

Defining geogenic background for site investigations – Combining petroleum forensic chemistry and geology

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Outline

- Framework for Forensic Chemistry
- Site data and examples from literature

All about hydrocarbons





Know your science

PHCs and PAHs

AB Tier 1

CCME CWS for PHCs Scientific Rationale 2008

CCME PAH guidance document 2010

Source-Pathway-Receptor considerations

Non-carcinogenic PAHs have been included as components of PHC Fractions (2 + 3) for derivation of guidelines.

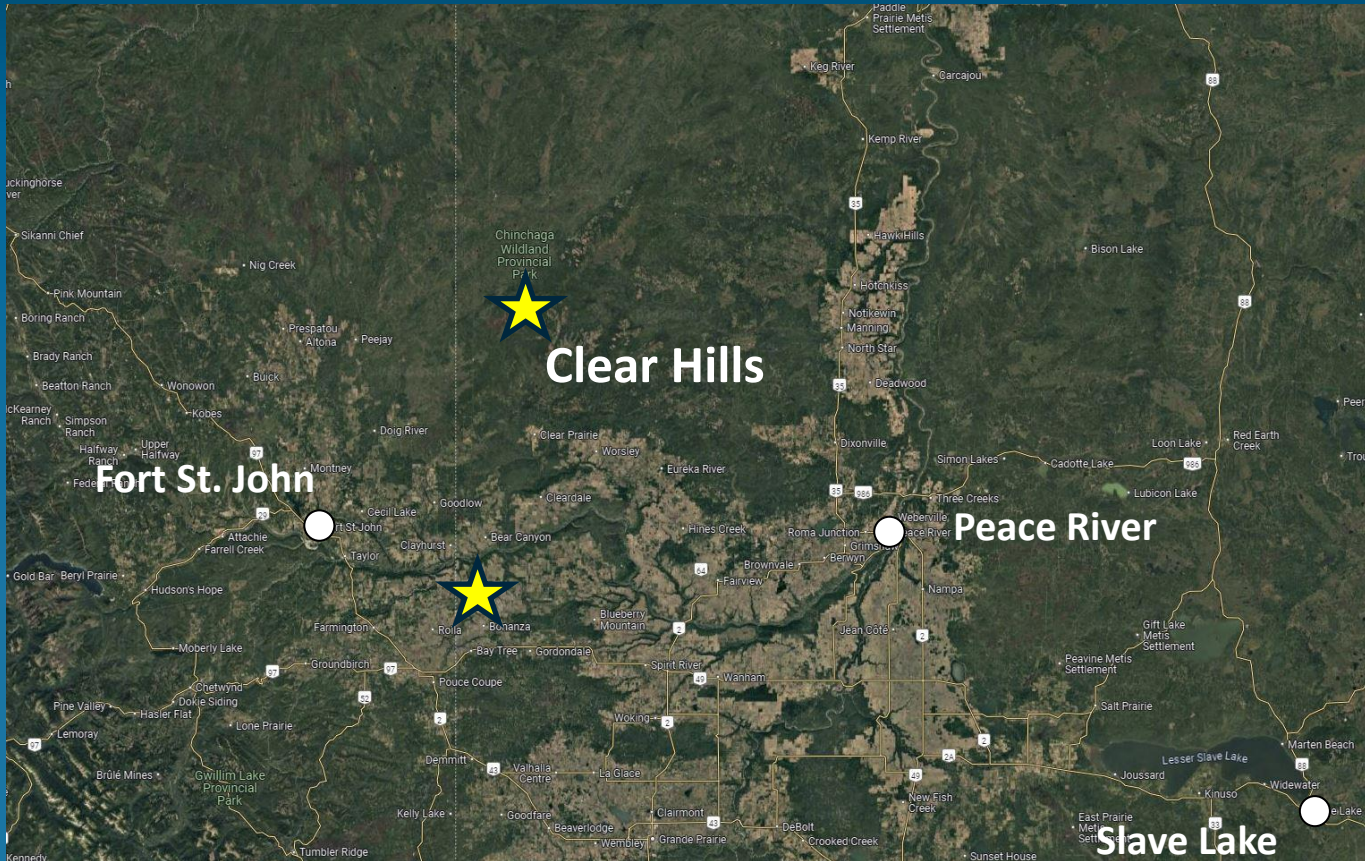
Exceptions:

- DUA or FAL receptor (realistically FAL is by far most strict)
- Sources with high concentration of PAHs such as creosote or combustion residues,
- If cannot limit analysis – can conduct forensic chemistry.

Big picture context

- Aromatics – BTEX and PAHs
- Focus on Peace River area
- Concepts are applicable everywhere
 - River sediments,
 - Quaternary deposits that include bitumen,
 - Bedrock and soil in AB foothills and Front Ranges, Hay-Zama, NE BC fields (Monias, Buick...)...

Area of Interest



The sites

Former Compressor Station

Identified PAHs above GL



Former Sweet Gas Plant

Identified BTEX and PAHs above GL



Characteristics not indicative of an anthropogenic source – condensate, diesel, crude oil, or combustion sources.

Analytical results – PHCs and BTEX

Location	Benzene	Toluene	Ethylbenzene	Xylenes	F1 C6-C10 - BTEX	F2 C>10-C16	F3 C>16-C34	F4 C>34
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
A	<0.005	<0.02	0.012	<0.03	<10	<25	<50	<100
A	<0.005	<0.02	<0.005	<0.03	<10	<25	<50	<100
A	<0.005	<0.02	<0.005	<0.03	<10	<25	<50	<100
B	<0.005	<0.02	<0.005	<0.03	<10	<25	<50	<100
B	0.037	0.04	0.109	0.11	<10	<25	<50	<100
B	0.043	0.06	0.13	0.12	<10	<25	<50	<100
B	0.048	0.05	0.136	0.11	<10	<25	<50	<100
C	<0.005	<0.02	<0.005	<0.03	<10	<25	<50	<100
C	<0.005	<0.02	<0.005	<0.03	<10	<25	<50	<100
C	0.015	0.03	0.121	0.1	<10	<25	<50	<100
C	0.048	0.09	0.148	0.16	<10	<25	<50	<100
D	<0.005	<0.02	<0.005	<0.03	<10	<25	<50	<100
D	<0.005	<0.02	<0.005	<0.03	<10	<25	<50	<100
D	0.052	0.06	0.125	0.12	<10	<25	<50	<100
D	0.038	0.02	0.1	0.1	<10	<25	<50	<100

