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Flash Pyrolysis of Anthropogenic and Natural Organic Matter in Polluted Sediments

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FLASH PYROLYSIS OF ANTHROPOGENIC AND NATURAL ORGANIC MATTER IN POLLUTED SEDIMENTS

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Key words: sediment contamination, environmental geochemistry, polycyclic aromatic compounds, PAHs, coal, coke, fly ash, pyrolysis-gas chromatography-mass spectrometry, organic petrography, Grand Calumet River, Illinois, Indiana

OBJECTIVES

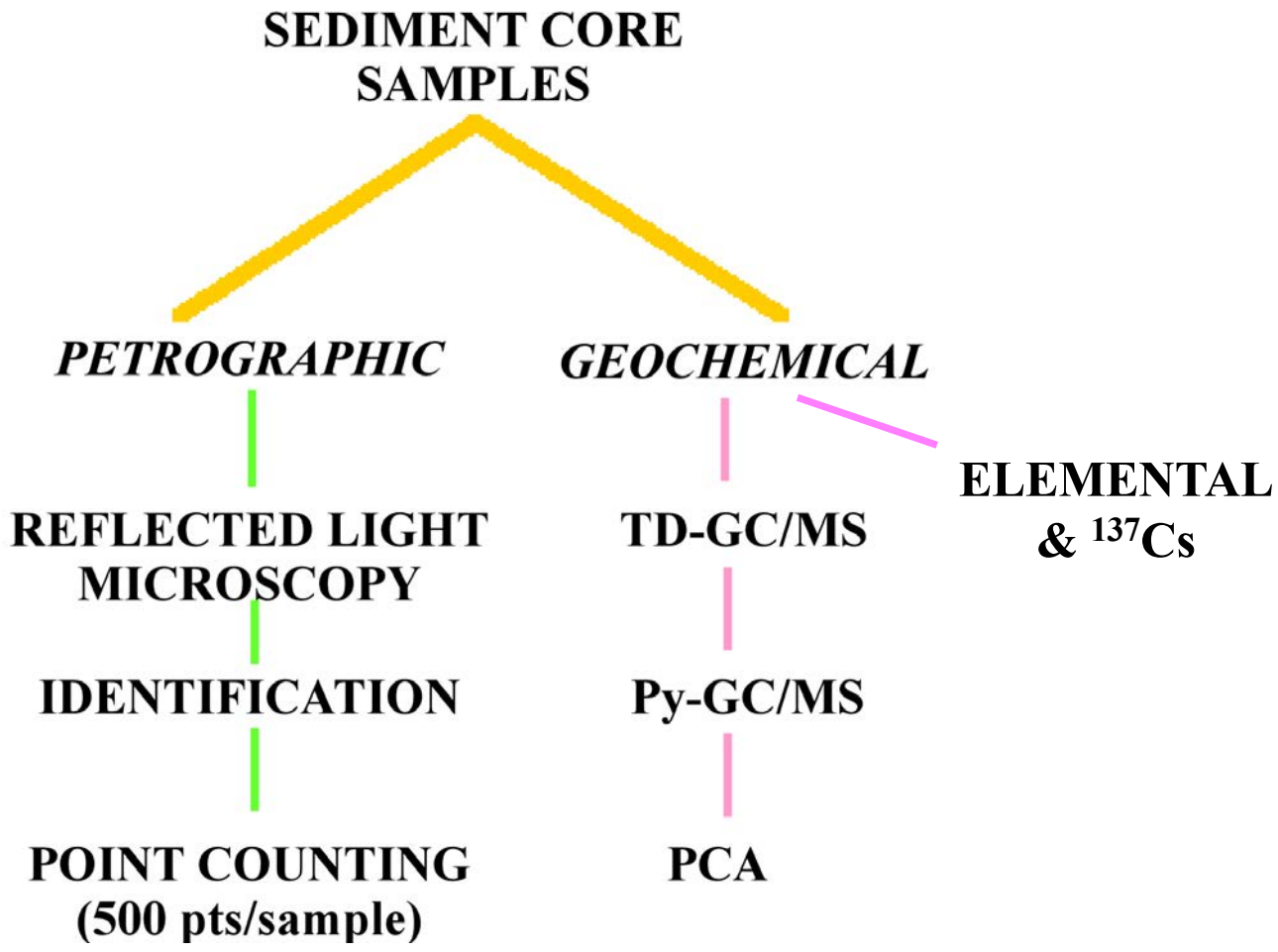
- Identify and quantify natural and anthropogenic OM in urban fluvial core sediments using optical and chemical methods.

- Determine possible sources of this OM.

