



chemistry
matters

*making environmental
data meaningful*

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

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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)

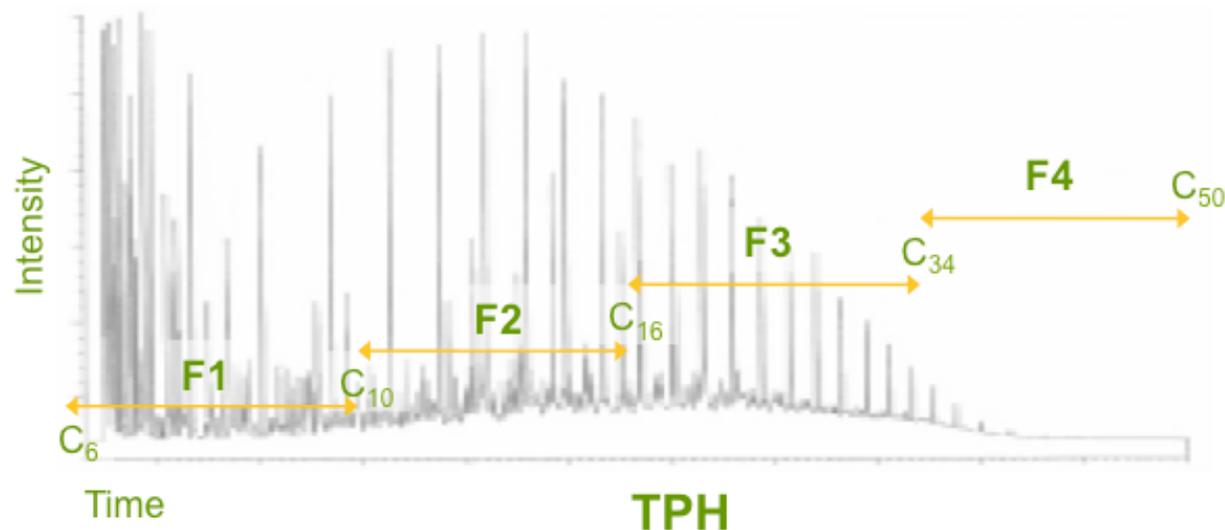
As stated by: Kurek et al 2013, PNAS:

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 ($T_{1/2}$ = **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...

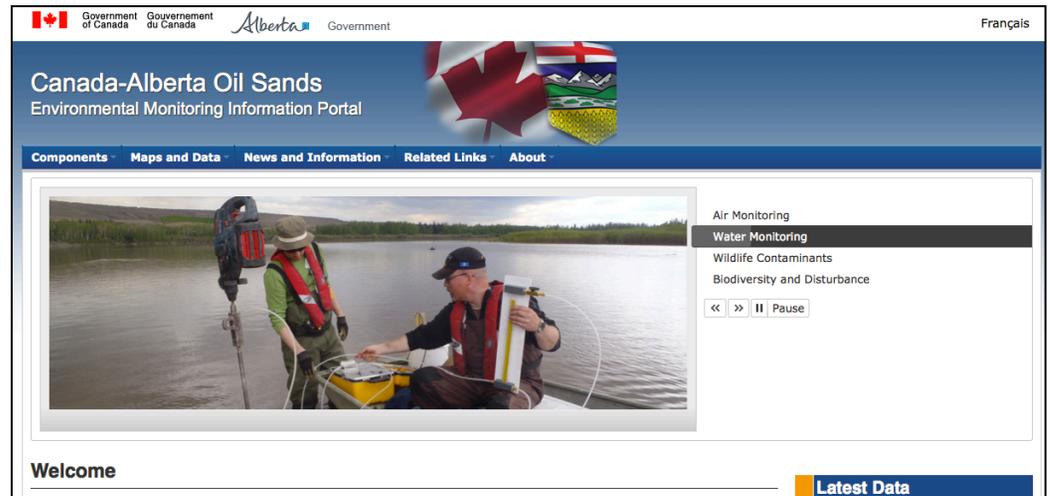
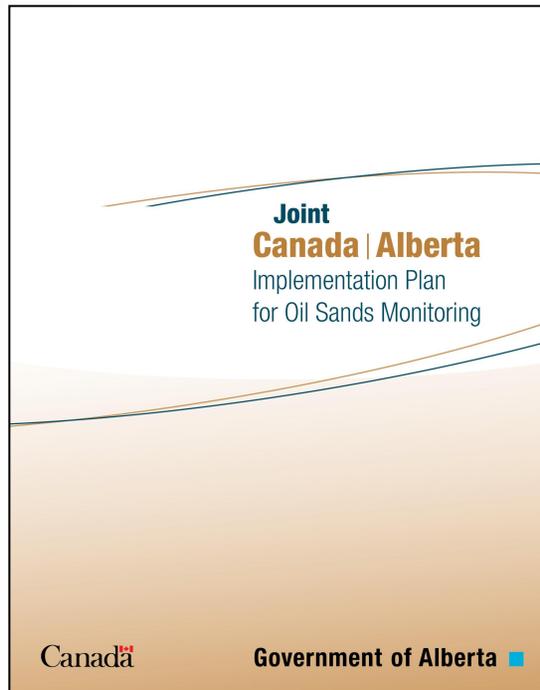


- Even Albertans don't trust their own scientists.



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)	%
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



Athabasca river and surrounding areas are impacted by oil sands development

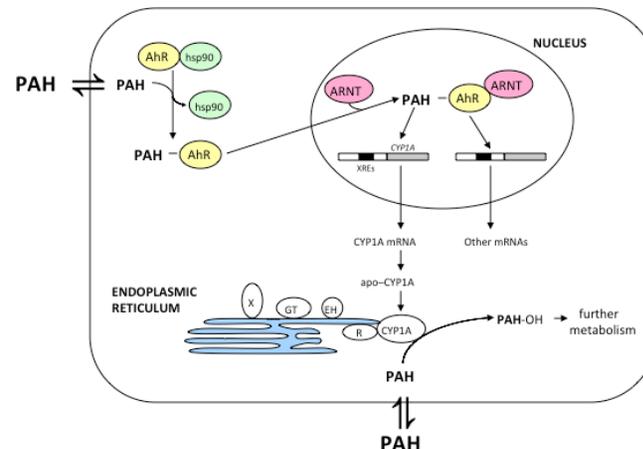
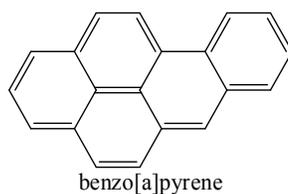


- Still be below guidelines for most targeted analytes



PAHs

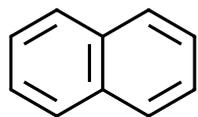
- Naturally present in oil sands at low % quantities (dust from open pit mining)
- Produced during combustion (upgrading)
- Resist degradation (persist in environment)
- Analytical methods available
 - Careful on method though...
- Well understood toxicity



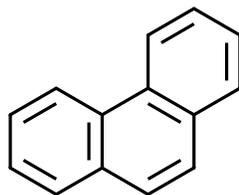


What are PAHs?

