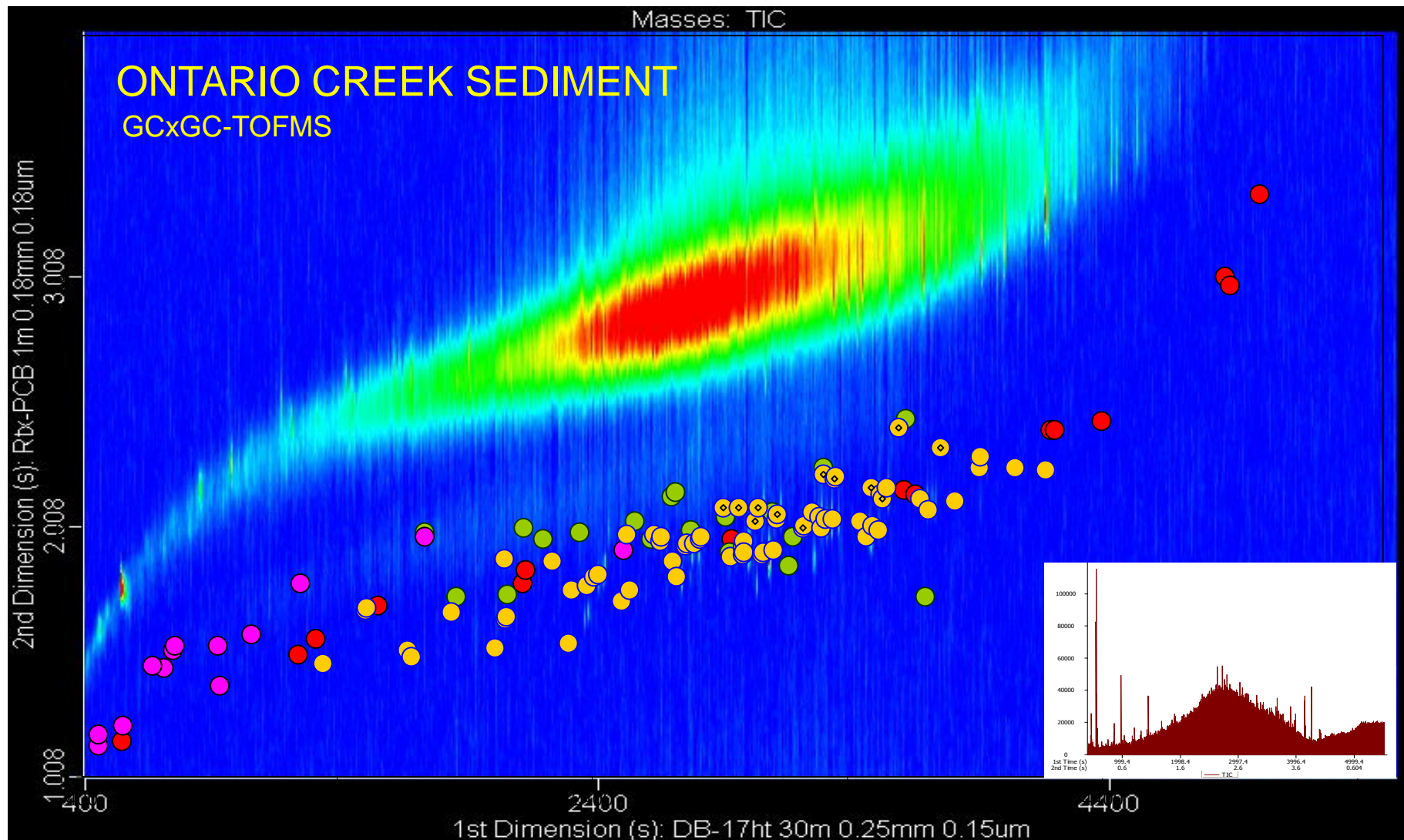
Improved resolving power

- Full scan mass spectrometric analysis enables identifications of unknown contaminants and matrix interferences
- Able to separate and resolve thousands of compounds

Useful tool for environmental contaminant analysis

- Resolution of complex mixtures that cannot be resolved on a single chromatographic medium or with a non-specific detector