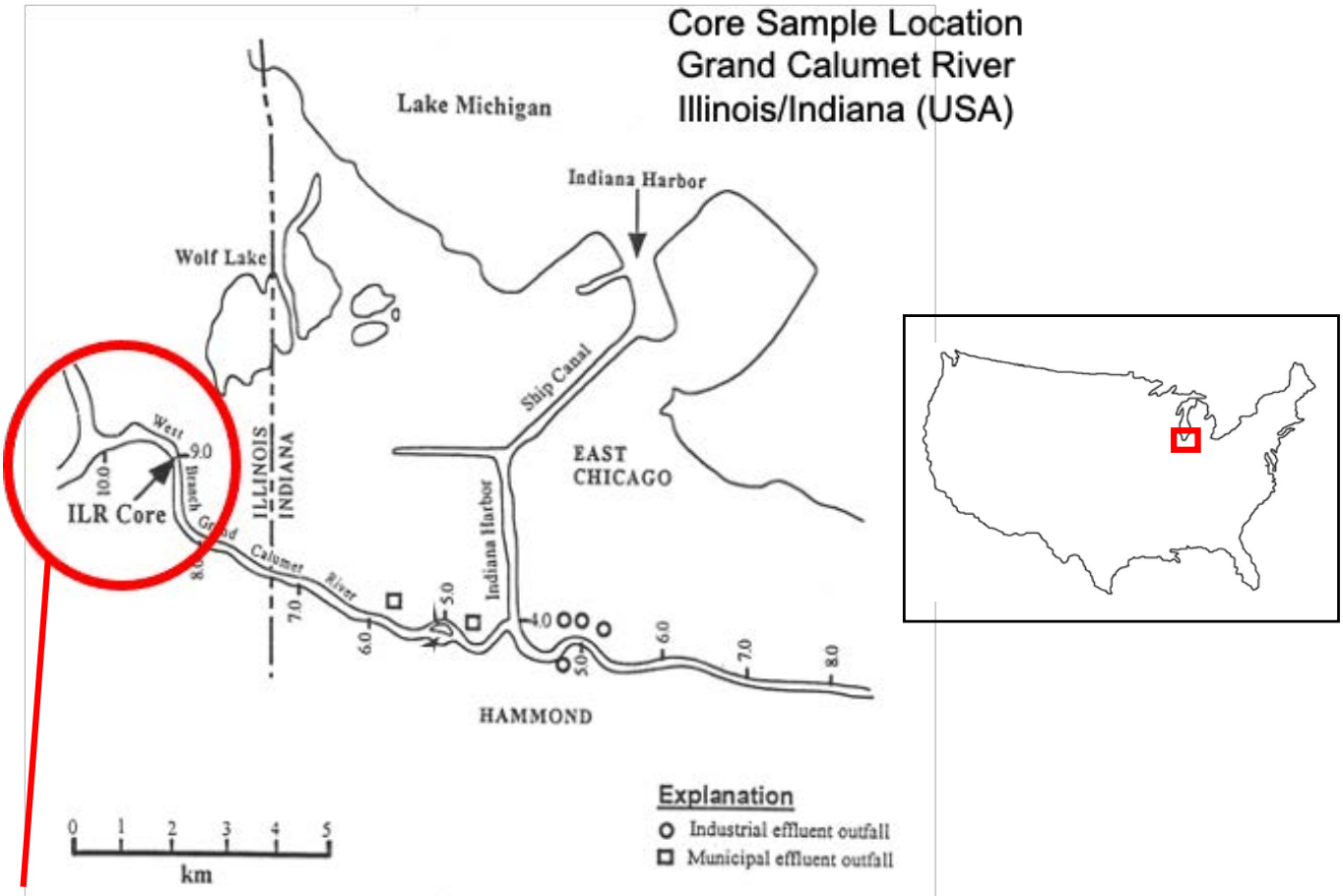
- Evaluate the OM assemblages in historical (stratigraphic) context.

- Establish compositional characteristics that can be used to distinguish between natural and anthropogenic sedimentary OM.

METHODS



Abdel Bagi et al., 1996, Pyrolysis Polluted Sediments



Core ILR recovered the top 310 cm of river sediment by vibracorer, from which 11 subsamples were taken for analysis.
The site is about 27 km south of central Chicago's Loop district.

Core sample location within the Calumet River / Indiana Harbor Canal system, as it appeared in 1951.
Major industrial sites are highlighted.

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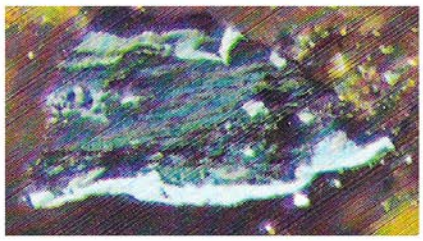
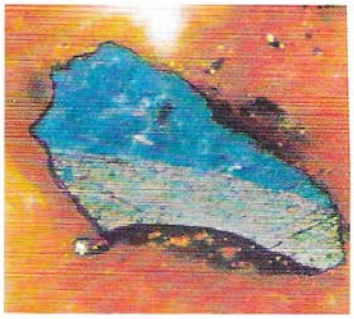
Organic Petrography