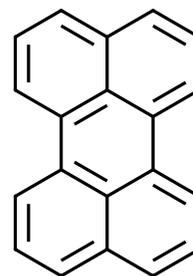
- Poly - multiple
- Cyclic - rings
- Aromatic – double bonds in a ring
- Hydrocarbons – contain carbon and hydrogen



naphthalene



phenanthrene

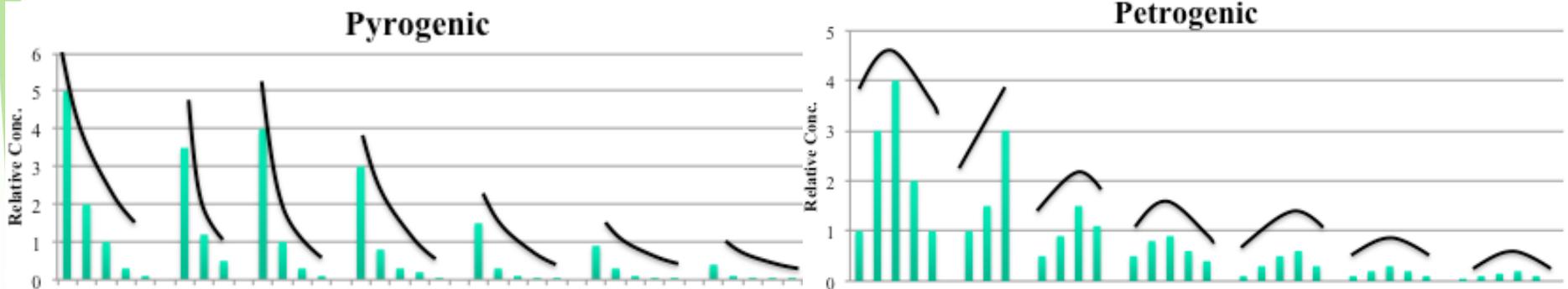
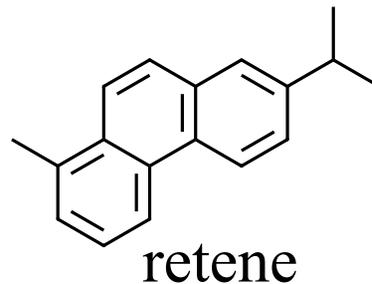


perylene

How are PAHs formed?

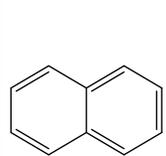
Three formation mechanisms:

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

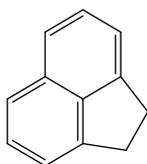




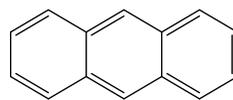
US EPA Priority Pollutants PAH Compounds



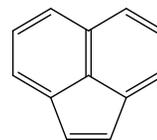
naphthalene



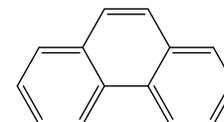
acenaphthene



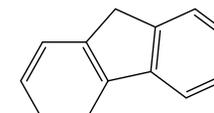
anthracene



acenaphthylene



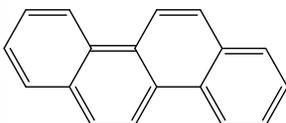
phenanthrene



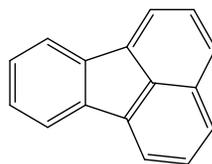
fluorene

LMW

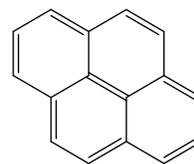
2-ring



chrysene

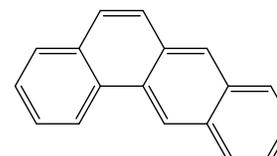


fluoranthene

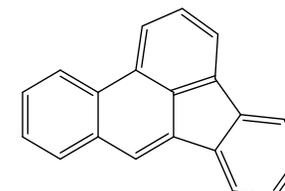


pyrene

3-ring



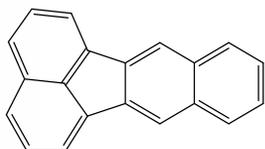
benzo[a]anthracene



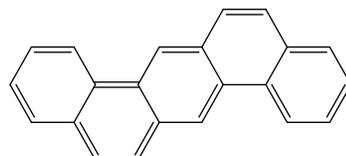
benzo[b]fluoranthene

HMW

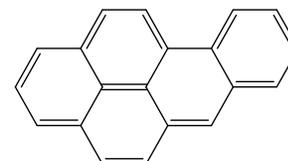
4-ring



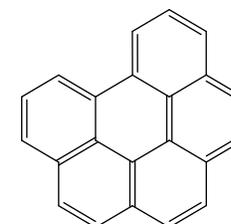
benzo[k]fluoranthene



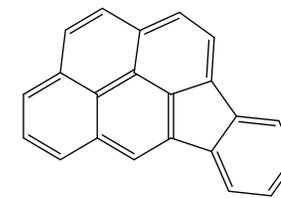
dibenz[a,h]anthracene



benzo[a]pyrene



benzo[ghi]perylene



indeno[1,2,3-cd]pyrene

5-ring

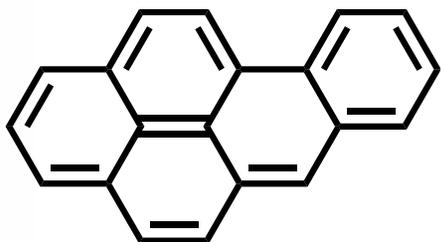
6-ring

List predates 1977



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



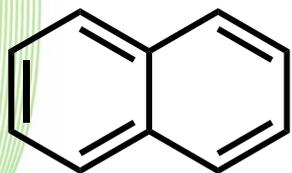
Benzo(a)pyrene

Difference in measuring 252
versus 252.30928

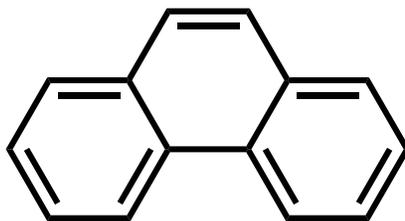
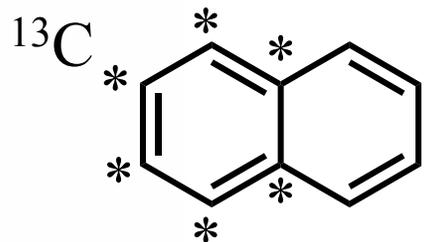
Internal Standards vs. Surrogates



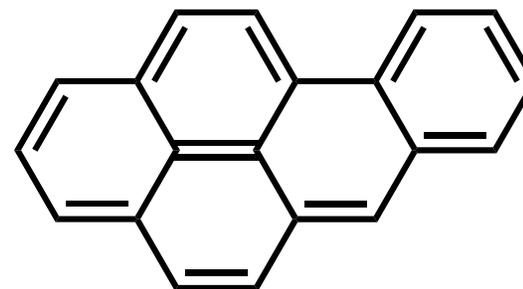
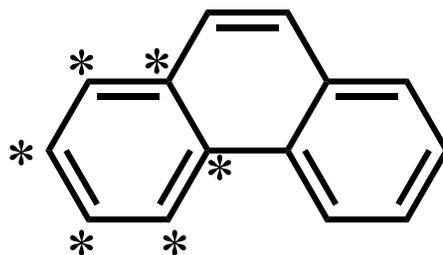
Quantification can be improved using isotopically labeled standards



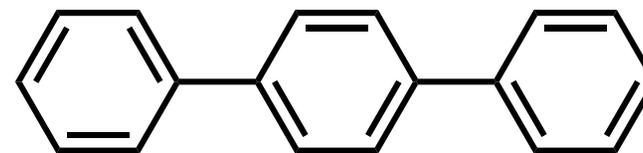
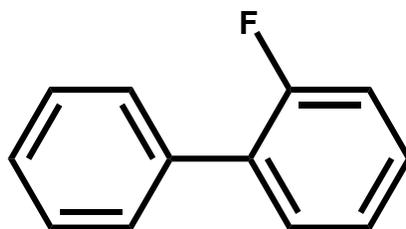
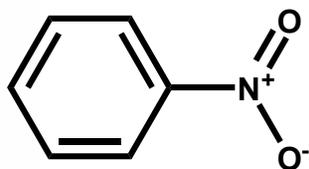
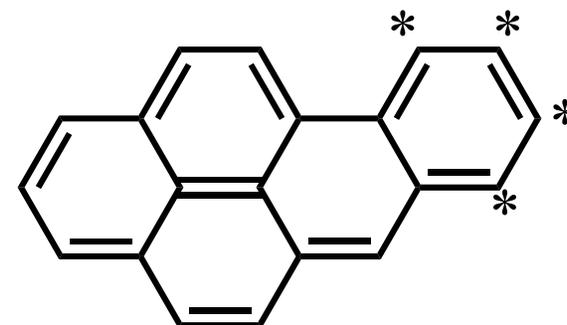
naphthalene



