Evaluation of Alberta Based Oils and Common Degradation Mechanisms by GCxGC

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ENERGY
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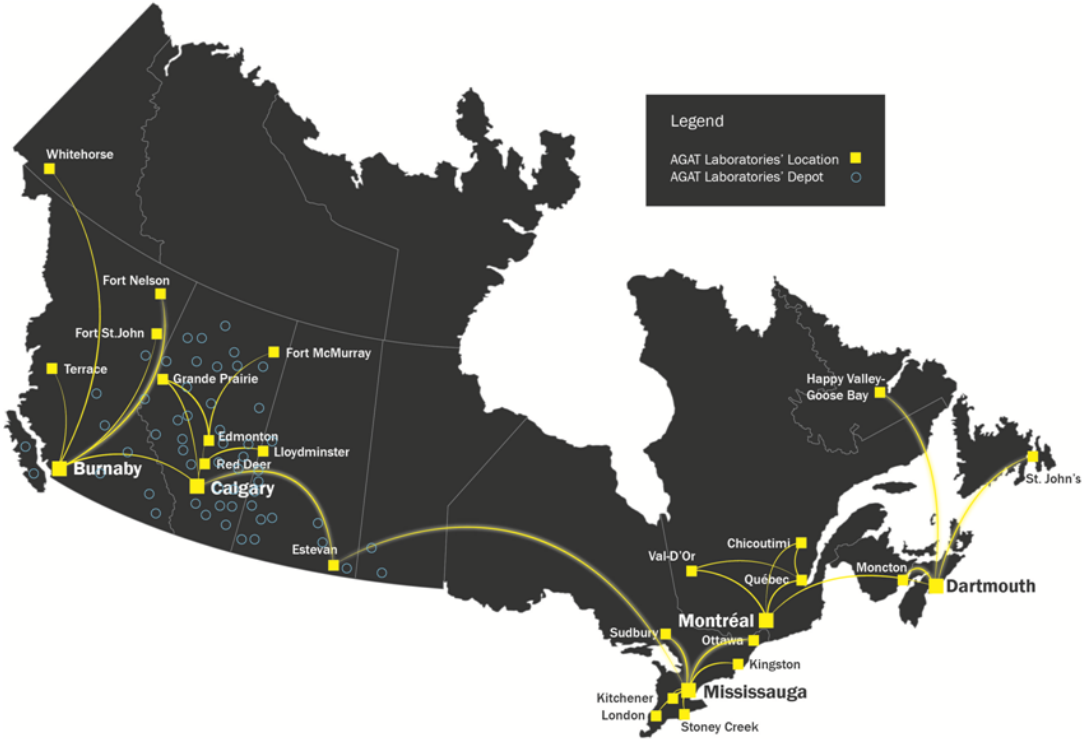
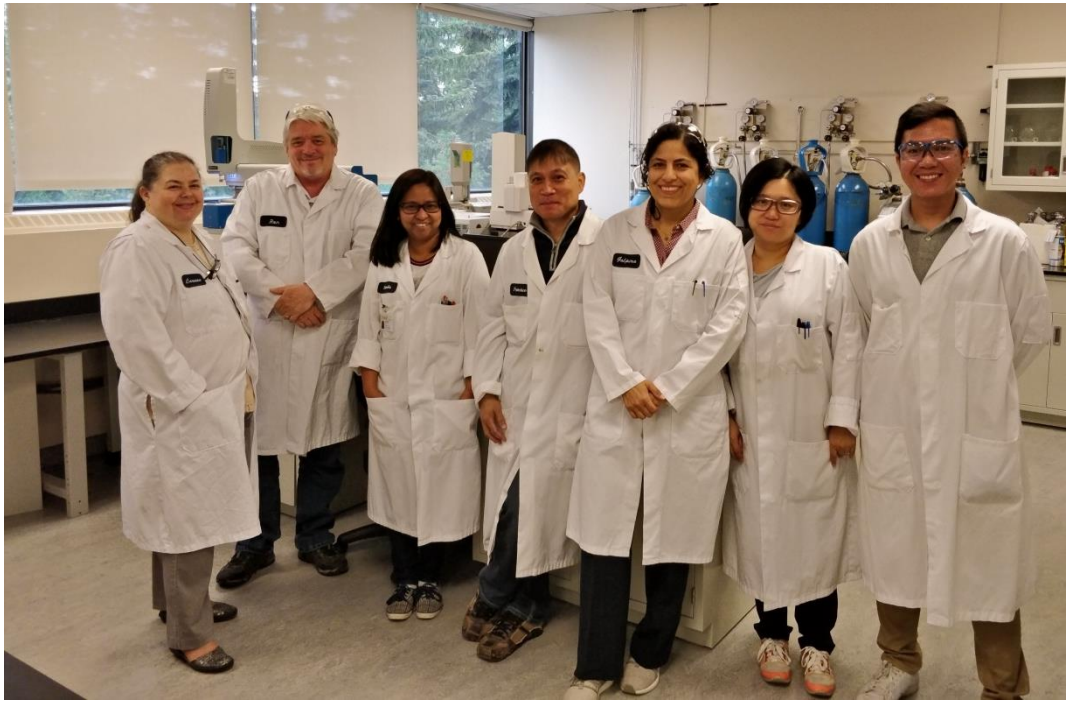
Spill Response and Mobile Lab Services

- Field and Laboratory Response
  - Mobile Lab
  - After Hours Service
  - 24hr Availability
  - Capacity Management

- Logistics
  - Sample Transportation
  - Courier Management
  - Command Center
  - Supply Management



Who We Are



AGAT Forensic Science Team

Environmental Forensics

Forensic analytical:
Environmental Forensics

- Is this contamination related to my activities or from another source?
- My site has multiple land use histories; what is the main product and when did the release occur?
- Are my exceedances related to natural hydrocarbon—or are they petrogenic?
- Is my site commingled?

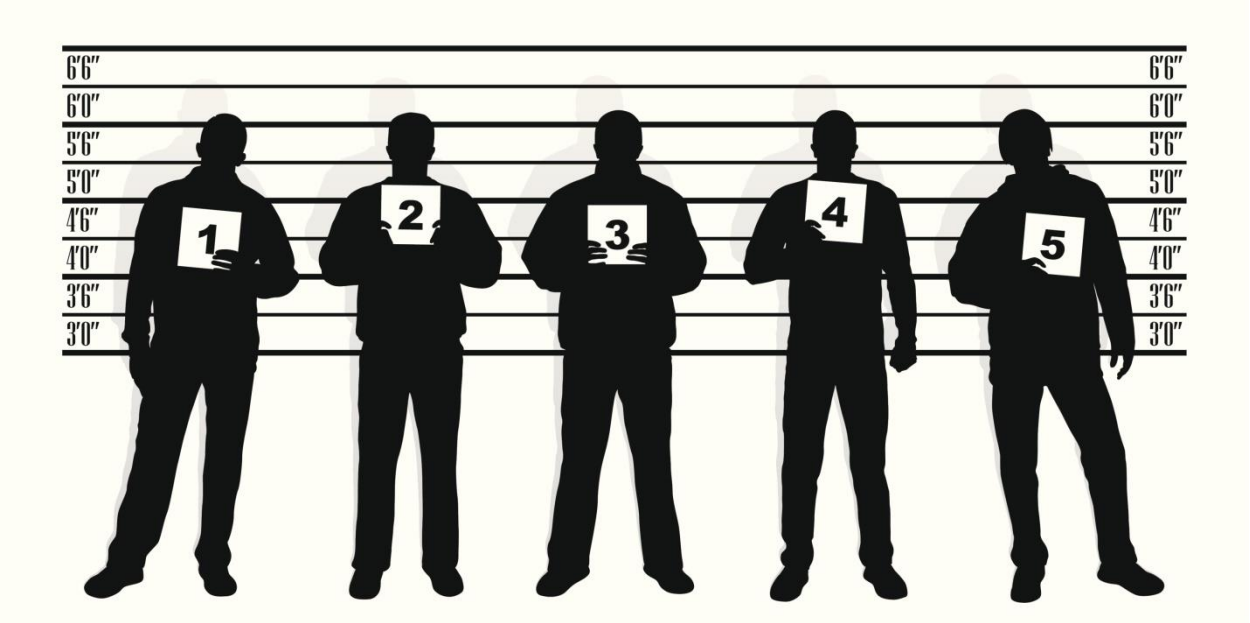
Environmental Forensics

Forensic analytical:
Environmental Forensics

The Fingerprint
Samples interpretation

Enables product type ID

To find the likely culprit it helps to have suspects



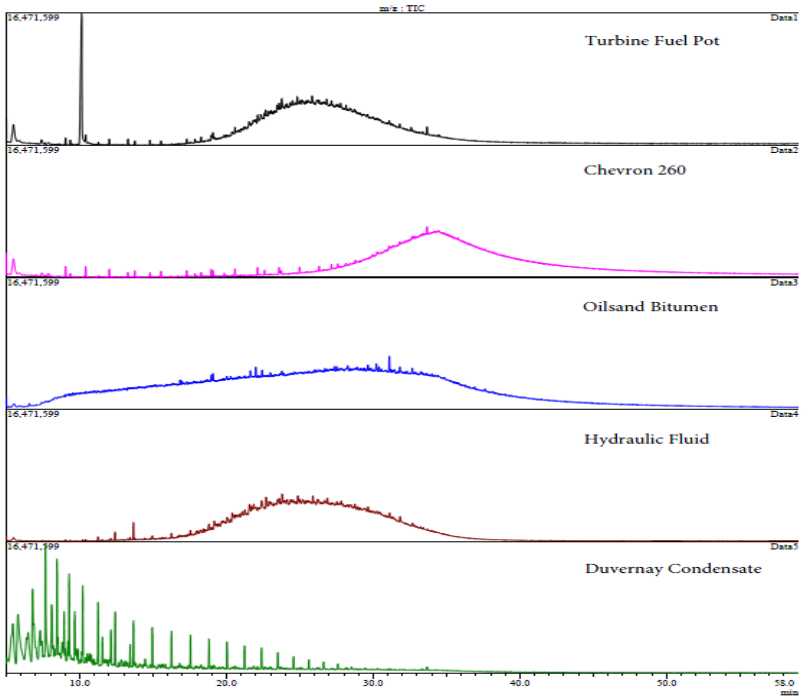
The usual suspects: While we have a large hydrocarbon library on hand, exemplars provided from a site enable more definitive and eloquent analysis.

Environmental Forensics

Forensic analytical:
Environmental Forensics

The Fingerprint

Exemplars (suspects) help to narrow the field. Especially when related products are involved.