Unweathered coal

Petroleum coke

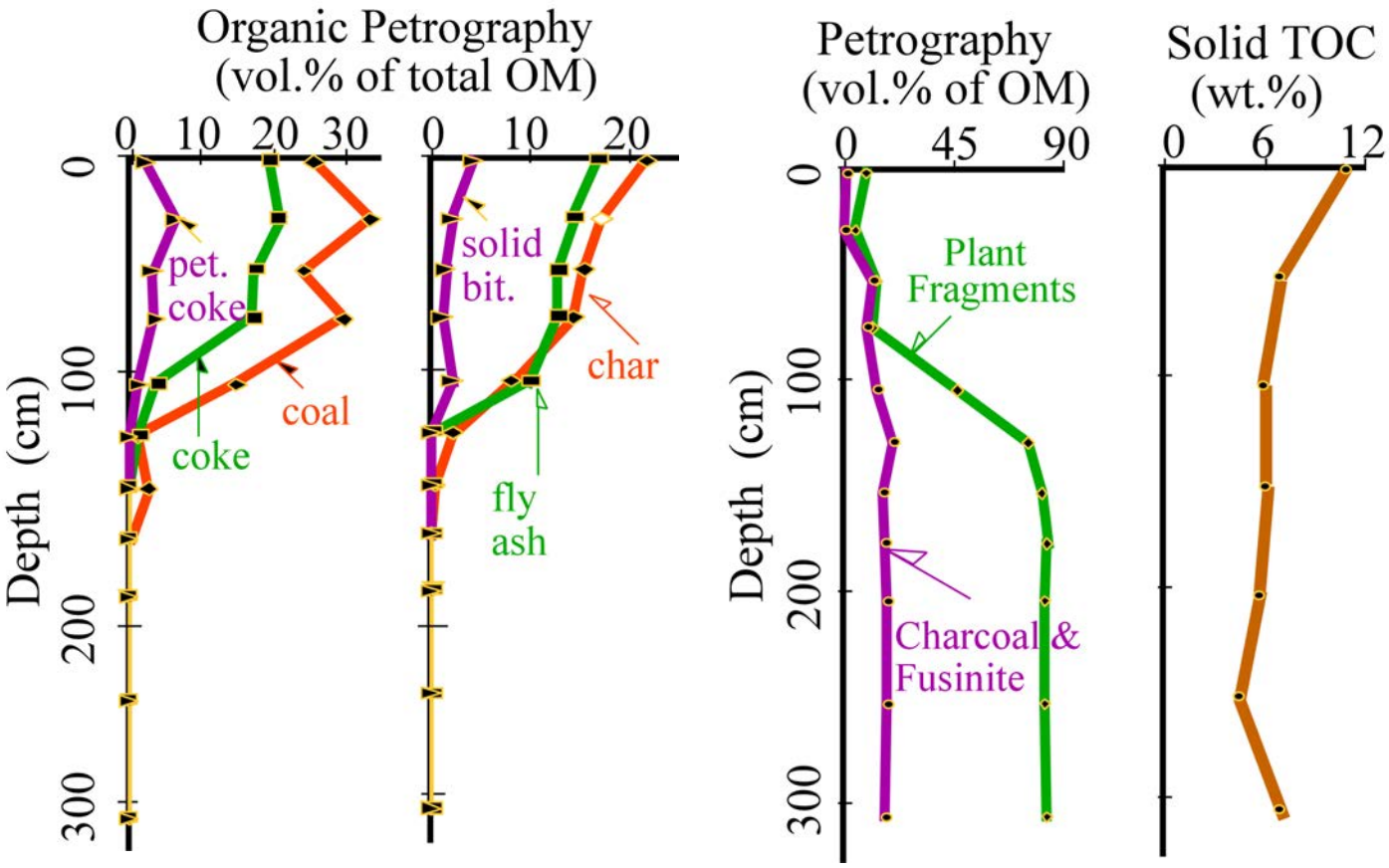


Metallurgical coke

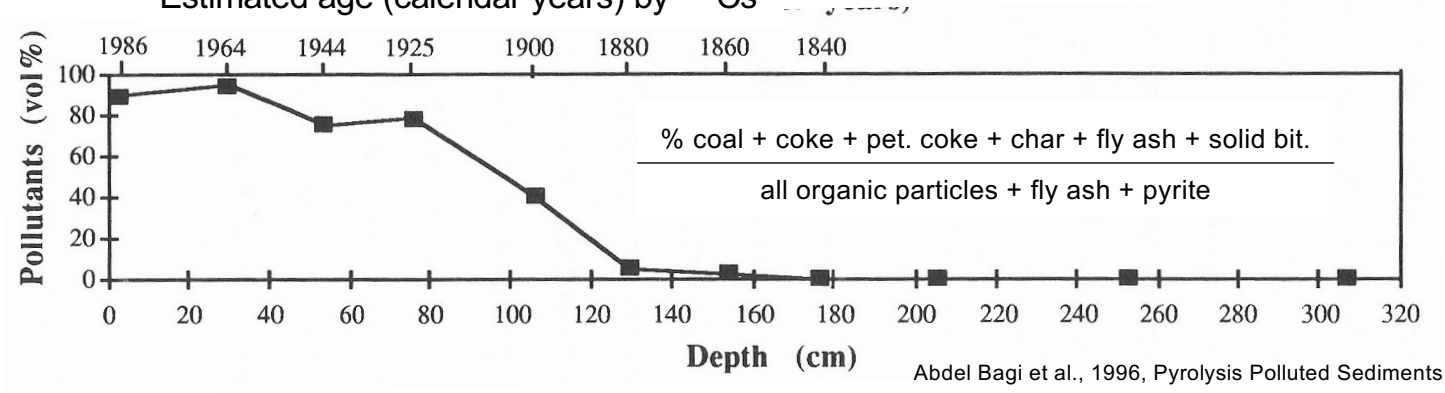
Examples of coal and coke particles from Core ILR sediments.
Reflected white light, oil immersion lens