phenanthrene



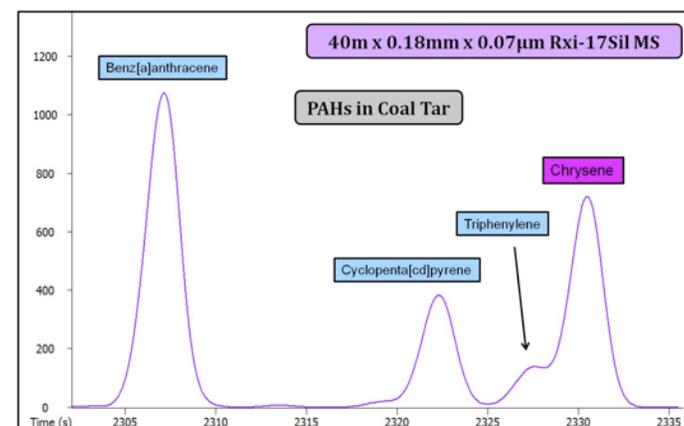
benzo(a)pyrene





Isotope Dilution Quantification

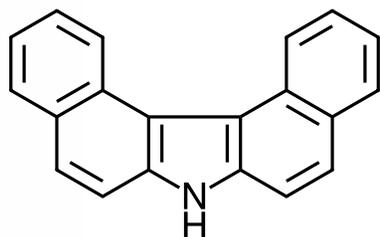
- Standards behave exactly like compounds being analyzed
- Loss of compounds during analytical method, included in measurement
- Matrix interferences in method, can usually be seen with standards as well
- THE most accurate measurement available



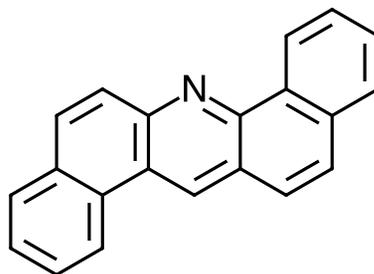
'New' PAHs



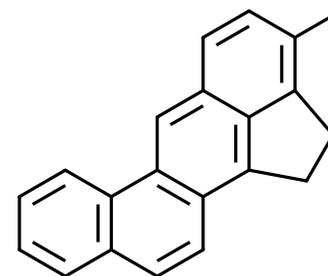
- EPA List of priority PAHs dates back pre-1977
- Upwards to 40 'parent' PAHs potentially to monitor
- Starting to look at heterocycles (O, N, S containing)



7H-dibenzo(c,g)carazole



dibenzo(a,h)acridine

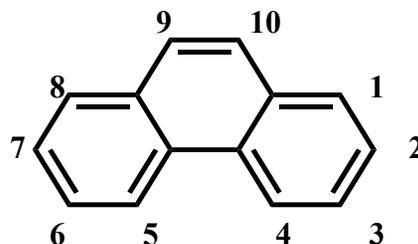


3-methyl chloanthrene

Expanding the List of PAHs

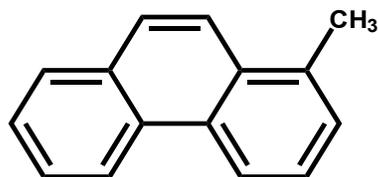


Alkylated-PAHs and Other PAHs



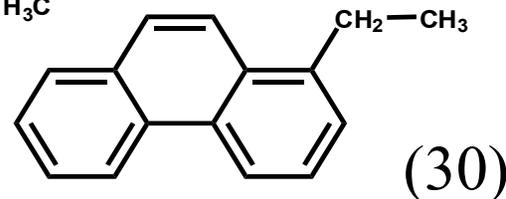
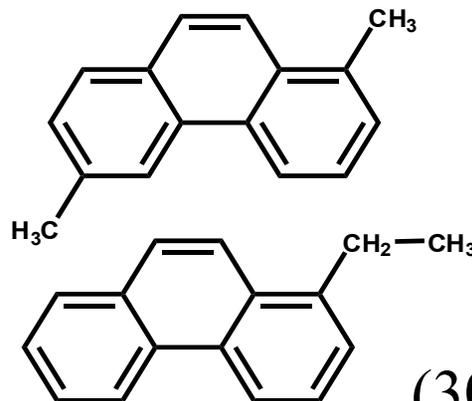
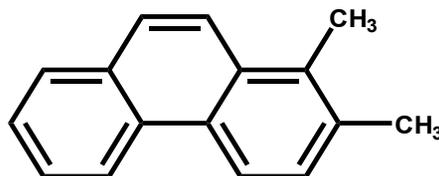
Phenanthrene

C1-Phenanthrenes



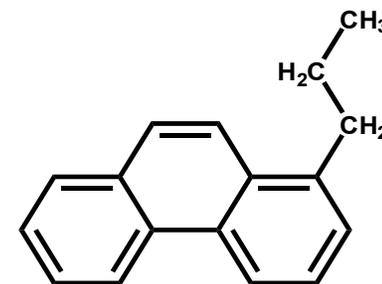
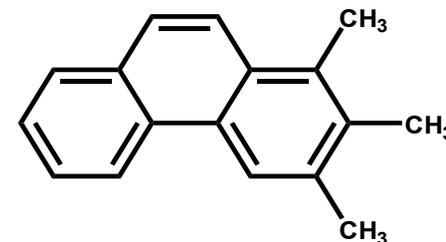
(5)

C2-Phenanthrenes



(30)

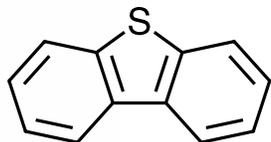
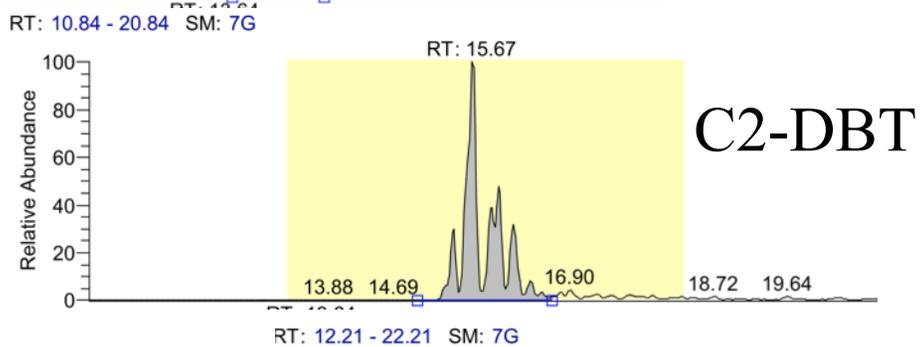
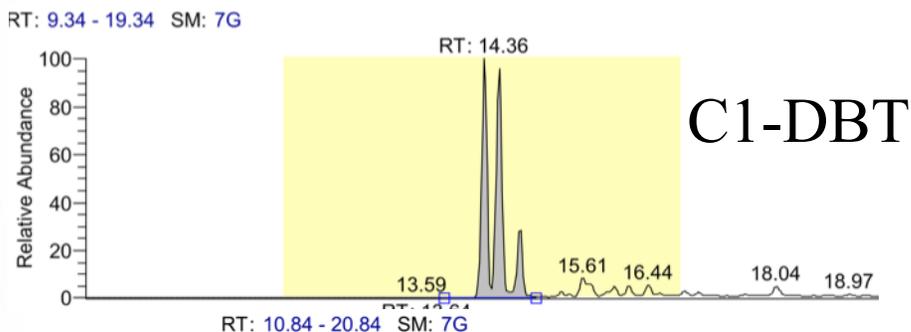
C3-Phenanthrenes



