Alkylated PAHs

Old pollutants, Novel approach

Mar 2026

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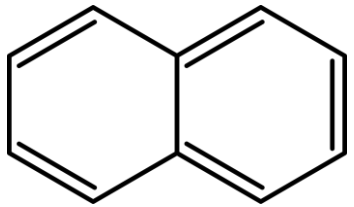
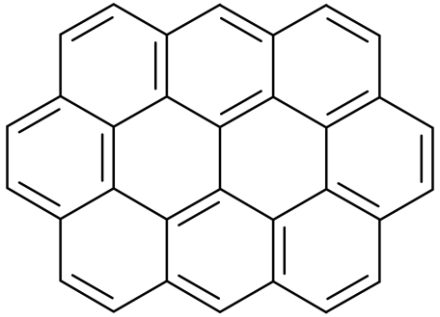
Quick background

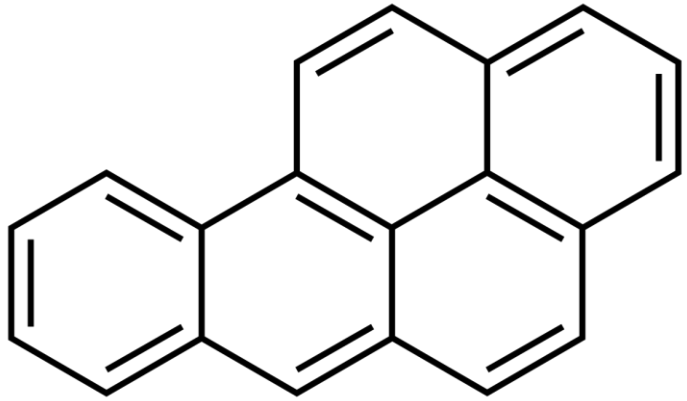
- Professional Chemist in BC
- Worked in a few labs = food, supplement, pharma, environmental
- Contract manufacturing supplements and pharmaceuticals
    - Sourced chemicals to fix issues and make runs more efficient
- Chemical ingredient distribution
    - Sold chemicals locally from Dupont, 3M, BASF etc

Y.N.W.A

PAHs: The compounds we know

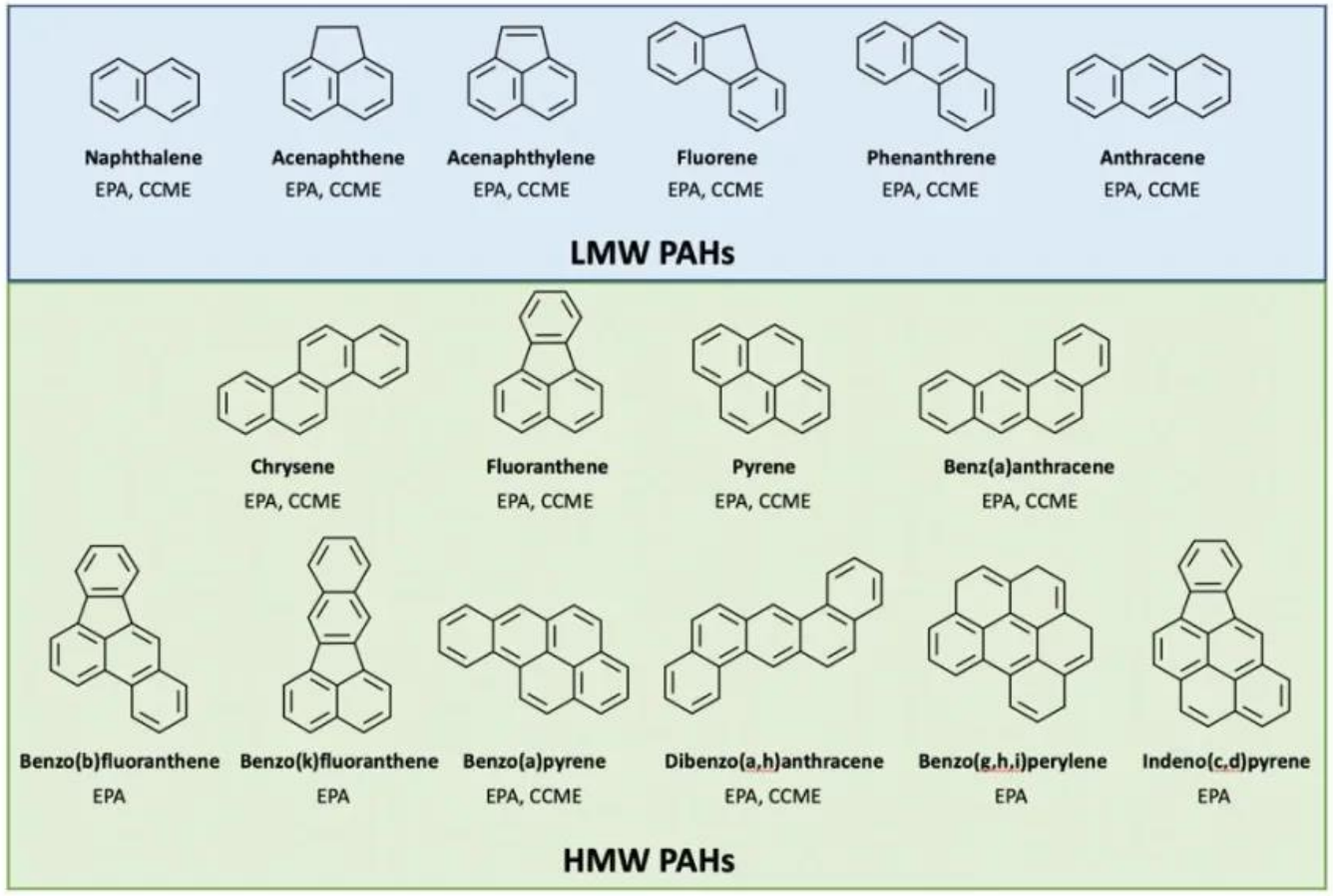






- Polycyclic Aromatic Hydrocarbons or PAHs are fused aromatic rings
- There are potentially 1000s, but when most people say PAHs they are looking at targeted list of 16-25
- Why do we care? They are persistent, and can cause long term health effects
- Where do they come from? Both naturally occurring and from human activity (combustion)

Are these just part of the picture?