50 µm

Coal cumbustion residue forming a thick-walled cenosphere



Estimated age (calendar years) by ^{137}Cs



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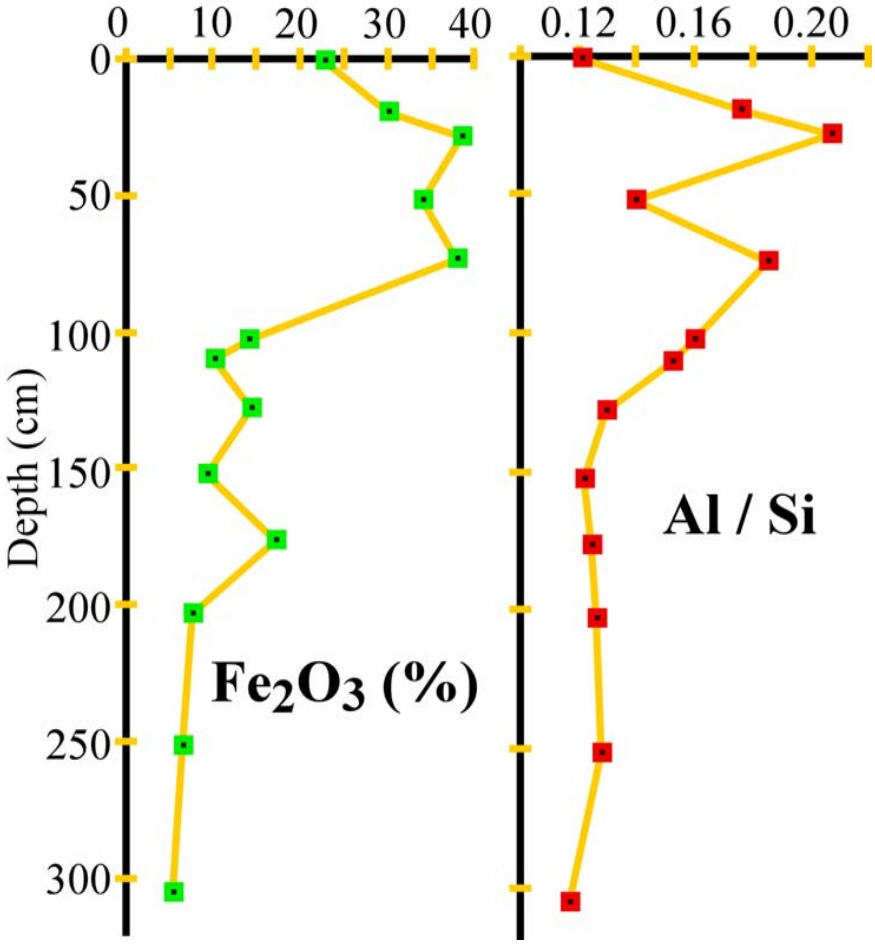
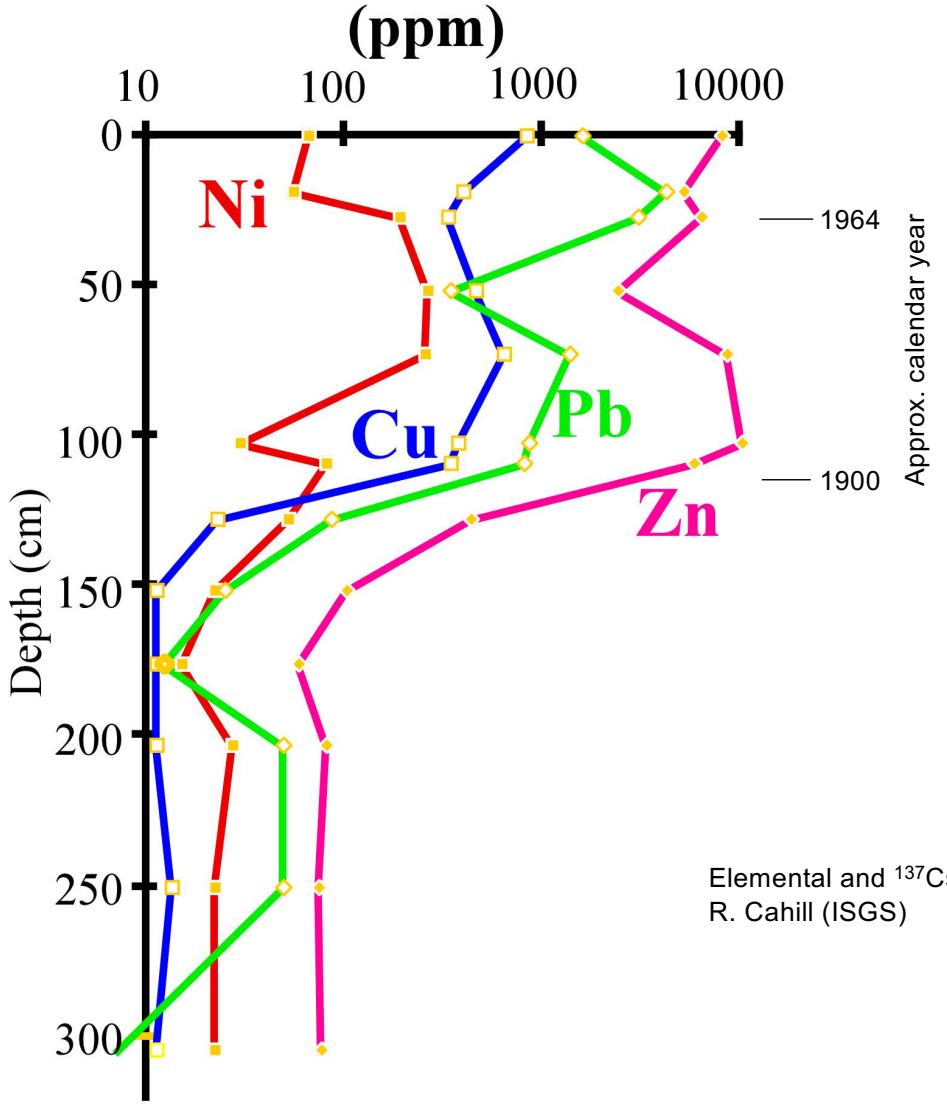
Major Elements



Trace Elements



Elemental and ^{137}Cs analysis by R. Cahill (ISGS)

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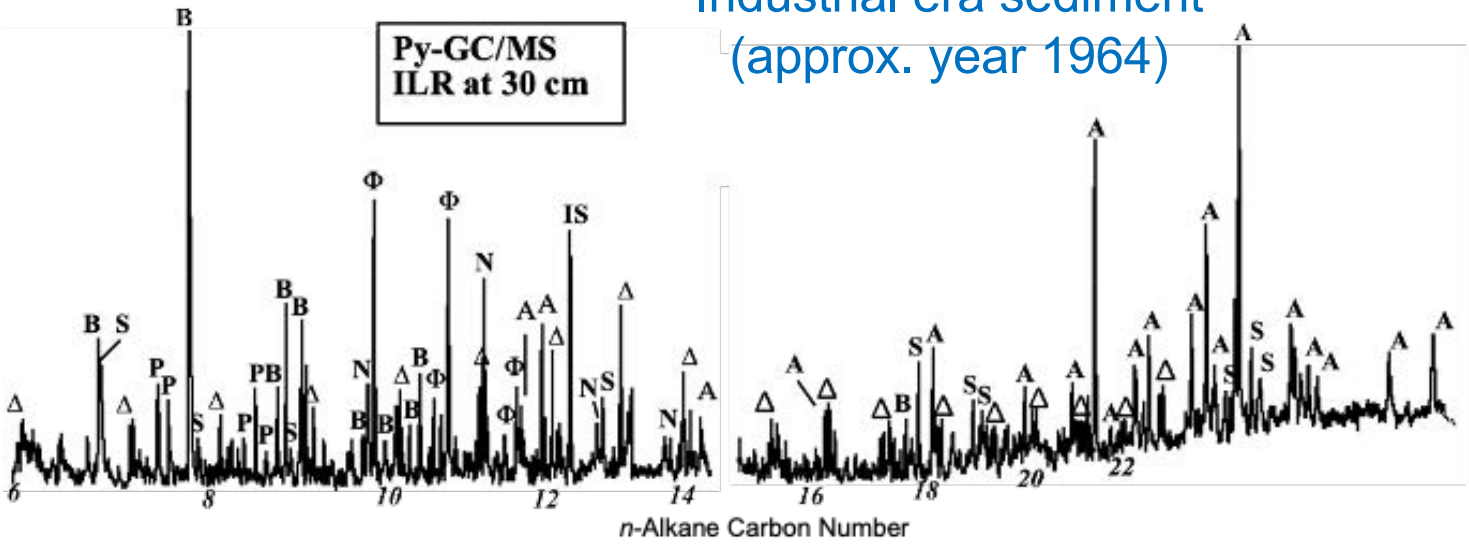
Core ILR sediment examples.
Pyrolysis-gas chromatography-mass spectrometry results.
Total ion current.