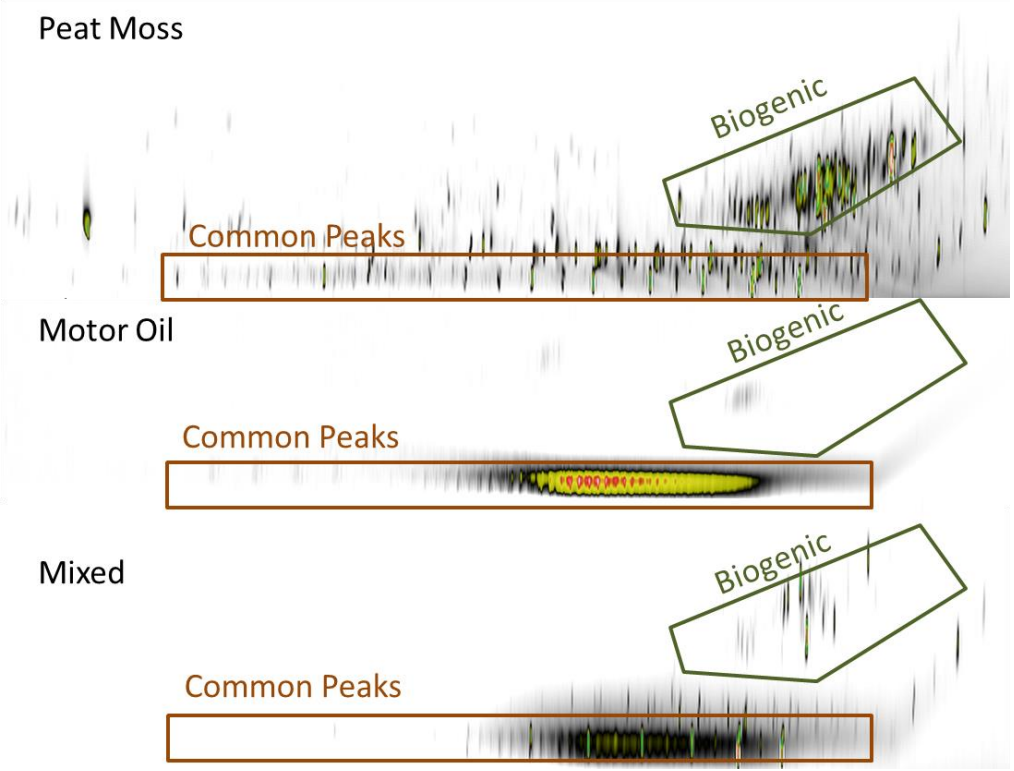
Total Ion Chromatograms (TIC) comparison of the Turbine Fuel Pot sample and comparison samples from the Agat Oil Forensic Library. The Turbine Fuel Pot sample is distinct from the other other types and most closely resembles the Hydraulic Fluid standard. The match is not exact and a further search of Hydraulic Fluids and Gear Oils used at the sample site may identify the unknown matching product.

Environmental Forensics

Forensic analytical:
Environmental Forensics

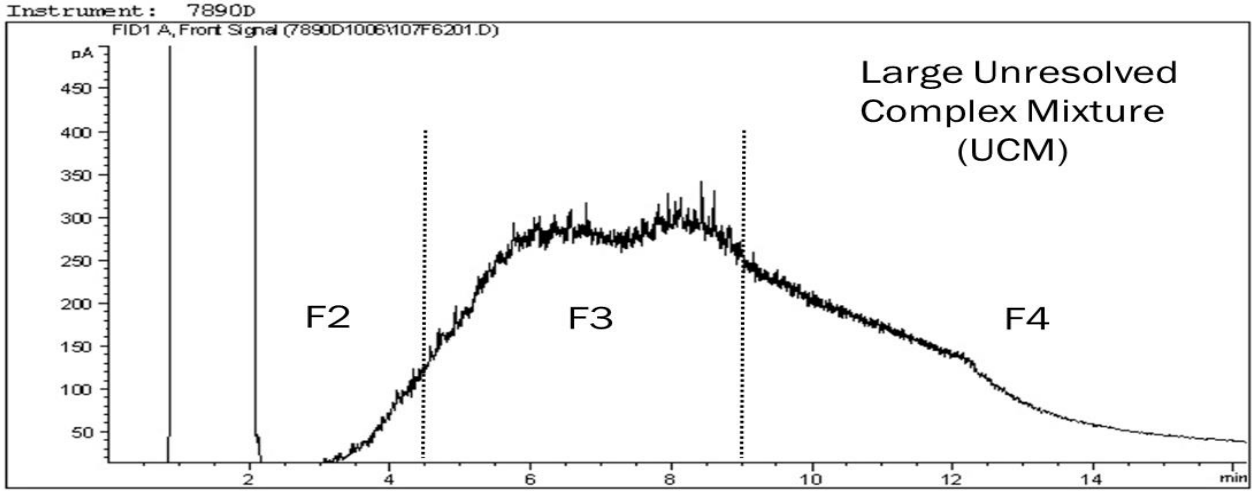
Diagnostics

- Comparison of signature compounds
- Similar to ILR work
- Biogenic toluene/peat

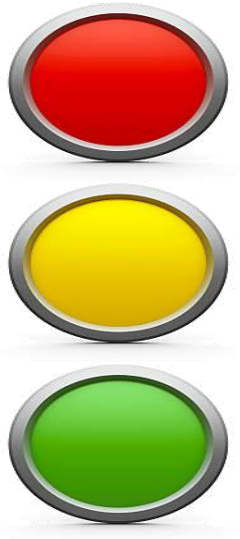


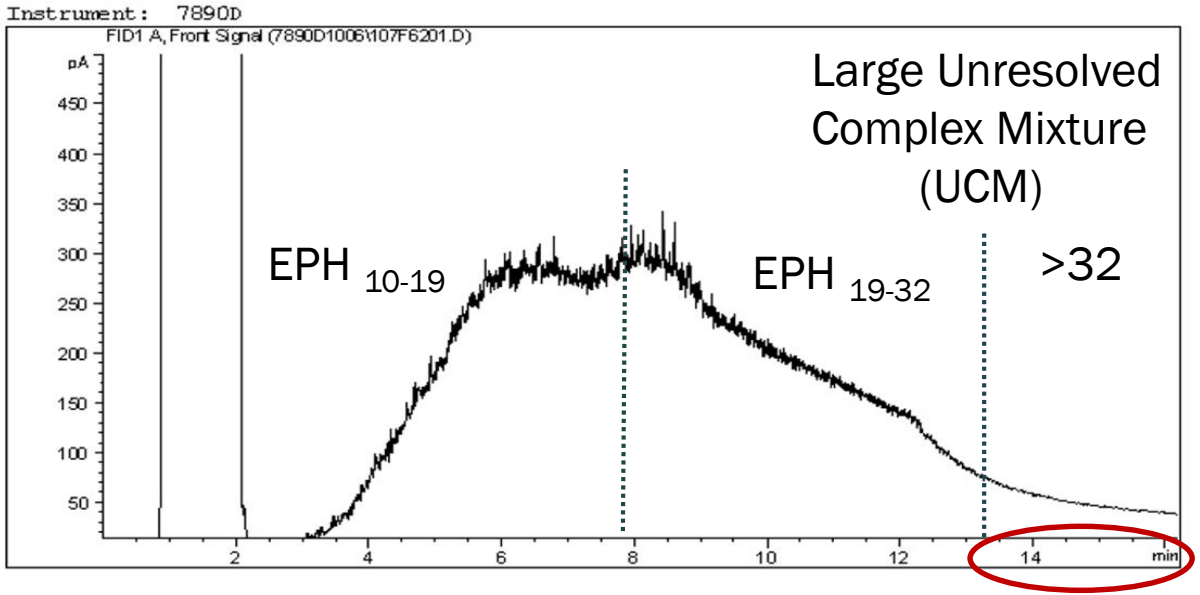
Why GCxGC?

Traditional GC can delineate some constituents in an oil sample, but not the details—compounds with similar properties can merge together into an Unresolvable Complex Mixture or “hump”



Routine GC-FID EPH





Stop Light
Interpretation: Subjective
"Can I make the yellow?"
Pro: Simple
Information: Limited

Routine Scans
Interpretation: Subjective
Accuracy: Low
Pro: Quantify Regulatory Hydrocarbons
Information: Limited

Product Fingerprinting

Signature Recognition

- Accuracy: Medium
- Multiple points of ID

X,Y, Pressure, Curvature, Acceleration

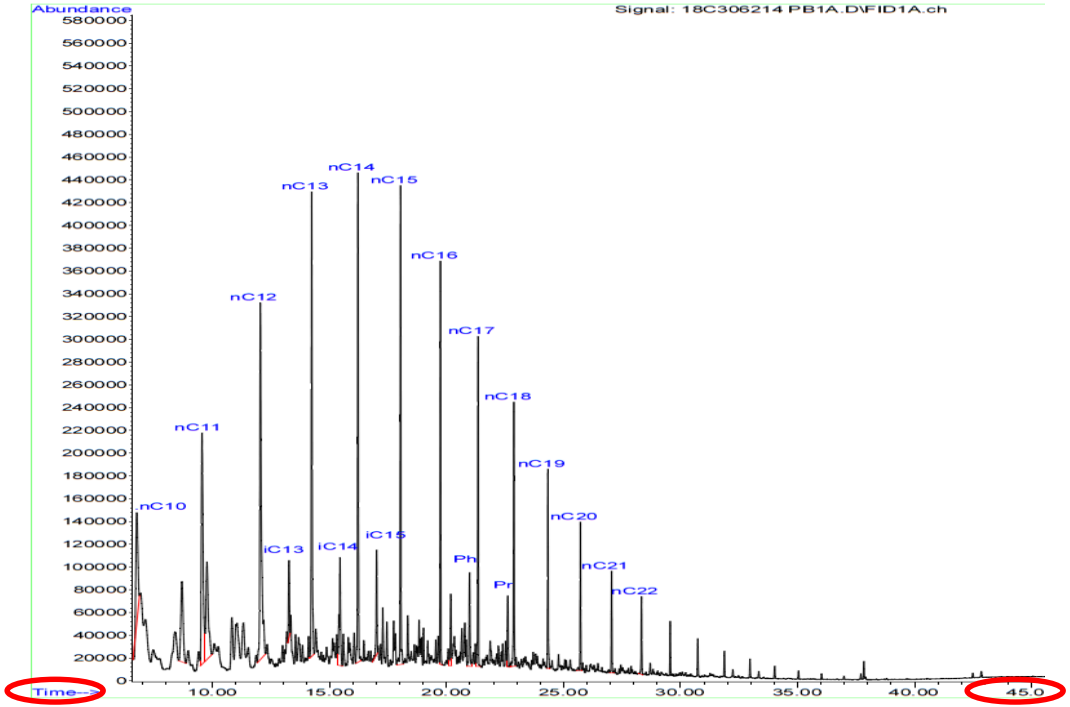
- Cost: Marginal
- Interpretation dependant

