chemistry matters

making environmental data meaningful

Environmental Forensics in the Oil Sands – What is it Telling Us?

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April 11, 2014

Watertech 2014

What is "Environmental Forensics" ?

The systematic examination of historical and environmental information (which may be used in litigation) to allocate responsibility for contamination

"The application of scientific methods to identify the origin and timing of a contaminant release"

Environmental Forensics of the Oil Sands

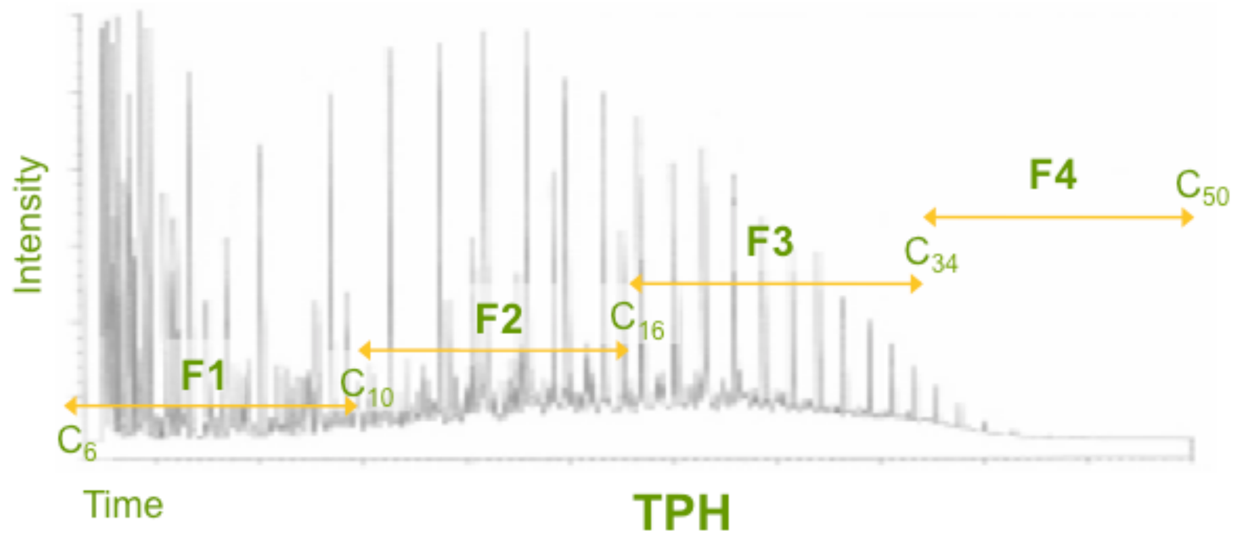
- NPRI (National Pollutant Release Inventory) did not require reporting of PAHs from industry facilities pre-2000
- No baseline completed in 1960s for PAHs
  - Instrumentation would not have allowed it if they did (all ND)

As stated by: Kurek et al 2013, PNAS:

A paradox exists between the pace and scale of oil sands development after ~1980 and the claims that development has minimal or no detectable impacts and that contaminants result mainly from natural sources (Natural sources cited in 2008 RAMP Report).

Monitoring Programs Limited

- Routine water quality and metals (sensitive enough indicators?)
- Benzene, Toluene, Ethyl-benzene, Xylenes ($T_{½}$ = days)
- Petroleum Hydrocarbon Fractions F1, F2, F3, and F4 (high DLs, in ppm)
- Polycyclic Aromatic Hydrocarbons (PAHs) (limited number and potentially high DLs, in ppb)



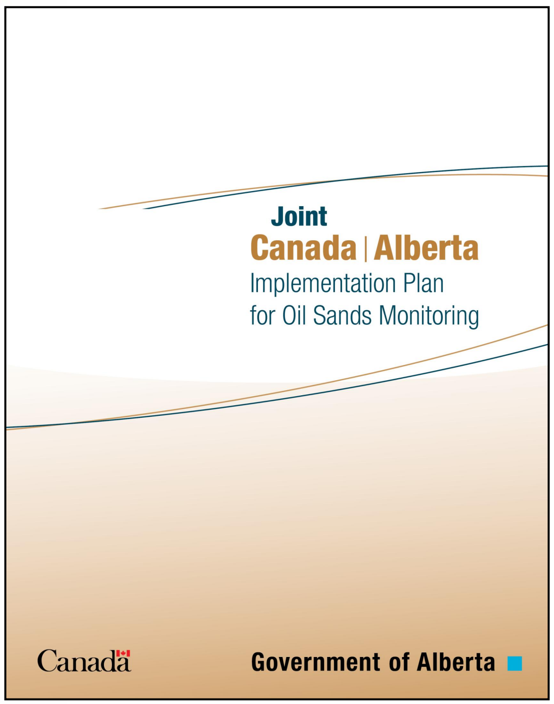
Trust level down in own province

- Ever feel that the odds are not in our favour…

- Even Albertans don't trust their own scientists.

Monitoring Changed Hands

- Proud to be Albertan, did not like to see loss of control
- Environment Canada scientists directed to study oil sands



EIAs for Oil Sands Development

- One researcher tried to find emissions data
- Mine dust may have been underestimated

PAC Emission by Source Type (Base Case)

PAC	Stacks (kg/d)	Plant Fugitives (kg/d)	Mine Fleet (kg/d)	Mine Face (kg/d)	Tailings Areas (kg/d)	Non-industrial (kg/d)	All (kg/d)	All %
Acenaphthene	0.27	0.00	1.95	0.00	0.00	0.16	2.38	0.8
Anthracene	0.29	0.00	1.27	0.00	0.00	0.10	1.66	0.6
Benz(a)anthracene	0.18	0.00	0.30	0.00	0.00	0.03	0.51	0.2
Benzo(a)pyrene	0.17	0.00	0.00	0.00	0.00	0.00	0.17	0.1
Benzo(b)fluoranthene	0.16	0.00	0.00	0.00	0.00	0.00	0.16	0.1
Benzo(g,h,i)perylene	0.17	0.00	0.00	0.00	0.00	0.00	0.17	0.1
Benzo(k)fluoranthene	0.16	0.00	0.00	0.00	0.00	0.00	0.16	0.1
Chrysene	0.19	0.00	0.34	0.00	0.00	0.03	0.56	0.2
Dibenz(a,h)anthracene	0.17	0.00	0.00	0.00	0.00	0.00	0.17	0.1
Fluoranthene	0.29	0.00	5.36	0.00	0.00	0.44	6.10	2.1
Indeno(1,2,3-cd)pyrene	0.18	0.00	0.00	0.00	0.00	0.00	0.18	0.1
Naphthalene	95.42	13.36	62.44	7.86	67.69	8.41	255.22	89.0
Phenanthrene	1.08	0.00	9.42	0.00	0.00	0.78	11.29	3.9
Pyrene	0.31	0.00	7.28	0.00	0.00	0.60	8.18	2.9
Total	**99.03**	**13.36**	**88.36**	**7.86**	**67.69**	**10.55**	**286.90**	**100.0**

NOTE:
Results are shown for the Base Case
Only the 14 PACs used for the water assessment are shown

Science is building…


Legacy of a half century of Athabasca oil sands development recorded by lake ecosystems

Joshua Kurek, Jane L. Kirk, Derek C. G. Muir, Xiaowa Wang, Marlene S. Evans, and John P. Smol

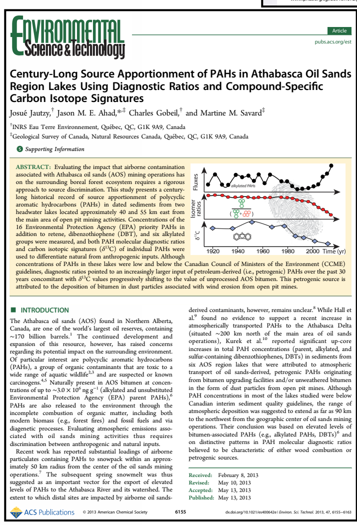

Evaluating officially reported polycyclic aromatic hydrocarbon emissions in the Athabasca oil sands region with a multimedia fate model

