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An Environmental Geochemical Study Of Connecticut Marsh Sediments

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Heller N.A., Kruge M.A., Varekamp J.C., Zierzow T., 2001, An environmental geochemical study of Connecticut marsh sediments. Geological Society of America Northeastern Section - 36th Annual Meeting, Burlington, Vermont, March 12-14.

<https://gsa.confex.com/gsa/2001NE/webprogram/Paper2850.html>

An Environmental Geochemical Study Of Connecticut Marsh Sediments

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ABSTRACT - Core material from *Spartina*-dominated Housatonic and Connecticut River estuarine sites (ranging from low to high marsh) were investigated in order to test the hypothesis that organic and inorganic pollutants preferentially accumulate in the low marsh environment. Radiometric data indicate that the low marsh setting experienced sedimentation rates an order of magnitude greater than that of the mid to high marsh. The low marsh sediments from the Housatonic tend to have significantly higher concentrations of trace metals (e.g., Cu and Zn, likely contributed by brass mills formerly active upstream). Petrographic examination of the samples under reflected white and blue light reveals fly ash, coke, char and coal particles. Molecular organic analysis by pyrolysis-gas chromatography/mass spectrometry demonstrates that the sediments enriched in anthropogenic trace metals and carbonaceous particles are also enriched in polycyclic aromatic hydrocarbons (PAHs) such as pyrene, chrysene and benzopyrenes, most likely combustion-derived. Long chain alkylamides are also unusually abundant in the pyrolyzates of these impacted sediments. These compounds are likely derived from bacterial organic matter in the sediments and we suggest that their presence could signal organic (i.e., sewage) contamination. These observations are reinforced by multivariate analysis of the combined organic/inorganic data set. The sediment cores serve in effect as archives documenting industrial pollution and environmental change in the estuaries over the last two centuries. The low marsh environments studied apparently provide a significant sink for pollutants when compared to mid and high marsh environments.

Reference: Heller N.A., 2000, Molecular biogeochemistry and pollutant geochemistry of estuarine sediments, Housatonic and Connecticut Rivers. MS Thesis. Southern Illinois University, Carbondale, 151 p.

Introduction

Hypothesis:

Organic and inorganic pollutants preferentially accumulate in the coastal low marsh environment.

Test:

Geochemical investigation of core material from *Spartina*-dominated Housatonic and Connecticut River estuarine sites (ranging from low to high marsh).

Methods

Core description

Radiometric dating:

^{210}Pb , $^{207}\text{Pb}/^{206}\text{Pb}$, ^{137}Cs

Major and minor elemental analysis

Organic petrology

Molecular organic analysis

Multivariate analysis (principal components)

Molecular Organic Analysis

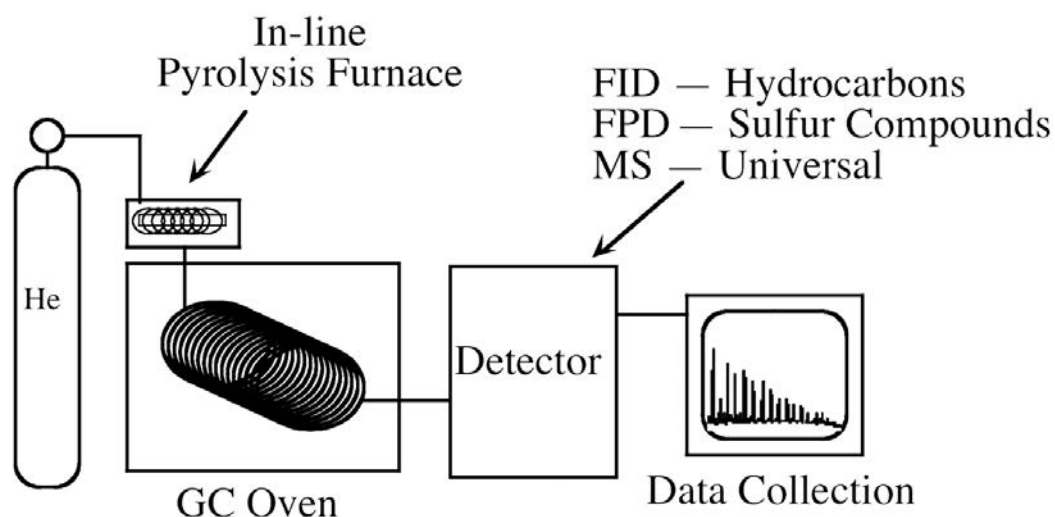
Pyrolysis-Gas Chromatography/ Mass Spectrometry (Py-GC/MS)

Advantages:

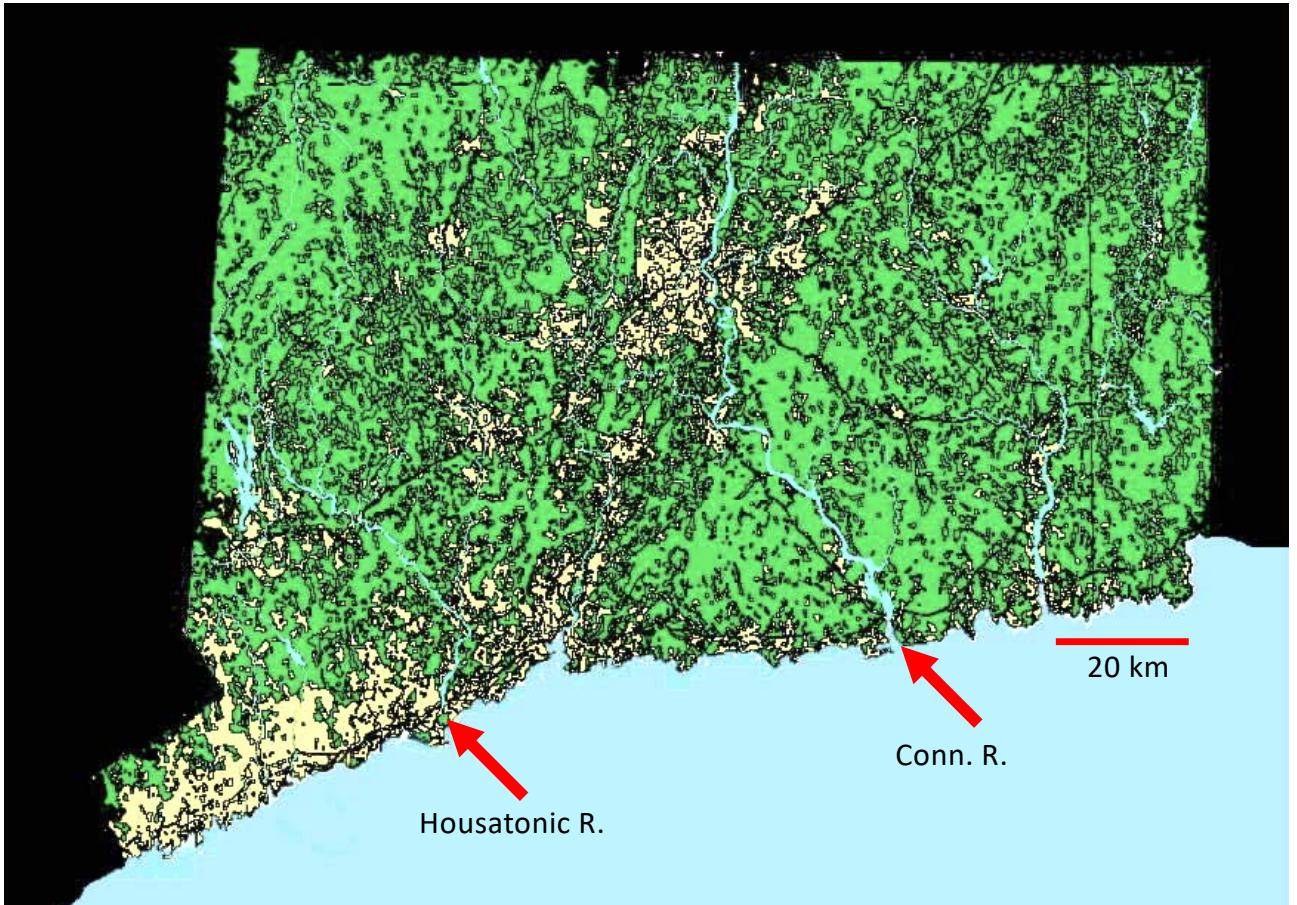
- milligram quantities of dry sediment
- minimal sample preparation
- rapid procedure