GC-FID/MS 'Signature'

- Resolution: Medium
- Multiple points of ID

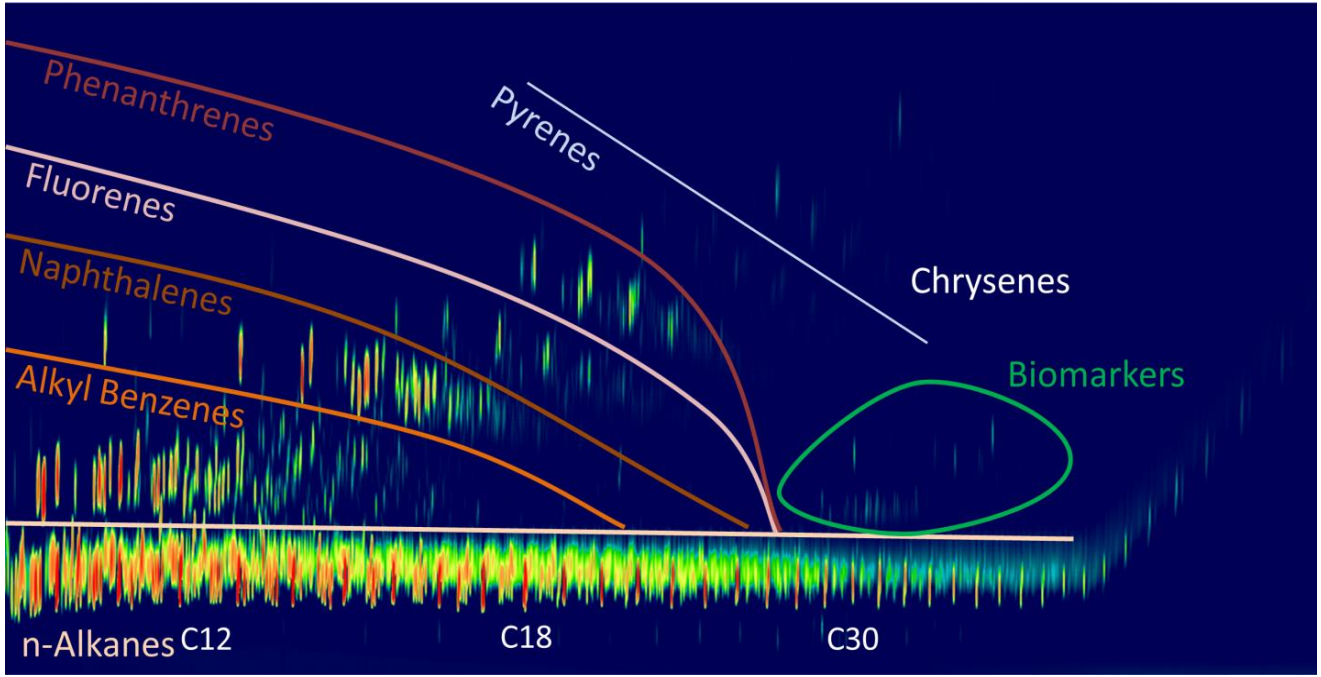
Ratios, profile matches, PCA…

- Multiple Runs
- Cost: Marginal
- Interpretation dependant



45+ min

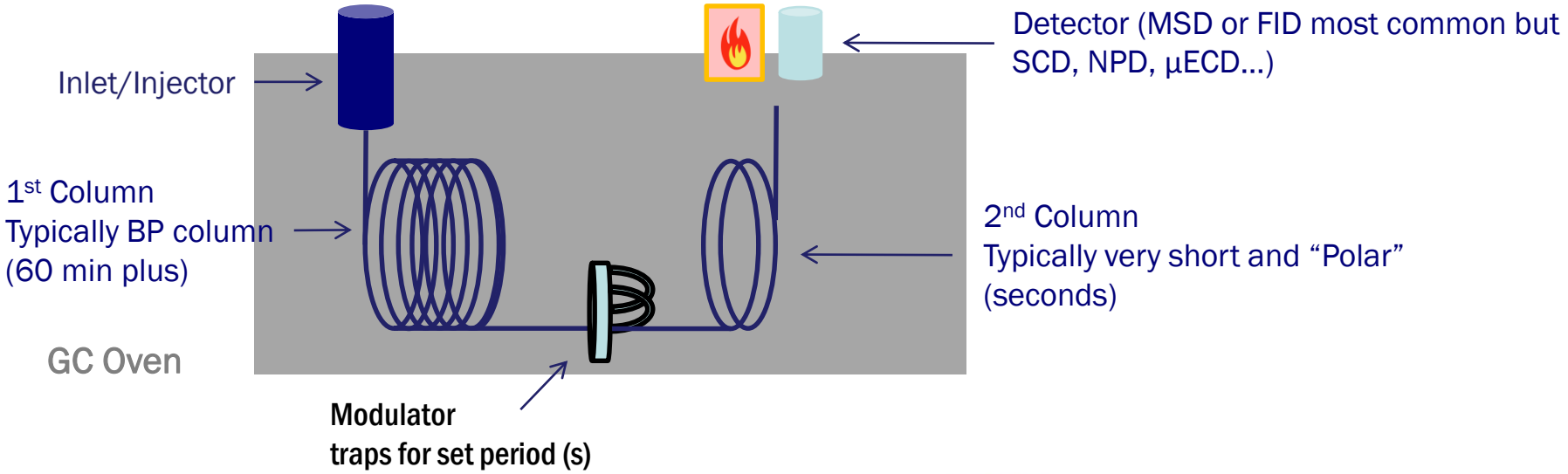
Gulf of Mexico Crude



What is GCxGC?

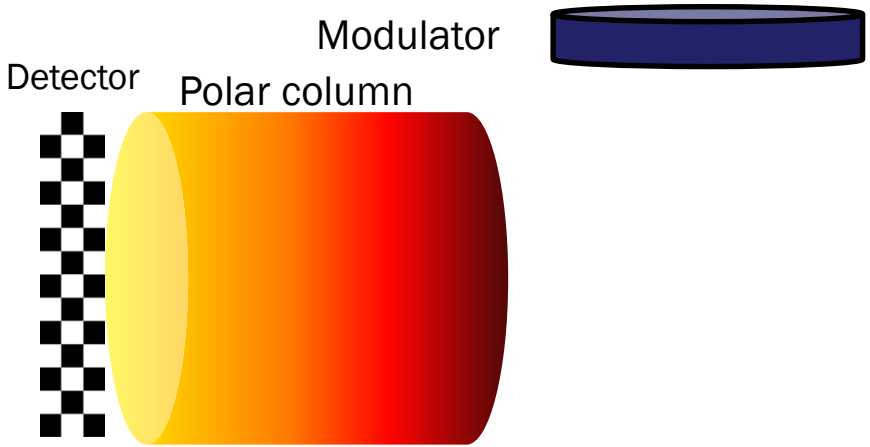
Many different names, GCxGC, Multi-dimensional GC, 2-D GC, GC^2....

Amounts to the same thing, 2 GC columns for multiple levels of separation.



How it works... (roughly)

Start! Non-Polar column



PAH determination

EPA 16 list created in 1970's based on :

- Availability of standards and detection by GC –MS or FID
- Environmental occurrance
- Proxy for other hard to detect or unknown toxicity
- *Known to be toxic ← Requires detection, isolation and characterization. Holistic approach typically unknown/difficult analytically and experimentally.

List has expanded to 23 routine; sometimes 34—but is far from comprehensive or representative of total PAHs

Uncharacterized A-PAHs can be present in variable amounts

*QSARS; TEST

PAH determination

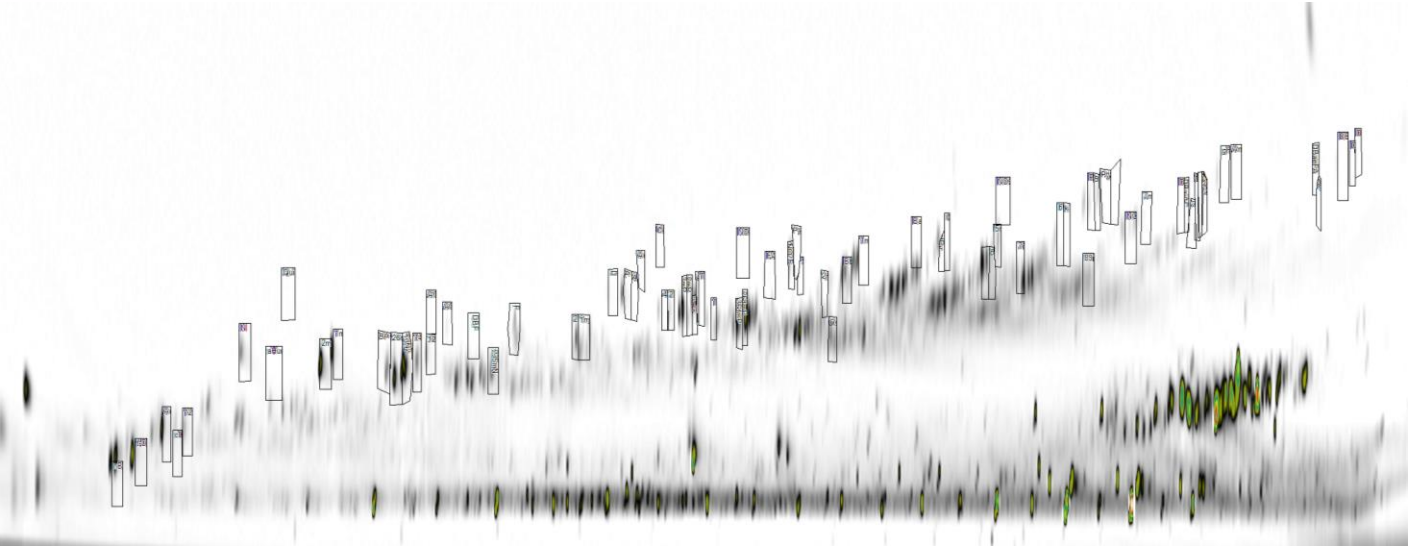
".....209 theoretical isomers of chlorinated biphenyls are possible....."