Abha Parajulee and Frank Wania


Atmospheric Environment

Calibration and application of PUF disk passive air samplers for tracking polycyclic aromatic compounds (PACs)

Tom Harner, Ky Su, Susie Genualdi, Jessica Karpowicz, Lutz Ahrens, Cristian Mihele, Jasmin Schuster, Jean-Pierre Charland, Julie Narayan


Environmental Science & Technology

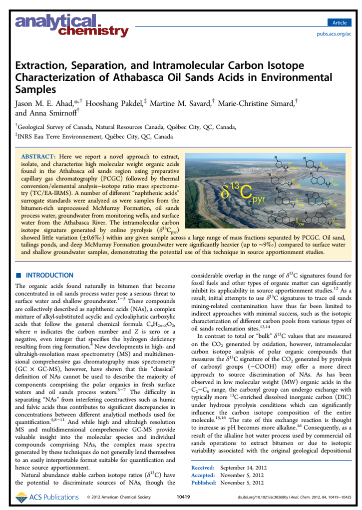
Century-Long Source Apportionment of PAHs in Athabasca Oil Sands Region Lakes Using Diagnostic Ratios and Compound-Specific Carbon Isotope Signatures

Josué Jautzy, Jason M. E. Ahad, Charles Gobeil, and Martine M. Savard


Environmental Science & Technology

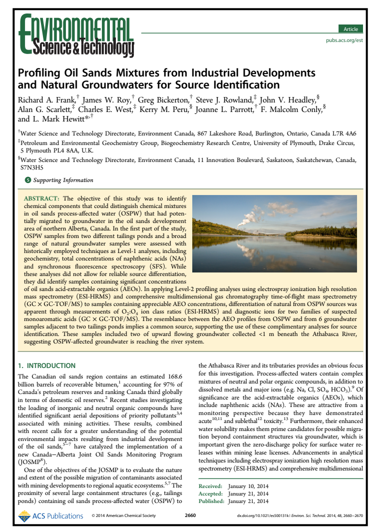
Characterization and Quantification of Mining-Related "Naphthenic Acids" in Groundwater near a Major Oil Sands Tailings Pond

Jason M. E. Ahad, Hooshang Pakdel, Martine M. Savard, Angus I. Calderhead, Paul R. Gammon, Alfonso Rivera, Kerry M. Peru, and John V. Headley


analytical chemistry

Extraction, Separation, and Intramolecular Carbon Isotope Characterization of Athabasca Oil Sands Acids in Environmental Samples

Jason M. E. Ahad, Hooshang Pakdel, Martine M. Savard, Marie-Christine Simard, and Anna Smirnoff


Environmental Science & Technology

Profiling Oil Sands Mixtures from Industrial Developments and Natural Groundwaters for Source Identification

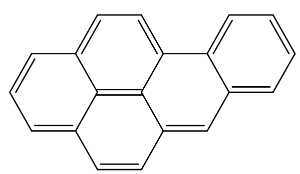
Richard A. Frank, James W. Roy, Greg Bickerton, Steve J. Rowland, John V. Headley, Alan G. Scarlett, Charles E. West, Kerry M. Peru, Joanne L. Parrott, F. Malcolm Conly, and L. Mark Hewitt

Athabasca river and surrounding areas are impacted by oil sands development

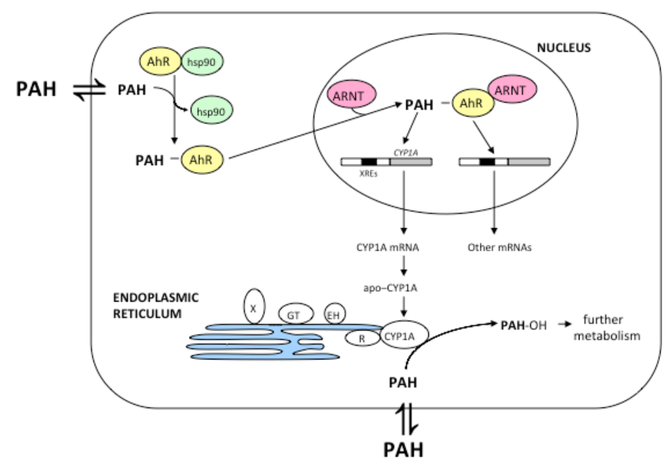
- Still be below guidelines for most targeted analytes

PAHs

- Naturally present in oil sands at low % quantities (dust from open pit mining)
- Produced during combustion (upgrading)
- Resist degradation (persist in environment)
- Analytical methods available
  - Careful on method though…
- Well understood toxicity

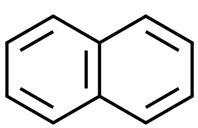


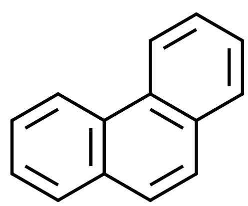
benzo[a]pyrene

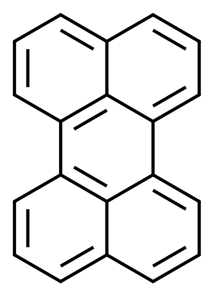


What are PAHs?

- Poly - multiple
- Cylic - rings
- Aromatic – double bonds in a ring
- Hydrocarbons – contain carbon and hydrogen


naphthalene

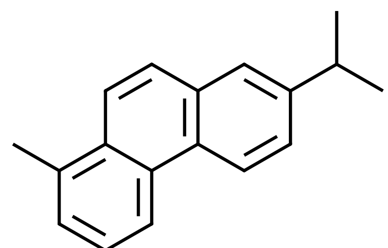

phenanthrene


perylene

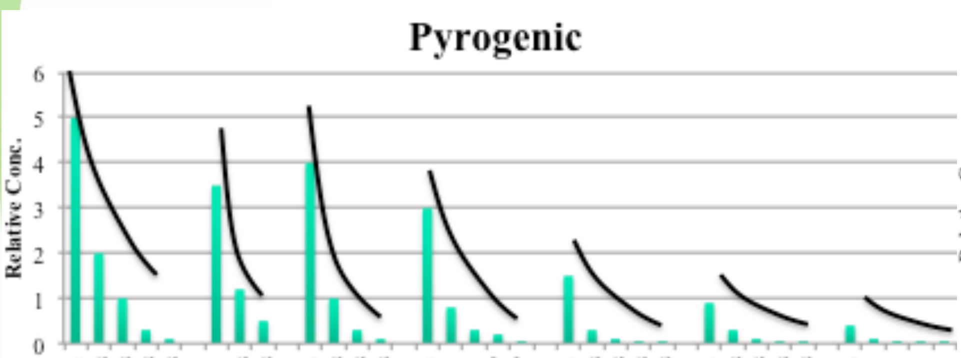
How are PAHs formed?