These parent PAHs are giving us a good outline of the general presence, risk etc
Outlines don't tell the entire story

Increasing data shows that alkylated PAHs often makes up the majority of PACs – **especially in petroleum impacted sites**

Not only that you miss understanding the true contamination, history, sources and more without their alkylated versions

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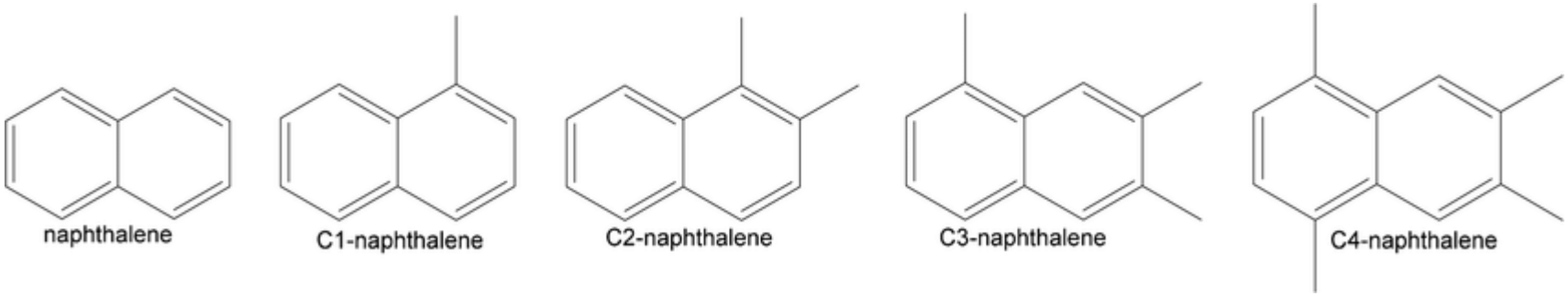
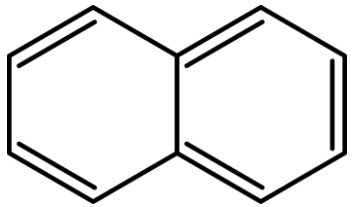
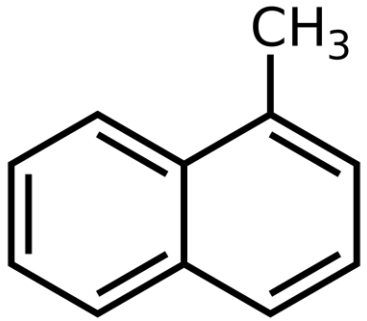
Parent vs Alkylated PAHs

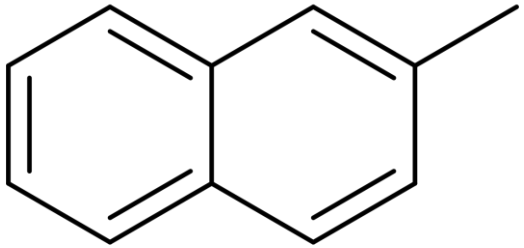


- Alkylated PAHs are just the parent PAHs with added alkyl side chains or groups
- We break these down into homolog groups = C1, C2 etc which are just the number of added carbon groups to the parent (not the specific ones)
- From an environmental standpoint, these small changes can mean very different behavior and diagnostic value

Parent vs Alkylated PAHs
Naphthalene example







- Naphthalene is the parent compound (solid at room temp), easily evaporates
  - Used in manufacturing

- 1-methylnaphthalene is a clear liquid also used in some manufacturing, while 2-methylnaphthalene is a solid, and can be used as a key ingredient to synthesize vitamin k

Parent vs Alkylated PAHs
Comparison of properties

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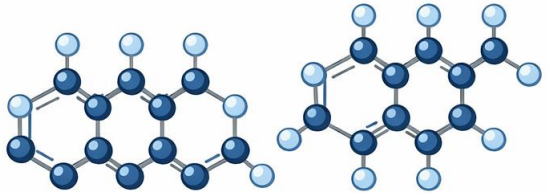
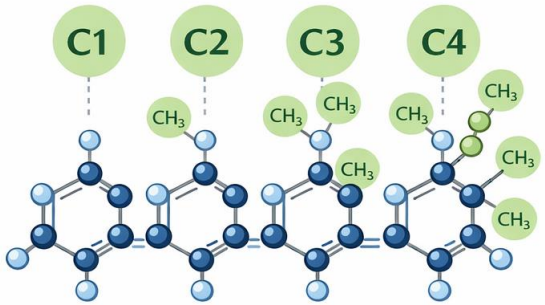
Parent PAHs



Phenanthrene

- Unsubstituted PAHs

Alkylated PAHs



C1- Phenanthrene | C2- Phenanthrene | C3- Phenanthrene | C4- Phenanthrene

- PAHs with alkyl side chains
- C1-Phenanthrenes
- C2-Phenanthrenes
- C3-Phenanthrenes
- C4-Phenanthrenes

- **More persistent** as the alkyl groups hinder degradation

- Less water soluble, hence they have a stronger affinity for **sediment and organic matter**

- Just as **toxic** (or more)

Parent vs Alkylated PAHs
Where do they come from?