".....(for PAHS) isomers ranged from 2 for C-1 naphthalene up to 19 502 for C-6 dibenzo(ah)anthracene. Heterocyclic PACs had similar numbers ranging from 4 isomers for C1 dibenzothiophene to 13 938 for C6 dibenzo[a,i]carbazole..."

Enumeration of the constitutional isomers of environmental relevant substituted polycyclic aromatic compounds *–Johnson et al. March 2018 Chemosphere 202*

Hundreds of thousands of substituted PAHs.
Ecotoxicity? Carcinogenicity? QSARS?

Fuel Oil #6 (spiked in Boreal Soil)

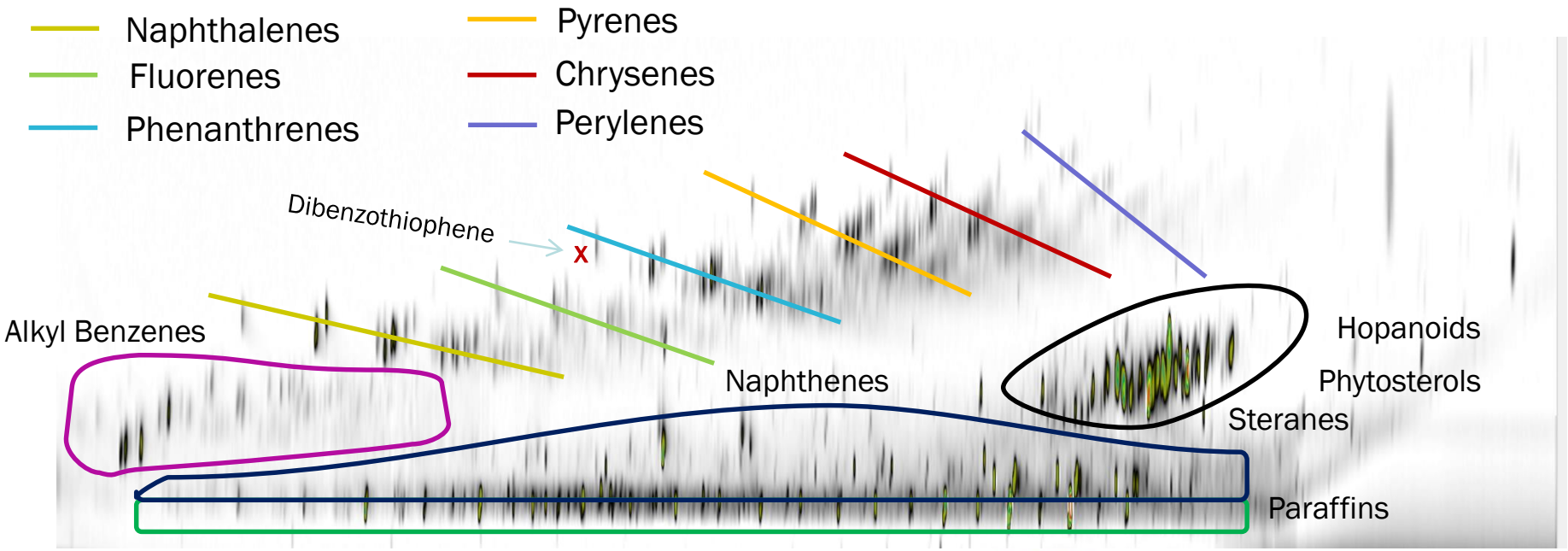


The sheer number of different PAHs that exist is difficult to comprehensively evaluate by any method. However, it is far more possible with GCXGC.

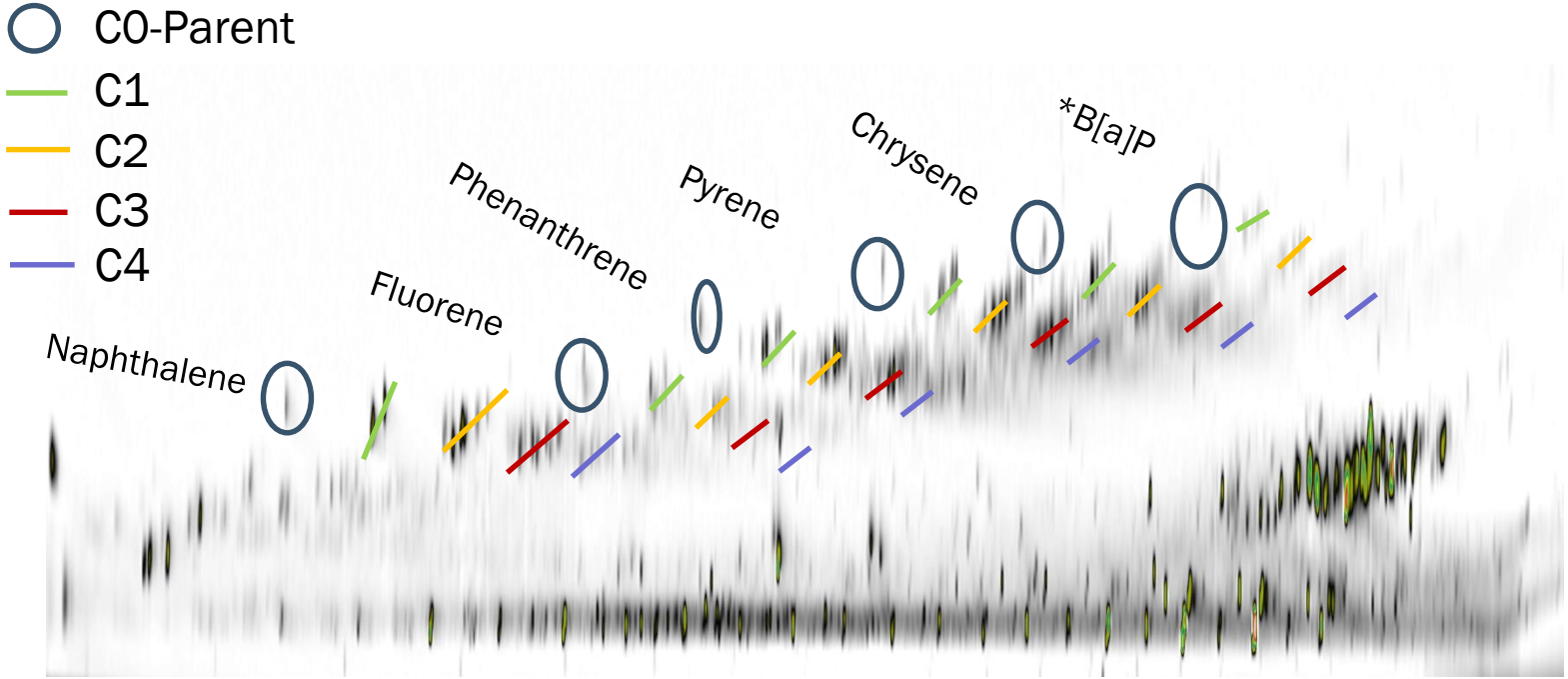
Not realistic or practical to look at each and every PAH
There are not standards available for the 100 000+ compounds for MS

....But what if we could identify quantify groups of PAHs easily?

Fuel Oil #6 (spiked in Boreal Soil)

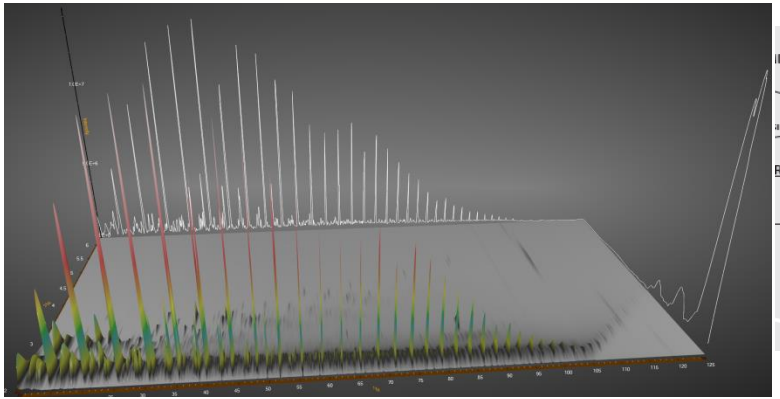


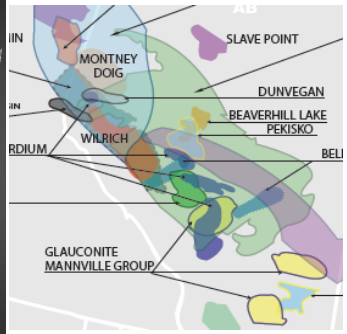
Fuel Oil #6 (spiked in NEBC Soil)



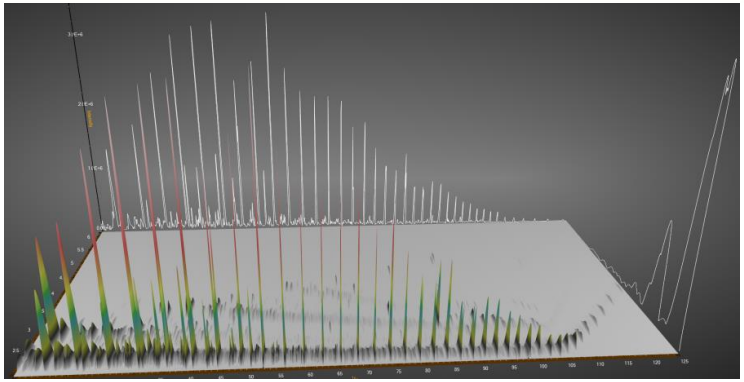
Characterization by class as well as unique identification and quantification as needed for tracking petroleum metabolites