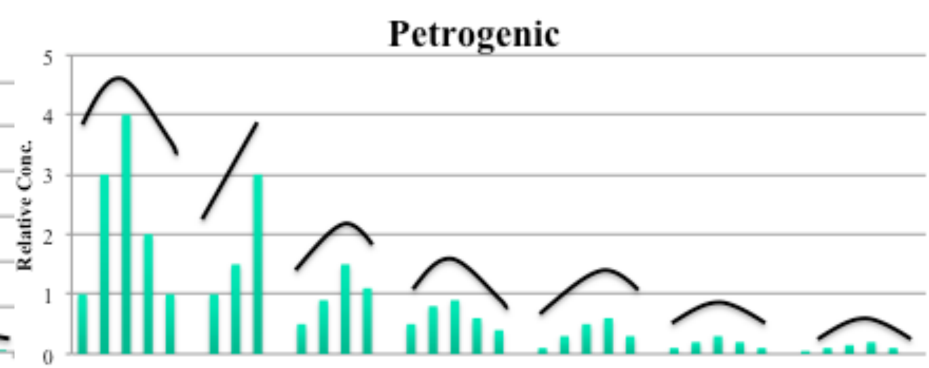
Three formation mechanisms:

- High temperature pyrolysis (pyrogenic)
- Low/moderate temperature diagenesis of organic matter (petrogenic)
- Natural biosynthesis by microbes and plants



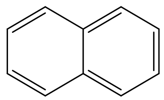
retene

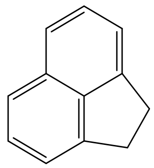


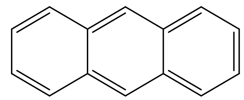


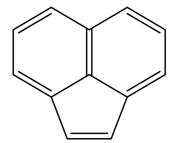
US EPA Priority Pollutants
PAH Compounds

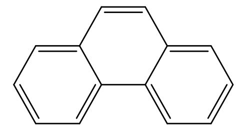
LMW

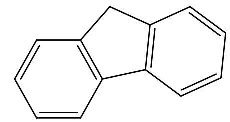

naphthalene


acenaphthene


anthracene

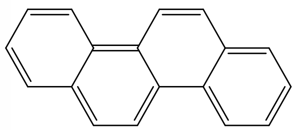

acenaphthylene

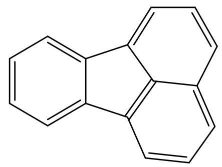

phenanthrene

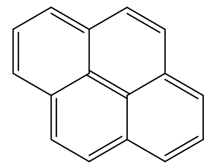

fluorene

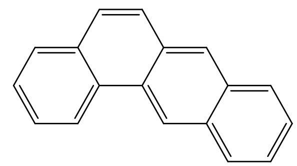
2-ring

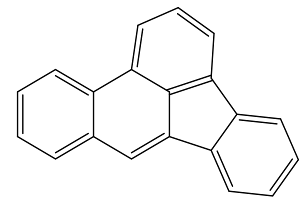
3-ring


chrysene


fluoranthene

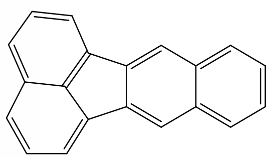

pyrene

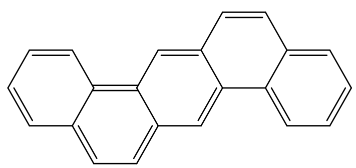

benzo[a]anthracene

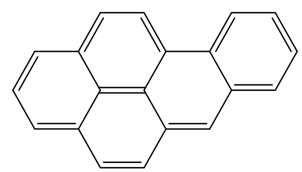

benzo[b]fluoranthene

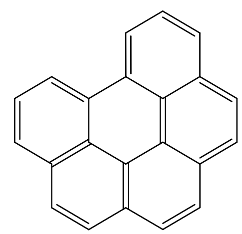
HMW

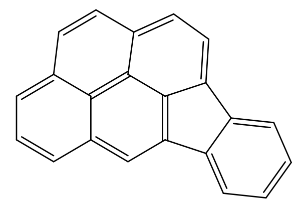
4-ring


benzo[k]fluoranthene


dibenz[a,h]anthracene


benzo[a]pyrene


benzo[ghi]perylene


indeno[1,2,3-cd]pyrene

5-ring

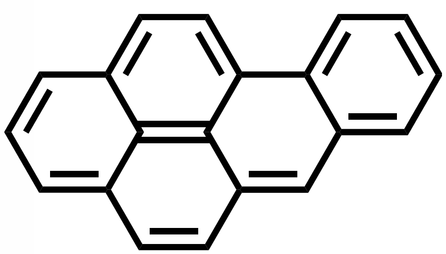
6-ring

List predates 1977

Analysis of PAHs

PAH Analysis

- Many interferences exist in low molecular weight range
  - Depends on matrix, clean up method
  - Need better ‘analytical cleanup’ or more specific detector
- Specificity of HRMS allows better accuracy and precision
- Comes at a cost – 4x
- Lowers DLs to ppt

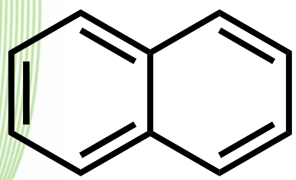


Benzo(a)pyrene

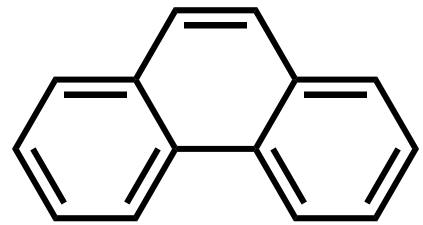
Difference in measuring 252 versus 252.30928

Internal Standards vs. Surrogates

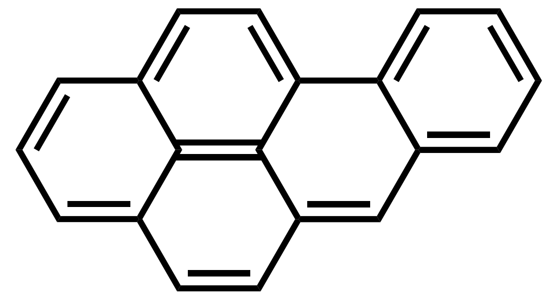
Quantification can be improved using isotopically labeled standards