Permits:

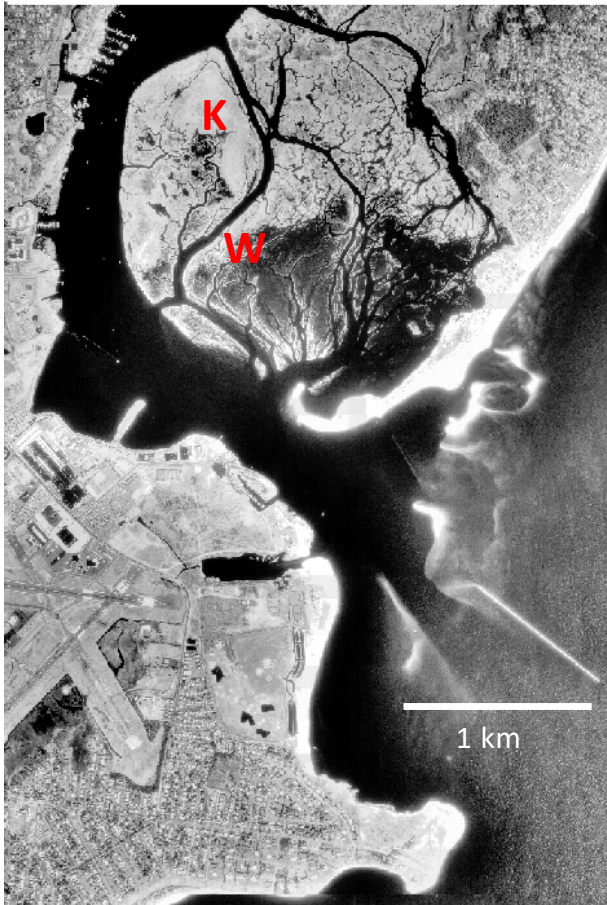
- 1) Thermodesorption of semi-volatile hydrocarbon pollutants
- 2) Biogeochemical profiling via systematic cracking of (fossil and sub-fossil) biopolymers



Analytical Pyrolysis - Gas Chromatography System



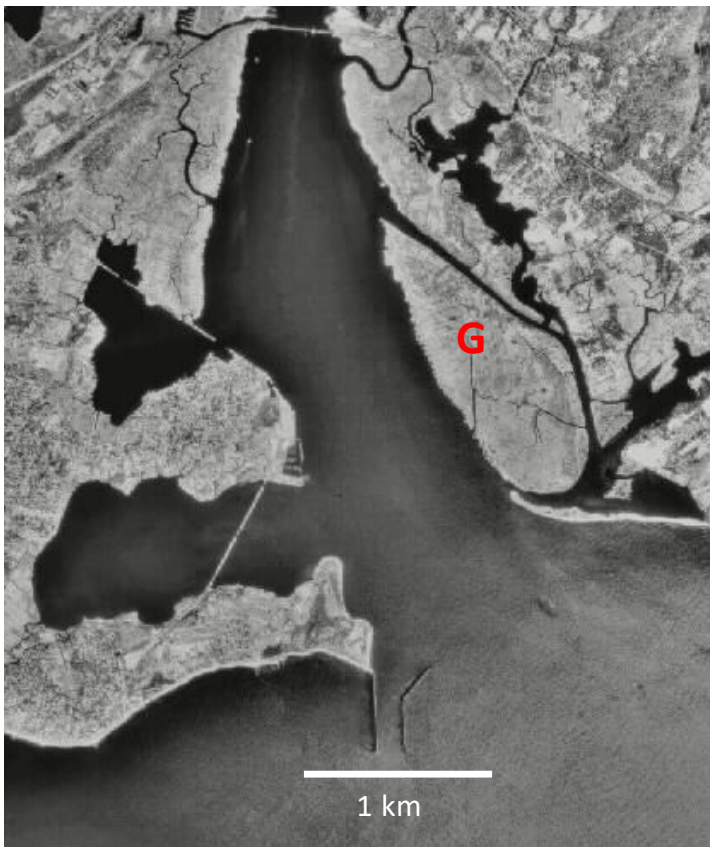
Peat Sampling Sites - Connecticut, USA
1) Mouth of the Housatonic River
2) Mouth of the Connecticut River