Detects and GL exceedances for aromatics.
Non-detect PHC Fractions

Analytical results - PAHs

Sample	Acenaphthene	Anthracene	Fluoranthene	Fluorene	Naphthalene	Phenanthrene	Pyrene	Benz[a]anthracene++	Benzo[b&f]fluoranthene++	Benzo[k]fluoranthene++	Benzo[g,h,i]perylene++	Benzo[a]pyrene++	Chrysene ++	Dibenz[a,h]anthracene++	Indeno[1,2,3-cd]pyrene++
A	<0.05	<0.0030	<0.010	<0.05	0.013	0.07	0.012	<0.01	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
A	<0.05	<0.0030	0.017	<0.05	0.016	0.07	0.012	<0.01	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
A	<0.05	<0.0030	0.037	0.07	0.048	0.39	0.057	0.02	0.09	<0.05	<0.05	<0.05	0.1	<0.05	<0.05
A	<0.05	<0.0030	0.032	<0.05	0.01	0.13	0.055	0.02	0.07	<0.05	0.05	<0.05	<0.05	<0.05	<0.05
A	<0.05	<0.0030	0.033	<0.05	0.014	0.07	0.054	0.02	0.07	<0.05	0.08	<0.05	<0.05	<0.05	<0.05
B	<0.05	<0.0030	<0.010	<0.05	<0.010	0.04	<0.010	<0.01	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
B	<0.05	<0.0030	0.023	<0.05	0.01	0.09	0.033	<0.01	0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
B	<0.05	<0.0030	0.042	0.05	0.053	0.41	0.073	0.02	0.1	<0.05	<0.05	<0.05	0.11	<0.05	<0.05
B	<0.05	<0.0030	0.031	0.05	0.019	0.18	0.06	0.02	0.08	<0.05	<0.05	<0.05	0.06	<0.05	<0.05
B	<0.05	<0.0030	0.037	0.11	0.027	0.37	0.078	0.02	0.09	<0.05	<0.05	<0.05	0.1	<0.05	<0.05
C	<0.05	<0.0030	<0.010	<0.05	<0.010	0.02	<0.010	<0.01	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
C	<0.05	<0.0030	0.037	0.06	0.054	0.31	0.073	0.02	0.09	<0.05	<0.05	<0.05	0.09	<0.05	<0.05
C	<0.05	<0.0030	0.027	<0.05	0.027	0.17	0.028	<0.01	0.06	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
C	<0.05	<0.0030	0.026	<0.05	0.023	0.19	0.041	0.01	0.06	<0.05	<0.05	<0.05	0.05	<0.05	<0.05
C	<0.05	<0.0030	0.027	<0.05	0.012	0.06	0.051	0.02	0.07	<0.05	0.07	<0.05	<0.05	<0.05	<0.05

Detects and GL exceedances for non-carcinogenics.

Framework for Forensic Chemistry

1. Information review

- Potential anthropogenic sources
- Potential natural sources

2. Additional data collection

- Tie the site data to literature.

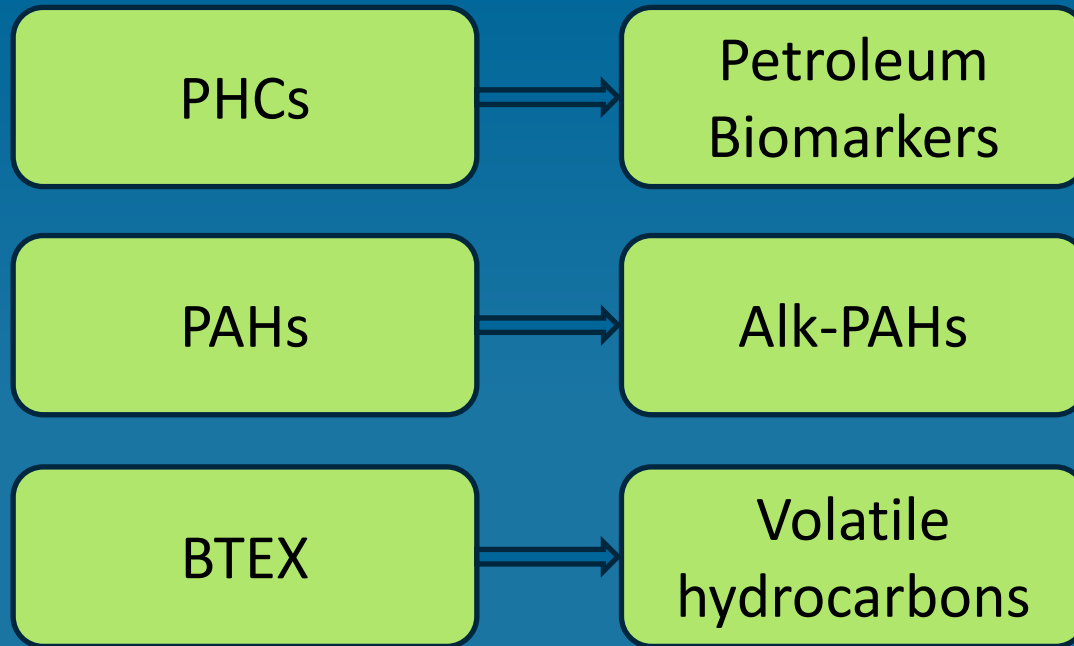
3. Interpretation

- PHCs, including chromatograms
- Standard PAHs
- Alkylated PAHs (PIANO, petroleum biomarkers...)