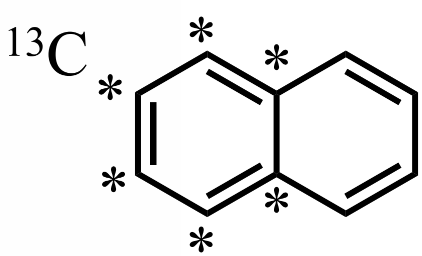
naphthalene

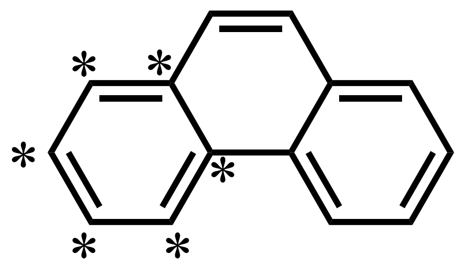


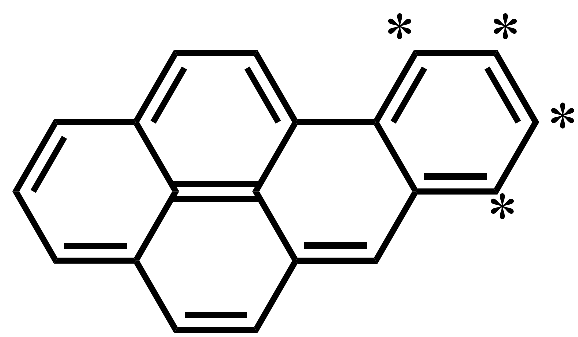
phenanthrene

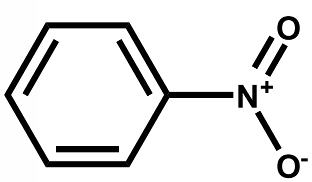


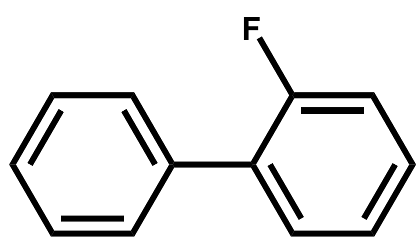
benzo(a)pyrene

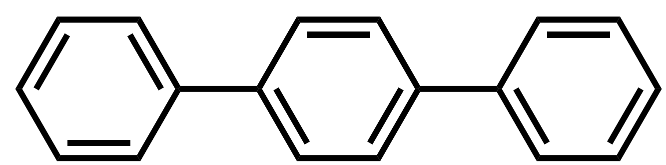






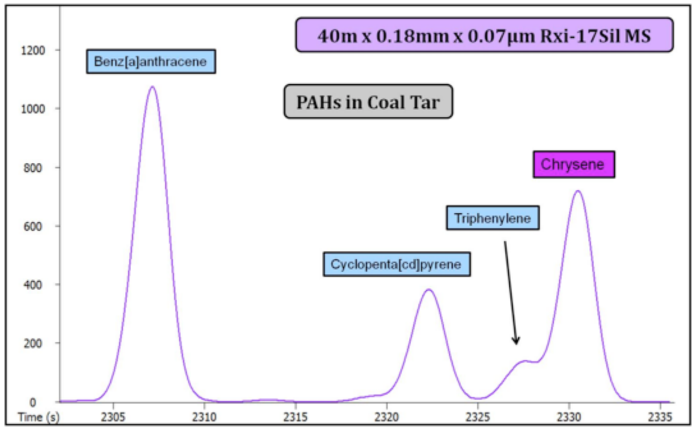






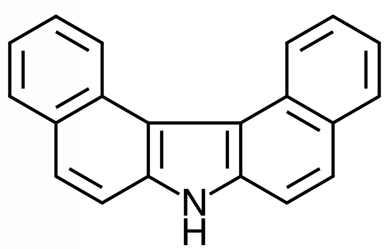
Isotope Dilution Quantification

- Standards behave exactly like compounds being analyzed
- Loss of compounds during analtyical method, included in measurement
- Matrix interferences in method, can usually be seen with standards as well
- <u>THE </u>most accurate measurement available

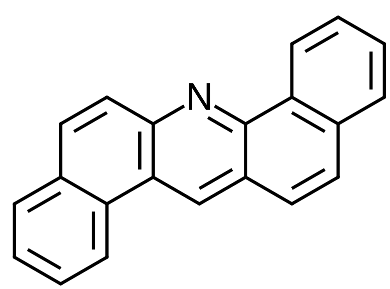


‘New’ PAHs

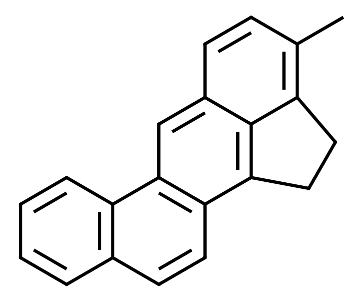
- EPA List of priority PAHs dates back pre-1977
- Upwards to 40 ‘parent’ PAHs potentially to monitor
- Starting to look at heterocycles (O, N, S containing)



7H-dibenzo(c,g)carazole



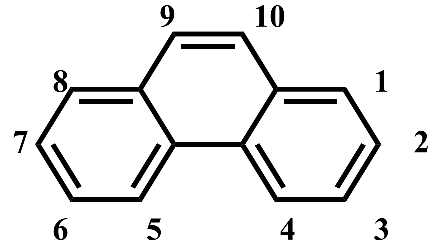
dibenzo(a,h)acridine



3-methyl chlolanthrene

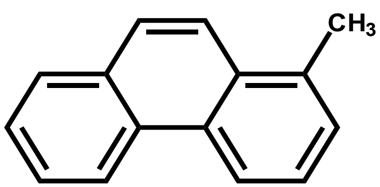
Expanding the List of PAHs

Alkylated-PAHs and Other PAHs



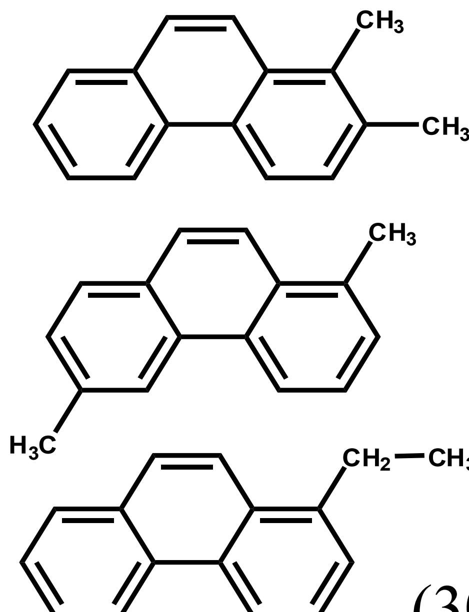
Phenanthrene

C1-Phenanthrenes



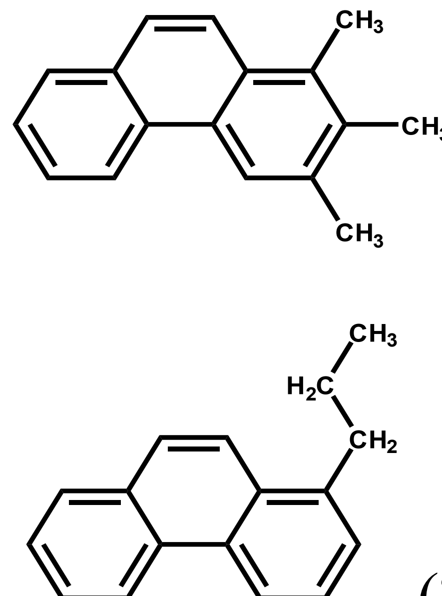
(5)

C2-Phenanthrenes



(30)