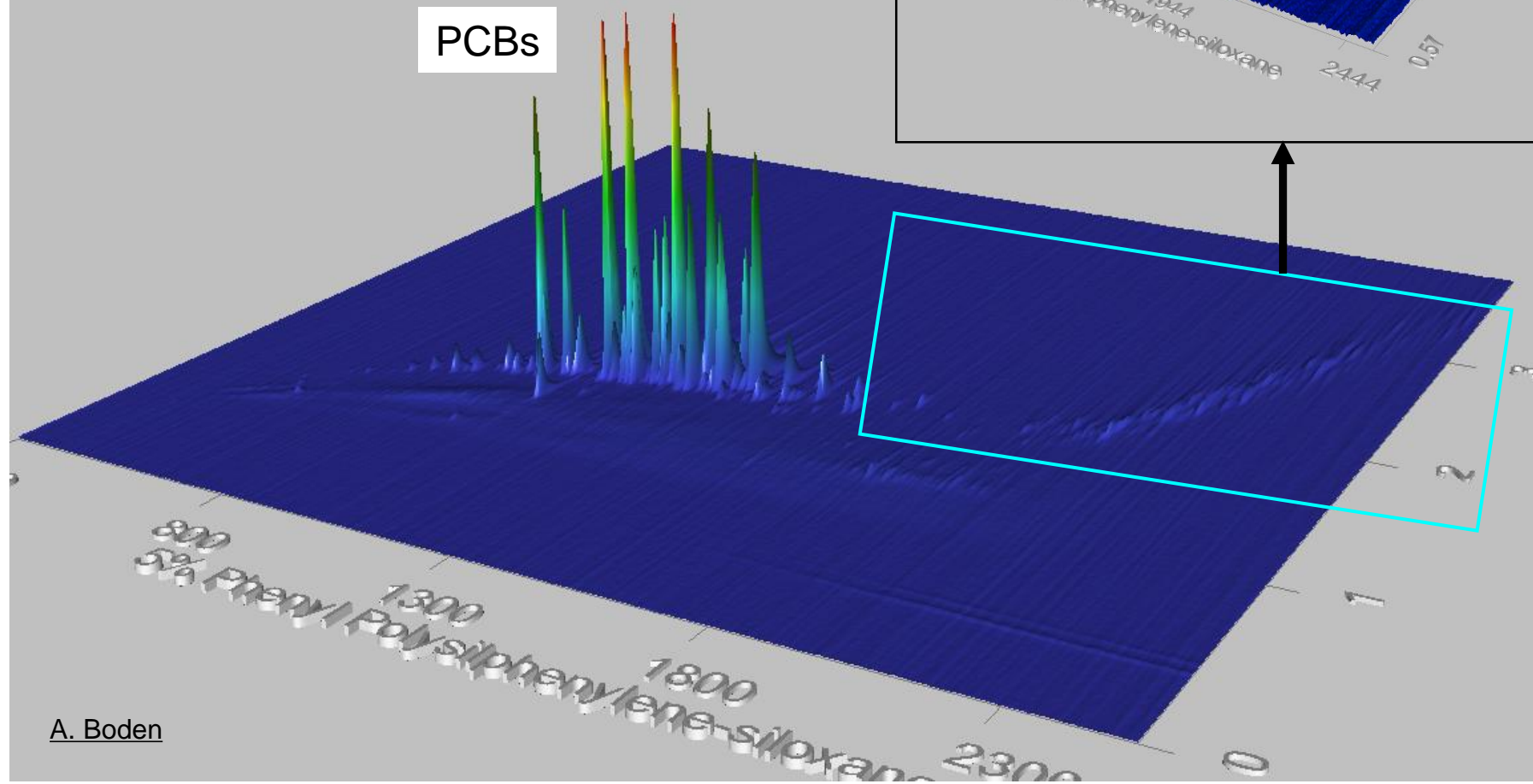




GCxGC-TOFMS – Biosolid Reactor Sludge

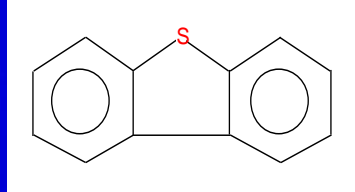
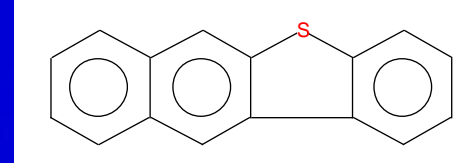
Chlorinated Terphenyls