Fingerprinting Oils

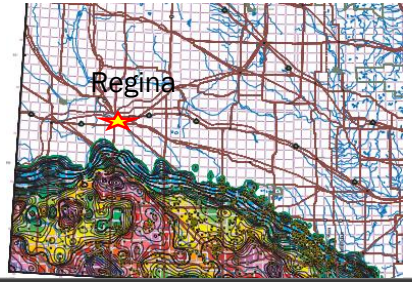


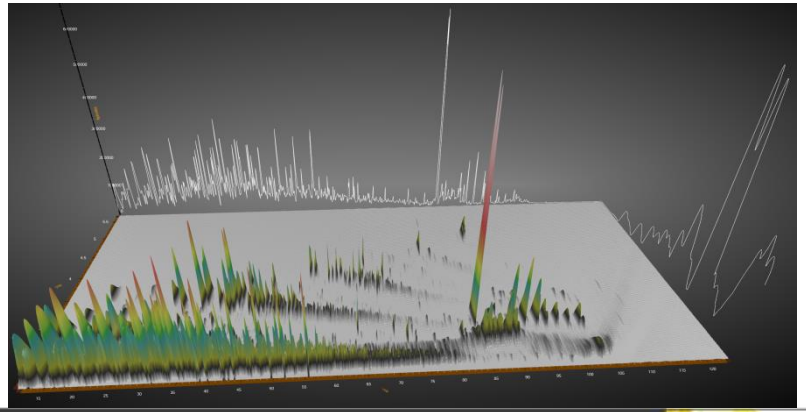


Oil 2 Glauconitic

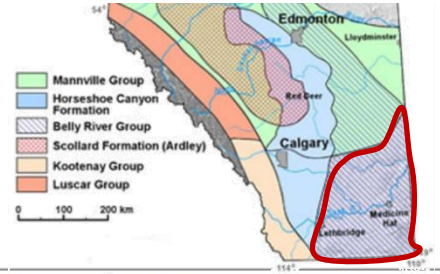


Oil 1 Alida Beds

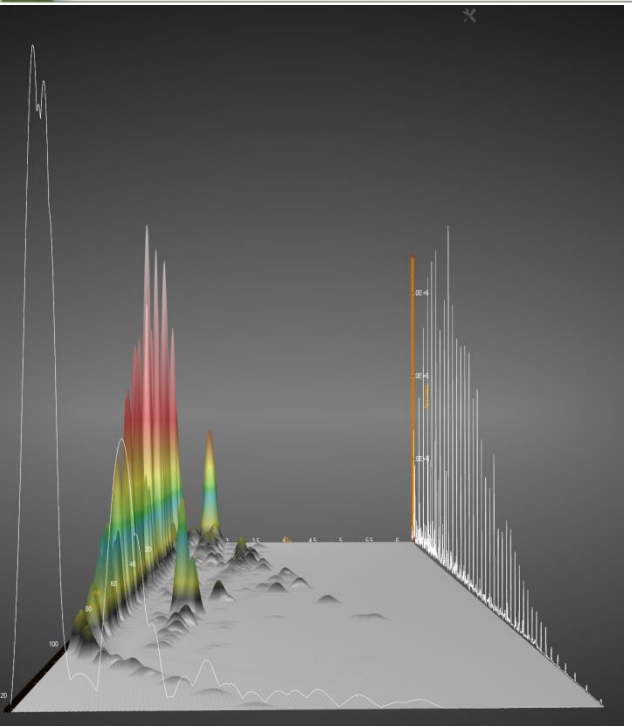




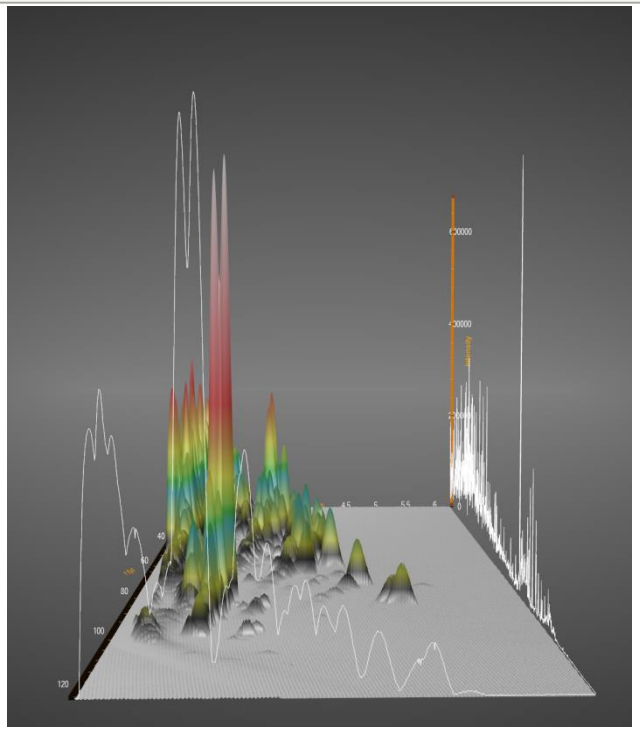
Oil 3 Belly River



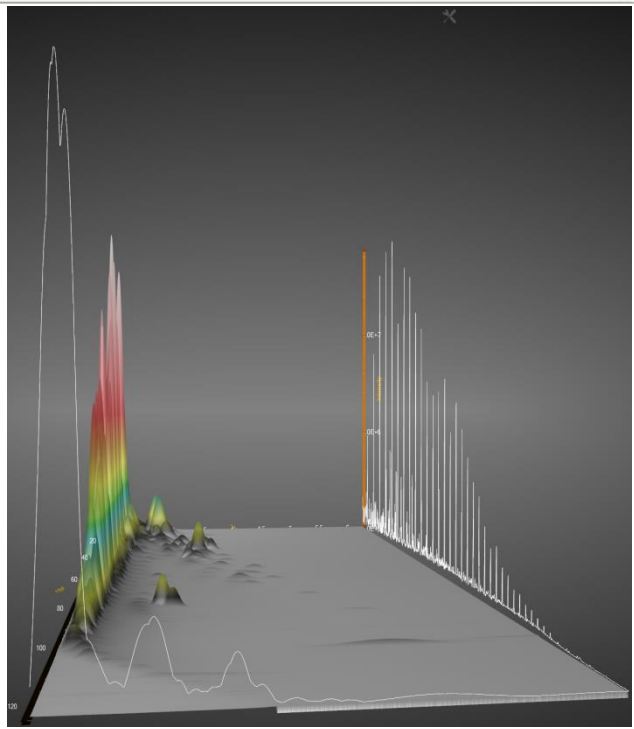
Identifying Oil Type



Oil 1



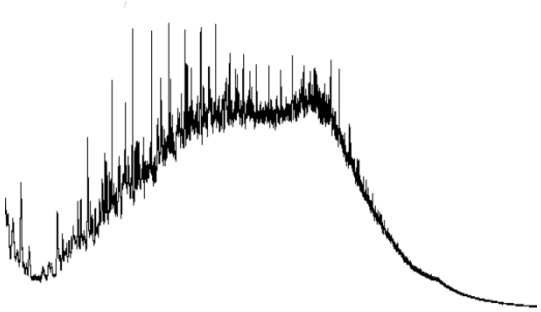
Oil 2



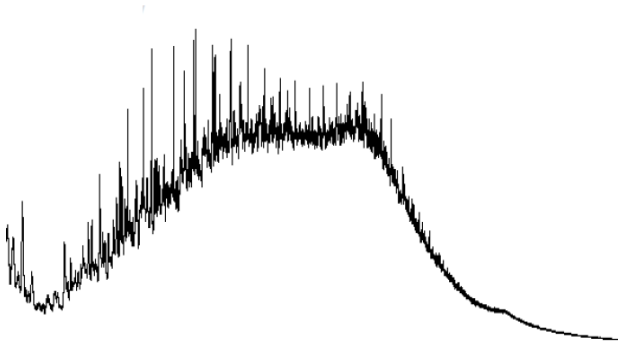
Oil 3

Identifying Oil Type

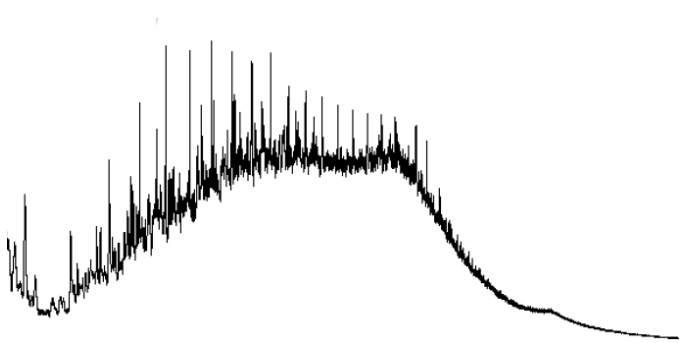
Those three were fairly easy. How about 3 DilBits from different regions?



Cold Lake Oil 1



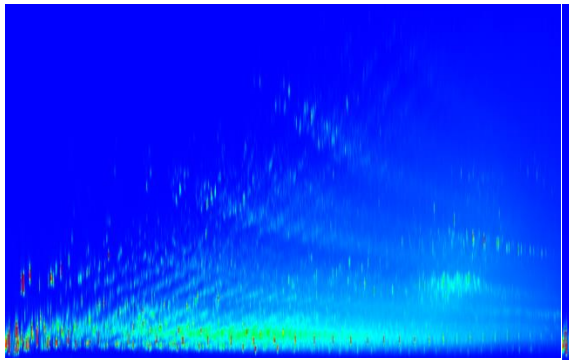
Athabasca Oil 2



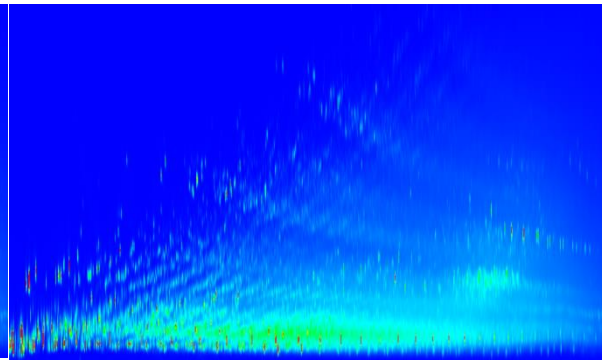
Peace Oil 3

Identifying Oil Type

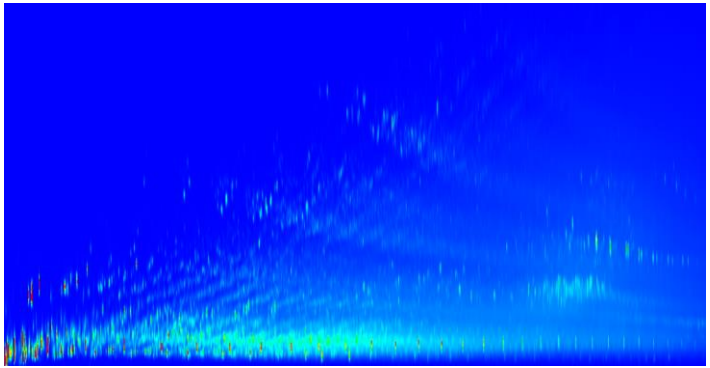
Those three were fairly easy. How about 3 DilBits from different regions?