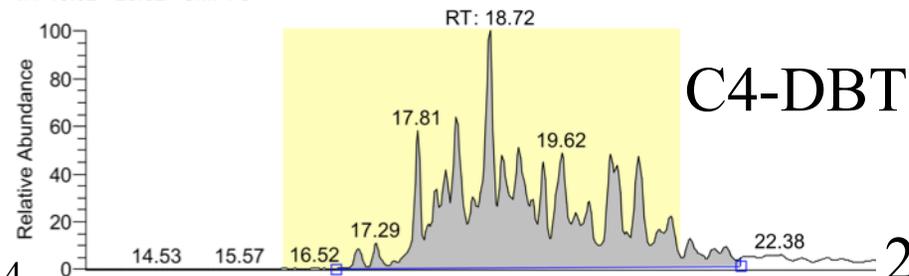
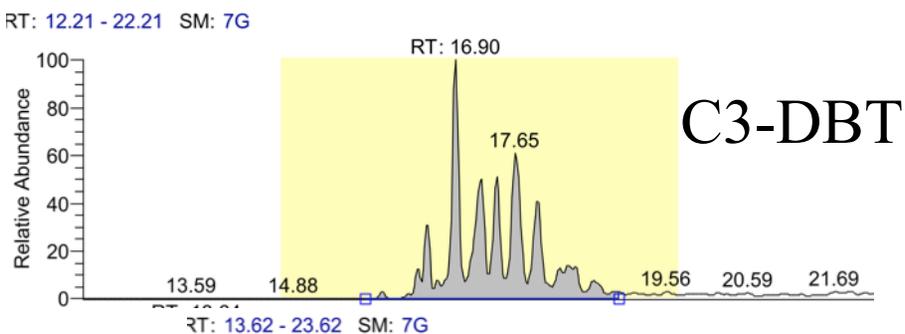
(?)

C4-Phenanthrenes... (?)

Chromatography Gets Busy



Dibenzothiophene



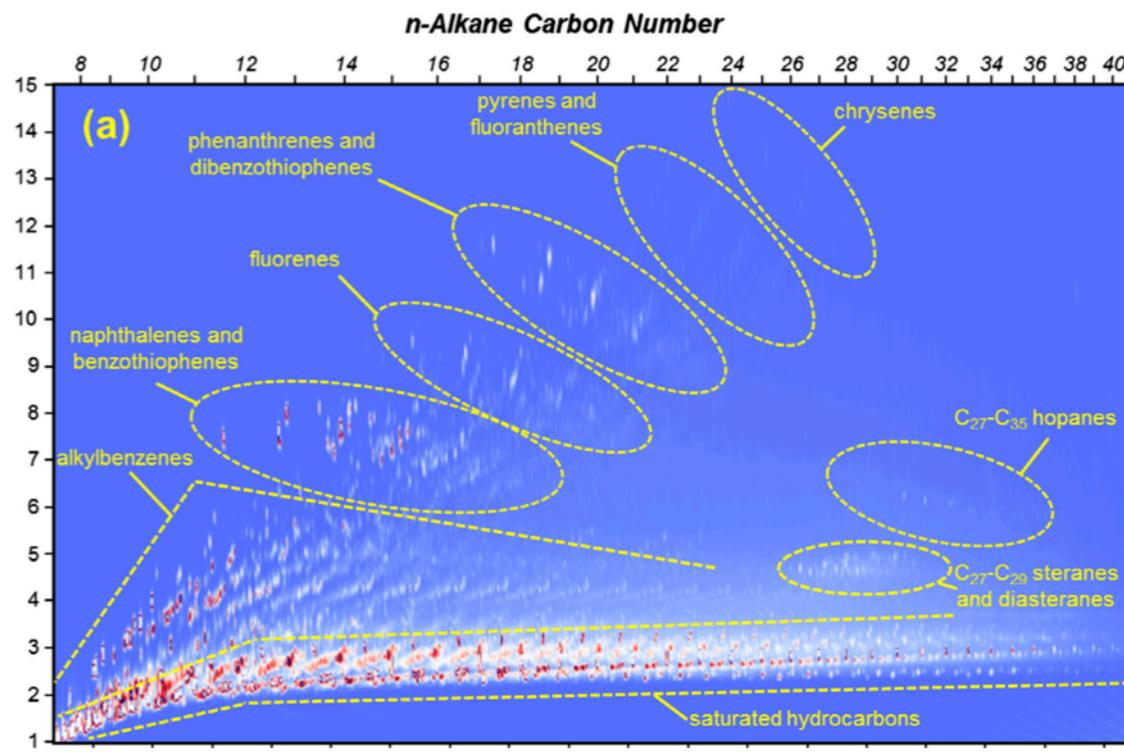
Each parent PAH has potentially 100s of alkylated homologues

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



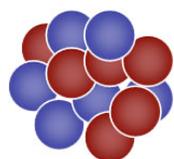


PAH Monitoring

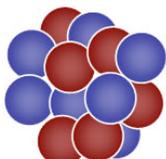
- Routine method no longer cuts it
- More analytes currently possible
- Better analytical standards and lower detection limits
- More analytes to be mandatory (in the future)
- All PAHs could be monitored, if desired



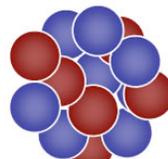
Isotopes on PAHs



carbon-12
98.9%
6 protons
6 neutrons



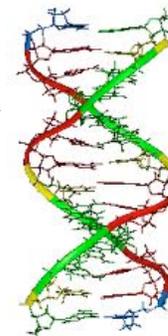
carbon-13
1.1%
6 protons
7 neutrons



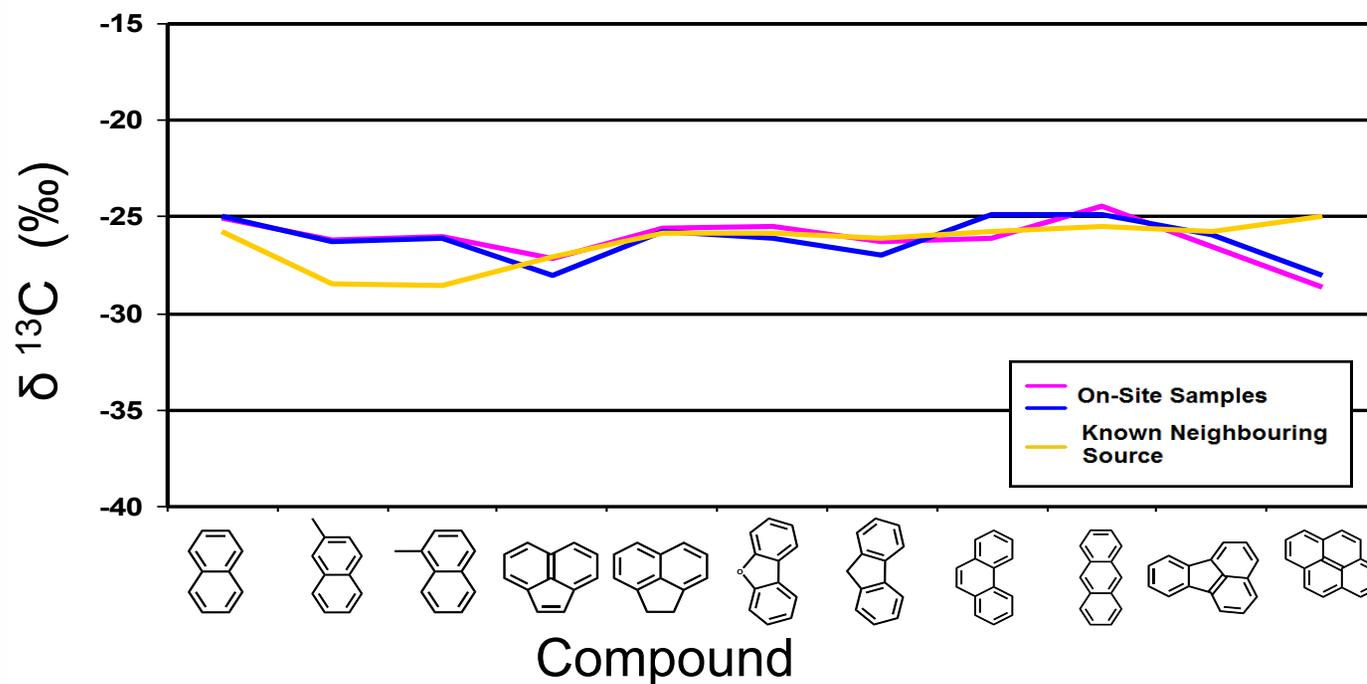
carbon-14
<0.1%
6 protons
8 neutrons

=

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

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 Jautry,¹ Jason M. E. Ahad,^{2,3} Charles Gobeil,¹ and Martine M. Savard¹