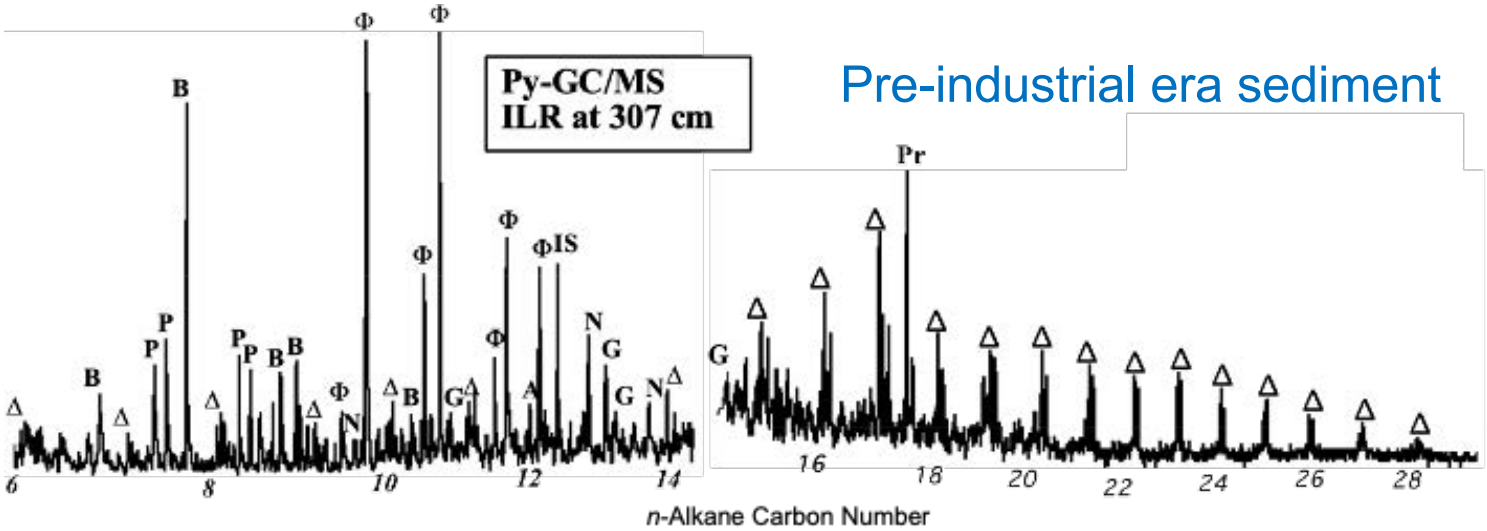
Pyrolysis at 610 °C for 20 sec.

Industrial era sediment
(approx. year 1964)



A – polycylic aromatic hydrocarbons (PAHs)
B – alkylbenzenes
G - methoxyphenols
IS – internal standard
N – azaarenes
P – pyrroles, pyridines
Pr – prist-1-ene
S – sulfur compounds
Δ – *n*-alkanes & alk-1-enes
Φ - phenols

Pre-industrial era sediment



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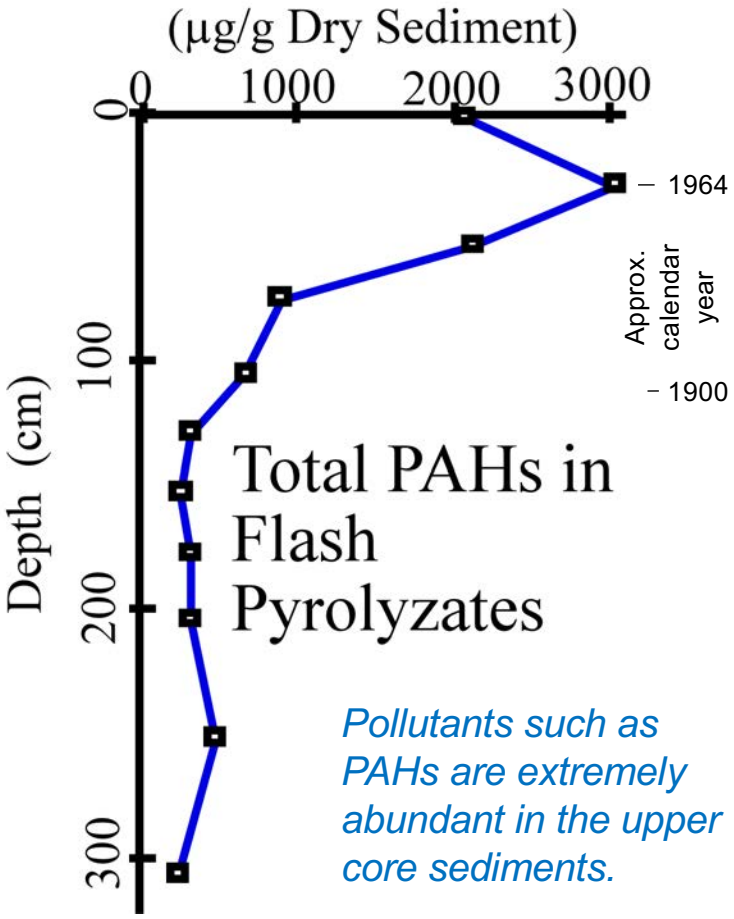
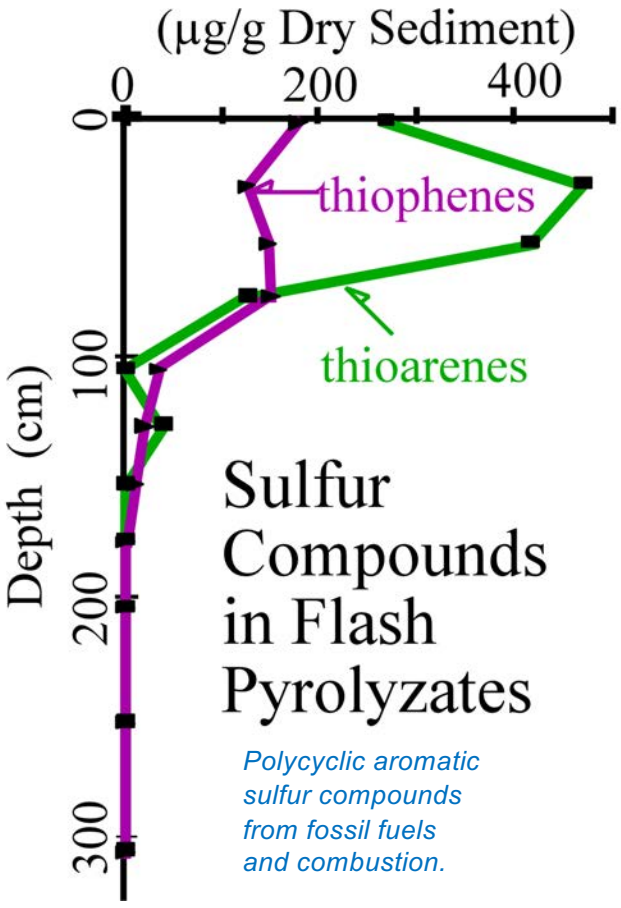
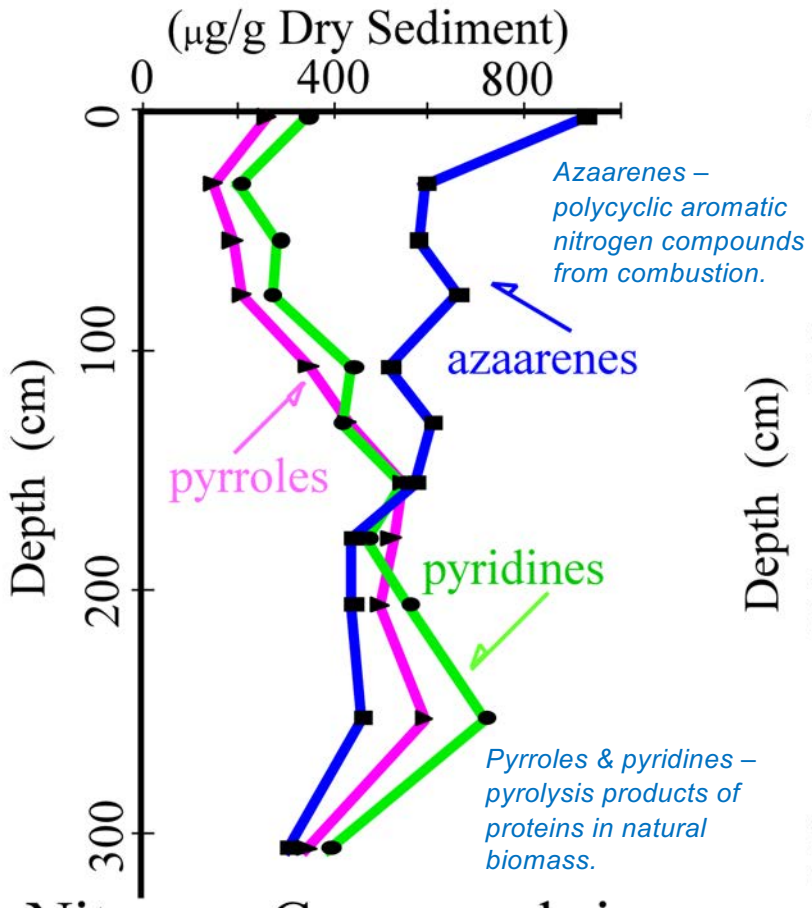
Pyrolysis-GC-MS results – CORE ILR sediments