Sampling Sites at the Housatonic R. Mouth

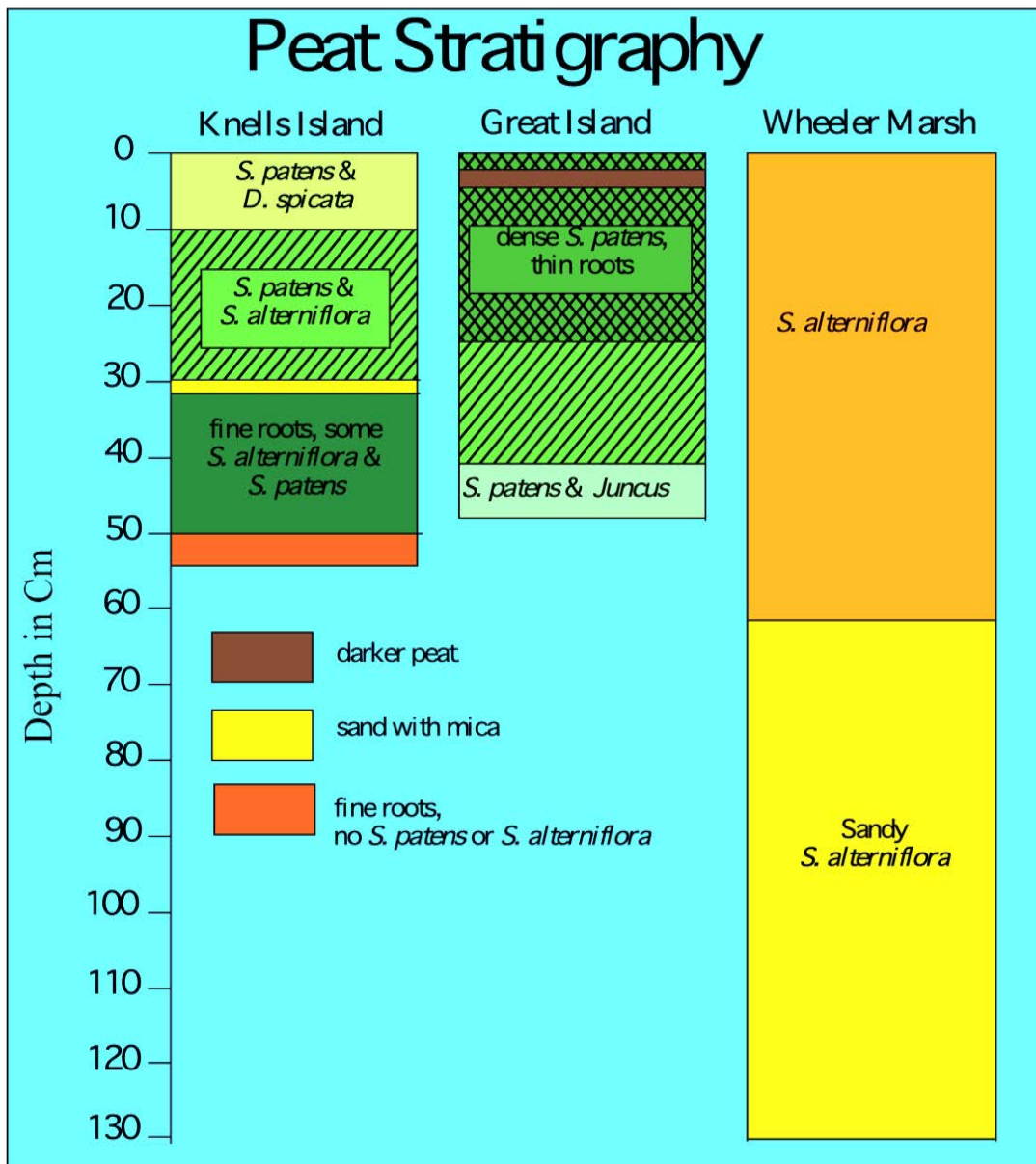
(K) Knells Island

(W) Wheeler Marsh

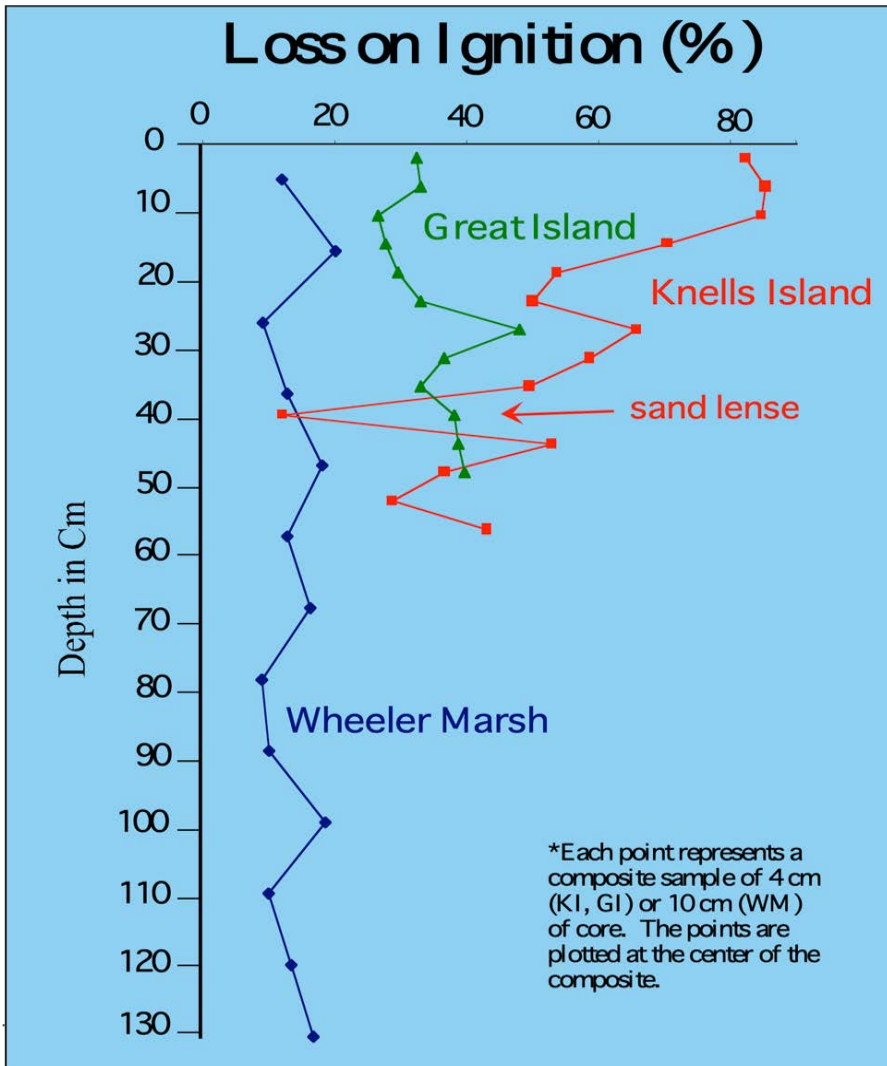


Sampling Site at the Connecticut R. Mouth

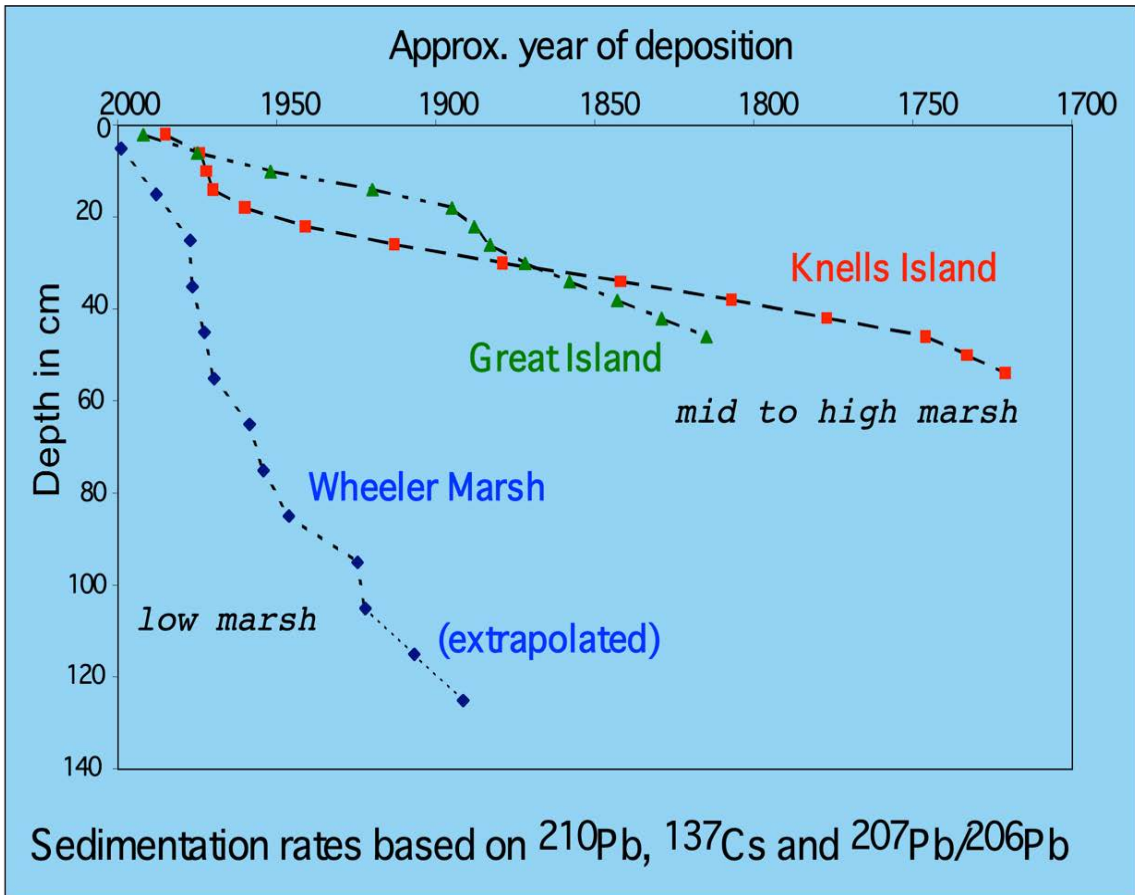
(G) Grand Island



- Stratigraphy of peat deposits encountered at the 3 sampling sites:
- 1) Knells Island (mid to high marsh, Housatonic River mouth)
 - 2) Great Island (mid to high marsh, Connecticut River mouth)
 - 3) Wheeler Marsh (low marsh, Housatonic River mouth)



Loss on ignition (LOI) results for the peat samples as a function of depth for the three cores. LOI is roughly proportional to the organic carbon content, notably lower in the sand lense in the Knells Island core.