¹NRS Eau Terre Environnement, Québec, QC, G1K 8A9, Canada
²Geological Survey of Canada, Natural Resources Canada, Québec, QC, G1K 8A9, Canada

Supporting Information

ABSTRACT: Evaluating the impact that airborne contamination associated with Athabasca oil sands (AOS) mining operations has on the surrounding boreal forest ecosystem requires a rigorous approach to source discrimination. This study presents a century-long historical record of source apportionment of polycyclic aromatic hydrocarbons (PAHs) in dated sediments from two headwater lakes located approximately 40 and 55 km east from the main area of open pit mining activities. Concentrations of the 16 Environmental Protection Agency (EPA) priority PAHs in addition to retene, dibenzofluorene (DBT), and six alkylated groups were measured, and both PAH molecular diagnostic ratios and carbon isotopic signatures ($\delta^{13}C$) of individual PAHs were used to differentiate natural from anthropogenic inputs. Although concentrations of PAHs in these lakes were low and below the Canadian Council of Ministers of the Environment (CCME) guidelines, diagnostic ratios pointed to an increasingly larger input of petroleum-derived (i.e., petrogenic) PAHs over the past 30 years consistent with $\delta^{13}C$ values progressively shifting to the value of unprocessed AOS bitumen. The petrogenic source is attributed to the deposition of bitumen in dust particles associated with wind erosion from open pit mines.

INTRODUCTION

The Athabasca oil sands (AOS) found in Northern Alberta, Canada, are one of the world's largest oil reserves, containing ~170 billion barrels.¹ The continued development and expansion of this resource, however, has raised concerns regarding its potential impact on the surrounding environment. Of particular interest are polycyclic aromatic hydrocarbons (PAHs), a group of organic contaminants that are toxic to a wide range of aquatic wildlife^{2,3} and are suspected or known carcinogens.^{4,5} Naturally present in AOS bitumen at concentrations of up to 12.17 mg kg⁻¹ (alkylated and unsubstituted Environmental Protection Agency (EPA) parent PAHs),⁶ PAHs are also released to the environment through the incomplete combustion of organic matter, including both modern biomass (e.g., forest fires) and fossil fuels, and via diagnostic processes. Evaluating atmospheric emissions associated with oil sands mining activities thus requires discrimination between anthropogenic and natural inputs. Recent work has reported substantial loadings of airborne particulates containing PAHs to snowpack, within an approximately 50 km radius from the center of the oil sands mining operations.⁷ The subsequent spring snowmelt was thus suggested as an important vector for the export of elevated levels of PAHs to the Athabasca River and its watershed. The extent to which dated sites are impacted by airborne oil sands-derived contaminants, however, remains unclear.⁸ While Hall et al.⁹ found no evidence to support a recent increase in atmospherically transported PAHs to the Athabasca Delta (located ~200 km north of the main area of oil sands operations), Kurek et al.¹⁰ reported significant up-core increases in total PAH concentrations (parent, alkylated and sulfur-containing dibenzofluorenes, DBT) in sediments from six AOS region lakes that were attributed to atmospheric transport of oil sands-derived petrogenic PAHs originating from bitumen upgrading facilities and/or unweathered bitumen in the form of dust particles from open pit mines. Although PAH concentrations in most of the lakes studied were below Canadian interim sediment quality guidelines, the range of atmospheric deposition was suggested to extend as far as 90 km to the northwest from the geographic center of oil sands mining operations. Their conclusion was based on elevated levels of bitumen-associated PAHs (e.g., alkylated PAHs, DBT)¹¹ and on distinctive patterns in PAH molecular diagnostic ratios believed to be characteristic of other wood combustion or petrogenic sources.

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

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The absence of well-executed environmental monitoring in the Athabasca oil sands (Alberta, Canada) has necessitated the use of indirect approaches to determine background conditions of freshwater ecosystems before development of one of the Earth's largest energy deposits. Here, we use highly resolved lake sediment records to provide ecological context to ~50 yr of oil sands development and other environmental changes affecting lake ecosystems in the region. We show that polycyclic aromatic hydrocarbons (PAHs) within lake sediments, particularly Cl-C4-alkylated PAHs, increased significantly after development of the bitumen resource began, followed by significant increases in dibenzofluorenes. Total PAH fluxes in the modern sediments of our six study lakes, including one site ~90 km northwest of the major development area, are now ~2–2.2 times greater than ~1960 levels. PAH ratios indicate temporal shifts from primarily wood combustion to petrogenic sources that coincide with greater oil sands development. Canadian interim sediment quality guidelines for PAHs have been exceeded since the mid-1980s at the most impacted site. A paleoecological assessment of *Daphnia* shows that the bivalve copepod has not yet been negatively impacted by decades of high atmospheric PAH deposition. Rather, coincident with increases in PAHs, climate-induced shifts in aquatic primary production related to warmer and drier conditions are the primary environmental drivers producing marked depthwise shifts of ~100% in PAH concentrations. RAMP data of PAH measures in Athabasca River Delta sediments showed increases of ~30% between 1999 and 2009 and yet no significant increases in PAHs from control sites (15). Others have challenged these findings. For example, based on three lake sediment records with well-dated hydrological settings >300 km north of the major development area, natural erosion processes in regional rivers were identified as the key vector of PAH delivery to sediments in recently flooded Athabasca Delta lakes (14). Analysis of PAHs in dated sediment cores from western Lake Athabasca and Richardson Lake in the Athabasca Delta also found no increase in total PAHs from the ~1950s to 1998 (23). The lack of consensus among the few temporal-focused PAH studies to date, and the shortcomings of oil sands monitoring programs to adequately recognize the deposition patterns of atmospheric contaminants (6, 7), leave justifiable cause for concern as to the ecological implications of oil sands development. Establishment of background PAH concentrations and historic loadings is essential and would allow the impacts of development, including industrial PAH contributions, to be compared with the natural range in variability and complexity of these contaminants in lake sediments from the region.

We used repeatedly in previous assessments of the impacts of the Alberta oil sands operations, insufficient monitoring data

ABSTRACT: Evaluating the impact that airborne contamination associated with Athabasca oil sands (AOS) mining operations has on the surrounding boreal forest ecosystem requires a rigorous approach to source discrimination. This study presents a century-long historical record of source apportionment of polycyclic aromatic hydrocarbons (PAHs) in dated sediments from two headwater lakes located approximately 40 and 55 km east from the main area of open pit mining activities. Concentrations of the 16 Environmental Protection Agency (EPA) priority PAHs in addition to retene, dibenzofluorene (DBT), and six alkylated groups were measured, and both PAH molecular diagnostic ratios and carbon isotopic signatures ($\delta^{13}C$) of individual PAHs were used to differentiate natural from anthropogenic inputs. Although concentrations of PAHs in these lakes were low and below the Canadian Council of Ministers of the Environment (CCME) guidelines, diagnostic ratios pointed to an increasingly larger input of petroleum-derived (i.e., petrogenic) PAHs over the past 30 years consistent with $\delta^{13}C$ values progressively shifting to the value of unprocessed AOS bitumen. The petrogenic source is attributed to the deposition of bitumen in dust particles associated with wind erosion from open pit mines.