Pollutants such as PAHs are extremely abundant in the upper core sediments.

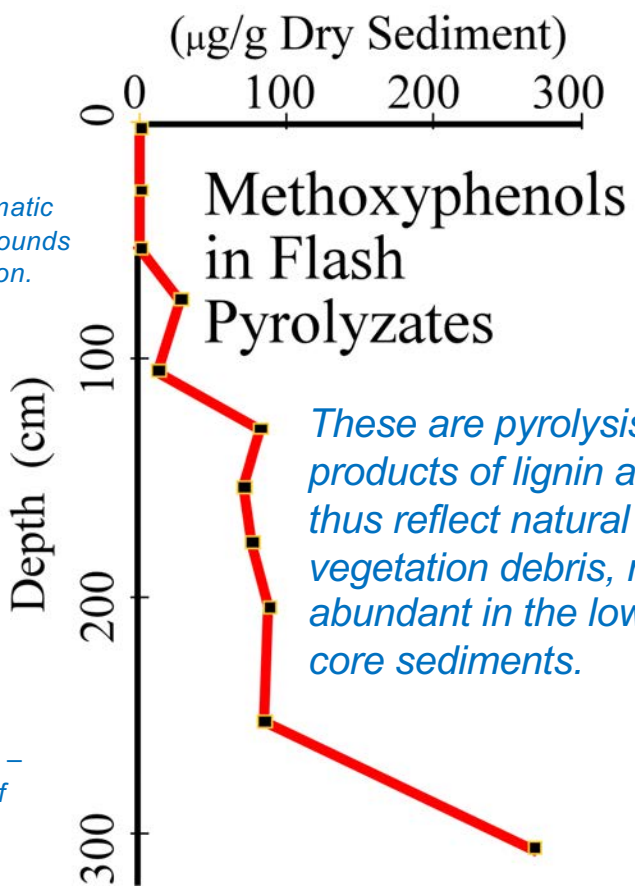


Polycyclic aromatic sulfur compounds from fossil fuels and combustion.



Azaarenes – polycyclic aromatic nitrogen compounds from combustion.

Pyrroles & pyridines – pyrolysis products of proteins in natural biomass.



These are pyrolysis products of lignin and thus reflect natural vegetation debris, most abundant in the lower core sediments.