- **Petrogenic (primary source):** naturally enriched in crude oil, petroleum products and coal
  - Fossil fuel marker
- **Pyrogenic (combustion):** formed during incomplete combustion or organic matter (forest fires)
  - Higher temp usually favours parent, while lower temp favours alkylation
- Diagenetic: Long term thermal maturation of sediments into rocks and fossil fuels

Are Alkyl PAHs important? Studies

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Assessment and Characterization of Alkylated PAHs in Selected Sites across Canada

by Andrzej Wnorowski * , David Harnish, Ying Jiang, Valbona Celo, Ewa Dabek-Zlotorzynska and Jean-Pierre Charland

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Alkylated Polycyclic Aromatic Hydrocarbons Are the Largest Contributor to Polycyclic Aromatic Compound Concentrations in the Topsoil of Huaibei Coalfield, China

MDPI International Journal of Environmental Research and Public Health (IJERPH)

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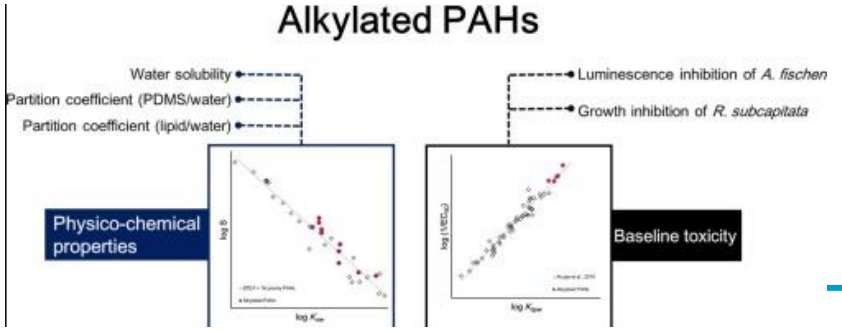
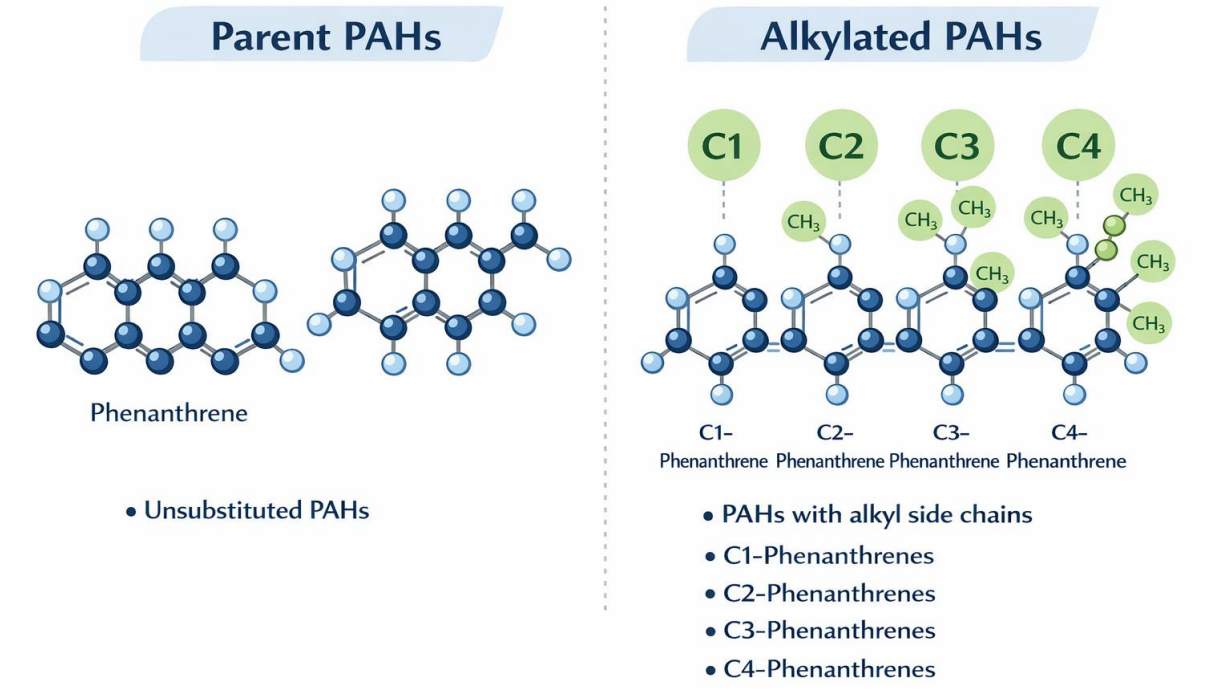
DOI:10.3390/ijerph191912733

Physico-chemical properties and toxicity of alkylated polycyclic aromatic hydrocarbons

Hyun-Joong Kang, So-Young Lee, Jung-Hwan Kwon



Why weren't we measuring them before?



- Early analytical methods did not have resolution for complex homolog groups
- As a result regulatory frameworks based on these methods focused on priority parent PAHs
- Number of compounds increased analytical complexity and cost (with many approaches)

- **Advances in instrumentation and data processing made routine analysis feasible**

How do we measure them

- Using GC MS/MS instrumentation (triple quad)
  - MS/MS needed to get breakdown of alkylated PAHs, compared to MS for parent PAHs
- Targets homolog series (C1-C4 alkylated groups) rather than single compounds
- Requires more advanced calibration and quality control
  - Specifically isotope labelled analogs of target PAHs

What value does this analysis bring?

- In petroleum related sources, alkylated PAHs are often more abundant than parent compounds
- This is especially true for crude oil, bitumen, and refined fuels we deal with in Alberta
- **Environmental Realism**
- **Source fingerprinting** from petrogenic vs pyrogenic, fresh vs weathered, different petroleum sources