Radiometrically determined sedimentation rates for the three peat cores. Note that these rates are much lower for the mid- to high marsh deposits at Great Is. and Knells Is. than in the low marsh setting at Wheeler Marsh, where sediment accumulated much more rapidly.

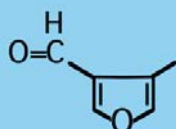


Wheeler Marsh (W) and Knells Island (K) sites in 1837.

Pyrolysis Products of Biogenic Organic Matter

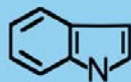
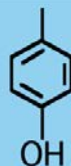
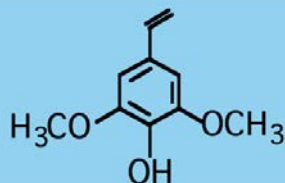
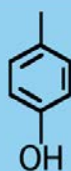


Aromatic



Polysaccharide-derived

Lignin-derived

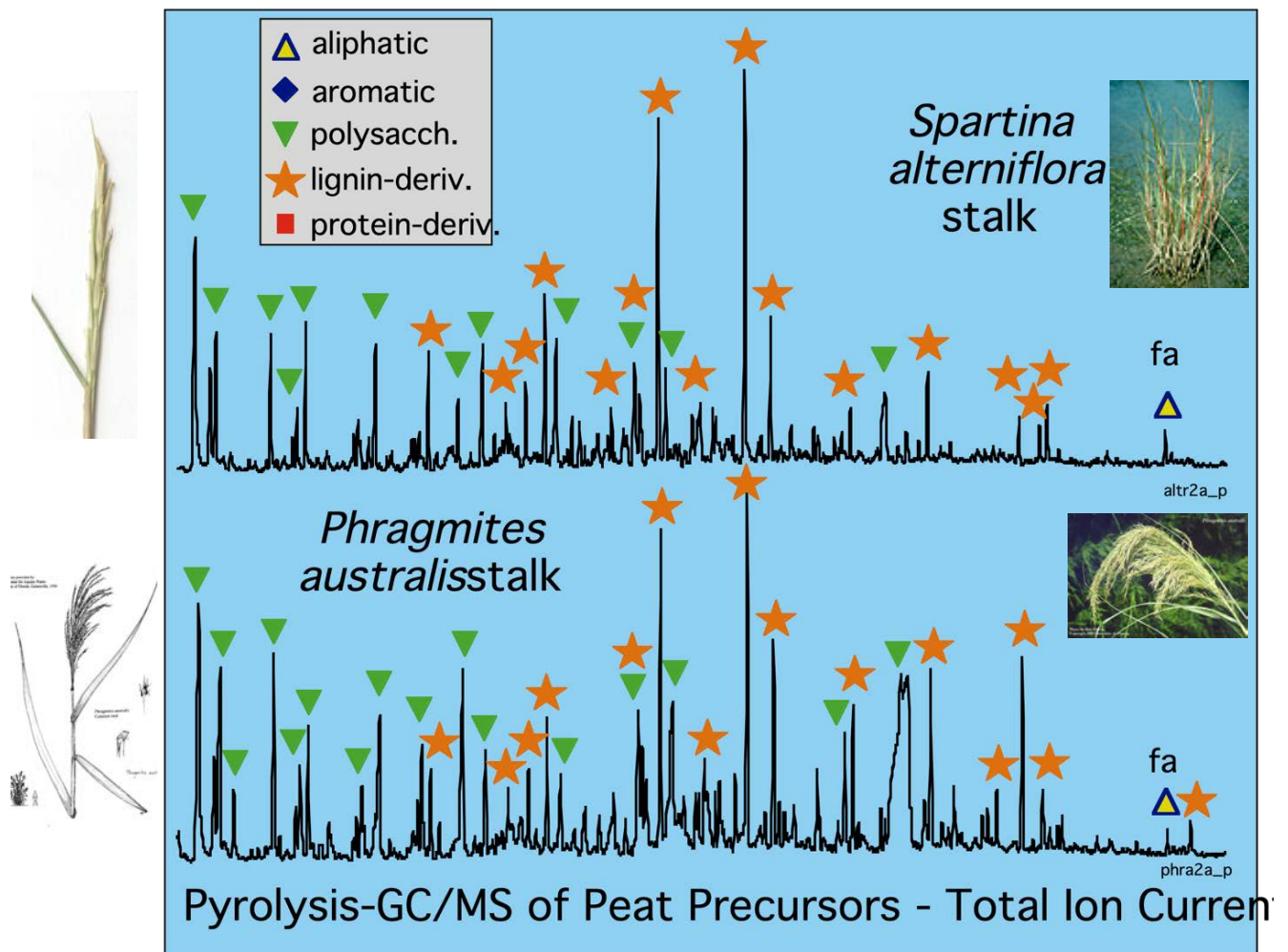


Protein-derived

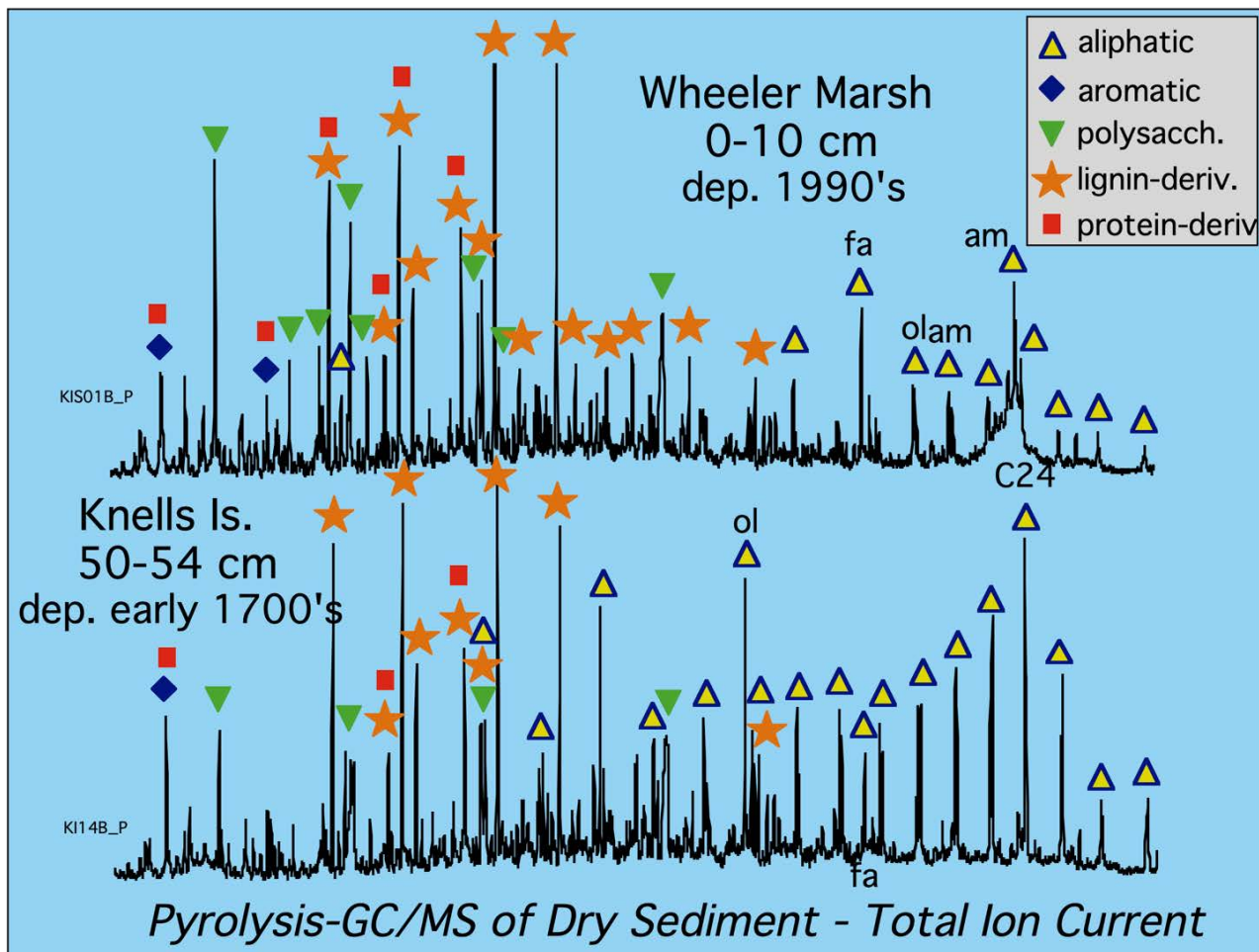
Examples from classes of typical pyrolysis products of biogenic organic matter.