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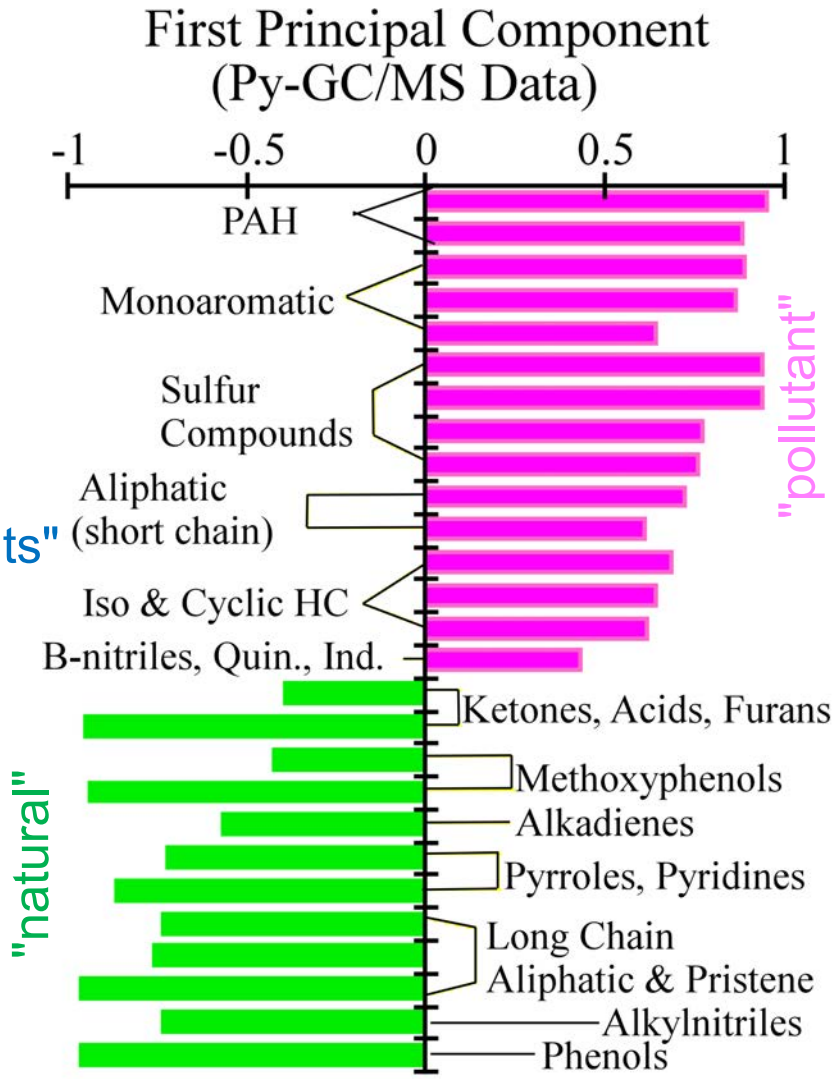
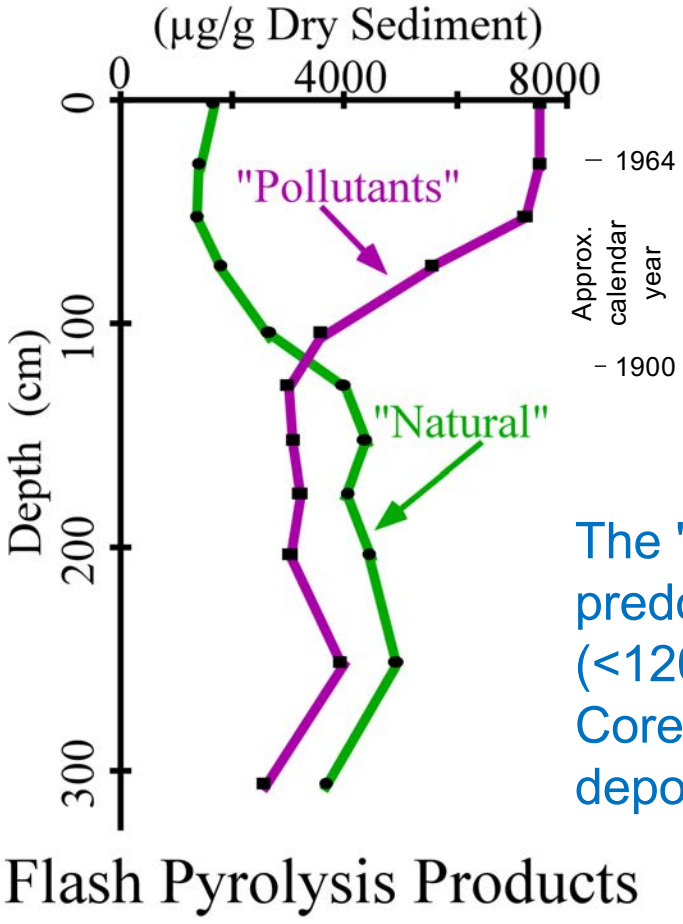
Principal components analysis of Py-GC-MS results reveals a sharp distinction between two groups of compounds: "anthropogenic pollutants" and "natural biomass pyroysis products".





Flash Pyrolysis Products

The "pollutants" predominate in the upper (<120 cm) sediments of Core ILR, i.e., those deposited after about 1900.