Interpretation vs Numbers

Patterns, not just concentrations

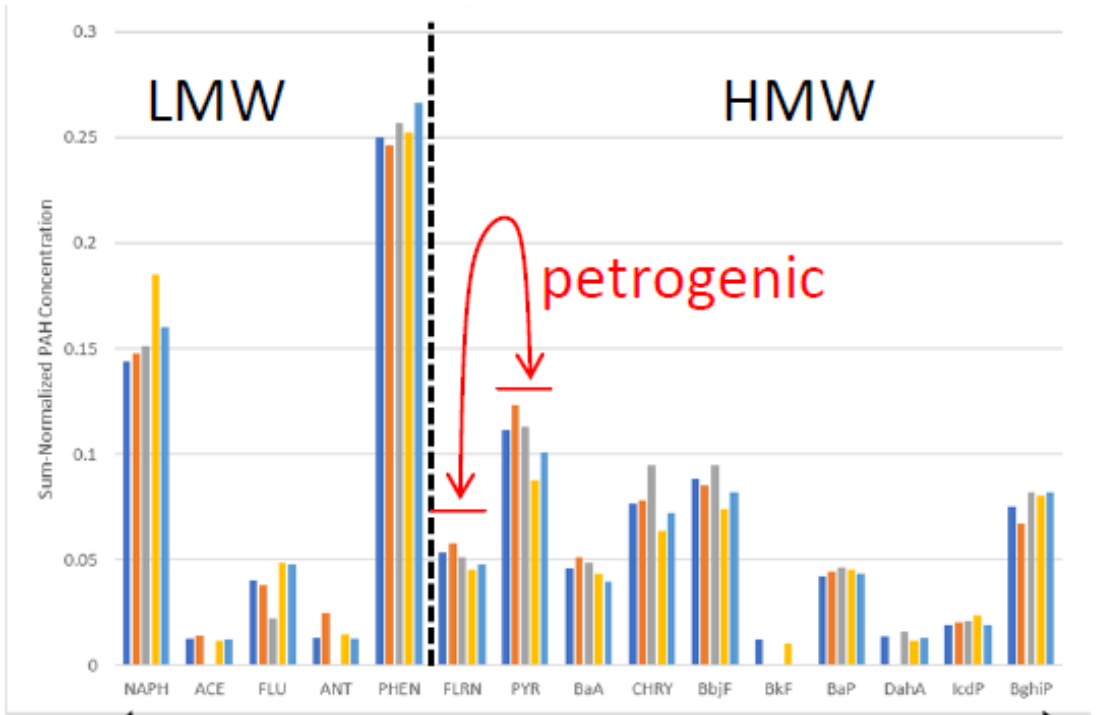
- Parent PAHs = how much contamination is present (regulatory)?
- Alkylated PAHs answer:
  - Where did it come from?
  - How weathered is it?
  - Does it match site history
- Value is in patterns and relative distributions (alkyl vs parent)

Site within floodplain

Exceedances for regulatory PAHs

Parent PAH fingerprint?

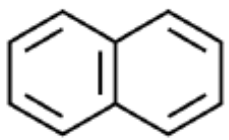
Basic fingerprint layout

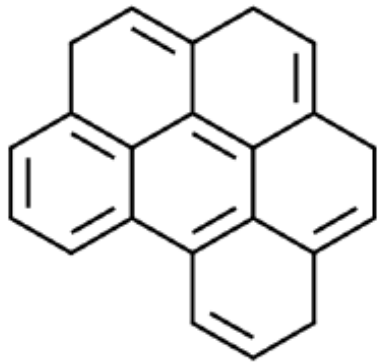


- One bar per PAH

(either as percentage or concentration)

- Compounds shown on graph with increasing molecular weight

naphthalene 

benzo[ghi]perylene 

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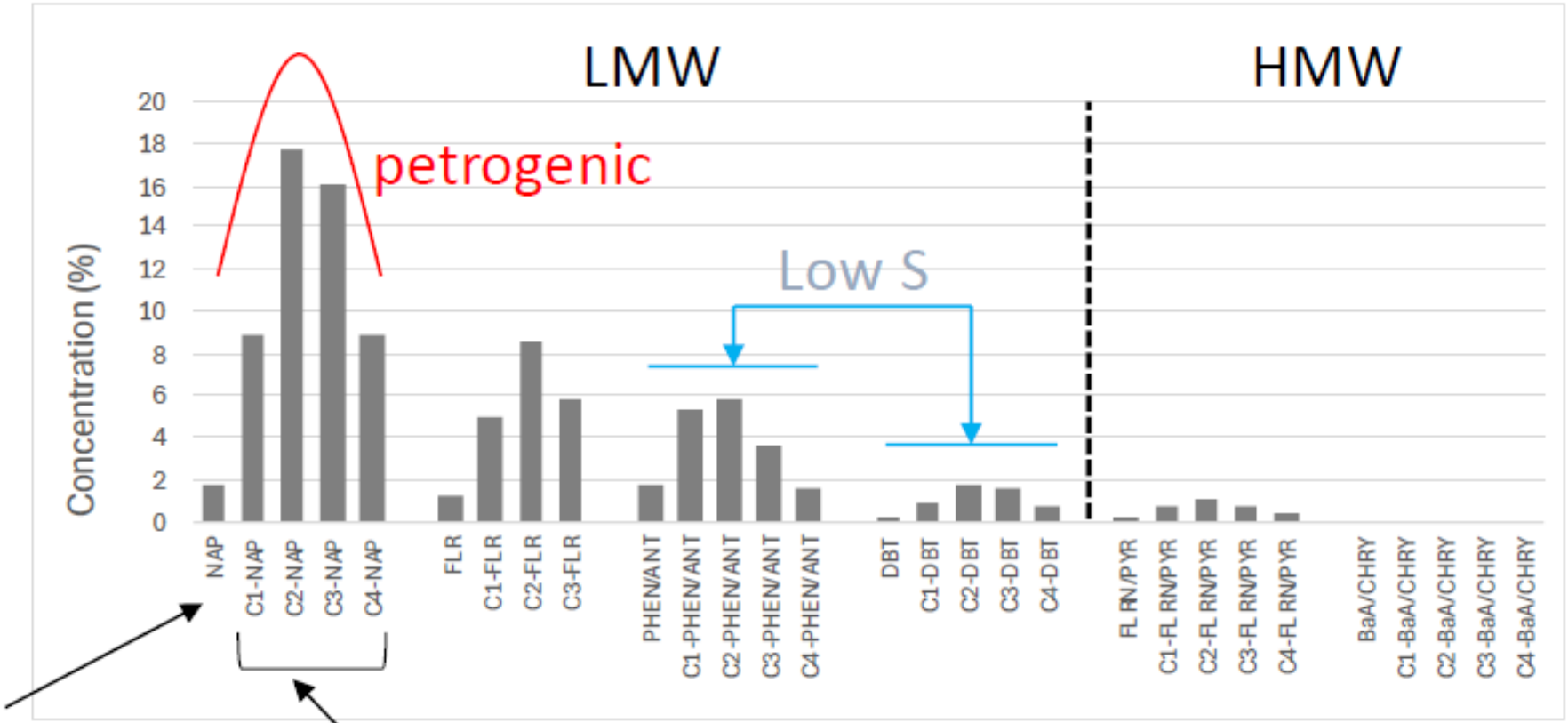
Site within floodplain

Exceedances for regulatory PAHs

Alkyl PAH fingerprint?