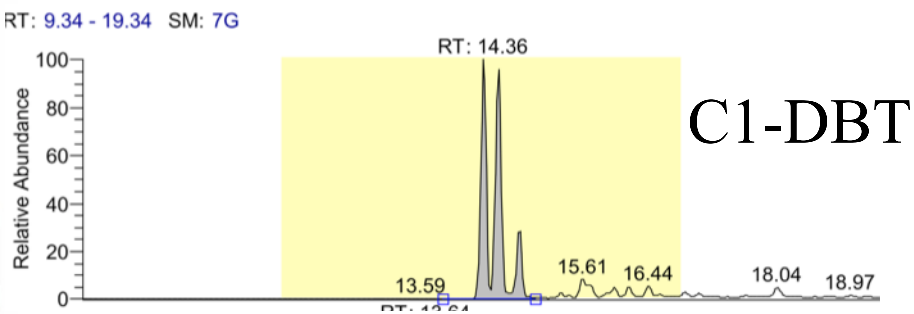
C3-Phenanthrenes

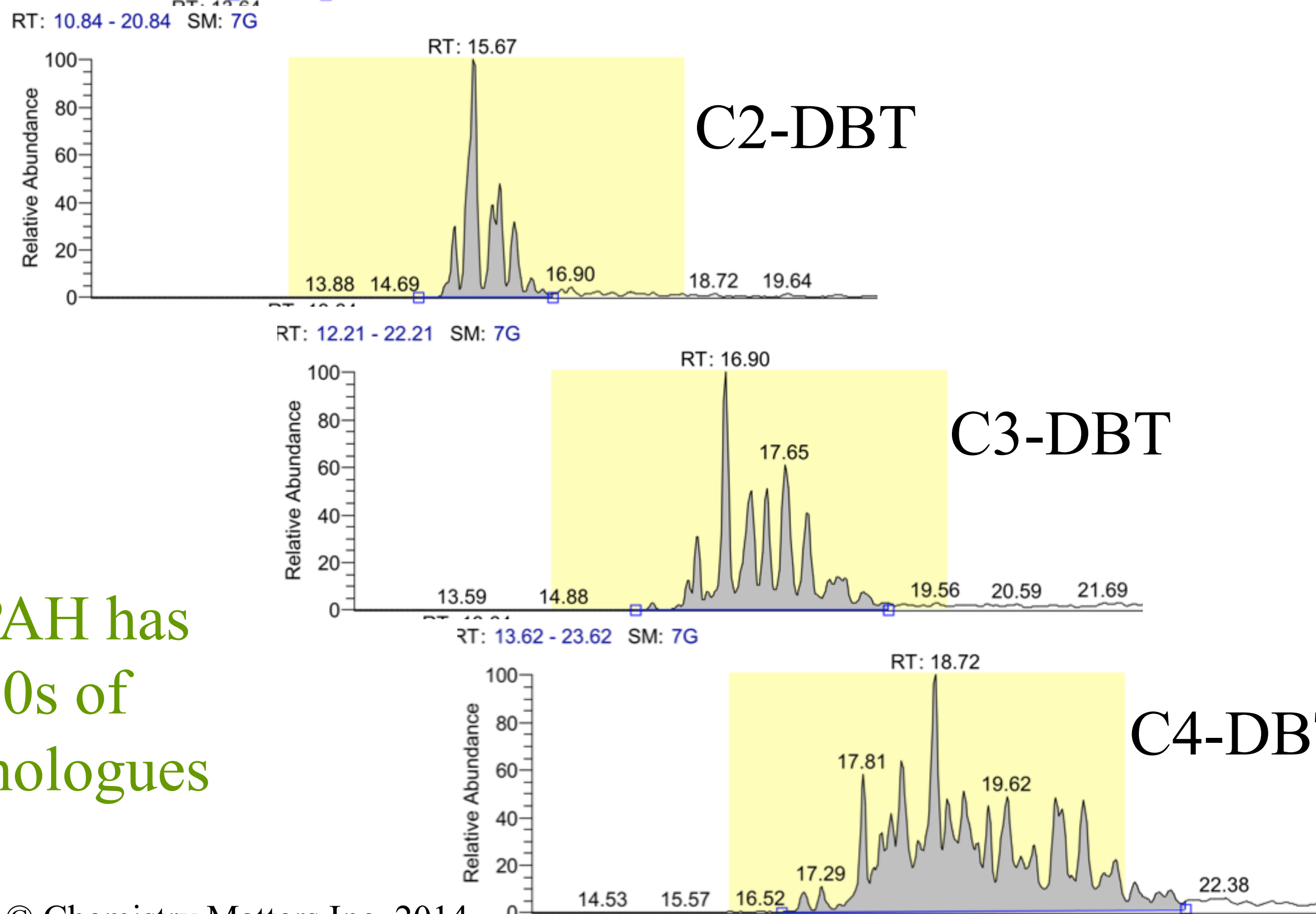


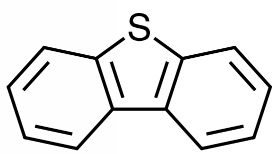
(?)

C4-Phenanthrenes… (?)

Chromatography Gets Busy







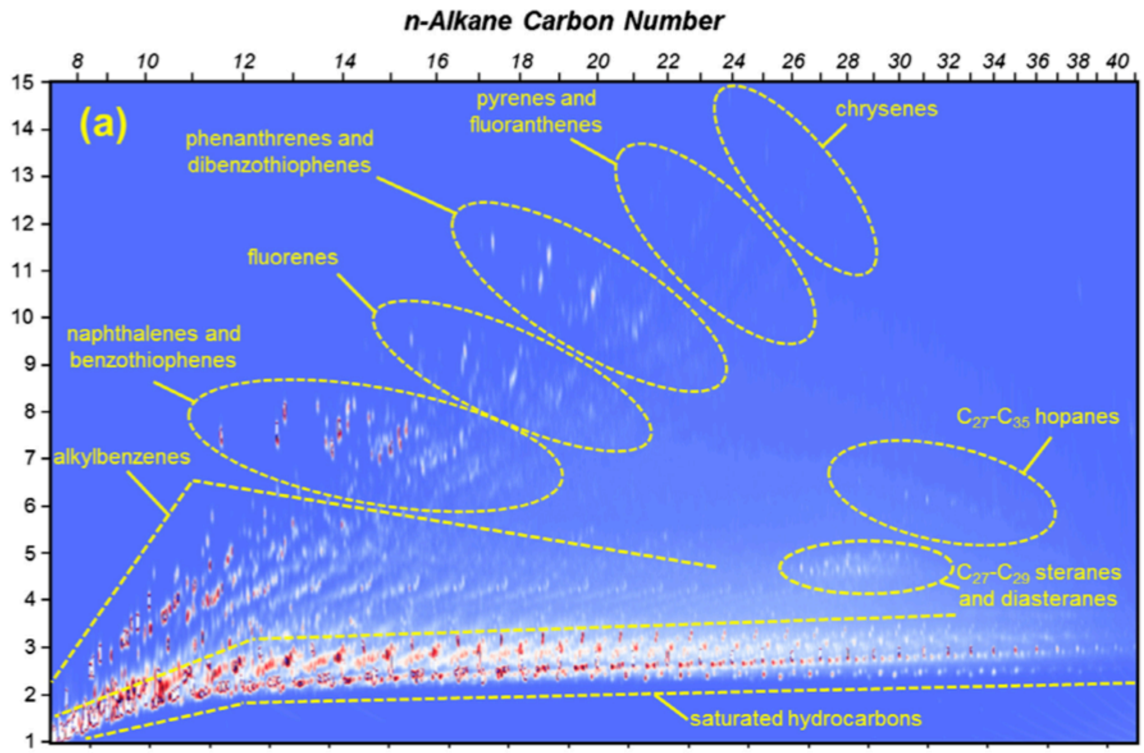
Dibenzothiophene

Each parent PAH has potentially 100s of alkylated homologues

Environmental Forensics in the Gulf Oil Spill

- Reddy et al. sampled oil directly above well to conduct comprehensive characterization
  - Gas isotopes, GOR, fluid characteristics, API etc.
  - Fingerprinted with 2D-GC-TOF
  - Could distinguish between crudes

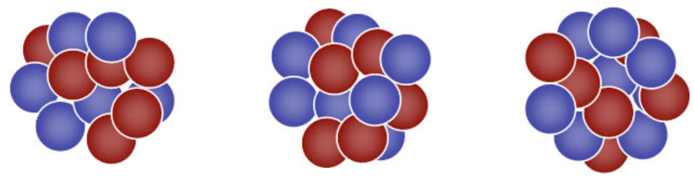
Reddy et al. 2011, PNAS Early Edition, p.1-6



PAH Monitoring

- Routine method no longer cuts it
- More analytes currently possible
- Better analytical standards and lower detection limits
- More analytes to be mandatory (in the future)
- All PAHs could be monitored, if desired