PCBs



Coal Tar Extract – fraction A2
SubPAC – sulfur heterocycles

**Benzonaphthothiophenes
(234 amu)**



2nd Dimension Column

4.22

3.22

2.22

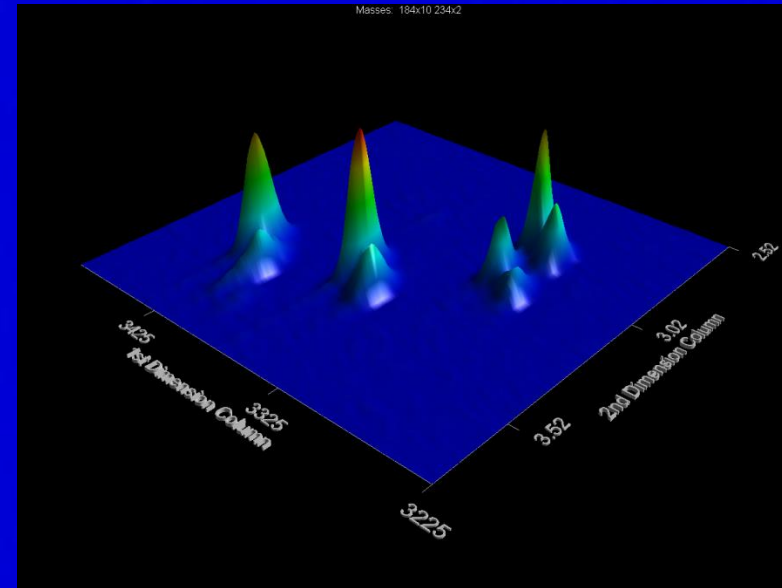
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3640