Cold Lake Oil 1



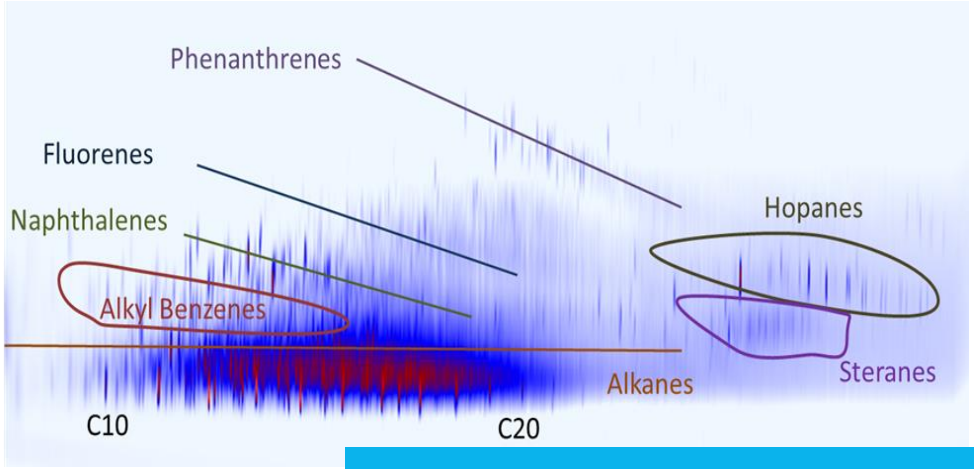
Athabasca Oil 2

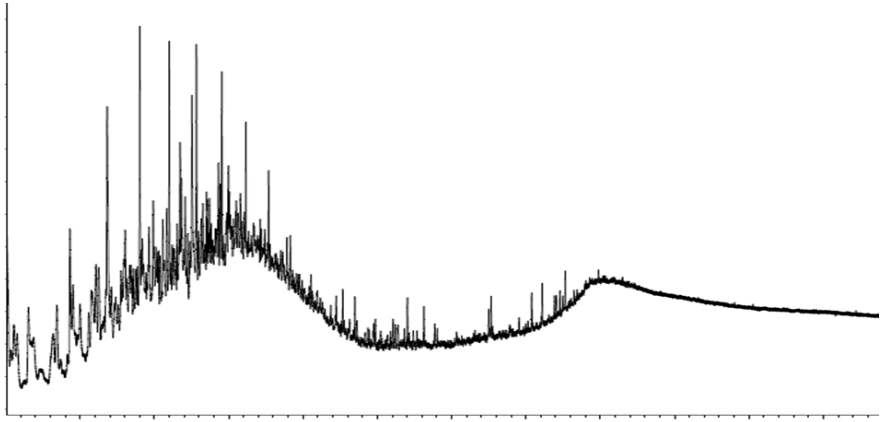


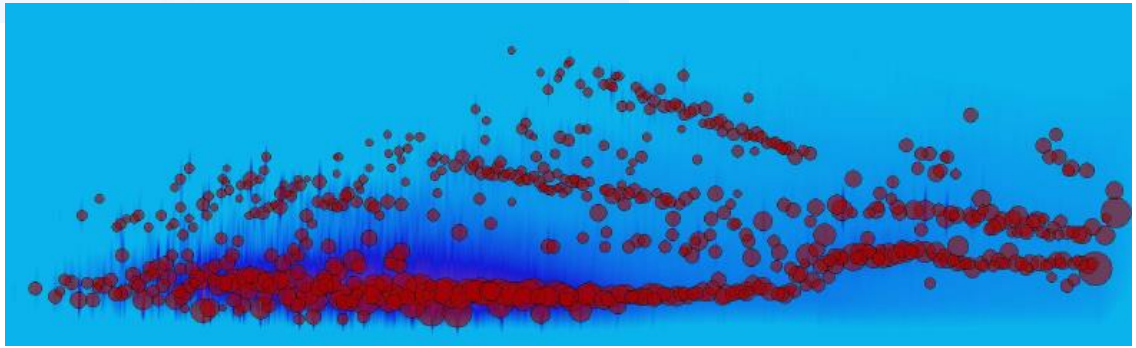
Peace Oil 3

Reddy 2015

Athabasca Diluted Bitumen

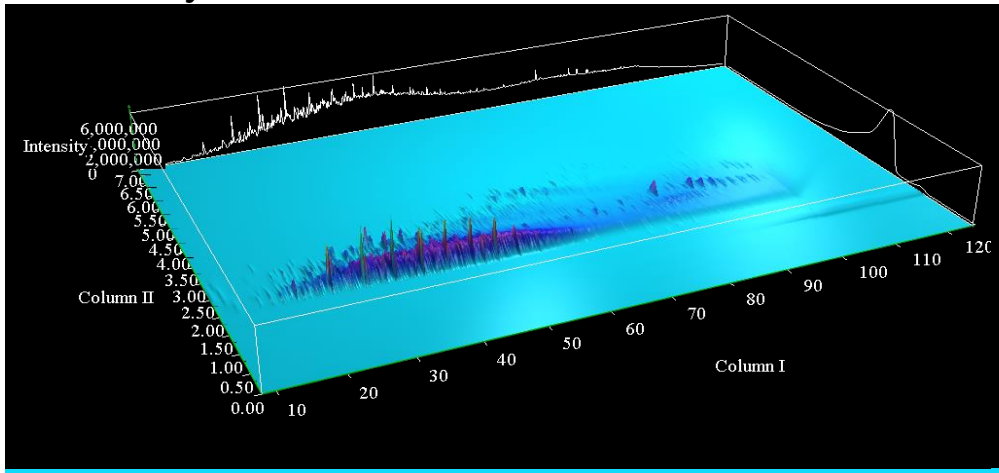




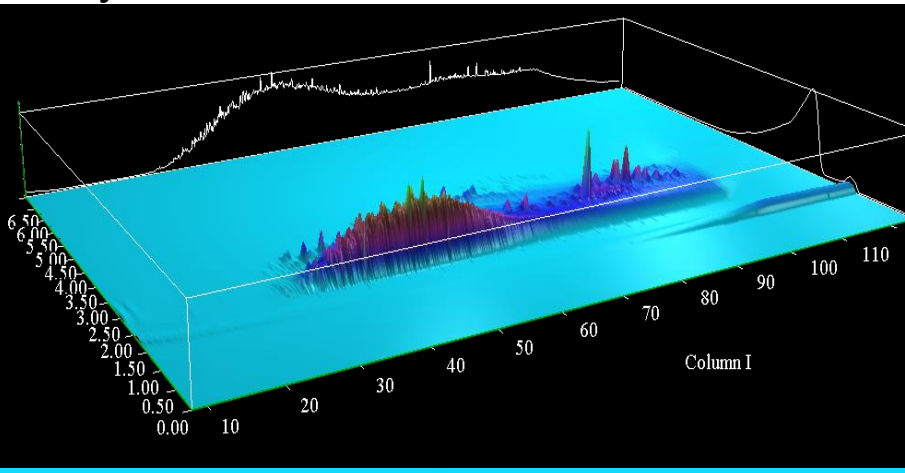


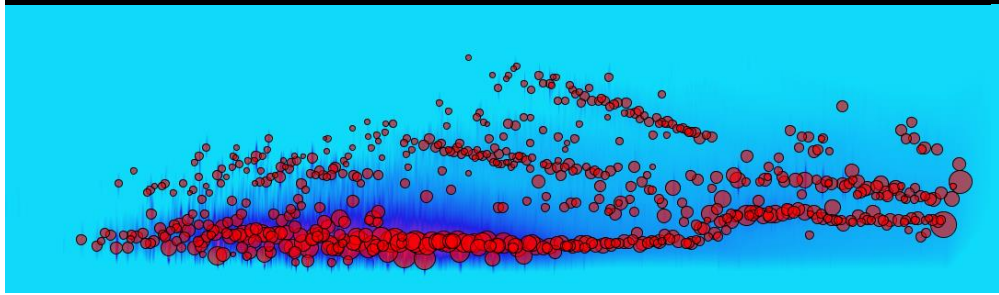
DilBit Weathering

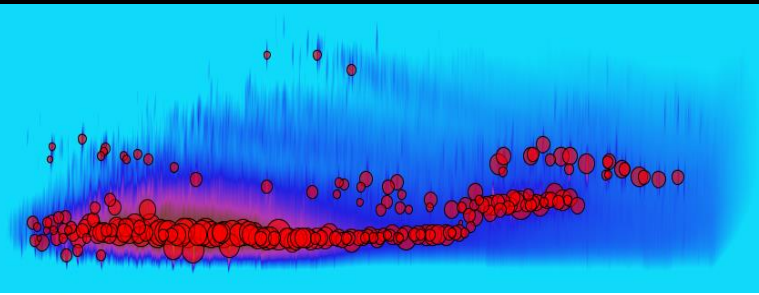
Day Zero



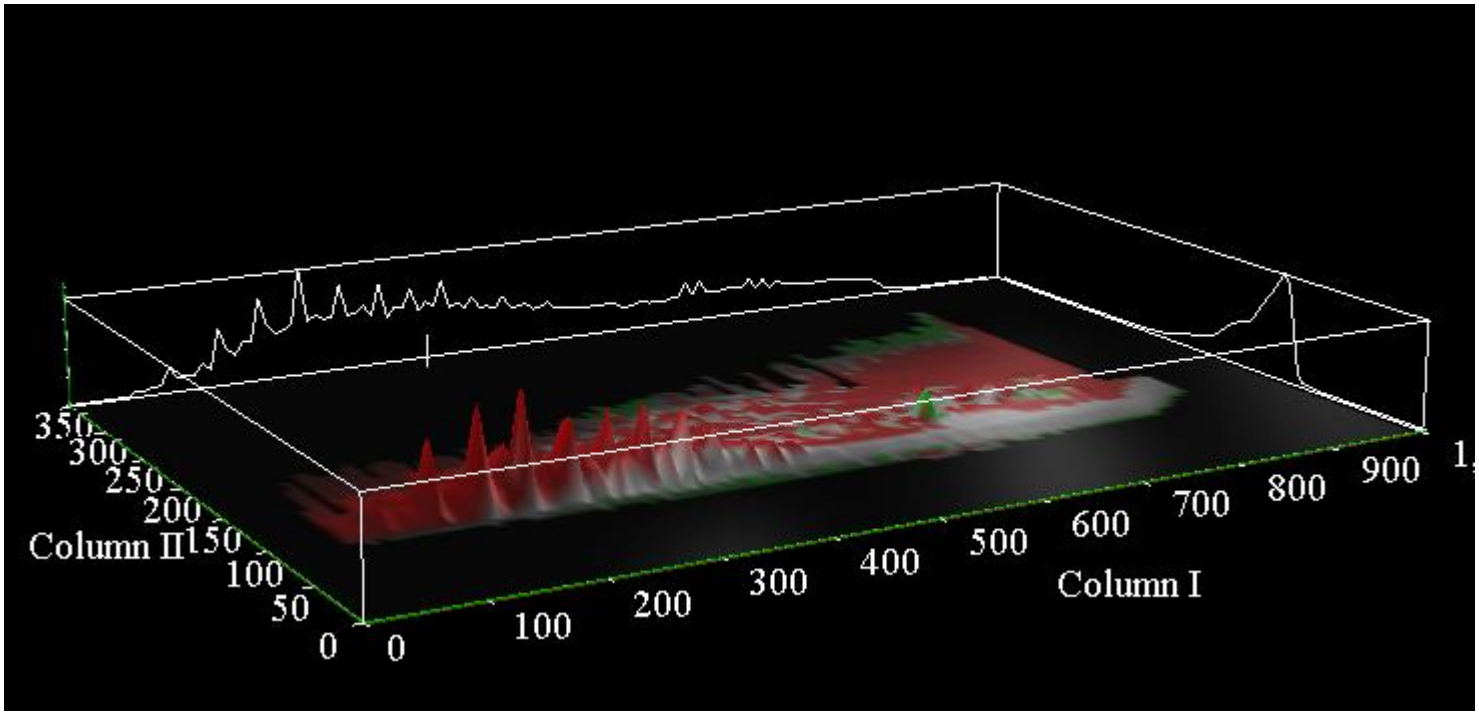
Day 60