Isotopes on PAHs



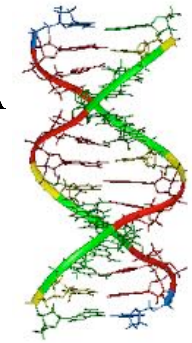
carbon-12
98.9%
6 protons
6 neutrons

carbon-13
1.1%
6 protons
7 neutrons

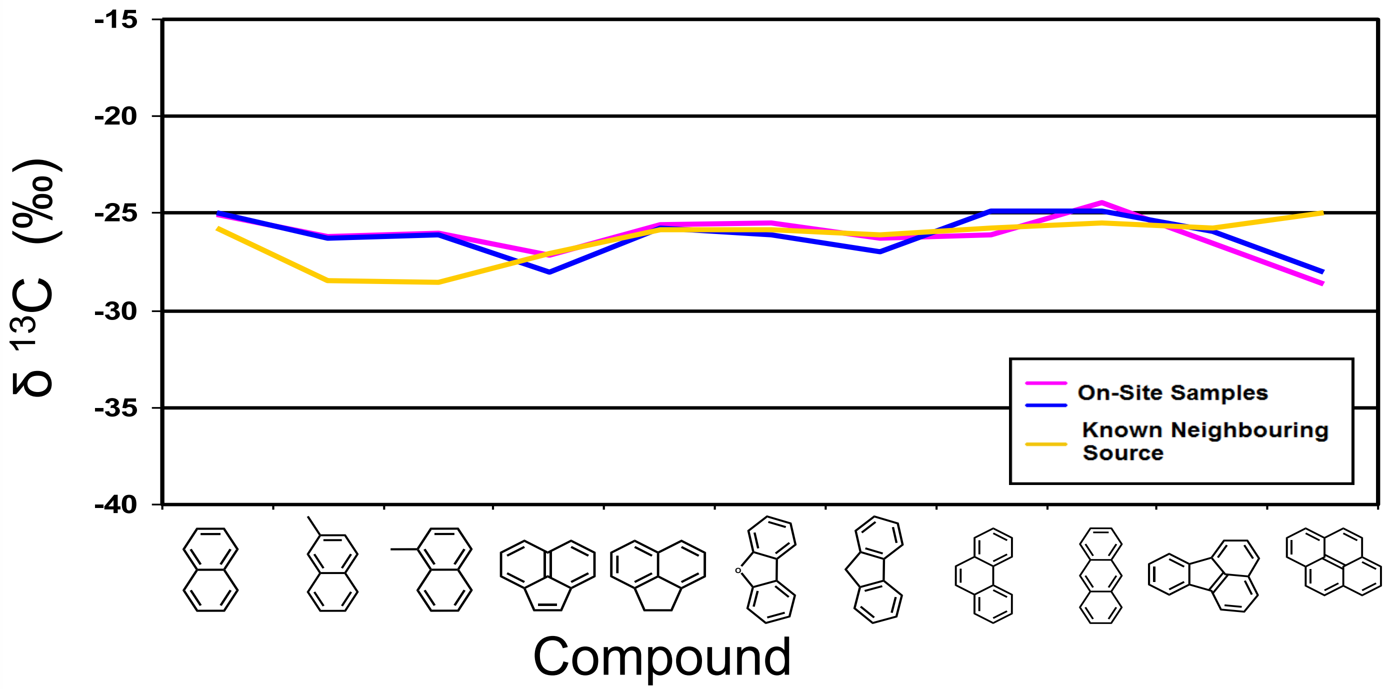
carbon-14
<0.1%
6 protons
8 neutrons

=

DNA

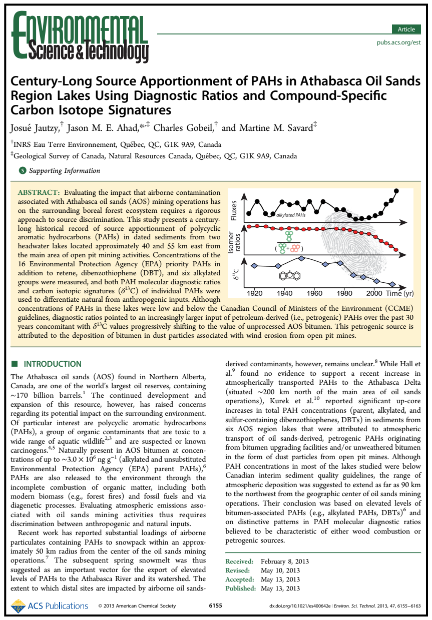


- Stable isotope data gives a “signature” to samples
- Samples may be linked or differentiated



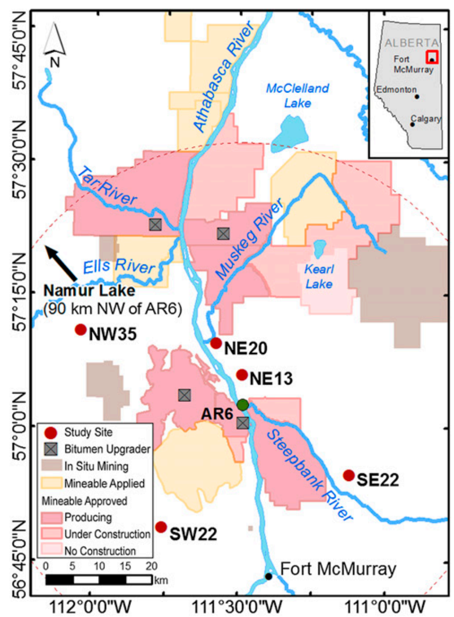
Oil Sands Environmental Forensics Studies

- Two independent studies:
  - Environment Canada and Queen’s University
  - Geological Survey of Canada
- Both confirmed increased PAHs due to oil sands development



PAHs in lake sediments

- Paleolimnological (*paleon*=old, *limne*=lake, *logos*=study)
- Sampled lake sediment (5 lakes, near field, 1 remote lake, far field)
  - Core samples
  - Extended PAHs
  - ^{210}Pb, ^{137}Cs, ^{226}Ra



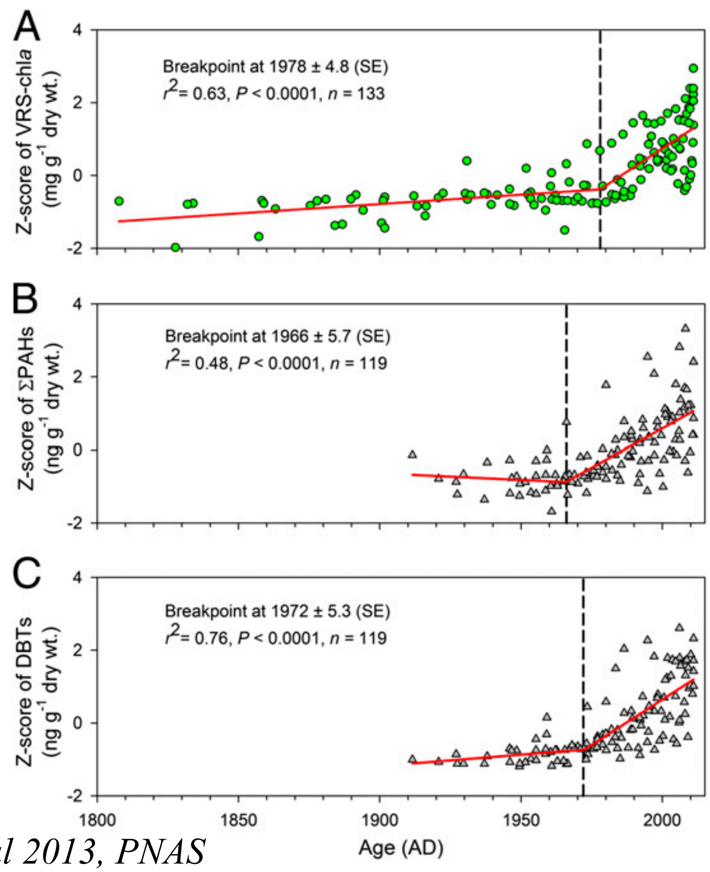

PNAS

Legacy of a half century of Athabasca oil sands development recorded by lake ecosystems