INTRODUCTION

The Athabasca oil sands (AOS) found in Northern Alberta, Canada, are one of the world's largest oil reserves, containing ~170 billion barrels.¹ The continued development and expansion of this resource, however, has raised concerns regarding its potential impact on the surrounding environment. Of particular interest are polycyclic aromatic hydrocarbons (PAHs), a group of organic contaminants that are toxic to a wide range of aquatic wildlife^{2,3} and are suspected or known carcinogens.^{4,5} Naturally present in AOS bitumen at concentrations of up to 12.17 mg kg⁻¹ (alkylated and unsubstituted Environmental Protection Agency (EPA) parent PAHs),⁶ PAHs are also released to the environment through the incomplete combustion of organic matter, including both modern biomass (e.g., forest fires) and fossil fuels, and via diagnostic processes. Evaluating atmospheric emissions associated with oil sands mining activities thus requires discrimination between anthropogenic and natural inputs. Recent work has reported substantial loadings of airborne particulates containing PAHs to snowpack, within an approximately 50 km radius from the center of the oil sands mining operations.⁷ The subsequent spring snowmelt was thus suggested as an important vector for the export of elevated levels of PAHs to the Athabasca River and its watershed. The extent to which dated sites are impacted by airborne oil sands-derived contaminants, however, remains unclear.⁸ While Hall et al.⁹ found no evidence to support a recent increase in atmospherically transported PAHs to the Athabasca Delta (located ~200 km north of the main area of oil sands operations), Kurek et al.¹⁰ reported significant up-core increases in total PAH concentrations (parent, alkylated and sulfur-containing dibenzofluorenes, DBT) in sediments from six AOS region lakes that were attributed to atmospheric transport of oil sands-derived petrogenic PAHs originating from bitumen upgrading facilities and/or unweathered bitumen in the form of dust particles from open pit mines. Although PAH concentrations in most of the lakes studied were below Canadian interim sediment quality guidelines, the range of atmospheric deposition was suggested to extend as far as 90 km to the northwest from the geographic center of oil sands mining operations. Their conclusion was based on elevated levels of bitumen-associated PAHs (e.g., alkylated PAHs, DBT)¹¹ and on distinctive patterns in PAH molecular diagnostic ratios believed to be characteristic of other wood combustion or petrogenic sources.

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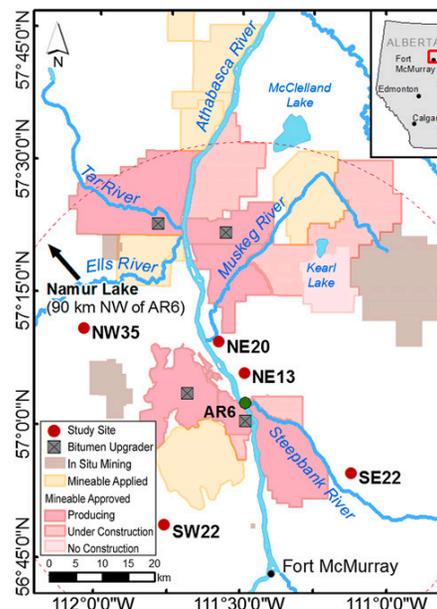
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PAHs in lake sediments



- 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

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The absence of well-resolved environmental monitoring in the Athabasca oil sands (Alberta, Canada) has necessitated the use of natural approaches to determine background conditions of freshwater ecosystems before development of one of the Earth's largest energy regions. Here, we use highly resolved lake sediment records to provide ecological context to ~50 yr of oil sands development and other environmental changes affecting lake ecosystems in the region. We show that polycyclic aromatic hydrocarbons (PAHs) within lake sediments, particularly C1-C4 alkylated PAHs, increased significantly after development of the bitumen reserves began, followed by significant increases in chlorobiphenyls. Total PAH fluxes in the modern sediments of four six study lakes, including one site ~90 km northwest of the major development area, were ~2.5–2.2 times greater than ~1960 levels. PAH ratios indicate temporal shifts from primarily wood combustion to petrogenic sources that coincide with greater oil sands development. Canadian interim sediment quality guidelines for PAHs have been exceeded since the mid-1980s at the most impacted site. A paleolimnological assessment of *Daphnia* shows that this sentinel organism has not yet been negatively impacted by decades of high atmospheric PAH deposition. Rather, consistent with increases in PAHs, climate-related shifts in aquatic primary production related to warmer and drier conditions are the primary environmental drivers producing marked declines in *Daphnia* from ~1960 to 1970. Because of the striking increase in PAHs, elevated primary production, and population changes, these oil sands lake ecosystems have entered new ecological states completely distinct from those of previous centuries.

atmospheric deposition | chlorobiphenyls | contaminants | environmental stressors | paleolimnology

Billions of sands in northern Alberta and Saskatchewan comprise 97% of Canada's proven oil reserves. They represent the world's third largest reserves (1) and are a significant North American economic driver, with ongoing growth forecasts. In 1960, oil production was 280,000 barrels per day. Production today is ~1.5 million barrels per day and is projected to increase by 50% (to 2.3 million barrels per day) between 2010 and 2025 (2). With stakeholders having polarized views on Canada's oil sands development, attention is focused on the region because of environmental and potential public-health concerns, as well as the significant economic benefits and evolving governance mechanisms and energy policies. Environmental concerns result primarily from the industrial activities associated with surface mining, site reclamation, and upgrading of bitumen. Collectively, these industrial activities have significant landscape disturbance and habitat loss (3, 4) and add to the controversy regarding water quantity and quality issues (5). The potential and realized emission of pollutants (6, 7), including greenhouse gases (8) and mercury (9), are also contentious. Some of the controversy results from a lack of reliable environmental monitoring for industrial activities from the establishment of the industry-funded Regional Aquatics Monitoring Program (RAM-IP) in 1997. Furthermore, weaknesses highlighted by scientific reviews of RAM-IP in its inability to recognize effects on biota (10–12), leads to additional criticism by some stakeholders.

A paradigm exists between the past and each of all lands development since ~1980 and the claims that development has resulted in detectable impacts and that contaminants result mainly from natural sources (13). Of particular concern are the atmospheric loading and distribution of contaminants associated with oil sands surface-mining and processing activities (6, 7, 14, 15), many of which are congeners and rank in the top 10 hazardous substances on the US Agency for Toxic Substances and Disease Registry (16). Polycyclic aromatic hydrocarbons (PAHs) are one such example, with natural and anthropogenic pathways to ecosystems (17). PAHs are a diverse group of organic compounds with multiple aromatic rings and are produced by the incomplete combustion of fossil fuel biomass. They are relatively soluble in water and tend to sorb to particles in the water column, potential to sorb organic ligands in aquatic biota, and, particularly in the presence of other stressors (18–21). With similar properties to PAHs, the sulfur-containing dibenzofurans (DBFs) and a related class of aromatic compounds, C1-C4-alkylated PAHs and DBFs are both recognized as prominent components of Athabasca oil sands bitumen (6, 22).