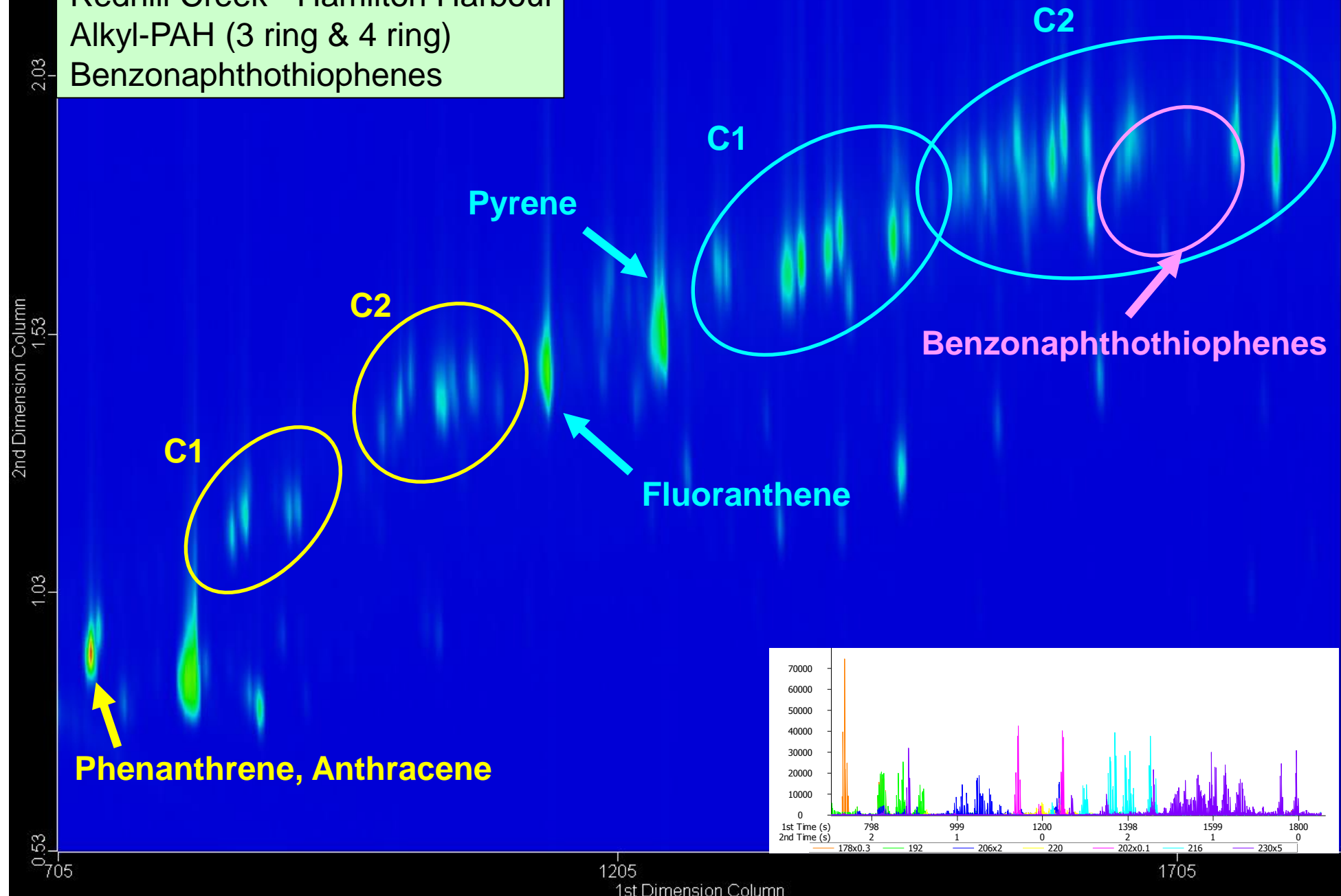
4140

4640

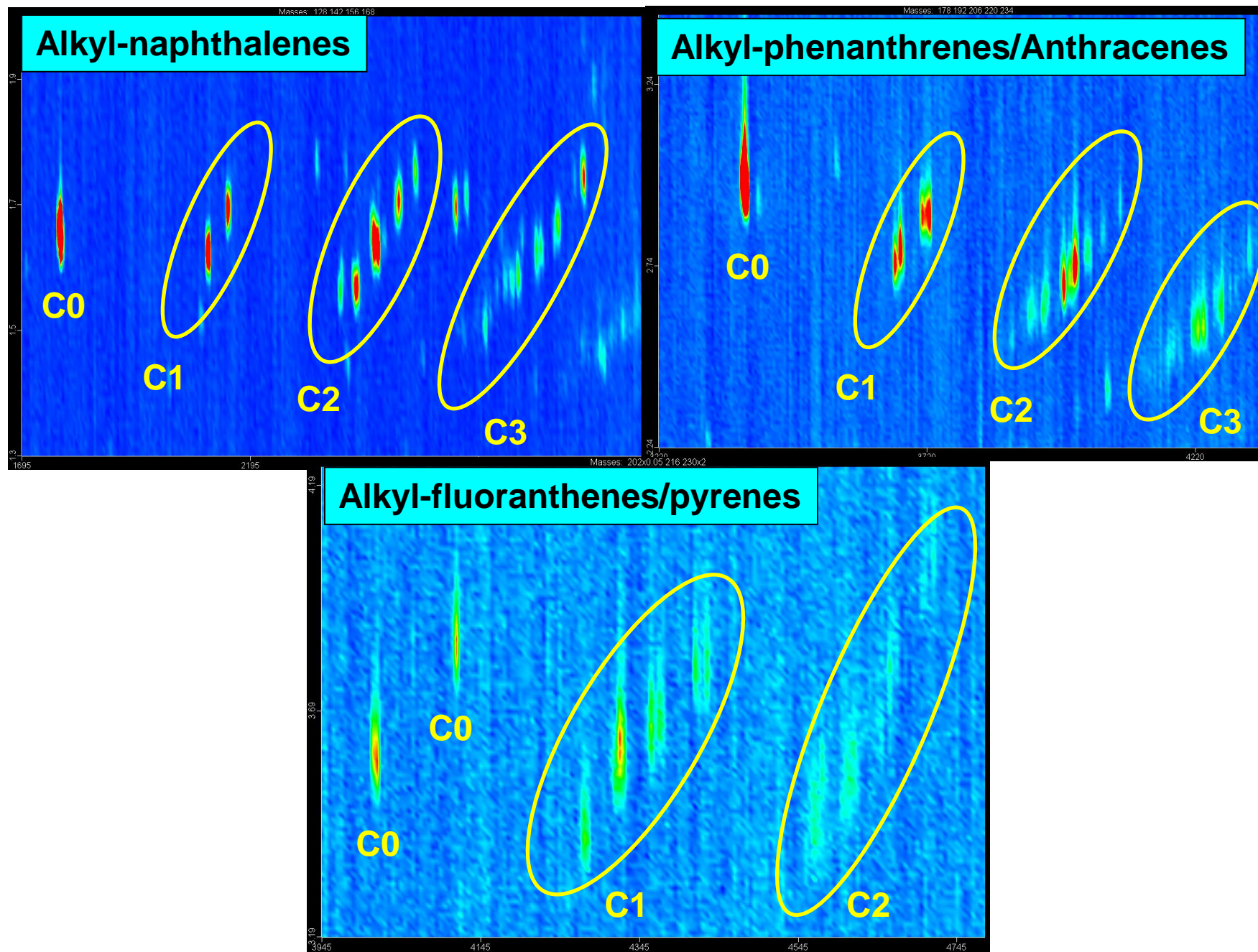
**Dibenzothiophene
Naphthothiophenes
(184 amu)**