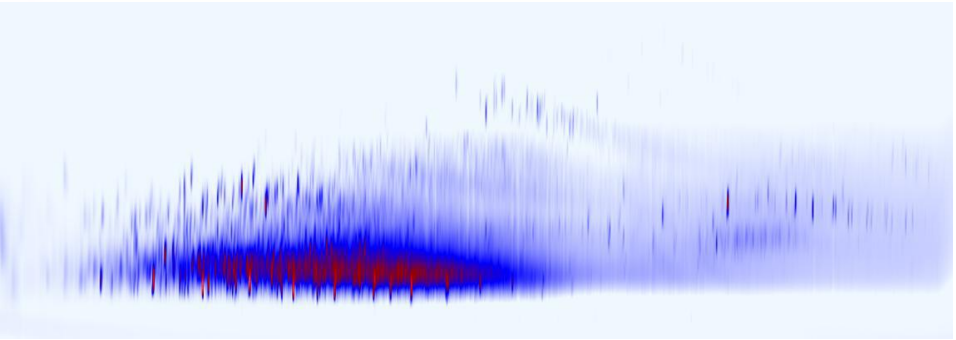


DilBit Weathering

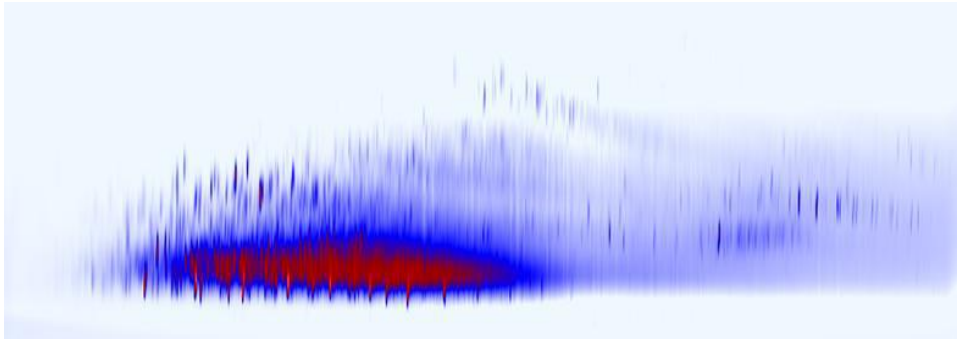


Difference Chromatogram

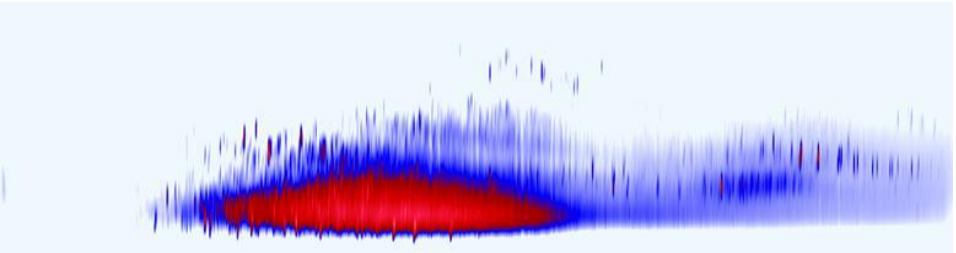
DilBit Weathering



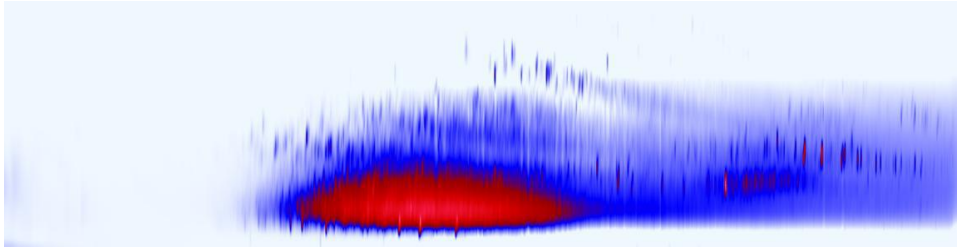
Day 0



Day 2

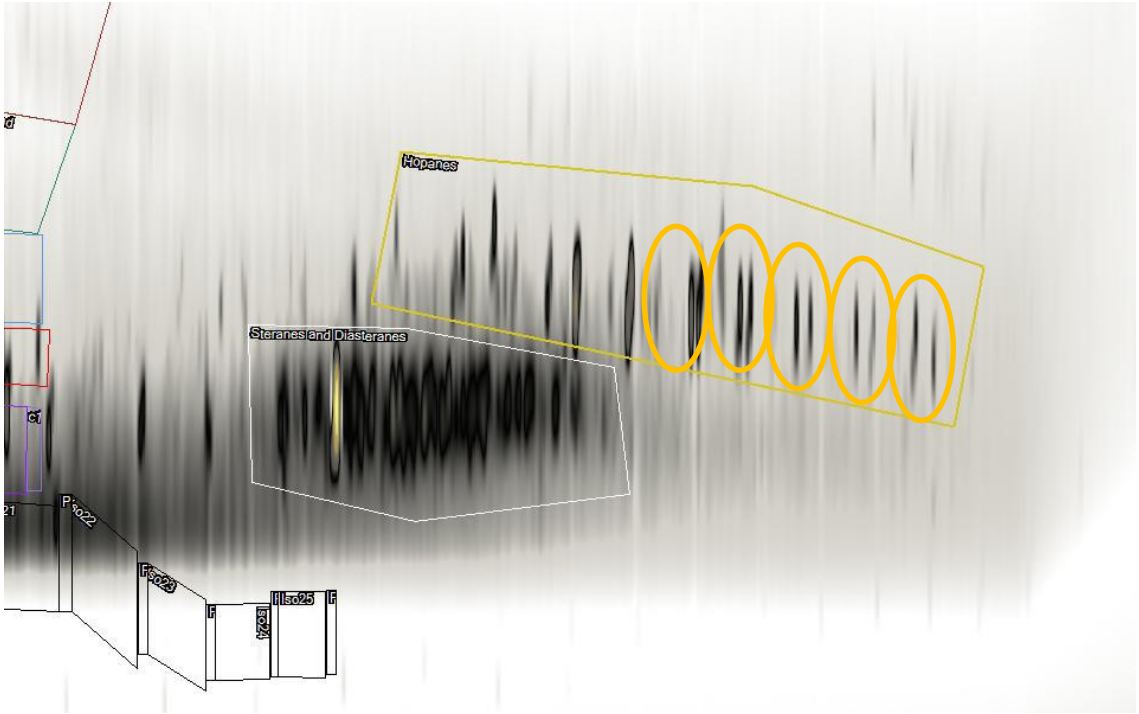


Day 7



Day 14

Biomarkers

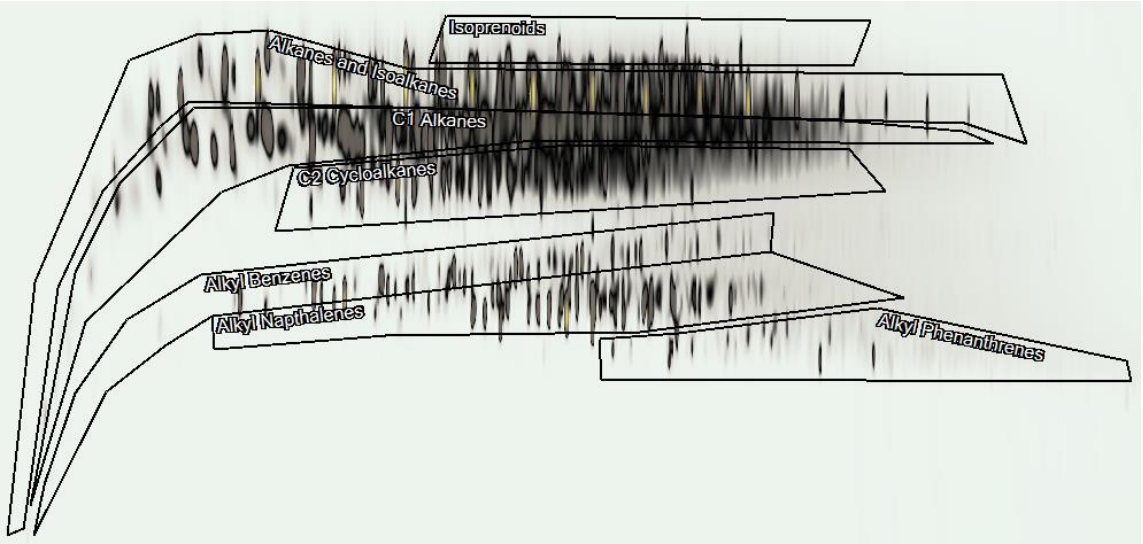


Biomarker region is very complex. Coelution of markers in GCMS TS, Tm, S/R Homo-hopanes. TA, MA steranes, diasteranes.