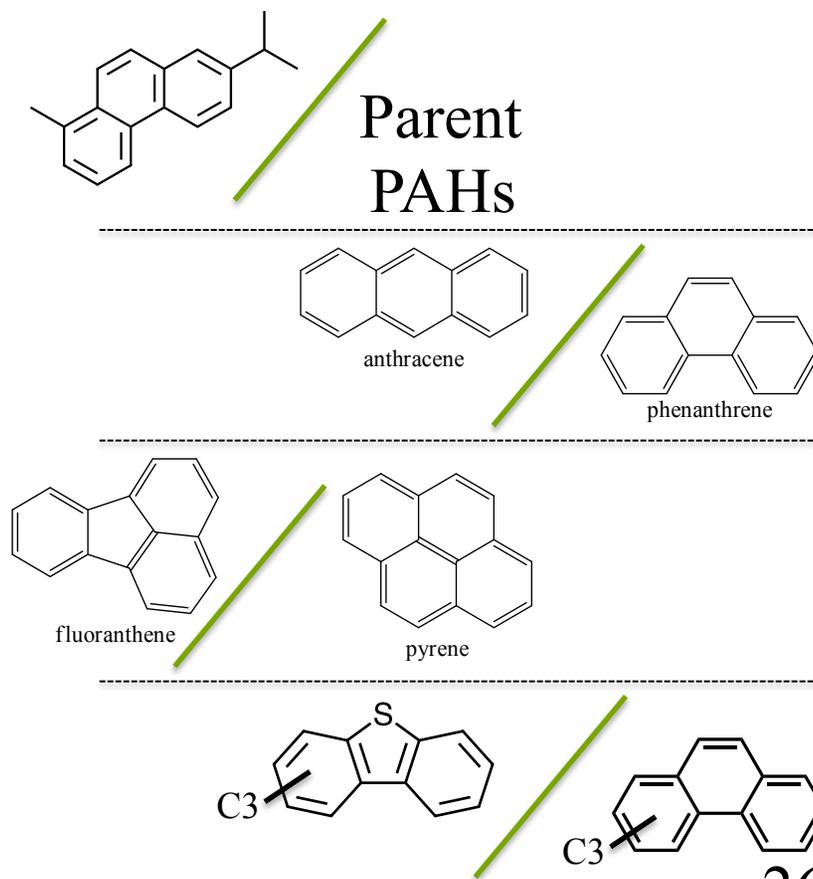
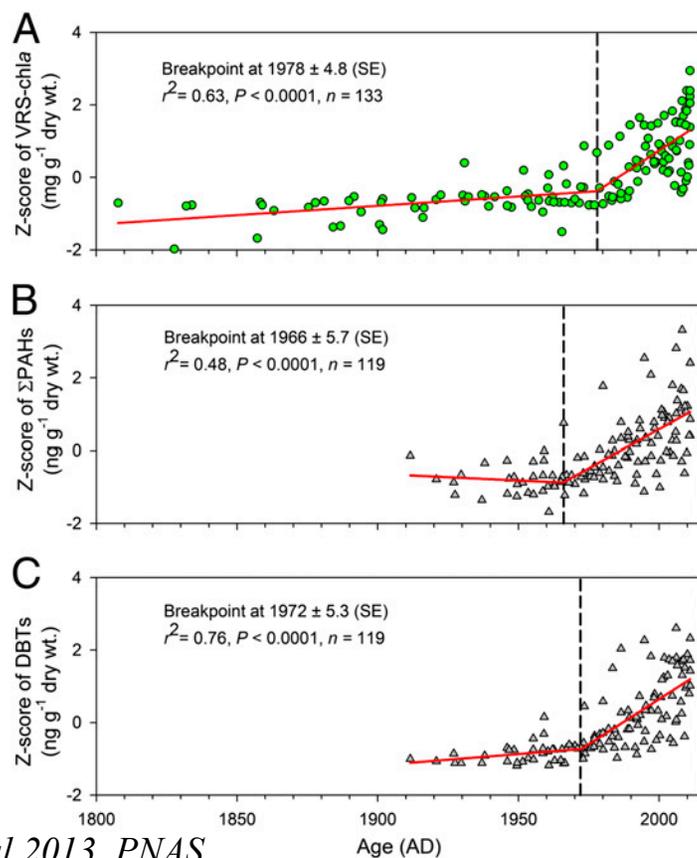
Almost two decades of environmental monitoring within the oil sands region has failed to establish background concentrations of highly toxic contaminants. RAM-IP data of PAH necessary to Athabasca River Delta sediments showed increases of ~30% between 1999 and 2009 and yet no significant increases in PAHs from control sites (15). Others have challenged these findings. For example, based on three lake sediment records within well-developed, non-impacted areas, natural processes in regional depositional basins appear to account for the increases in PAHs (23). However, a recent study of PAH delivery to sediments in seasonally flooded Athabasca Delta lakes (14). Analysis of PAHs in dated sediment cores from western Lake Athabasca and Richardson Lake in the Athabasca Delta also found no increases in total PAHs from the ~1960s to 1990s (24). The lack of consensus among the few temporal-focused PAH studies to date, and the shortcomings of oil sands monitoring programs to adequately recognize the deposition patterns of atmospheric contaminants (6, 7), have justifiable cause for concern as to the ecological implications of oil sands development. Establishment of background PAH concentrations and biotic loading is essential and would allow the assessment of development, including industrial PAH contributions, to be compared with the natural range in variability and composition of these contaminants in lake sediments and corroborated in previous assessments of the impacts of the Athabasca oil sands operations, insufficient monitoring data

*Author contributions: J.K., D.C.G.M., X.W., M.S.E., and J.P.S. designed research; J.K., D.C.G.M., X.W., M.S.E., and J.P.S. performed research; J.K., D.C.G.M., X.W., M.S.E., and J.P.S. analyzed data and wrote the paper. The authors declare no conflict of interest. This article is a PNAS Direct Submission. J.P.S. is a guest editor invited by the Editorial Board. Address correspondence to J.P.S. at jpsmol@queensu.ca. This work was supported by the Natural Sciences and Engineering Research Council of Canada. We thank the Athabasca Regional Aquatics Monitoring Program (RAM-IP) in 1997. Furthermore, weaknesses highlighted by scientific reviews of RAM-IP in its inability to recognize effects on biota (10–12), leads to additional criticism by some stakeholders.

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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

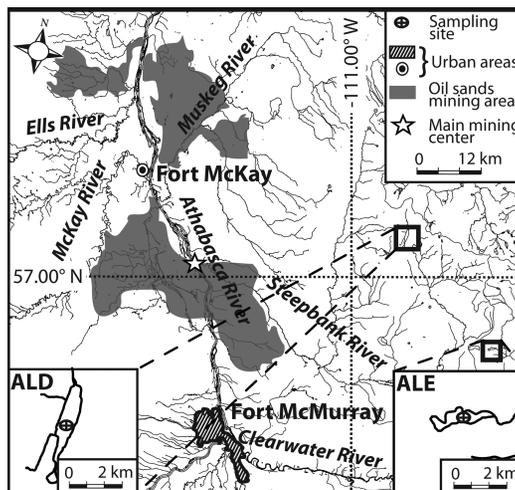
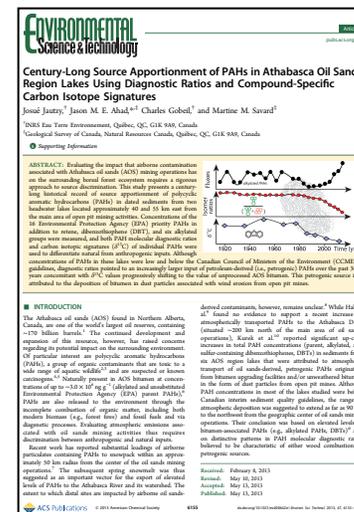
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PAHs in lake sediments



- 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

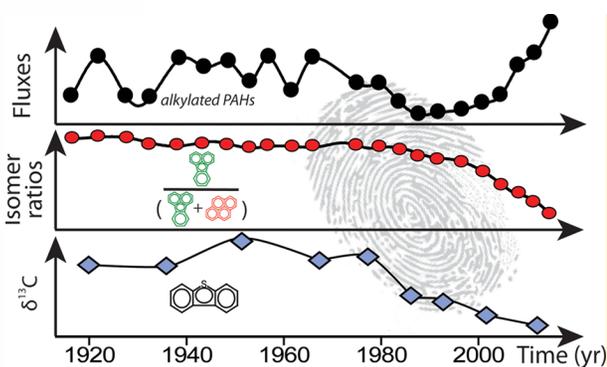
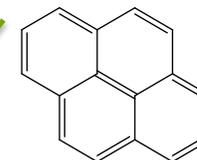
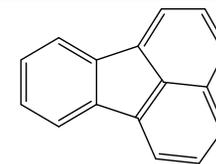
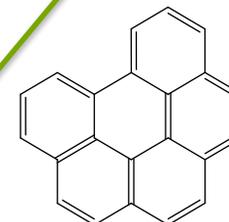
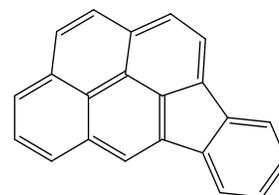