4. Conclusion - SSROs / complete exclusion of COC

Additional data collection

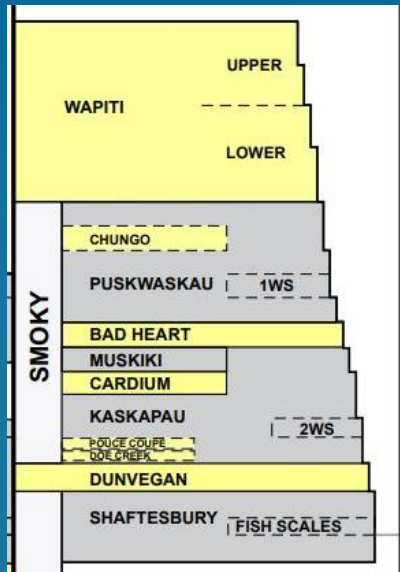
Select representative samples



Information review

Geological expectations - bedrock

- Interbedded marine and non-marine shales and sandstones - Hydrocarbon-bearing



Bituminous coal

Oil kerogen

Oil kerogen

Lignite / Sub-bituminous coal

Immature oil kerogen

Geological expectations - soil

- The surficial geology in the area is comprised of glaciolacustrine deposits.
- These contain “a high proportion of material derived from the local Cretaceous bedrock.”
- Inclusions will contain coal / oil kerogen

Geology – Chemistry

Organic Geochemistry 39 (2008) 801–819



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Contents lists available at ScienceDirect

Organic Geochemistry

journal homepage: www.elsevier.com/locate/orggeochem

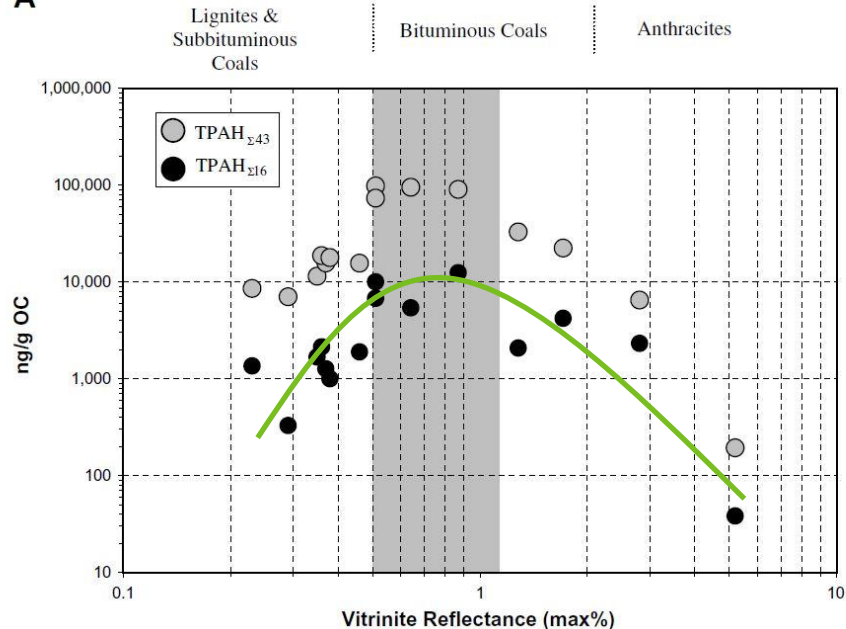


Concentration and character of PAHs and other hydrocarbons in coals of varying rank – Implications for environmental studies of soils and sediments containing particulate coal

Scott A. Stout*, Stephen D. Emsbo-Mattingly

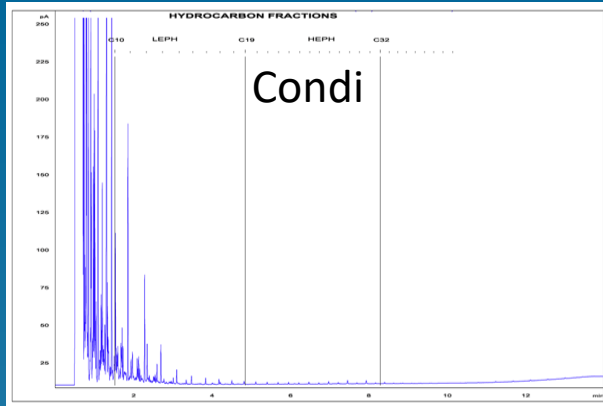
NewFields Environmental Forensics Practice, LLC, 300 LedgeWood Place, Suite 305, Rockland, MA 02370, United States

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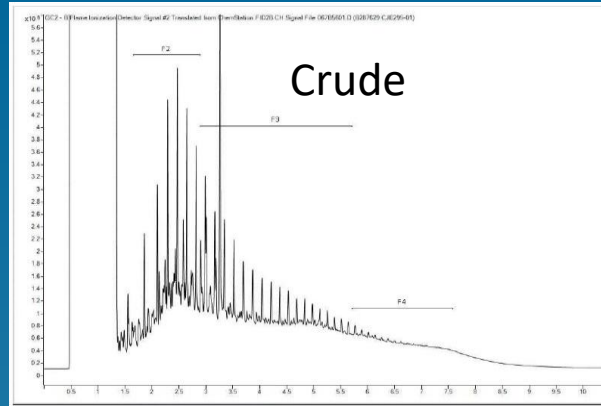