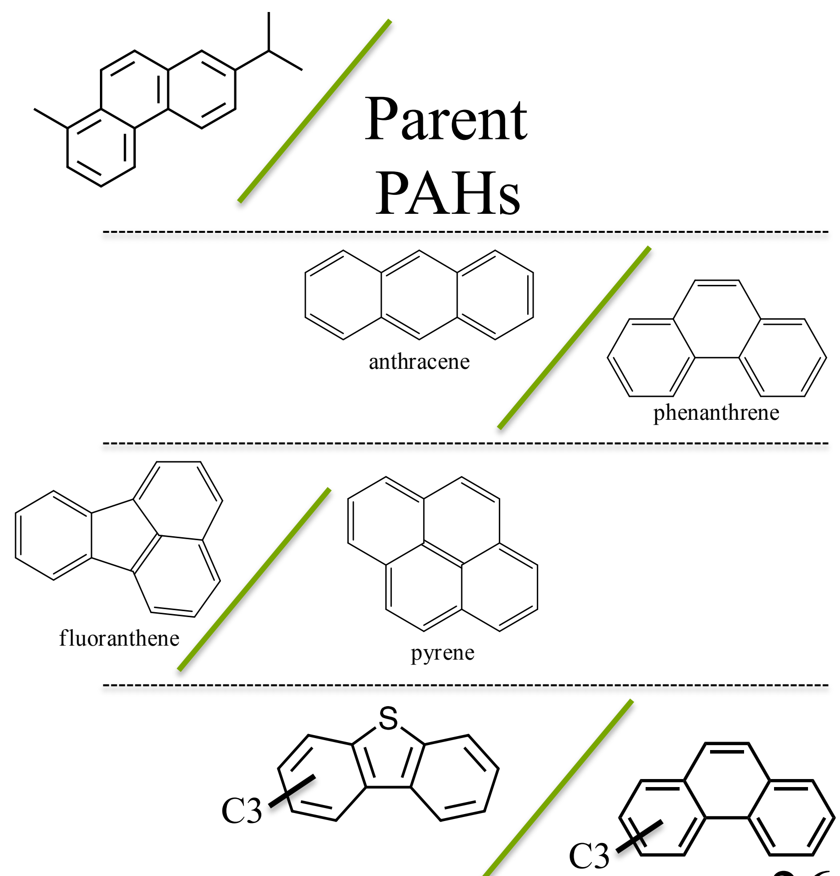
Kurek et al 2013, PNAS

PAHs in lake sediments

- Showed increase of PAHs by decade
- PAH diagnostic ratios switched from wood burning to unweathered petrogenic source



Kurek et al 2013, PNAS



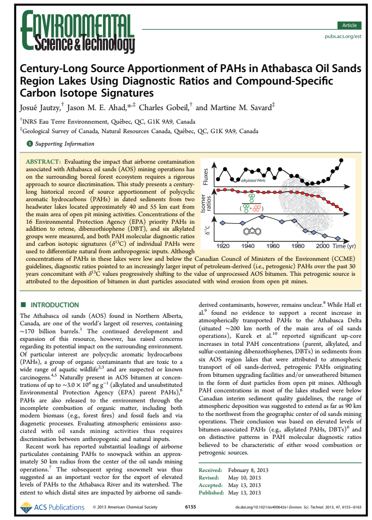
PAHs in lake sediments

- 1960s showed sharp increase (coincides with development)
- Prevailing wind direction, higher increase – surface dust from open pit mining suggested culprit
- First scientifically defensible study showing increase in PAHs as a result of oil sands development
- Can now establish baseline PAHs and can monitor current and future inputs

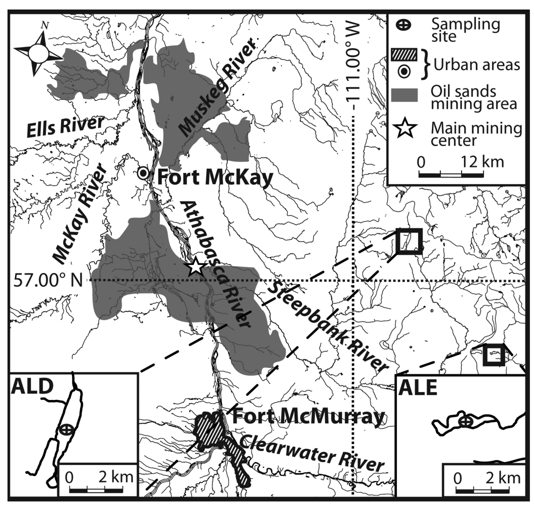
Kurek et al 2013, PNAS

PAHs in lake sediments

- Sampled 2 headwater lake sediment cores
  - Extended PAHs
  - ^{210}Pb, ^{137}Cs, ^{226}Ra
  - Added stable isotope analysis of selected PAHs – C1-Fluorene; DBT; Retene



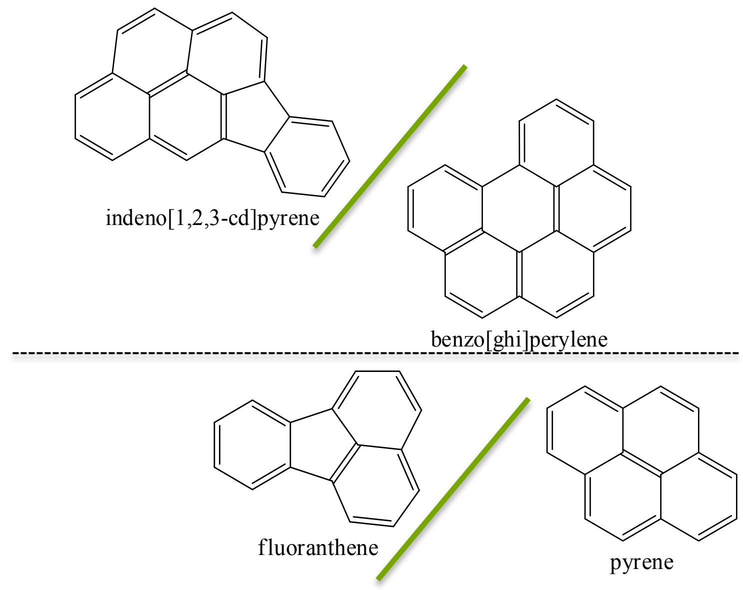
- No McMurray crop out near either lake

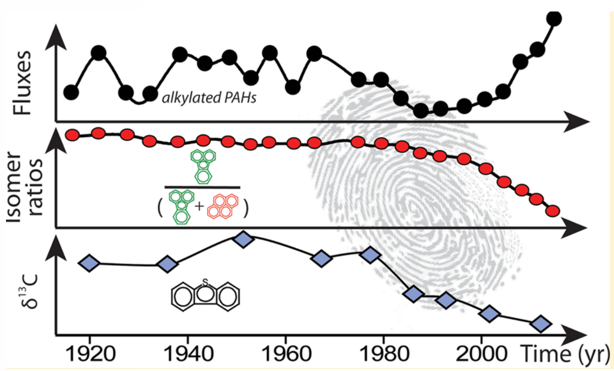


Jautzy et al 2013, ES&T

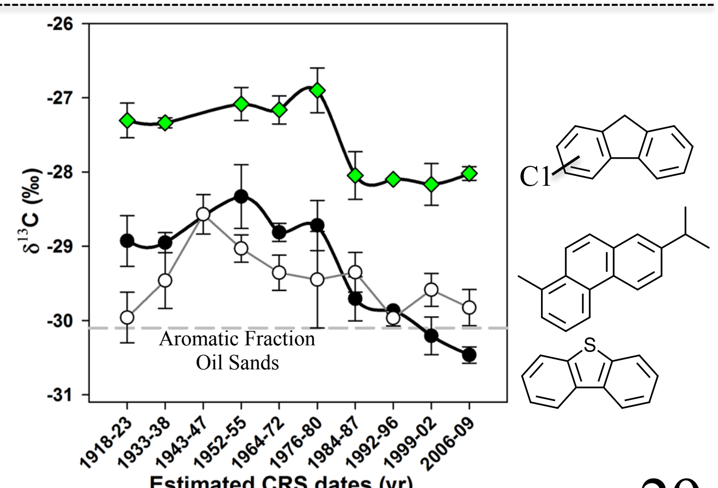
PAHs in lake sediments

- Ratios indicate shift from combustion to petrogenic origin
- Isotopes shift towards depleted aromatic signal of oil sands
- All data points to shift near 1980 in this area