Suspended Sediments
Redhill Creek - Hamilton Harbour
Alkyl-PAH (3 ring & 4 ring)
Benzonaphthothiophenes



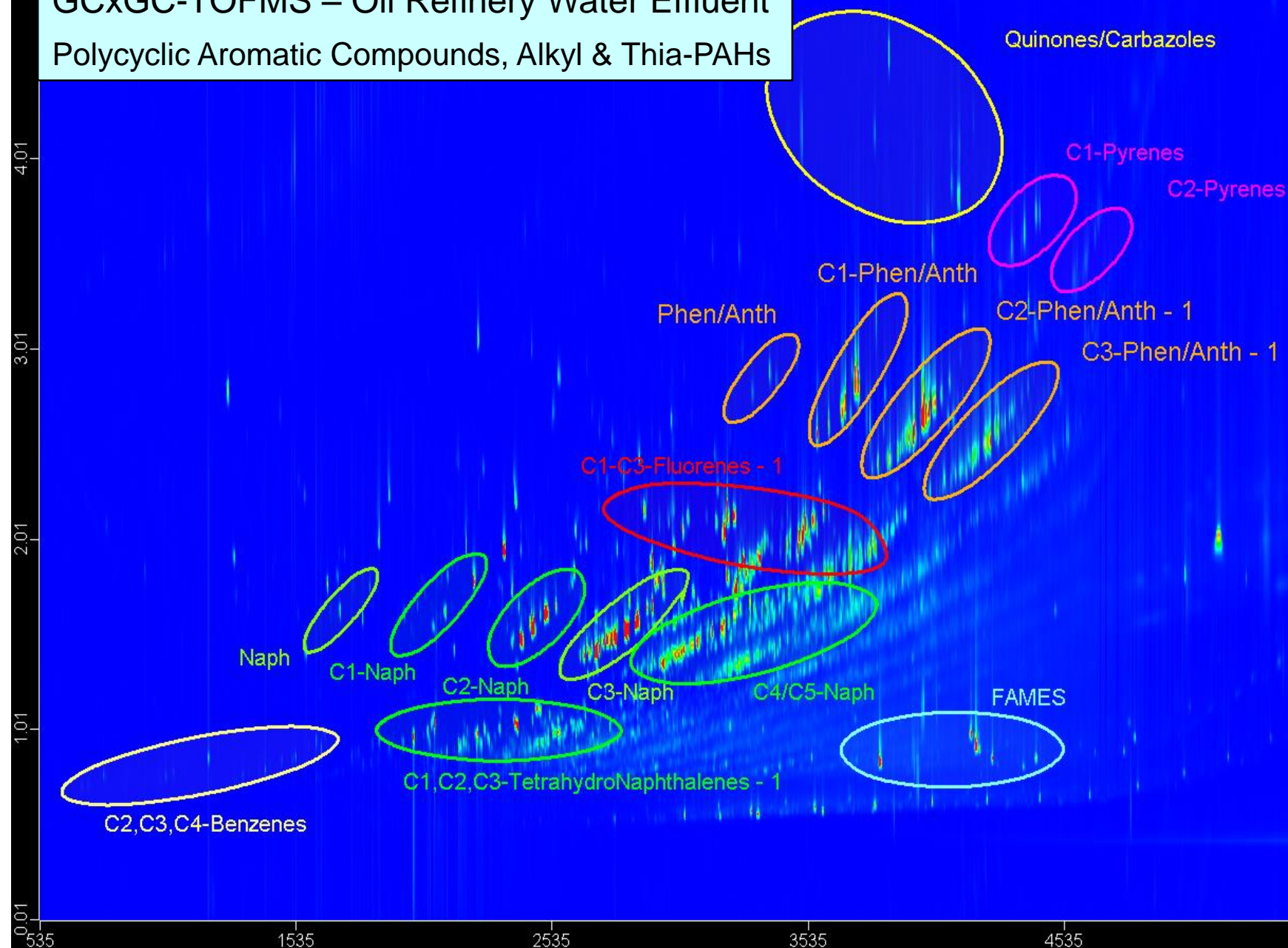
Air Particulate Sample: Long range transport, Yukon (Little Fox Lake)