Alkylated PAH fingerprint layout

no weathering



Parent PAH

Alkylated PAHs

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Petrogenic vs Pyrogenic
Primary source vs combustion

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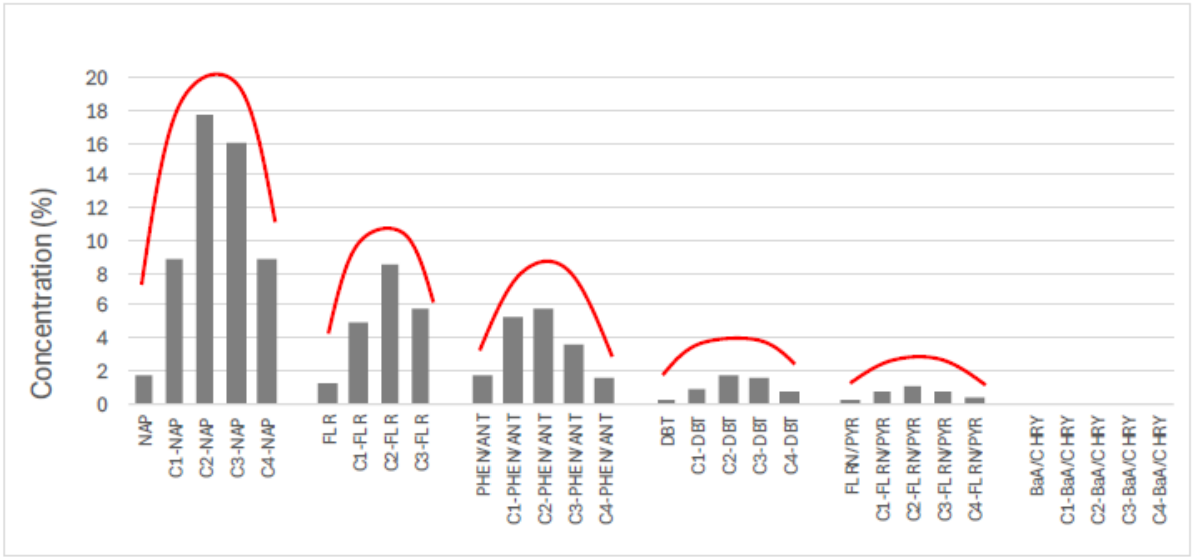

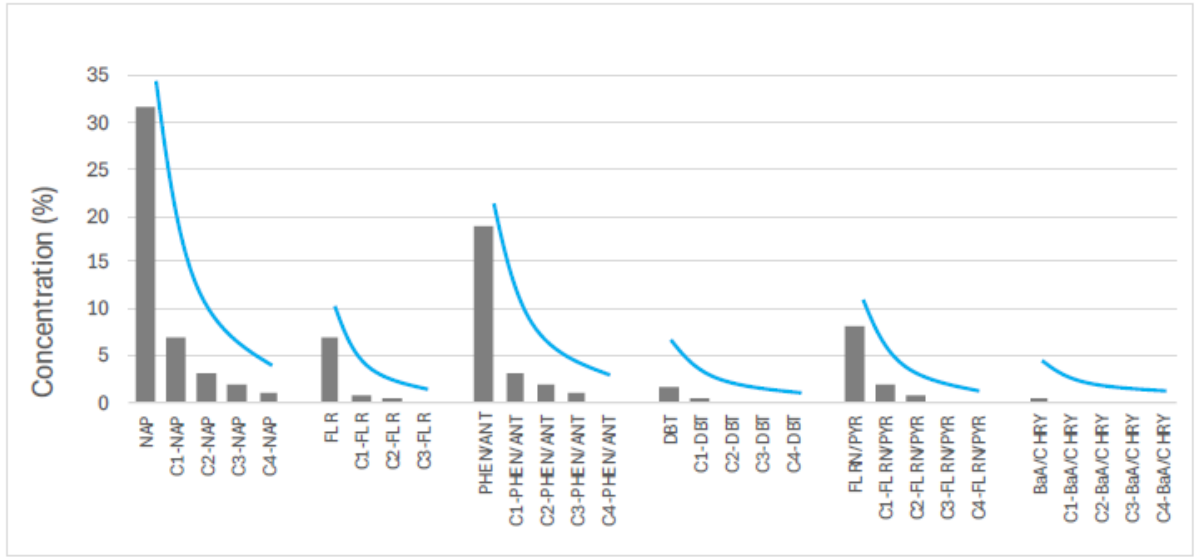

Petrogenic PAHs have hump pattern.*

Pyrogenic PAHs have scree shape.

(*But not always!)