Anthropogenic sources

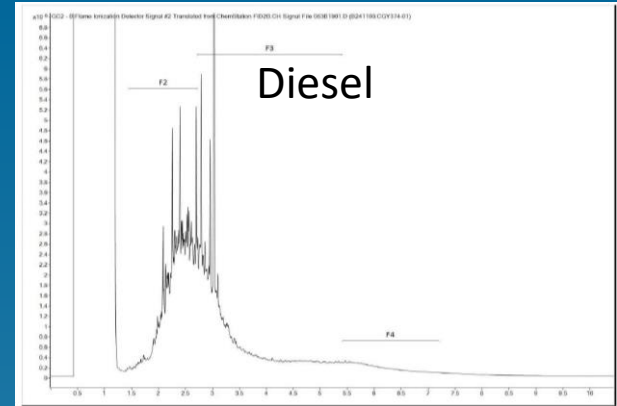
Start with review of PHC chromatograms



PHC F1-F2



PHC F1-F4

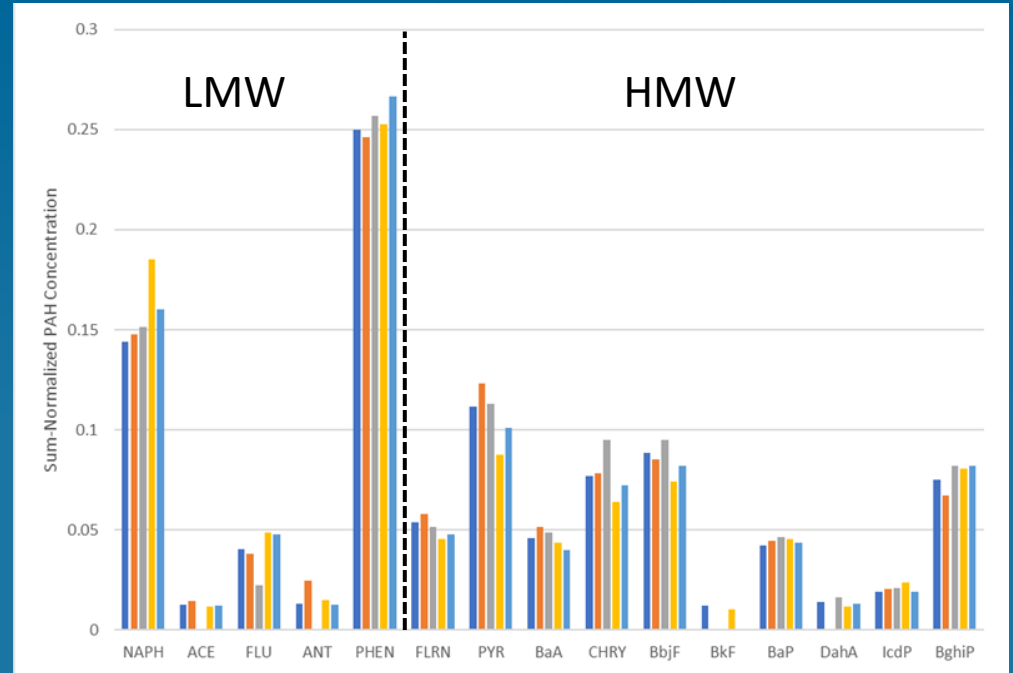


PHC F2-F3

Fingerprinting for PAHs

Example – HV bituminous coal

Standard PAHs
Normalize data
Multiple samples
LMW->HMW



Fingerprinting for PAHs

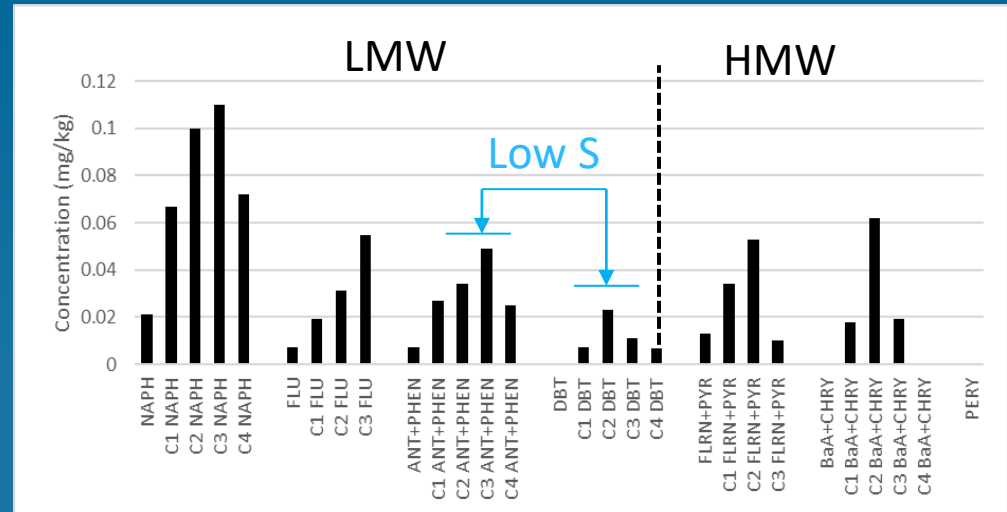