Jautzy et al 2013, ES&T

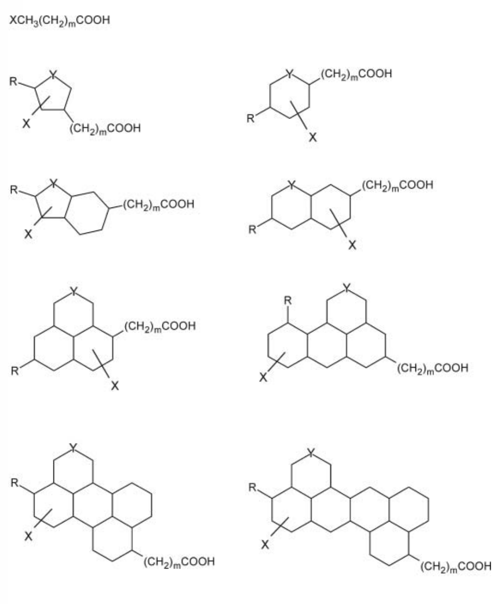


Monitoring Oil Sands

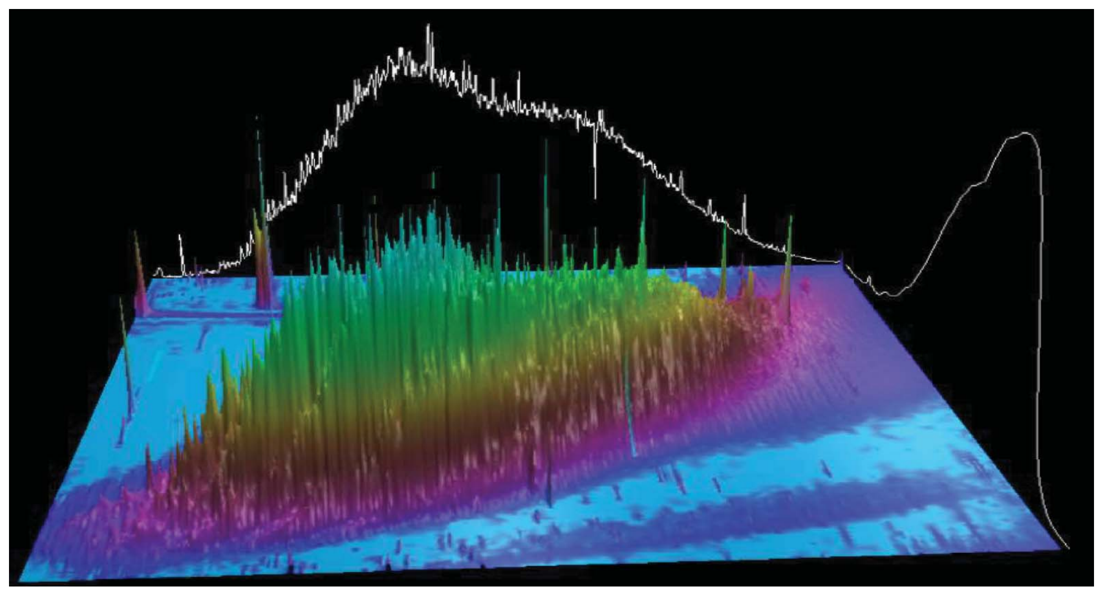
- Pre-development baseline can now be established
  - Important in studying current loadings and inputs for future oil sands development (EIAs)
- Oil sands have impact on surrounding environment that is measurable
  - Need non-traditional analytes (some that are not regulated) to allocate source

Naphthenic acids

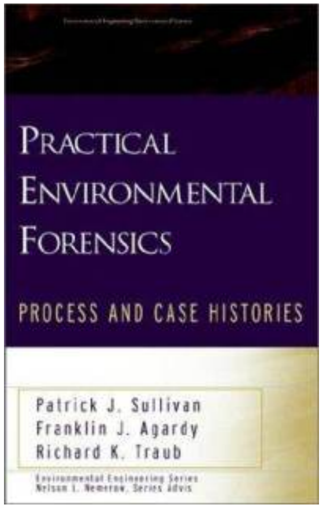
- Its not a recreational drug
- If you don’t know what it is, you should learn
- 1000s of compounds – water soluble and have known toxicity
  - And a fingerprint…

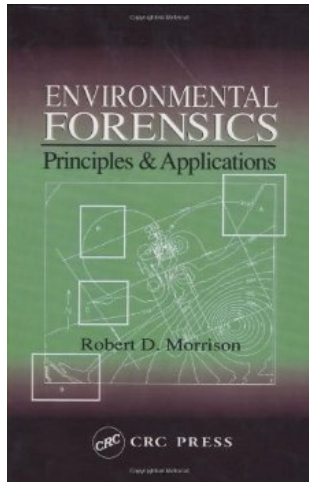


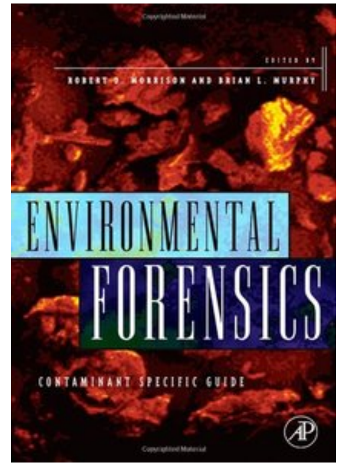
R = alkyl group
X = COOH, R, OH, SO_x, NO_x, SH
Y= C, S, N
note: ring structures may not be fully saturated

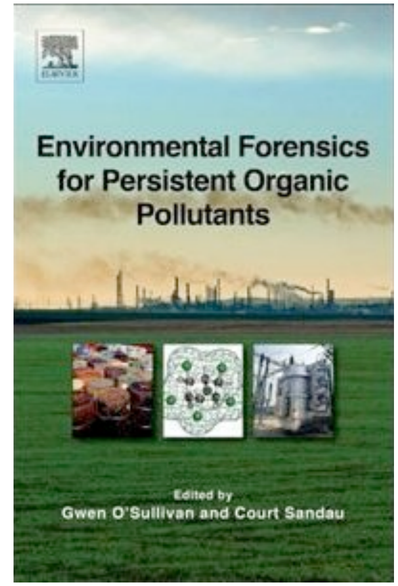


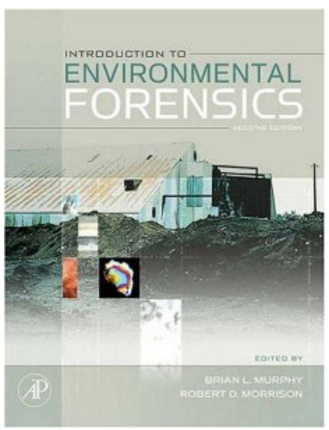
Environmental Forensics Resources

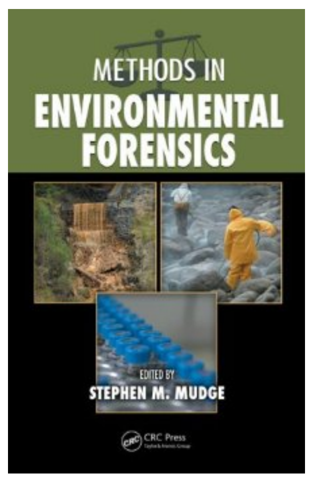


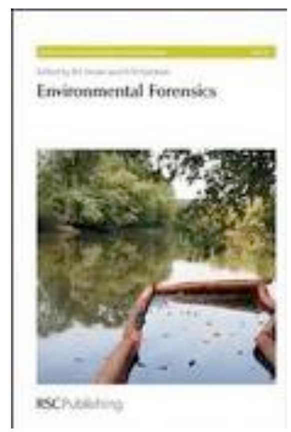


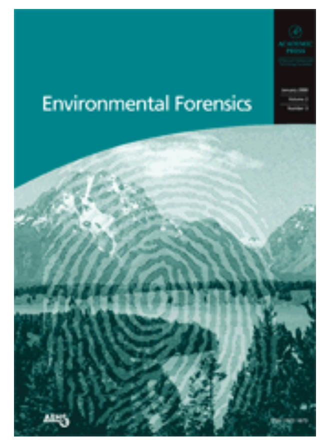












Questions?

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