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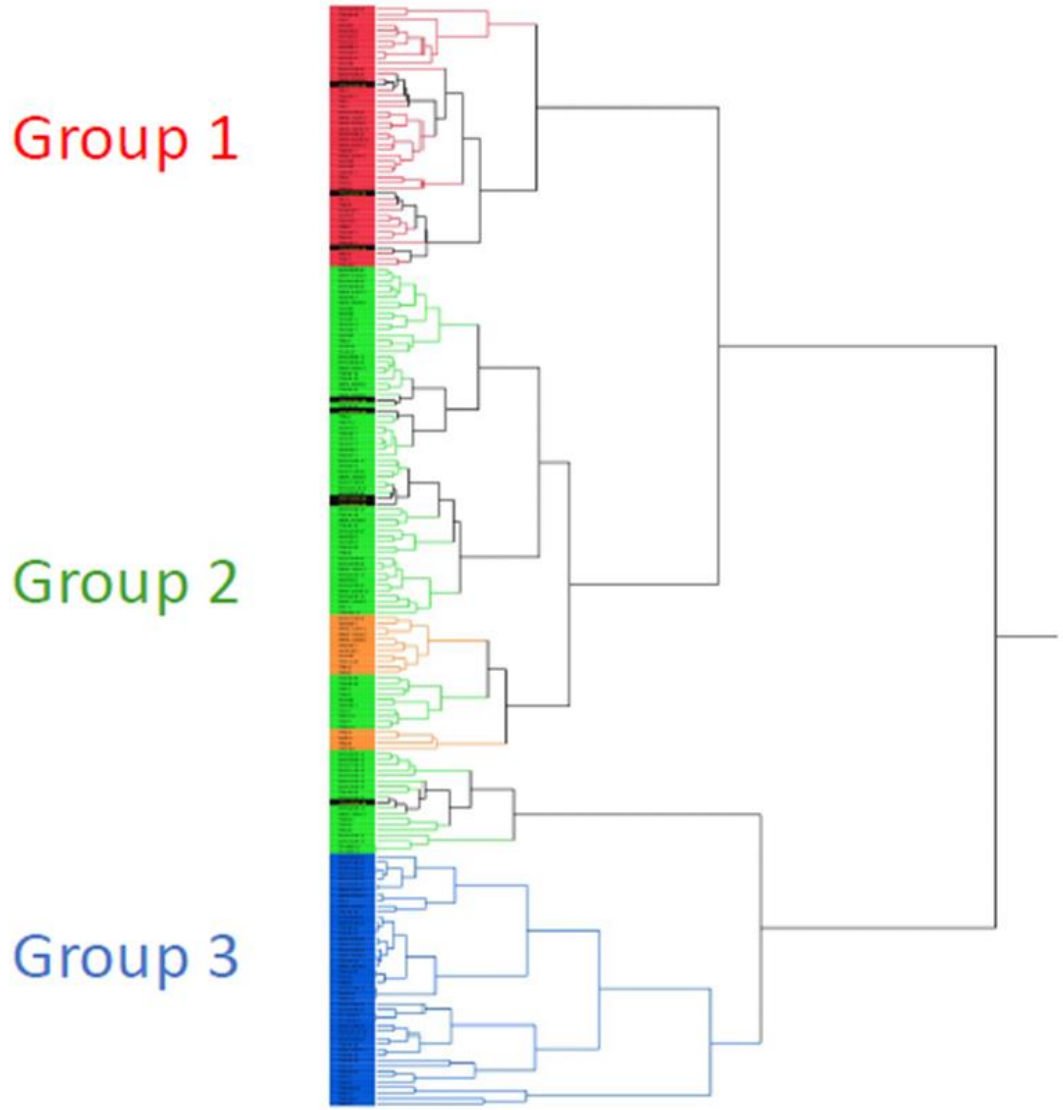
Dive into site more with HCA

- Floodplain location
- Mixed ash-type waste
- Natural coal geology
- Exceedances above guideline

Group samples based on similar fingerprint



What does each fingerprint tell us?

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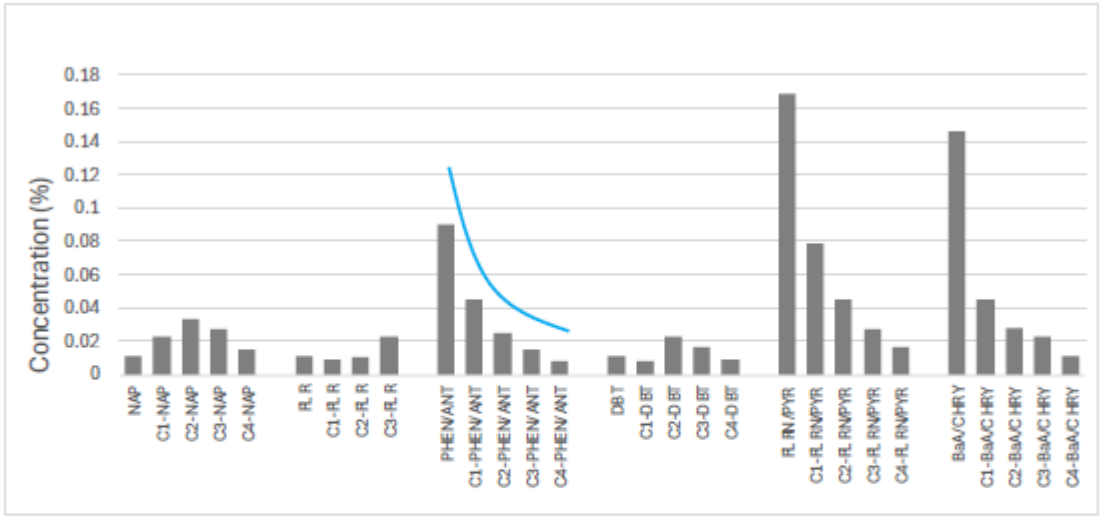
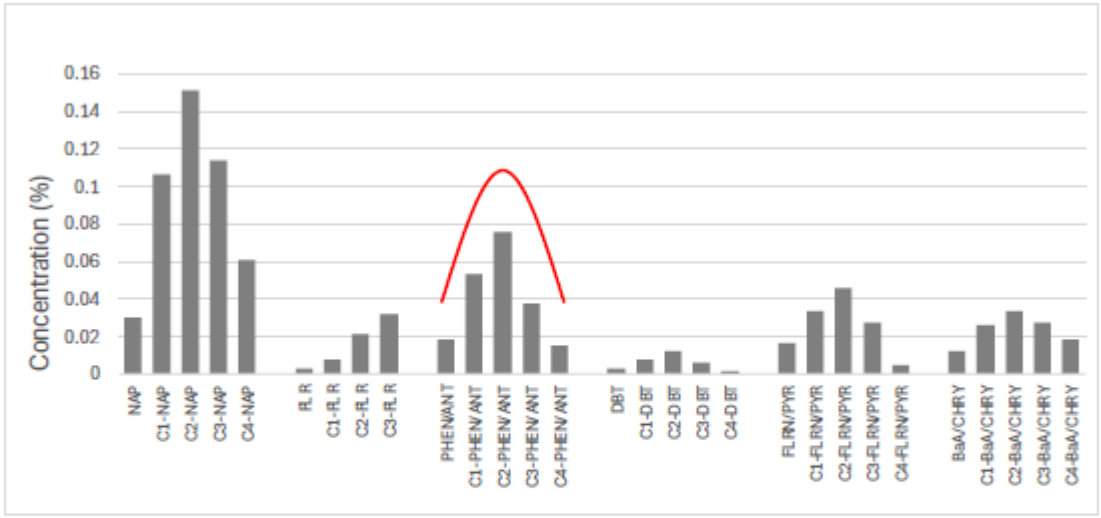
Group 1