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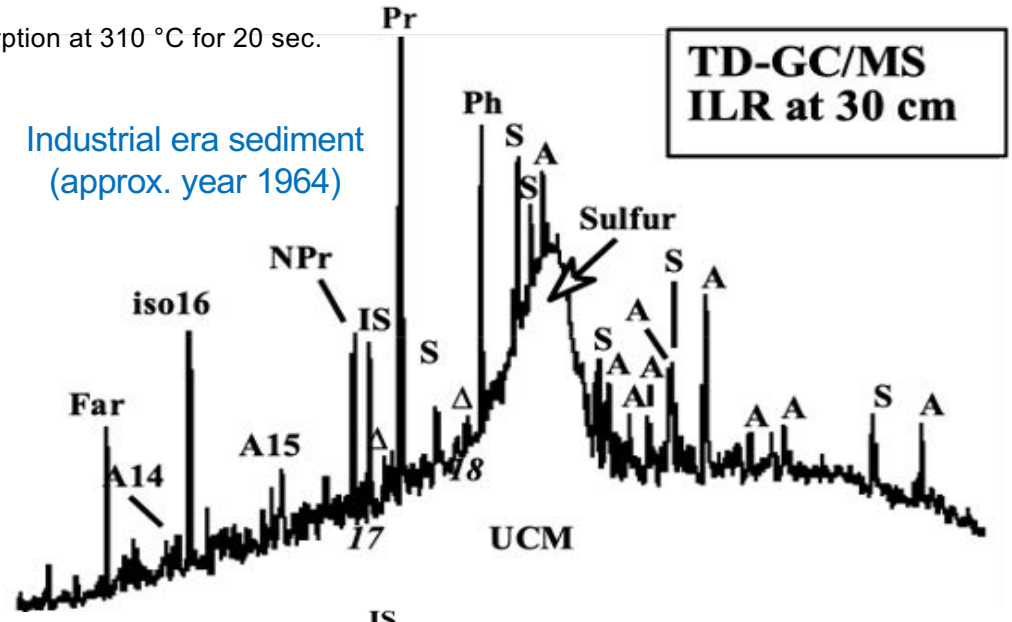
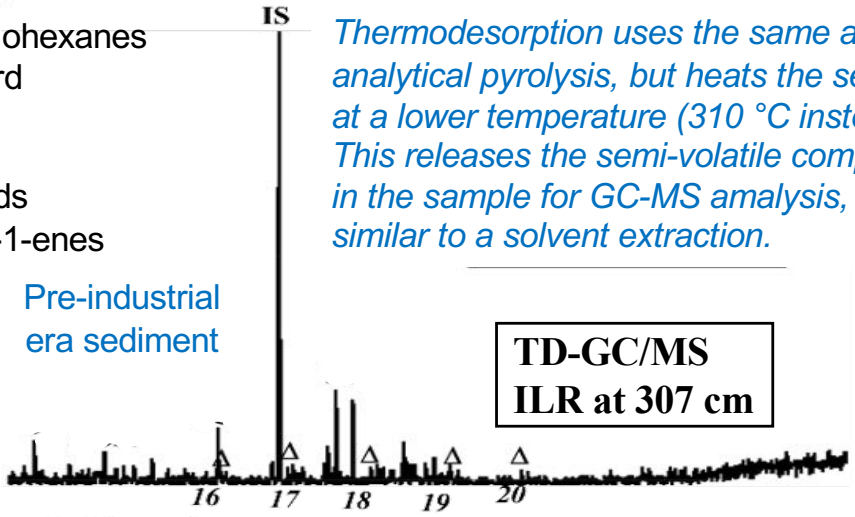
Core ILR sediment examples.
Thermodesorption-gas chromatography-mass spectrometry results.
Total ion current.

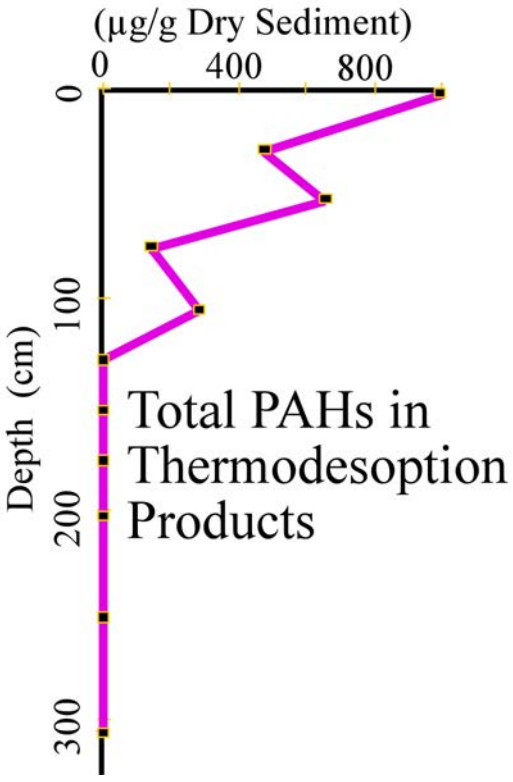
Thermodesorption at 310 °C for 20 sec.

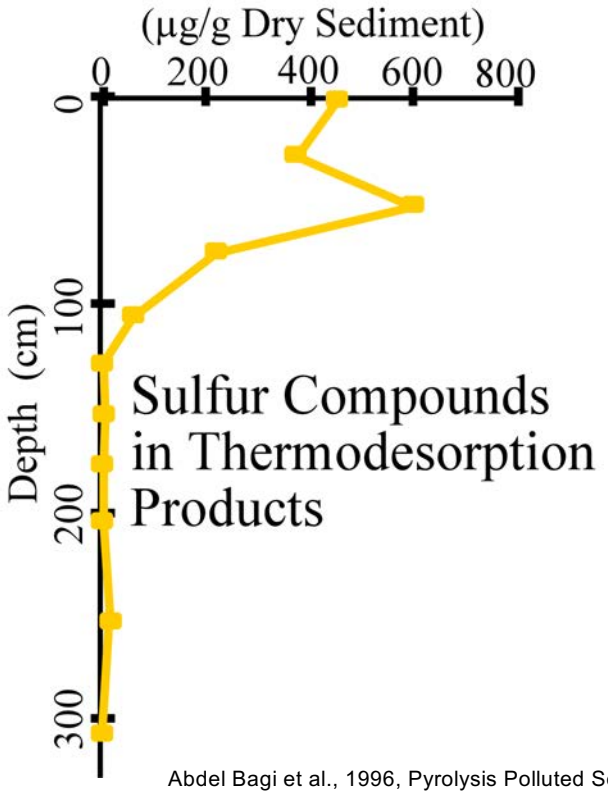


A – PAHs
A14, A15 – alkylcyclohexanes
IS – internal standard
Pr – pristane
Ph - phytane
S – sulfur compounds
Δ – *n*-alkanes & alk-1-enes

Thermodesorption uses the same apparatus as analytical pyrolysis, but heats the sediment sample at a lower temperature (310 °C instead of 610). This releases the semi-volatile compounds present in the sample for GC-MS amalysis, giving results similar to a solvent extraction.







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CONCLUSIONS

Organic Petrography

- Anthropogenic material dominates sedimentary OM in upper core.

- Plant fragments in older sediments reflect the pristine, pre-industrial environment.

- Vertical distributions of anthropogenic and natural sedimentary OM in core document local industrial development.

Metals

- High concentrations of heavy metals indicate contamination of industrial period sediments.

Organic Geochemistry

- Flash pyrolyzates of sediments from the industrial period contain high concentrations of PAHs, thioarenes and azaarenes.

- Pyrolyzates from pre-industrial sediments contain higher relative concentrations of methoxyphenols, pyridines and pyrroles.

- TD-GC/MS indicated petroleum contamination in industrial period sediments, evidenced by isoprenoids, alkylcyclohexanes, the UCM and alkylated 2- and 3-ring PAHs.

- TD-GC/MS in conjunction with Py-GC/MS and petrography proved to be effective in characterizing sediments contaminated with both solid and liquid pollutants.