

# Compound-specific Radiocarbon Analysis to Evaluate the Contribution of Peace River Floodings to the PAH Background in the Peace-Athabasca Delta.

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## Introduction

WHERE?



No large-scale bitumen surface mining in the Peace River watershed.

Natural bitumen outcrops on river banks.

WHY?

Oil sands located in a sensitive & complex environmental system.

Rapid growth of oil sands industry:

--> questioning the environmental impacts.

Focus on: Polycyclic Aromatic Hydrocarbons (PAHs).

--> hazardous and carcinogenic organic compounds.

--> produced by: - incomplete combustion of biomass (modern or fossil).  
- maturation of kerogene towards fossil fuel.  
- early stage diagenesis.

Establishing PAH background crucial in this region for source apportionment.

HOW?

Natural chronological record used:

--> <sup>137</sup>Cs & <sup>210</sup>Pb dated lake sediment core.

--> novel approach based on <sup>14</sup>C content of specific PAH<sub>alkyl</sub> source discrimination.

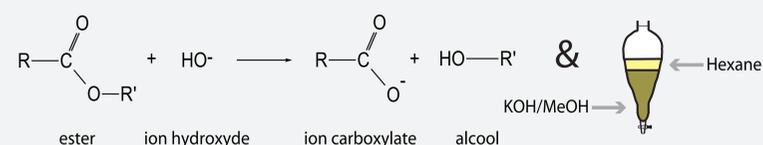
--> able to estimate the relative contribution of fossil vs modern PAH fraction modern (f<sub>modern</sub>)

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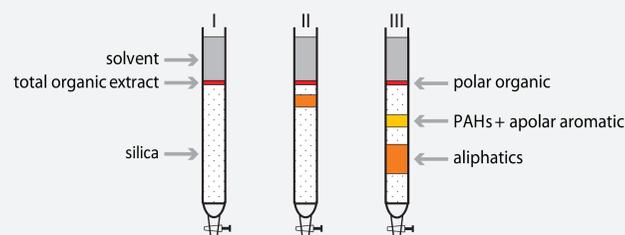
## Methods

### MARS & Soxhlet Extraction

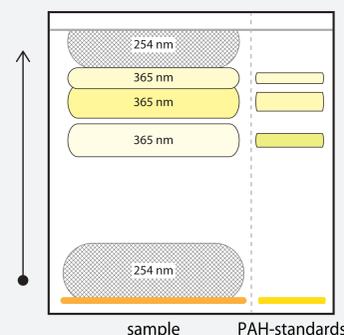
### Saponification & Liquid/Liquid Extraction



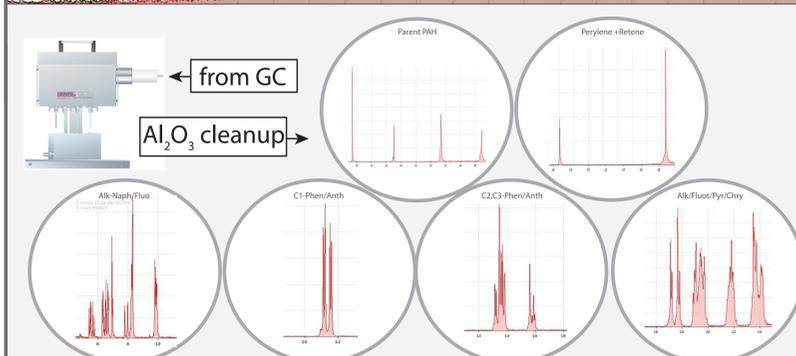
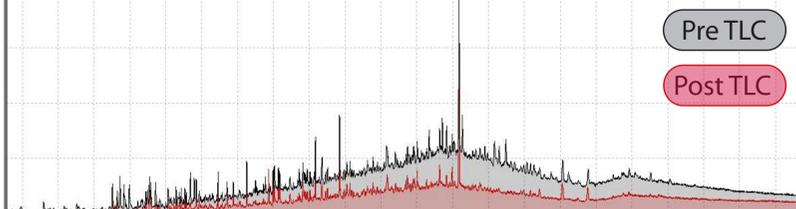
### Silica-gel Cleanup



### TLC



### PAH Harvest (using PcGC)



AMS measurements

mass balance calculation:

$$\Delta^{14}C_{\text{sample}} = \Delta^{14}C_{\text{modern}} f_{\text{modern}} + \Delta^{14}C_{\text{fossil}} f_{\text{fossil}}$$

Radiocarbon dead =  $\Delta^{14}C = -1000 \text{ ‰}$

## Results & Discussion

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PAH diagnostic ratios shows only a fossil fuel source in the entire sedimentary sequence --> not sensitive enough for this type of environment.

need to refine fingerprinting...