Group 2



Combustion source

Site anthropogenic impact

Petrogenic - Bituminous coal

Comparable with the river sediment

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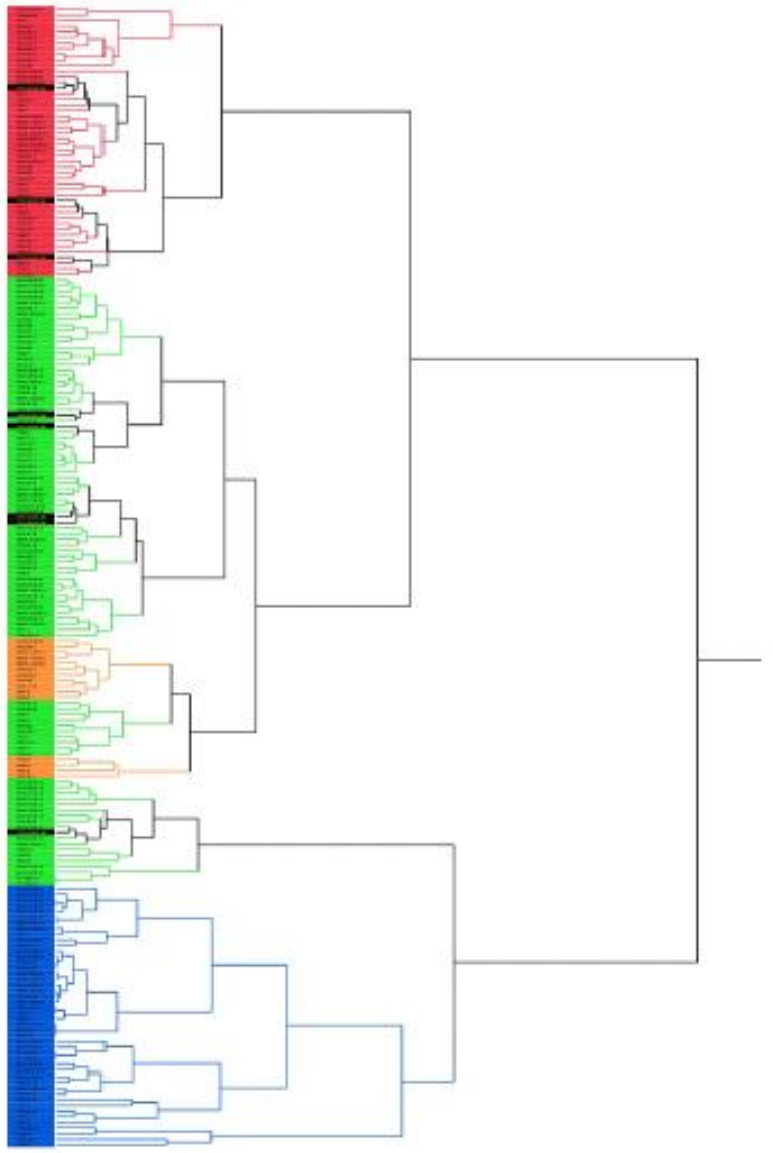
impact area

background

low detection
(no exceedances)



This changes delineation, and thus changes liability.

Same exceedance, different story

We don’t need to clean up natural sources!

Weathering

Will our exceedances resolve themselves naturally

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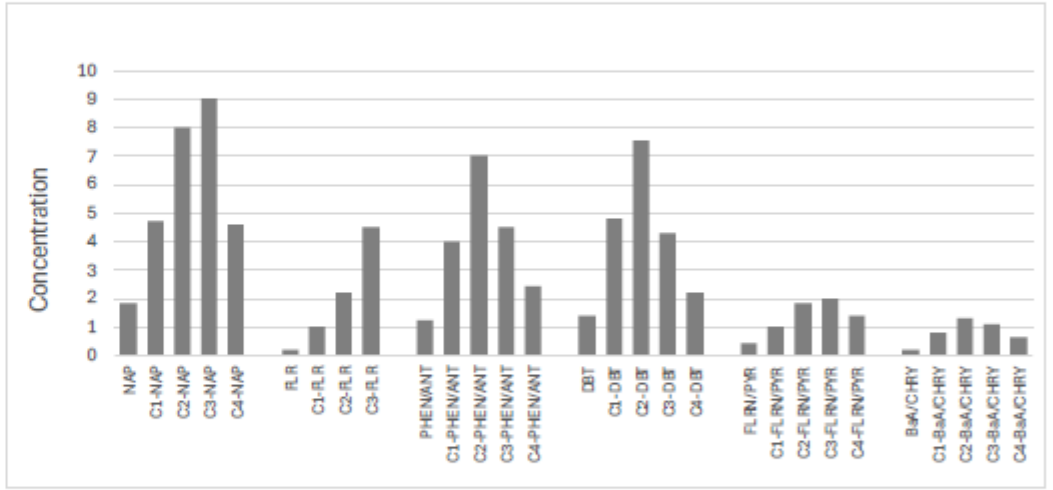
F&T of oil release

- Oil release into aquatic environment
- Deposited along shoreline
- Residual oil exposed to weathering
- What can we say about degradation rate over time (natural attenuation)