- ▲ aliphatic
- ◆ aromatic
- ▼ polysacch.
- ★ lignin-deriv.
- protein-deriv.

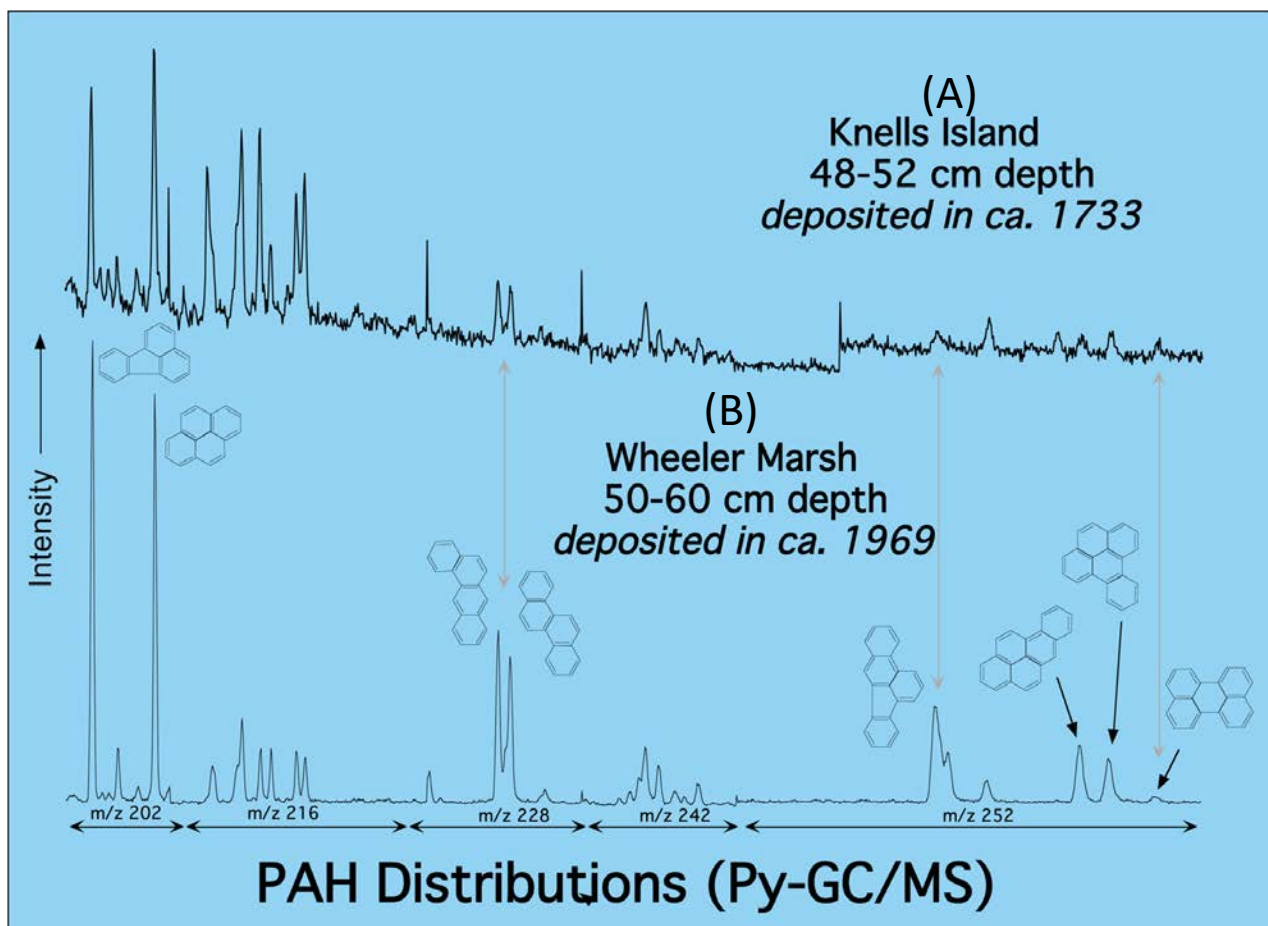
These symbols are used to mark the peaks corresponding to these compound classes on the following Py-GC-MS traces.