$\Delta^{14}C$  of specific PAHs:

Sediment TOC : increasing trend for f<sub>modern</sub> (from 20 to 36%)

--> flood frequency decrease associated with climate change.<sup>(1)</sup>

All PAH groups are < 12% modern, even though perylene and retene believed to be related to modern biomass diagenesis or combustion.<sup>(3,4)</sup>

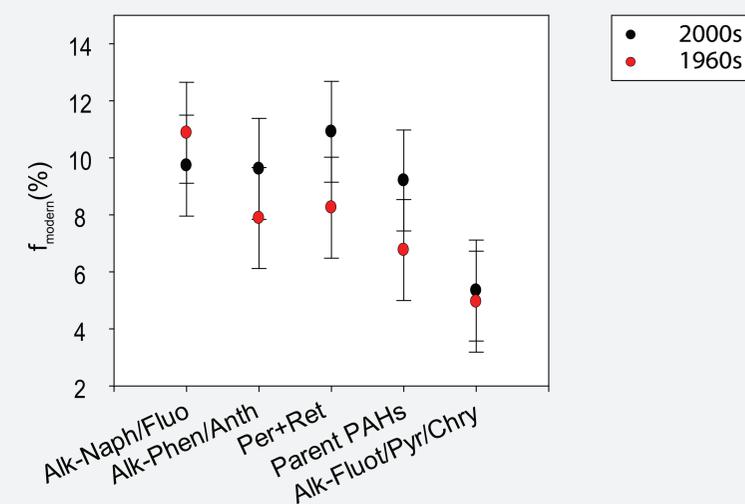
Bacterial community selection --> metabolize fossil organic compound

Variation between top and bottom layer of the core within the error bars

However...

All PAHs except Alk-Naph/Fluo groups show an increasing trend for the modern fraction.

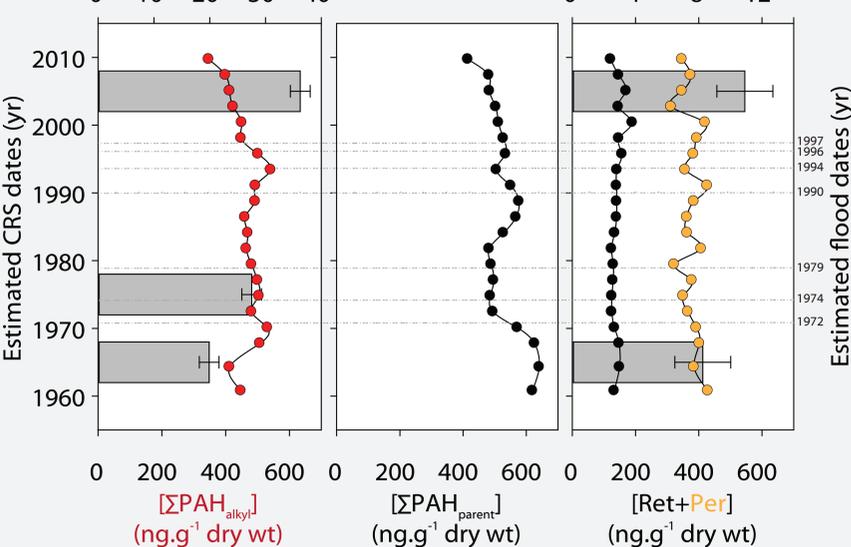
Mining related PAHs in this region --> particulate transport<sup>(5)</sup> --> unlikely to reach this remote area. Light PAHs more volatile --> could be transported further.



## Results & Discussion

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f<sub>modern</sub> sediment TOC (%) 0 10 20 30 40  
f<sub>modern</sub> Ret+Per (%) 0 4 8 12



[PAH]:

> ISQGs for phenanthrene, benz[a]anthracene, dibenz[a, h]anthracene.

Alkylated PAH peak correlated with ice jam floods reported for this lake (C/N ratio & magnetic susceptibility profile).<sup>(1)</sup>

PAH<sub>alkyl</sub> often related to fossil fuel, but can be produced by forest fire or during diagenesis.<sup>(2,3)</sup>

No correlation between [Ret] and [PAH<sub>alkyl</sub>] profile.

--> [PAH<sub>alkyl</sub>] unlikely related to forest fire events.

## Take Home Conclusions

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(1) PAH<sub>alkyl</sub> naturally occurring in this lake from outcrops erosion/river transport/ lake deposition during major flood events.

(2) More than 85% of the PAH<sub>alkyl</sub> are bitumen related.

(3) Less frequent flooding events in the last 10 years resulted in slightly less input of bitumen related PAHs.

## To be continued...

(1) Compound specific  $\Delta^{14}C$  on specific PAHs group from the 1970s layer.

(2) Assess and model the input of bitumen derived PAHs into Athabasca Lake.

(3) Use of dual compound specific  $\delta^{13}C$  &  $\delta^2H$  on light M.W. PAHs for further source characterization.

### References

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