Example – HV bituminous coal

Alkylated PAHs

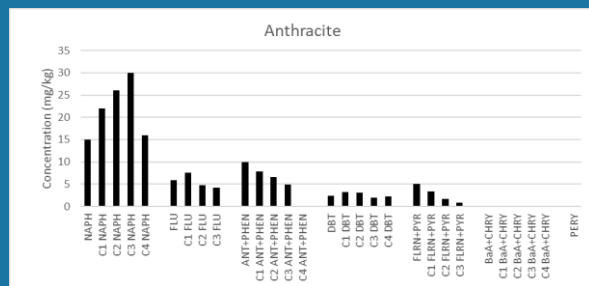
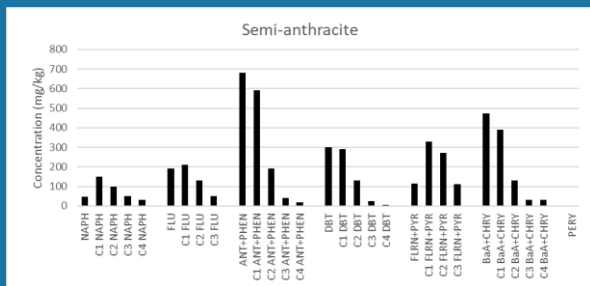
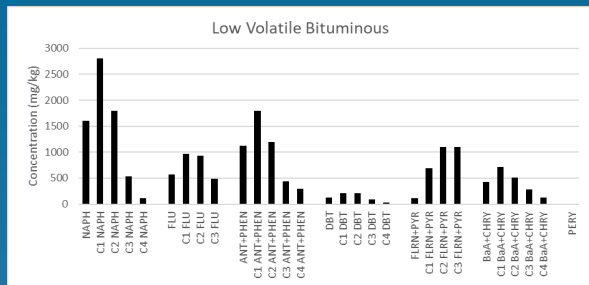
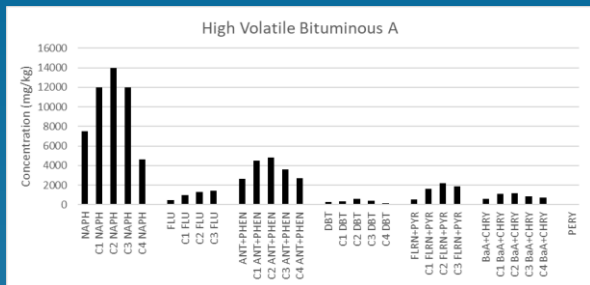
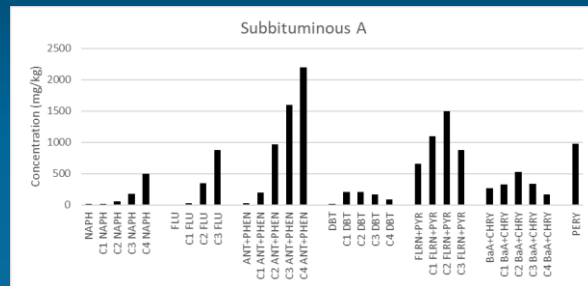
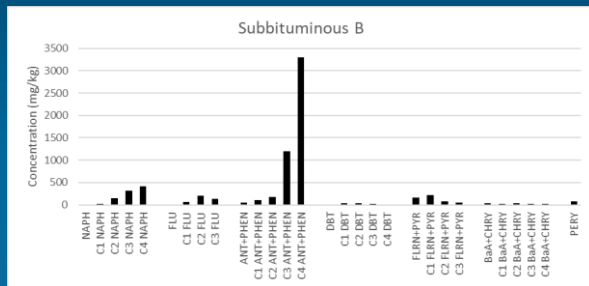
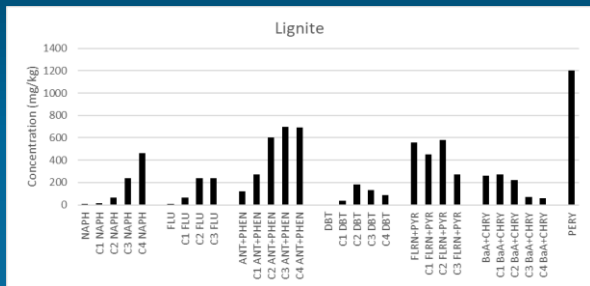
Prepare data – combine
some PAHs