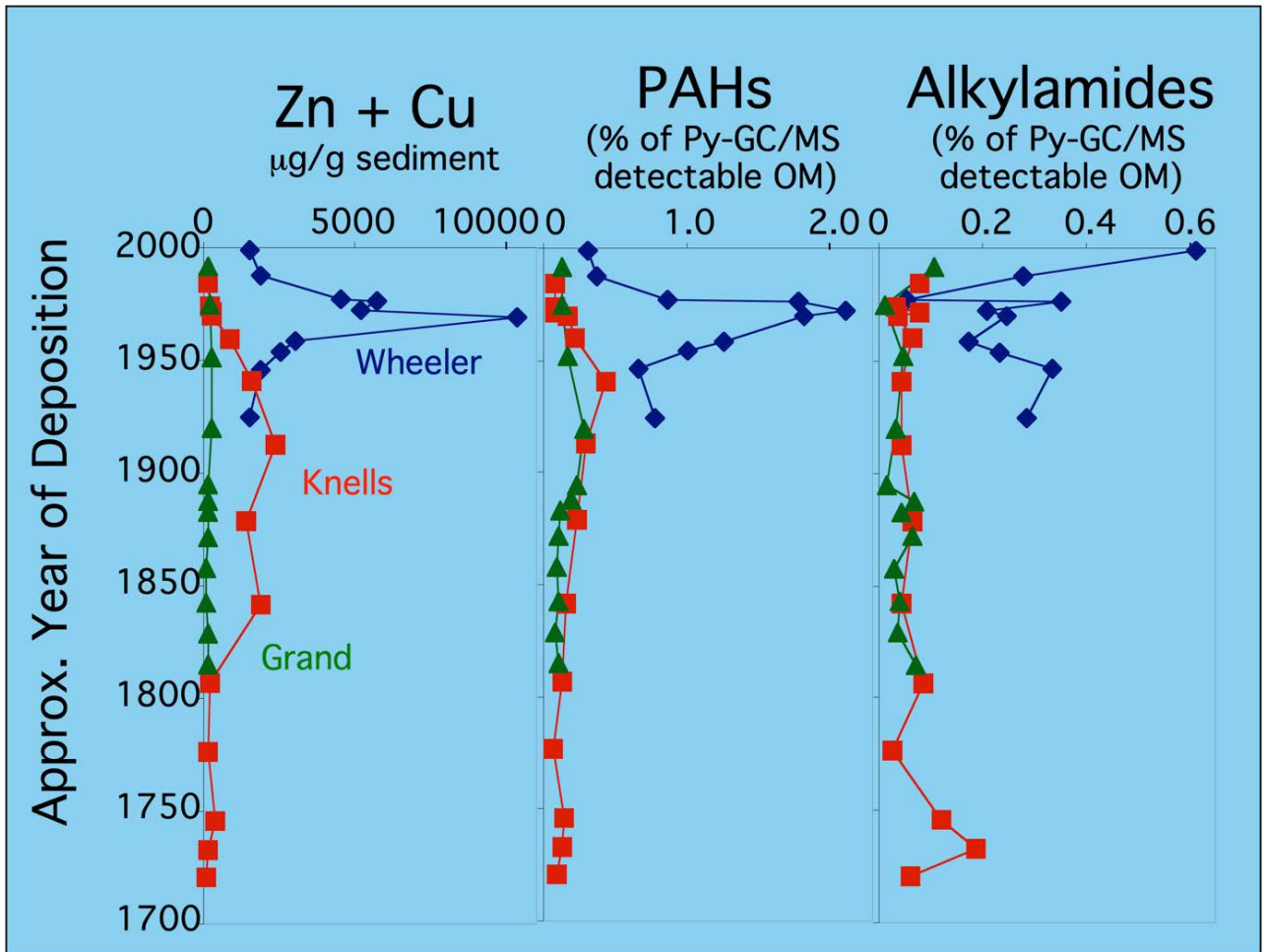
Pyrolysis-GC-MS traces (total ion current) of showing the results of the analysis of fresh stalks of the dominant marsh plants in the studied areas. 1) *Spartina alterniflora*. 2) *Phragmites australis*. Note the predominance of polysaccharide (▼) and lignin (★) derivatives.



Py-GC-MS traces showing results from the analysis of two representative peat samples. 1) Recent deposited peat from the top of the Wheeler Marsh core. 2) Several century-old peat from the Knells Island core. As with the pyrolyzates of the fresh plants, polysaccharide (▼) and lignin (★) derivatives are important. Protein derivatives (■) are also relatively abundant in the case of the younger sample, while aliphatic compounds (△) are strongly evident in the older, more degraded peats.

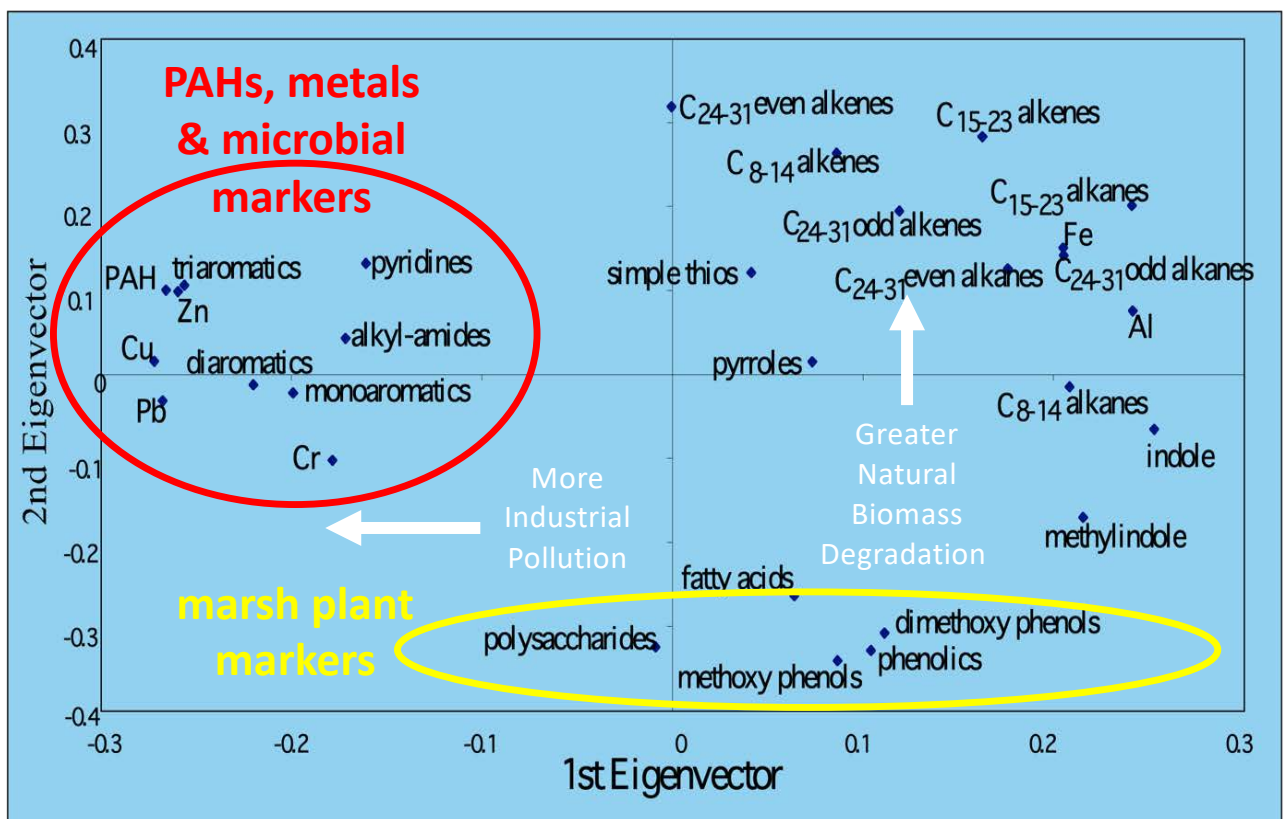
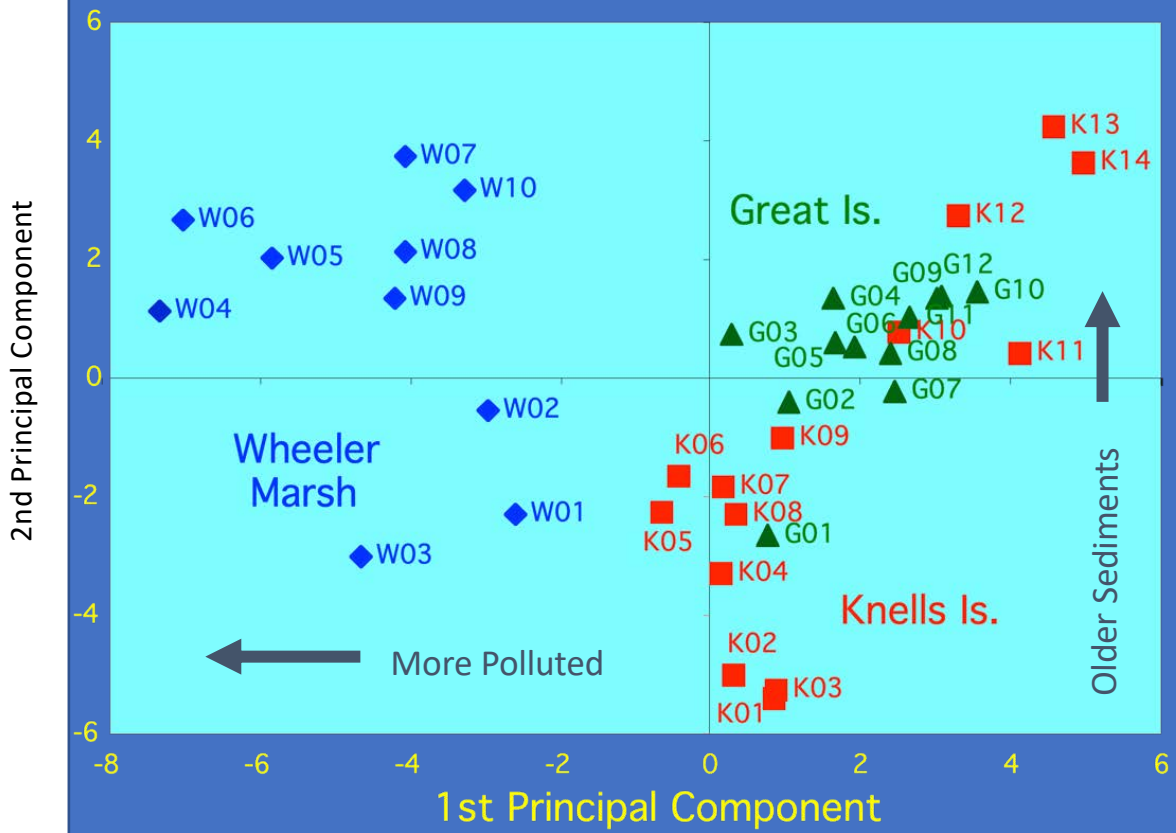