Masses: TIC

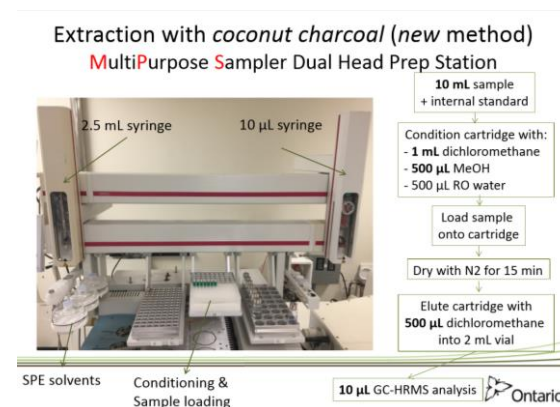
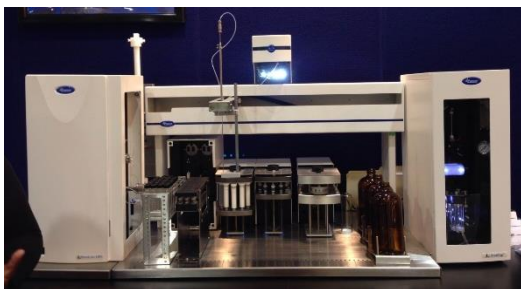
GCxGC-TOFMS – Oil Refinery Water Effluent

Polycyclic Aromatic Compounds, Alkyl & Thia-PAHs



Advancing Sample Preparation: What's Next?

- On-line unified analytical system - extraction system in-line with chromatographic separation and MS/MS detection in a single flowpath for high sensitivity. Reduction in sample size, organic solvent usage, compound degradation, time and cost.
- Automated small-scale SPE: robotic extraction of water by SPE direct to analysis; fractionation of n-alkanes/PAHs. Lowering detection limits with advanced mass spectrometry.
(e.g., E. Korenkova; 1,4-dioxane in water by automated SPE with large volume injection GC-HRMS).



- Bluetooth smart chemical measurements: transmitting measurement data to tablet platforms (graphing, data logging/sharing).
- Further multidimensional chromatography development for pollution source identifications in complex environmental samples.

Greening Analysis with Greater Efficiency

We can green our analyses with greater efficiency by:

- adopting small-scale extractions with integrated cleanups
- reducing preparation time while maintaining/improving data quality
- minimizing waste mgmt. requirements, reuse & recycle labwares
- create comprehensive analyses with multiple contaminant groups
- improving the health & safety profile and environmental impacts of the laboratory.

Thank you: Organic Contaminants Section, Laboratory Services Branch,
MOECC

D. Morse – OCS manager, H. Doai – DBP water/PAH biota analysis, R. Burton – PAH water/soil analysis
K. Asemota – PAH biota analysis, P. Yang, G. Ladwig – initial DBP, A. Muscalu, V. Pantelic –PCB data

Thank you for listening...