Single sample is best

LMW- \rightarrow HMW

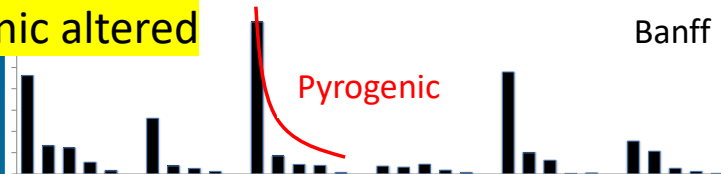


Alkylated PAHs – coal types



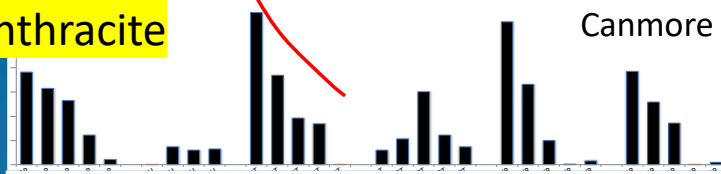
Alkylated PAHs – Bow Valley

Pyrogenic altered



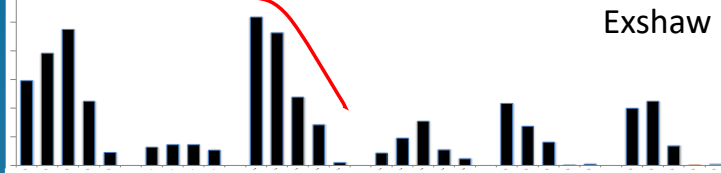
Banff

Semi-anthracite

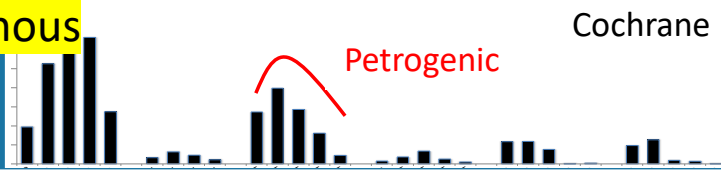


Canmore

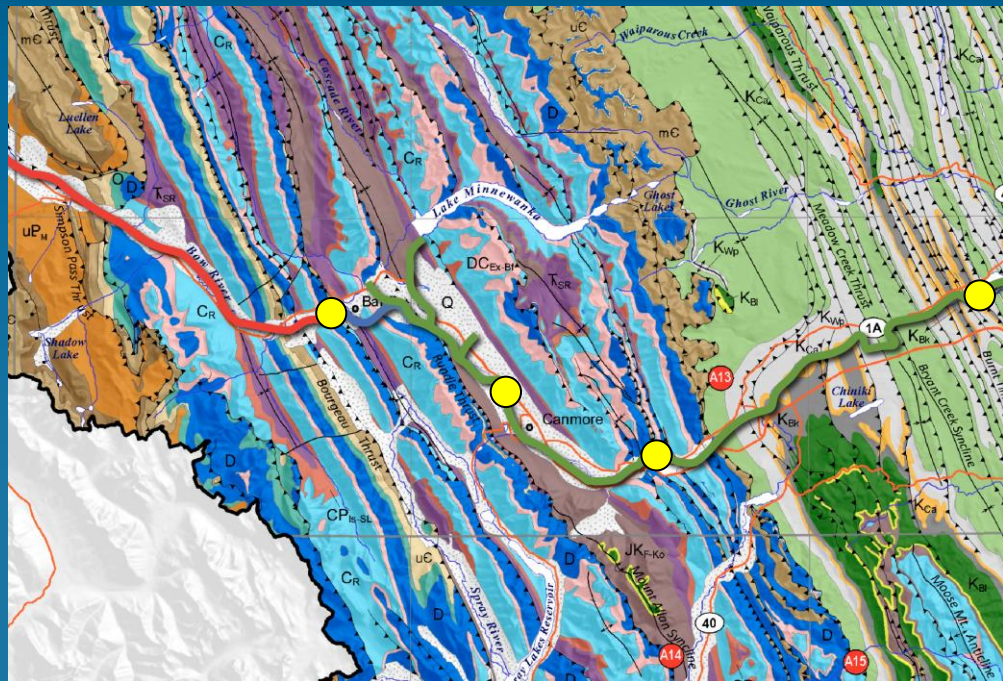
Exshaw



Bituminous



Cochrane



Data interpretation

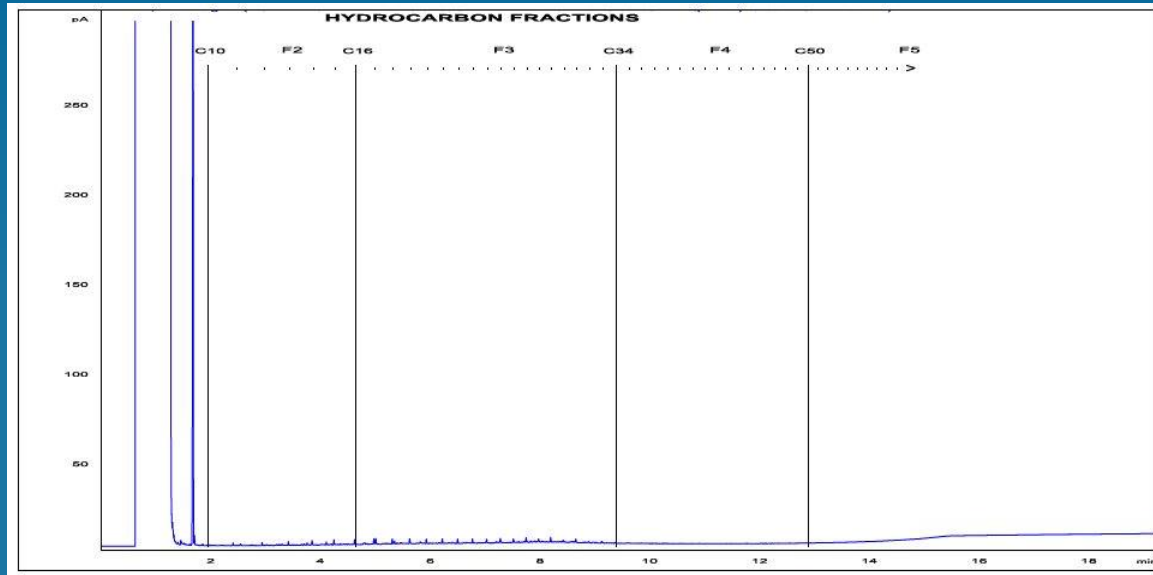
PHCs

PAHs

Alkylated PAHs

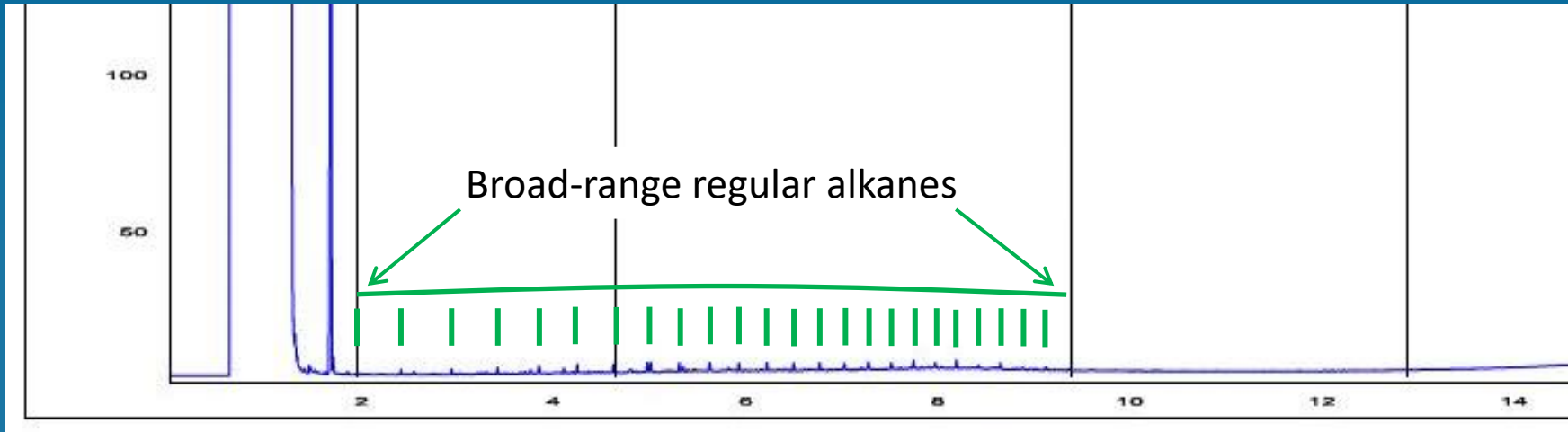
PHCs

- Use of chromatograms... to contrast with anthropogenic sources.
- All samples show low or no PHCs detected