Polycyclic aromatic hydrocarbons (PAHs) are notably evident in the Wheeler Marsh peat (B) deposited in about the year 1969, while faint in the pre-industrial era (early 18th century) peat collected at Knells Island (A). The PAH fingerprint in (B) is typical of industrially-impacted 20th century sediments, e.g., by fossil fuels and their combustion products, as well as the coal tar by-products of manufactured gas plant operations.

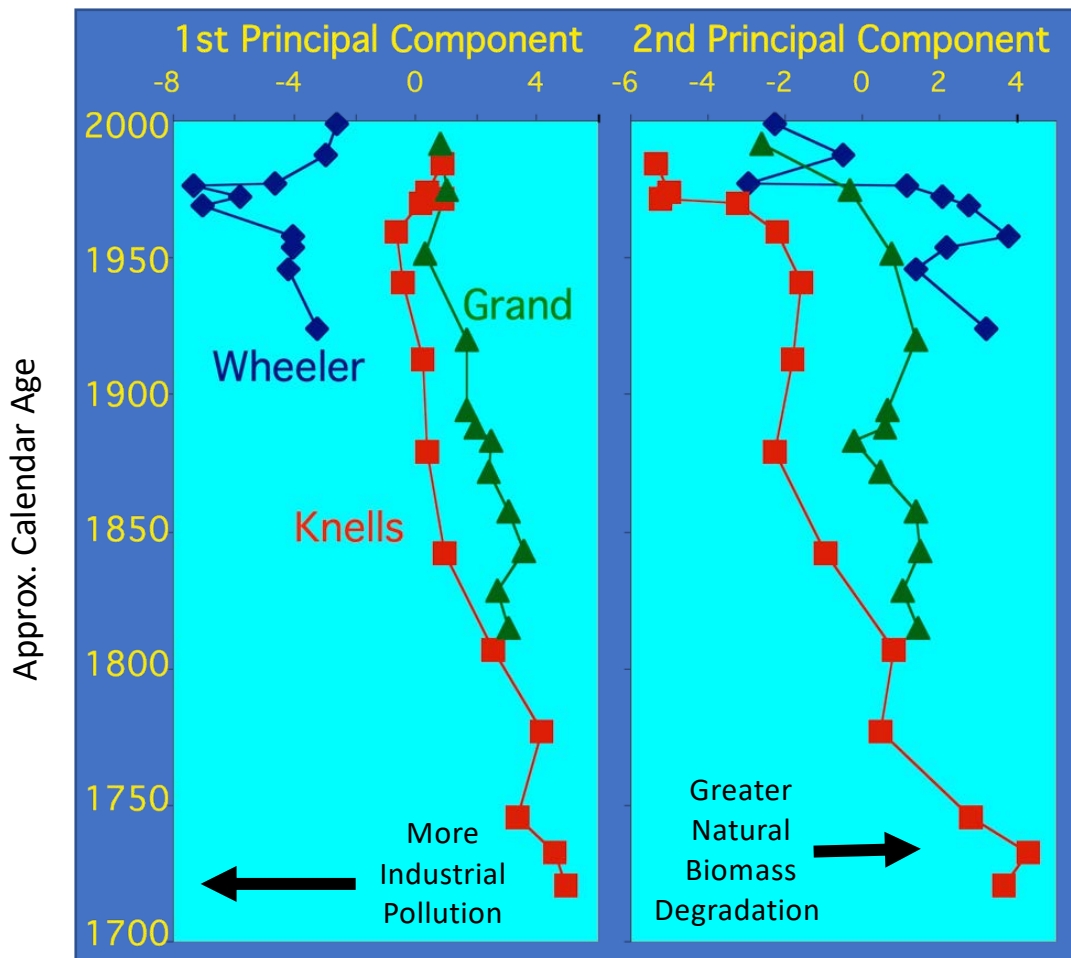


Contents of various industrial-era contaminants as a function of estimated time of deposition at the three core locations. 1) Zinc and copper. 2) PAHs. 3) Alkylamides. Note that the low marsh deposits (Wheeler Marsh site) show the highest concentrations, clearly peaking post-1950 in the case of the metals and PAHs. The alkylamides abundant in the Wheeler Marsh core pyrolyzates are likely microbial, at least in part from sewage released into the river during the 20th century.