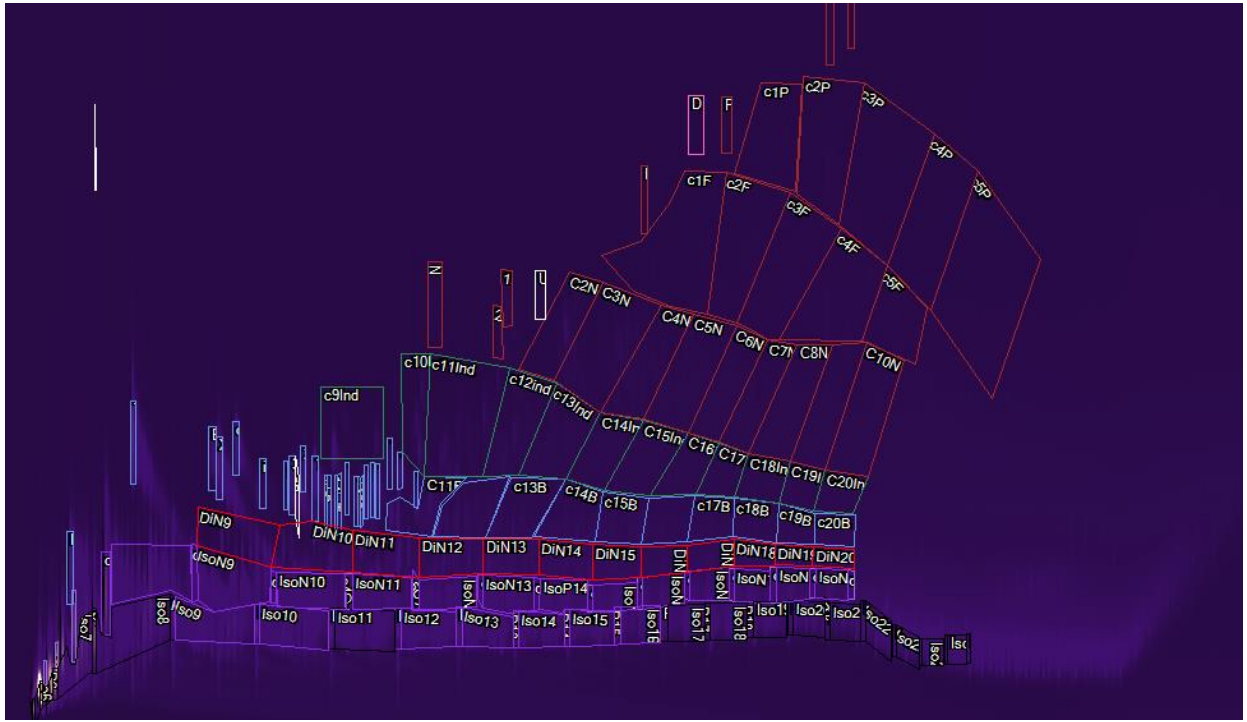
Thermal maturity, etc

Fingerprinting Condensates

Best approach for overall analysis of hydrocarbon classes, most naphthas and gasolines
Generally 1 D suffers from separation of saturates and monoaromatics; 2D enables clear separation



PIONA



Groups cluster well in 2D space; relatively easy to parse

Modified PIONA type analysis

Comprehensive “PIONA”

GCXGC group type analysis

C_{no}	n-P	iso-P	n-CC5/6	iso-N	DiN	mono-Ar	N mono Ar	di AR	N Di Ar	Tri Ar	N Tri Ar	
6	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	
7	0.00	0.00	0.00	0.00	0.14	0.47	0.25	0.52	0.00			
8	0.02	0.22	0.17	0.13	0.02	0.42	0.71	0.63	0.77	0.75	0.66	
9	2.65	0.95	0.90	0.60	0.76	0.72	0.50	0.42	0.65	0.43	0.84	
10	3.50	0.11	0.12	0.15	0.10	0.75	0.71	0.82	0.44	0.89	0.62	
11	5.64	0.11	0.12	0.15	0.10	0.32	0.38	0.57	0.96	0.18	0.59	
12	1.45	3.30	3.30	5.51	4.41	0.08	0.56	0.61	0.83	0.53	0.84	
13	0.91	0.63	0.41	0.30	0.07	0.92	0.55	0.02	0.27	0.81	0.89	
14	0.53	0.53	0.91	0.38	0.48	0.10	0.35	0.82	0.59	0.83	0.21	
15	0.32	0.93	0.50	0.45	0.22	0.13	0.60	0.28	0.81	0.52	0.23	
16	0.24	0.46	0.69	0.22	0.90	0.54	0.62	0.26	0.65	0.72	0.96	
17	0.90	0.30	0.75	0.50	0.32	0.06	0.81	0.25	0.12	0.13	0.15	
18	0.25	0.45	0.52	0.44	0.91	0.09	0.82	0.67	0.14	0.39	0.88	
19	0.05	0.14	0.51	0.13	0.16	0.03	0.11	0.86	0.91	0.06	0.43	
20	0.10	0.06	0.29	0.18	0.54	0.46	0.86	0.11	0.47	0.59	0.28	
21	0.05	0.25	0.41	0.32	0.03	0.04	0.87	0.14	0.22	0.23	0.97	
22	0.04	0.01	0.01	0.28	0.07	0.27	0.32	0.03	0.15	0.17	0.17	
23	0.00	0.04	0.06	0.02	0.09	0.03	0.02	0.03	0.01	0.02	0.04	
24	0.00	0.09	0.04	0.02	0.06	0.08	0.04	0.06	0.05	0.10	0.06	total
total	16.65	8.60	9.72	9.77	9.39	5.51	9.09	7.11	8.01	7.35	8.81	100.00

Cno- Carbon Number, n-P: Normal Paraffins, isoP: Isoparrafins; n-C5/6: n-alkane, cyclopentane cyclohexane; isoN: Isonaphthenes; diN: diNapthenes; Mono Ar: monoaromatics; n-mono Ar: naphthenic mono aromatics; Di Ar: Diaromatics; N-DiAR: naphthenic diaromatics; TriAr: Triaromatics; N Tri Ar: naphthenic triaromatics.

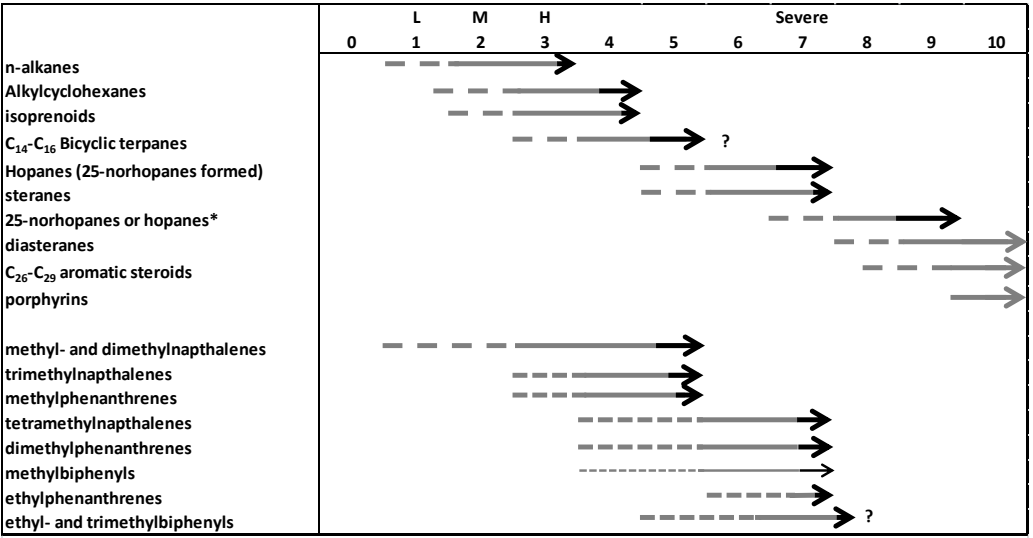
GCXGC PIONA style analysis

Quantitative nature of FID; easy for response factor

Weathered Diesel

- Petroleum releases can be challenging to ‘age’ there is a lot of variability and it is important to know the ‘mode’ of release; Chronic releases have a different appearance than acute or catastrophic releases.
- Compositional changes in samples can help ascertain this—but need to a representative group of geospatial samples to make the best use of the chemistry data. (ex. at least two samples from the source and the outer plume edge.)
- Weathering mechanisms dependant on site conditions and release; degradation typically relies on the availability of water, energy, oxygen, nutrients, etc.
- For example, low temperatures (Northern Canada) and a thick release profile (>15cm) can appear fresher than thin layers at lower latitudes.
- Field conditions such as pH, DO, conductivity, etc. aid in identifying the likely weathering ‘regime’
- Good info in good results out ☺

Weathering Stages



Recreated from Peters *et al* (2005). The extent of biodegradation of mature crude oil can be ranked on a scale of 1—10 based on differing resistance of compound classes to microbial attack. Biodegradation is quasi-sequential because some of the more labile compounds in the more resistand compound classes can be attacked before complete destruction of less resistant classes (from Peters and Moldowan, 1993). Arrows indicate where compound classes are first altered (dashed lines), substantially depleted (solid grey), and completely eliminated (black), Sequence of alteration of alkylated polyaromatic hydrocarbons is based on work by Fisher *et al.* (1996b; 1998) and Triolo *et al.* (1999). Degree of biodegradation from Wenger *et al.* (2002) reflects changes in oil quality (L,

*Hopanes degraded without the formation of 25-norhopanes.

Weathering regime:	Very aggressive	Aggres-sive	Moderate	Weak	Very Weak
Fresh fuel	0	0	0	0	0
Kaplan Stages:					
1. Abundant *n*-alkanes	<0.25	0-2	0-4	0-8	0-10
2. Light *n*-alkanes removed, benzene & toluene removed	<0.5	2-4	4-8	8-16	10-20
3. Middle-range *n*-alkanes removed, ethylbenzene & xylenes removed	<1	4-6	8-12	16-24	20-30
4. More than 50% of the *n*−alkanes removed	<2	6-8	12-16	24-32	30-40
5. More than 90% of *n*-alkanes removed, alkyl-benzenes and alkyl-*cyclo*-hexanes begin to degrade	<3	8-10	16-20	32-40	40-50
6. All n-alkanes removed, alkyl-benzenes	<4	10-12	20-24	40-48	50-60
7. Isoprenoid removal significant	<5	>12	>24	>48	>60

Kaplan Stages (Oudiijk 2009)

Benefits Using GCxGC

- The power of GCxGC provides enhanced specificity and peak capacity with increased resolving power that can separate diagnostic biomarkers from potential interferences.
- GCxGC provides a structured chromatogram, which allows compound identification that would be impossible with GC due to the complexity of crude oil.

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Thank you!

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QUESTIONS AND DISCUSSION

Thank you!!