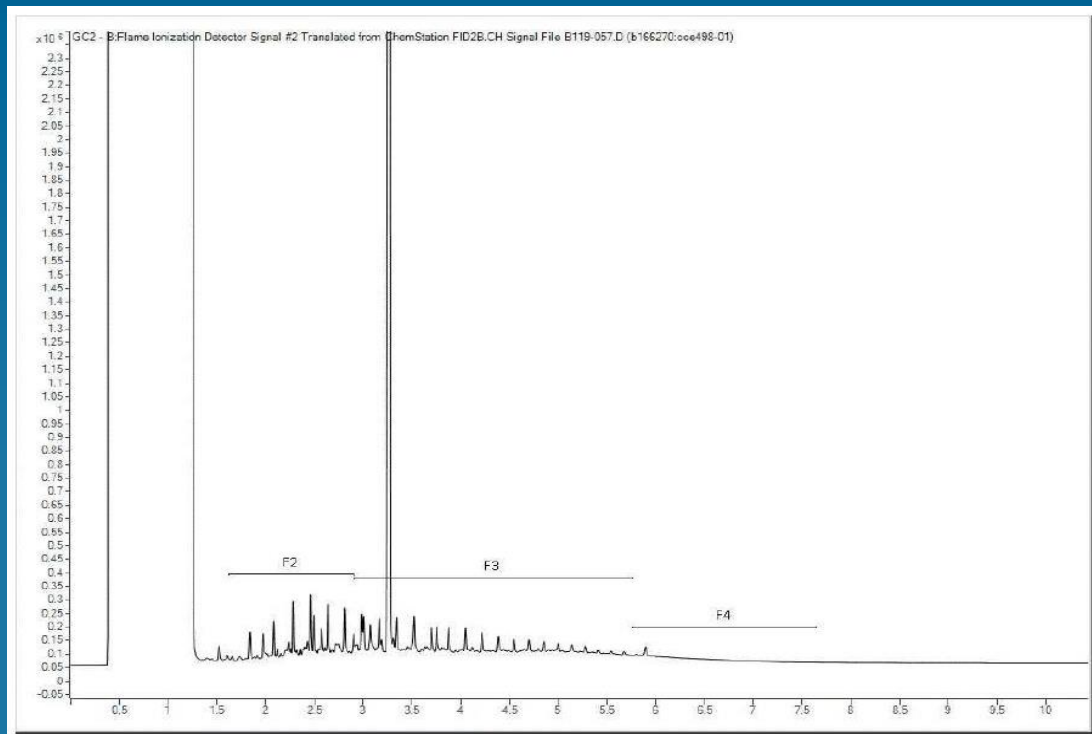
PHCs

- Coal - Low or no PHCs detected



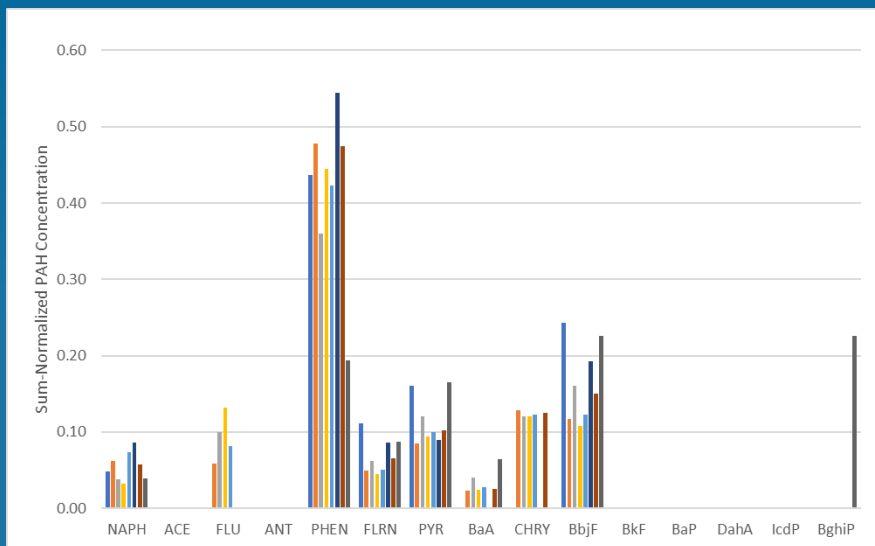
Coal sample

HV bituminous coal

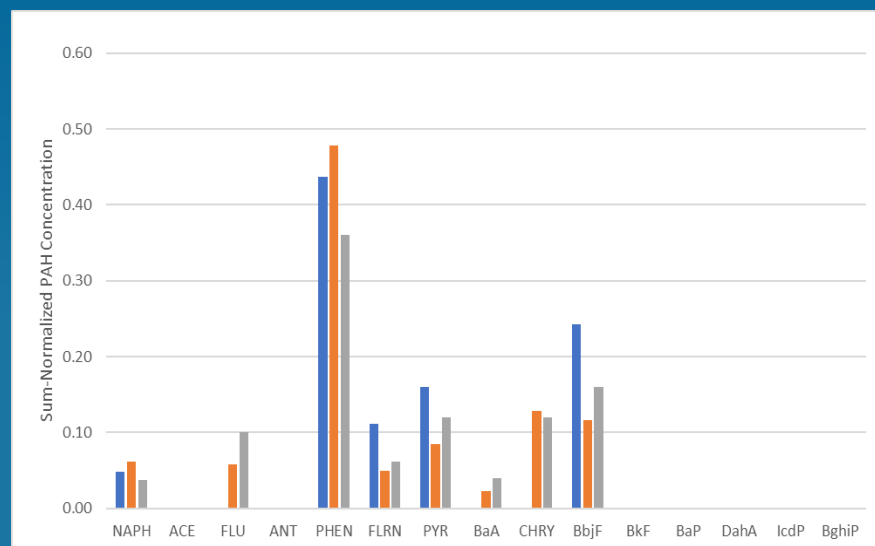


PAHs - Site background

Site APECs

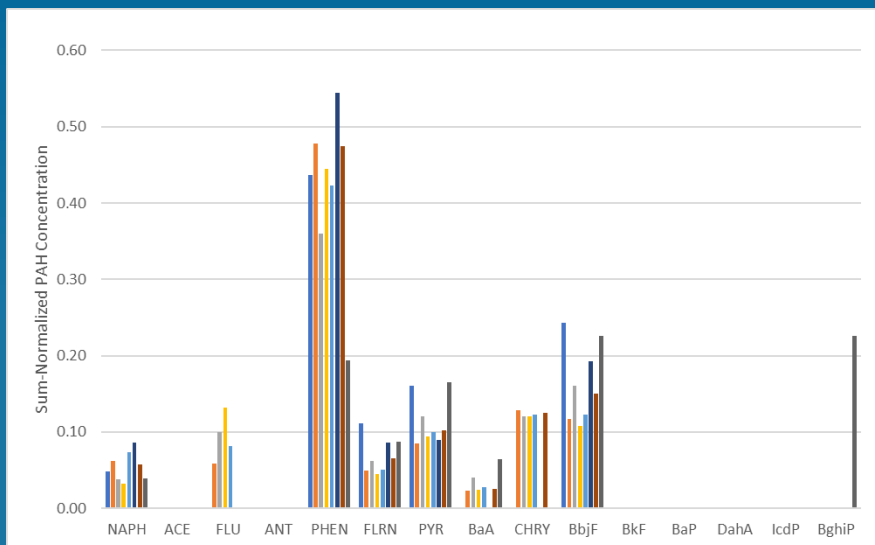


Site background

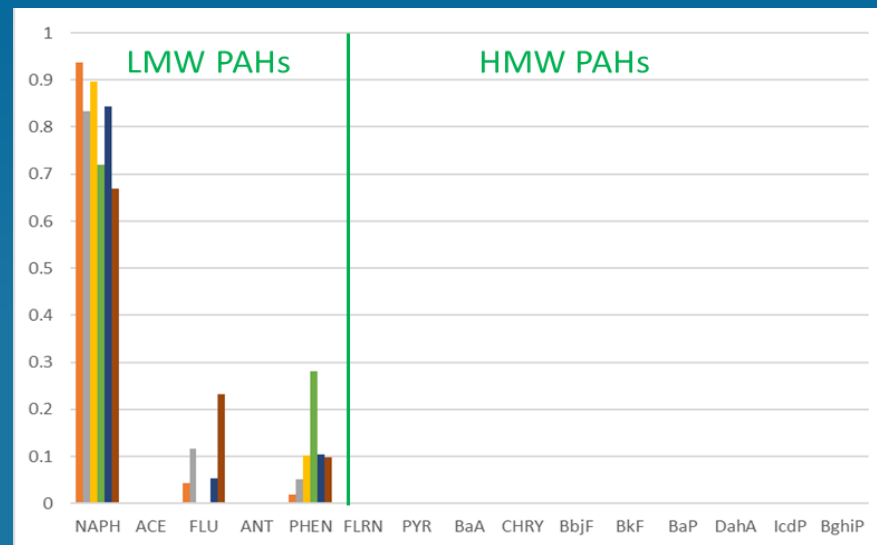


PAHs - Anthropogenic

Site APECs

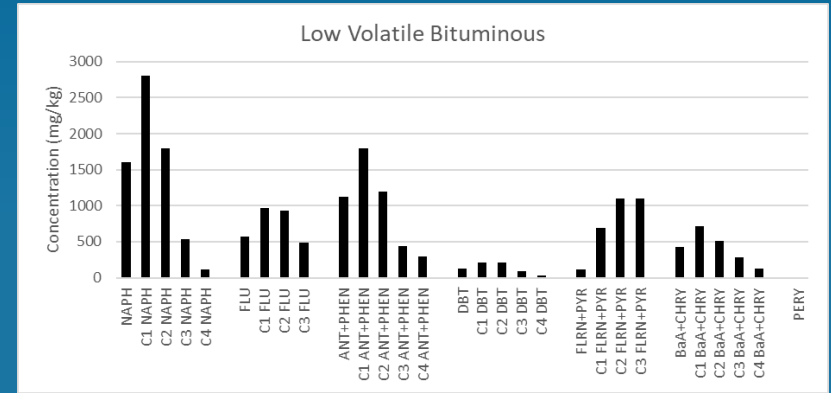
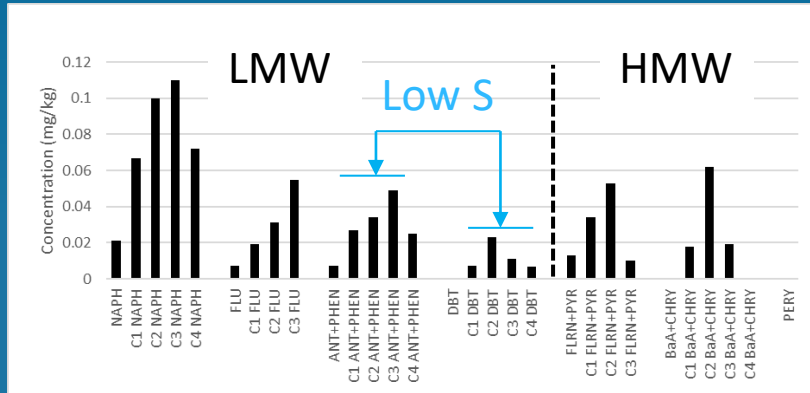


Example condensate



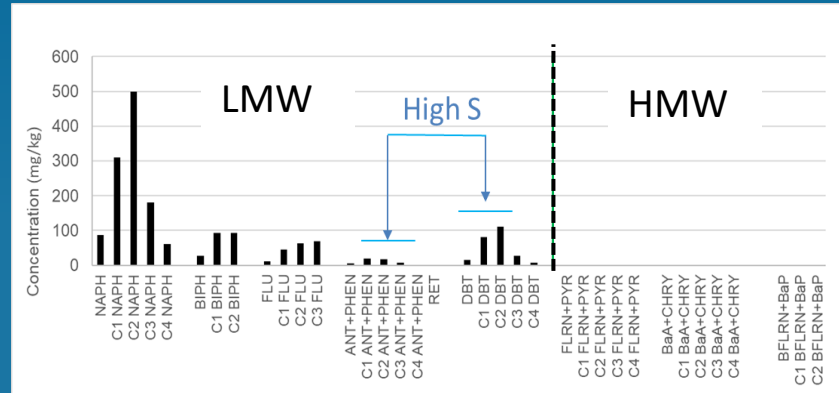
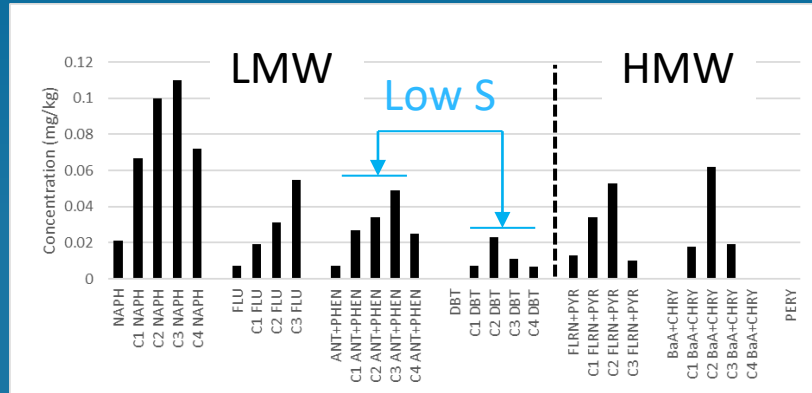
Alk-PAHs

- Geogenic natural source
- Bituminous coal, low sulphur coal



Alk-PAHs

- Anthropogenic source
- Condensate



Data Interpretation

- PHCs

Data and chromatograms no indication of anthropogenic sources, typical for bituminous coal.

- PAHs

Fingerprints comparable with background, no anthropogenic.

- Alk-PAHs

Fingerprints comparable with background, no anthropogenic, typical for bituminous coal.

Summary

- Bedrock inclusions in soil retain many characteristics of source rock. This includes coal or oil kerogen. Typical in this area bituminous coal.
- Represent data so it can be interpreted.
- PHC, PAH, alk-PAH consistent from background and across the sites.
- Exclude all BTEX and PAH exceedances, no need for SSRO in this instance.

Contact Us

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