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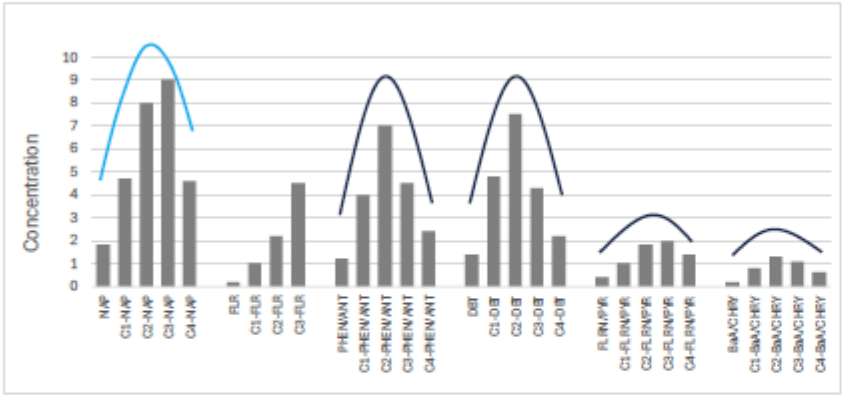
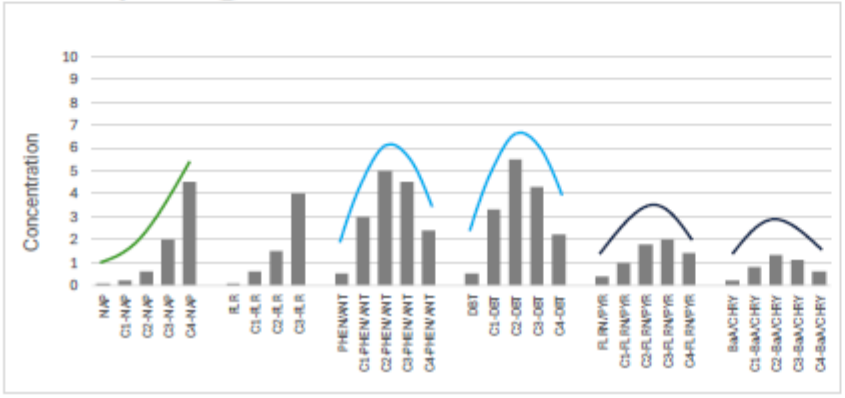
Alkylated PAH results

First sampling event



Light weathering of naphthalenes

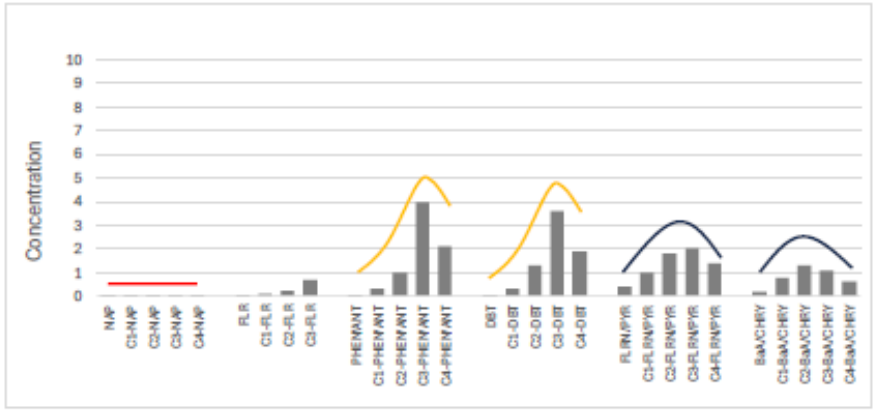
Second sampling event



Weathering progressing into 3-ring PAHs

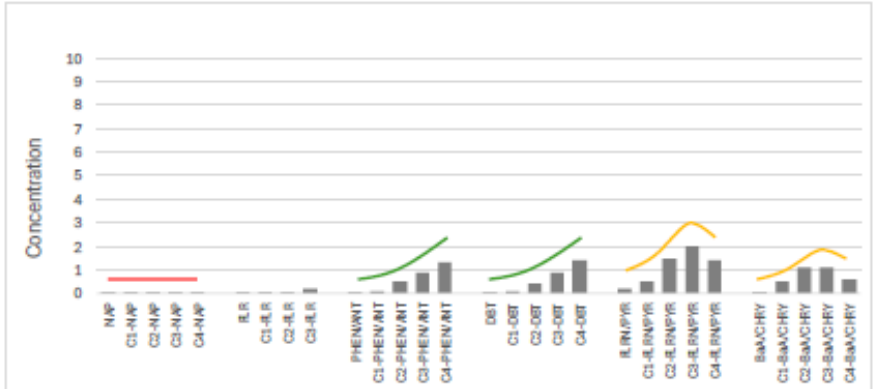
Alkylated PAH results

Third sampling event



Loss of naphthalenes, moderate weathering of 3-ring PAHs

Fourth sampling event



Weathering progressing into 4-ring PAHs

Oil release naturally degrading

Degree of weathering

	Naphthalenes	Phenanthrenes	Pyrenes	BaA/CHRY
First sampling event	Light	None	None	None
Second sampling event	Strong	Light	None	None
Third sampling event	Full	Moderate	None	None
Fourth sampling event	Full	Strong	Moderate	Light

Natural attenuation progressing steadily

Risk decreasing

Why do alkylated PAHs matter?

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Parent PAHs Only

Limited resolution — general trends only

Parent + Alkylated PAHs

Same site — much clearer picture

Key Advantages

- Better understanding of your site and contamination allows for better site model
  - Allows for focus on key exceedances
  - Cost savings, defensible conclusions
  - Understanding of natural attenuation

- Better chemistry leads to better decisions!

- Draft assessments by Health Canada suggest we need to move beyond standard list (underestimating toxicity by up to 6 times!)
- CCME push to develop alkyl-specific benchmarks as they are more persistent in Canadian aquatic environments.

THANK YOU

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