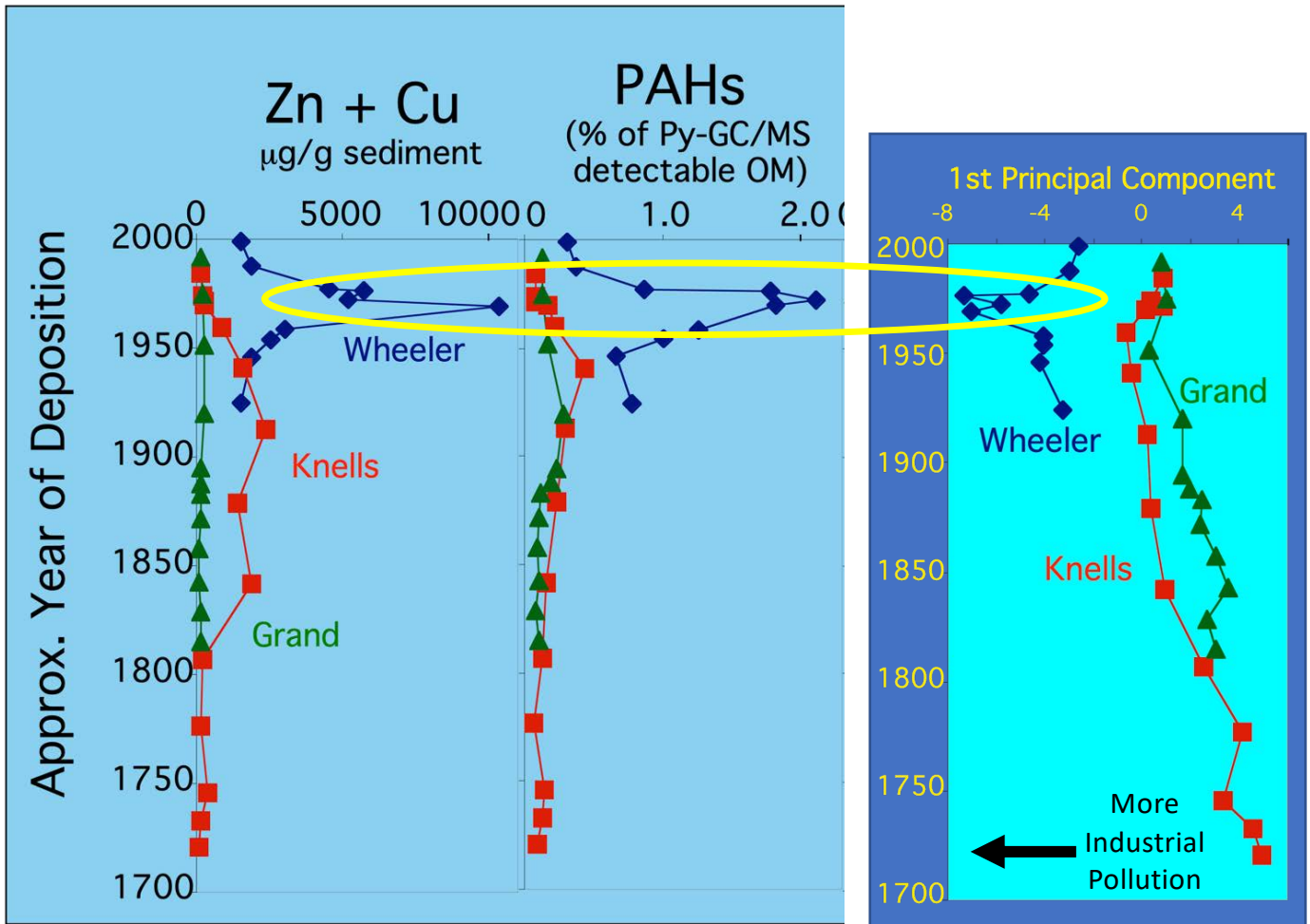
Principal Components Analysis Based on 19 Organic Compound Classes and 6 Metals



First two principal components and their eigenvectors. Mid-core samples from Wheeler Marsh are the most contaminated. "Fresh" peat in the upper core sections is less degraded.



As shown by the eigenvectors in the previous slide, the 1st principal component becomes more negative with increasing inorganic and organic pollution, while the 2nd principal component increases in the older, more degraded peats deeper in the cores.



What might have produced the sharp increase in pollutants seen in the Houstatonic River deep marsh core (Wheeler) post-1950?



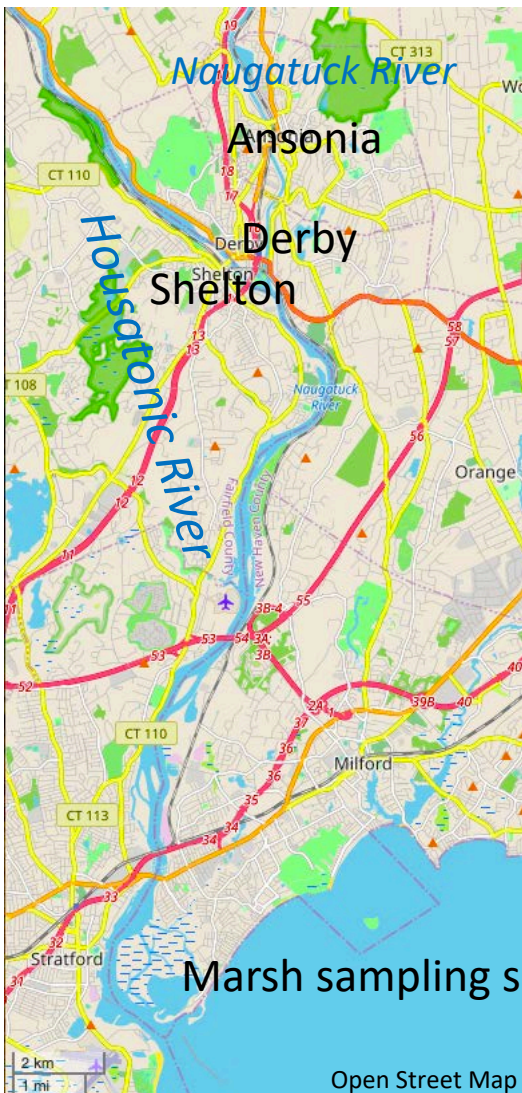
Derby - 1876



Ansonia - 1858



Ansonia - 1935

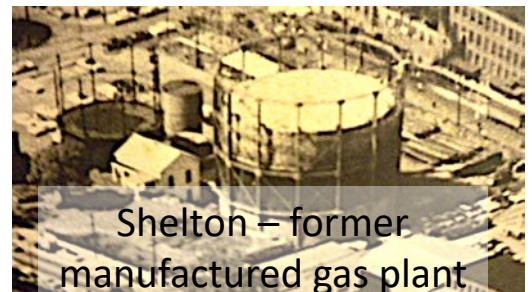


Marsh sampling site

Open Street Map

The valley of Naugatuck River - a major tributary to the Housatonic River once known as Connecticut's "dirtiest river" - was the site of intensive industrialization beginning in the 19th century.

The formerly industrial cities of Ansonia, Derby and Shelton sit at the confluence of the Naugatuck and Housatonic Rivers (~17 km upstream of the sampled marsh sites).



Shelton - former manufactured gas plant

“Black Friday”

August 19, 1955

**Naugatuck River Flood,
Ansonia & Derby (CT)**

**(Photos: Collection of the
Derby Public Library)**



In 1955, the Naugatuck River suffered a major flood, severely impacted the riverside factories, including the American Brass Company works.

This severe flooding event upstream of the marsh would likely have mobilized metals (Cu, Zn) and PAHs from (e.g.) manufactured gas plants.



Conclusions

Radiometric data indicate that the low marsh setting experienced *sedimentation rates* an order of magnitude greater than that of the mid to high marsh.

The low marsh sediments from the Housatonic tend to have significantly higher concentrations of *trace metals* (e.g., Cu and Zn, likely contributed by brass mills formerly active upstream, mobilized during the major 1955 flood event).

Petrographic examination of the samples under reflected white and blue light reveals *fly ash, coke, char and coal* particles.

Molecular organic analysis by Py-GC/MS demonstrates that the sediments enriched in anthropogenic trace metals and carbonaceous particles are also enriched in *PAHs* such as pyrene, chrysene and benzopyrenes, most likely *derived from fossil fuel combustion and/or manufactured gas plant residues*, likely also mobilized by the flood.

Long chain *alkylamides* are also unusually abundant in the pyrolyzates of these impacted sediments. These compounds are likely derived from *microbial* organic matter in the sediments and we suggest that their presence could signal organic (i.e., *sewage*) contamination.

Observations are reinforced by *multivariate analysis* of the combined organic/inorganic data set.

The *sediment* cores serve in effect as *archives* documenting industrial and urban pollution and environmental change in the estuaries over the last two centuries.

The *low marsh* environments studied apparently provide a significant *sink for pollutants* when compared to mid and high marsh environments.

Thanks to: K. Meigs, T. Hoffman, T. Kuder, J. Crelling, S. Ishman