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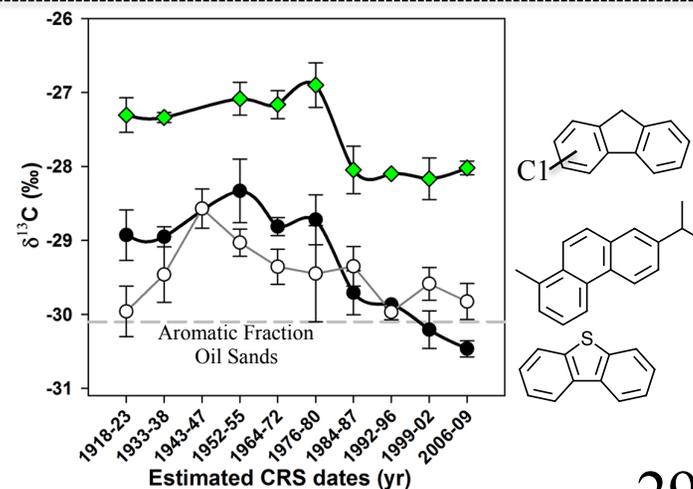


PAHs in lake sediments

- 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

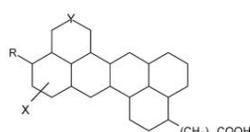
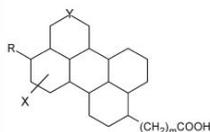
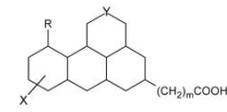
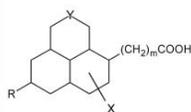
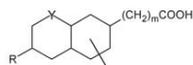
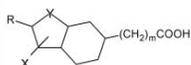
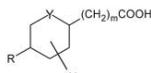
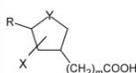
- Pre-development baseline can now be established
 - Important in studying current loadings and inputs for future oil sands development (EIAs)
- Oil sands have impact on surrounding environment that is measurable
 - Need non-traditional analytes (some that are not regulated) to allocate source



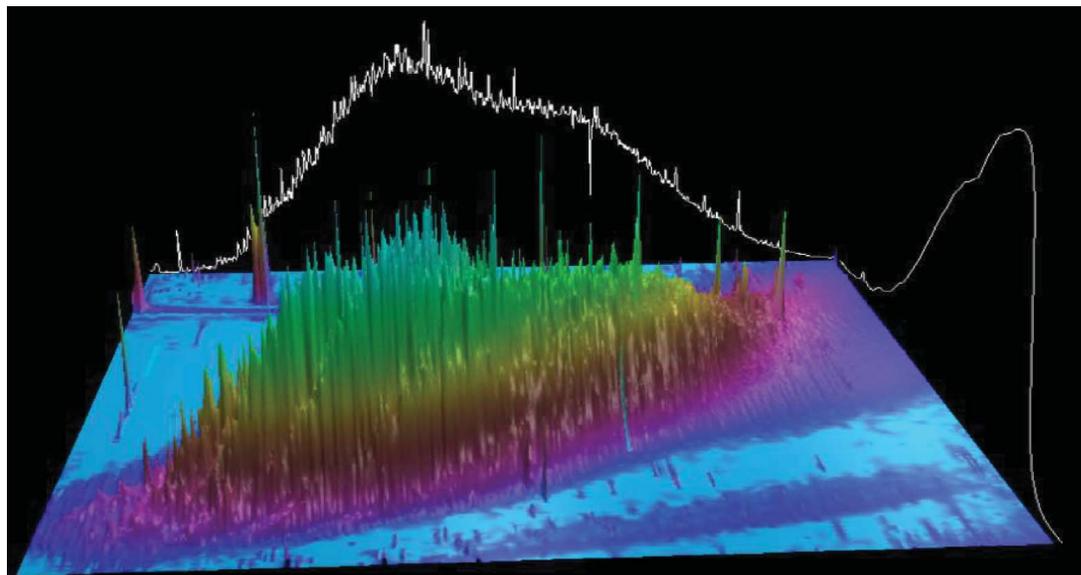
Naphthenic acids

- 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...

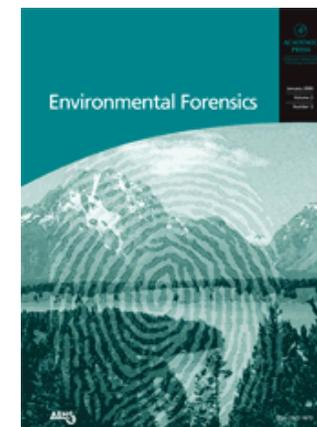
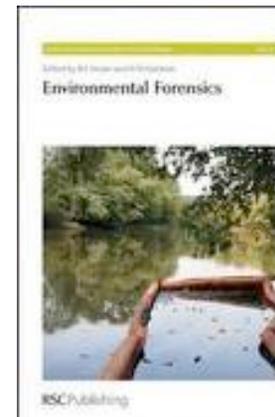
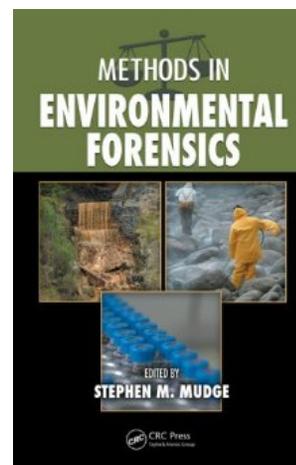
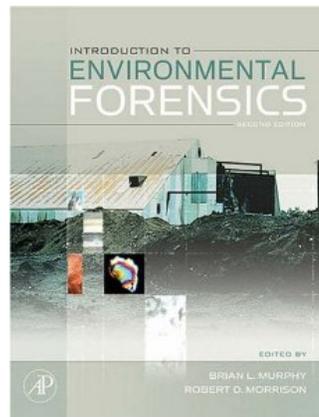
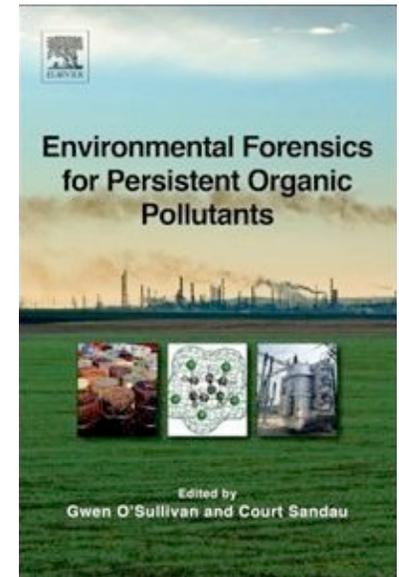
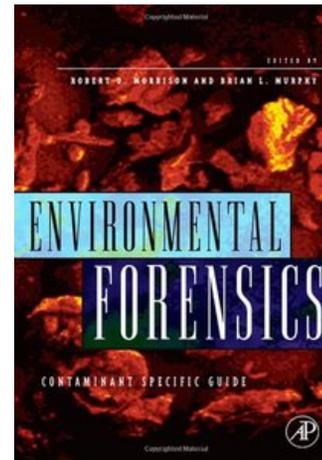
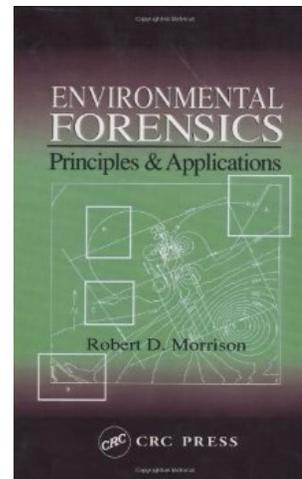
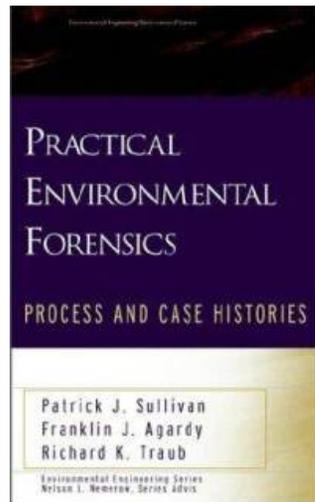
$XCH_2(CH_2)_mCOOH$



R = alkyl group
X = COOH, R, OH, SO₃, NO₂, SH
Y = C, S, N
note: ring structures may not be fully saturated



Environmental Forensics Resources





Questions?

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