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Biogeochemistry and Contaminant Geochemistry of Marine and Estuarine Sediments, New Haven, Connecticut (USA)

Michael A. Kruege¹ and Gaboury Benoit²

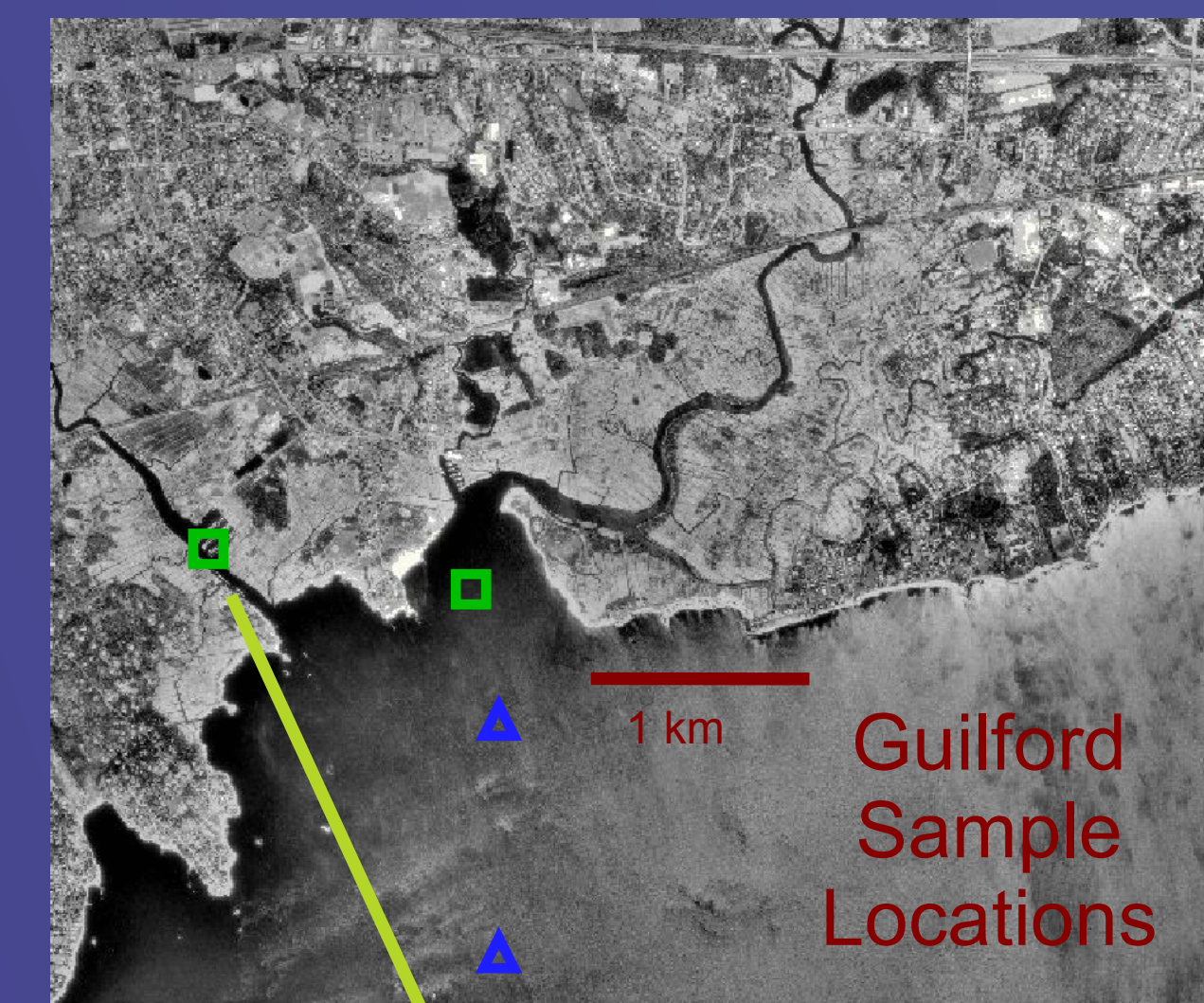
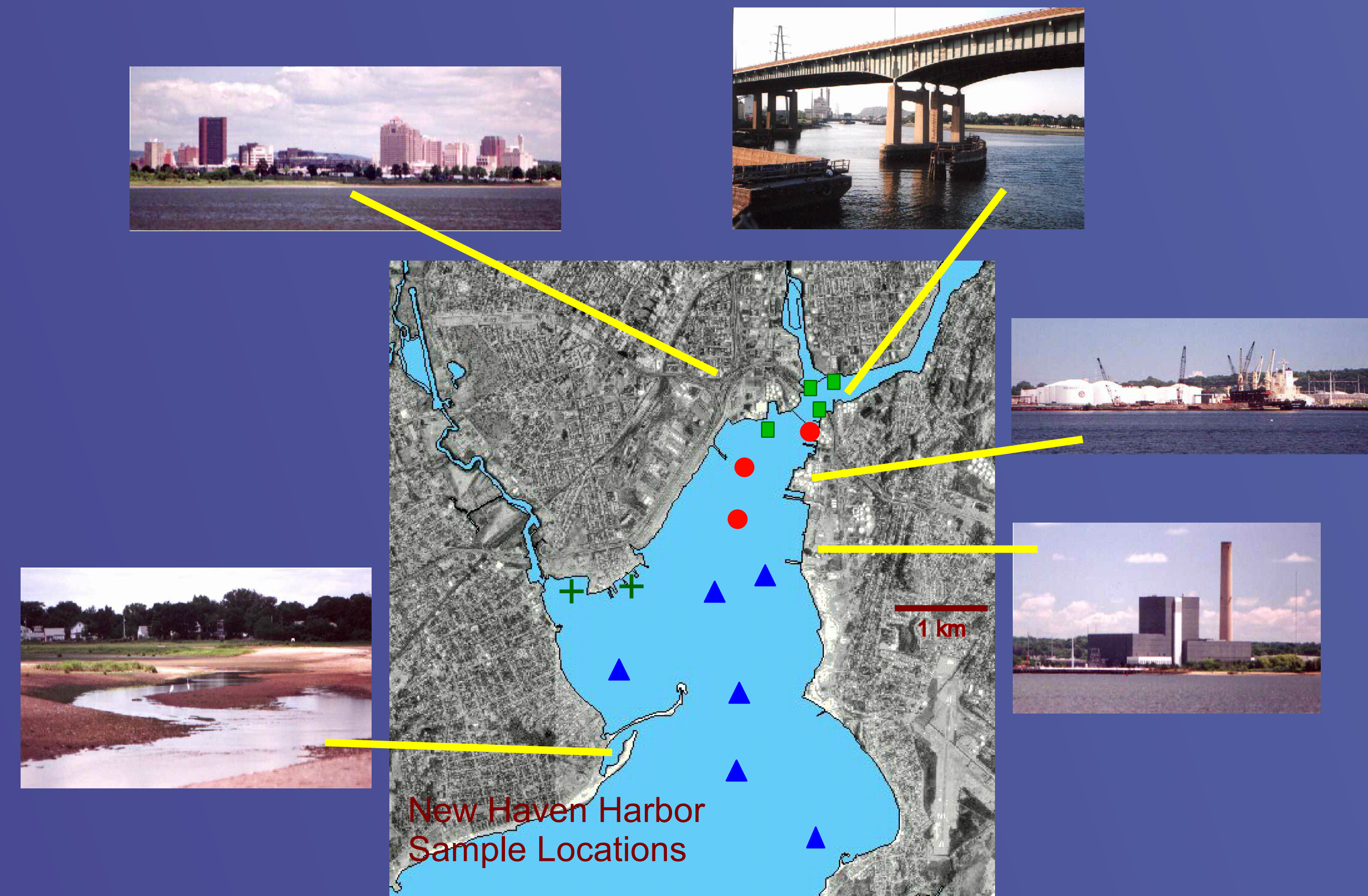
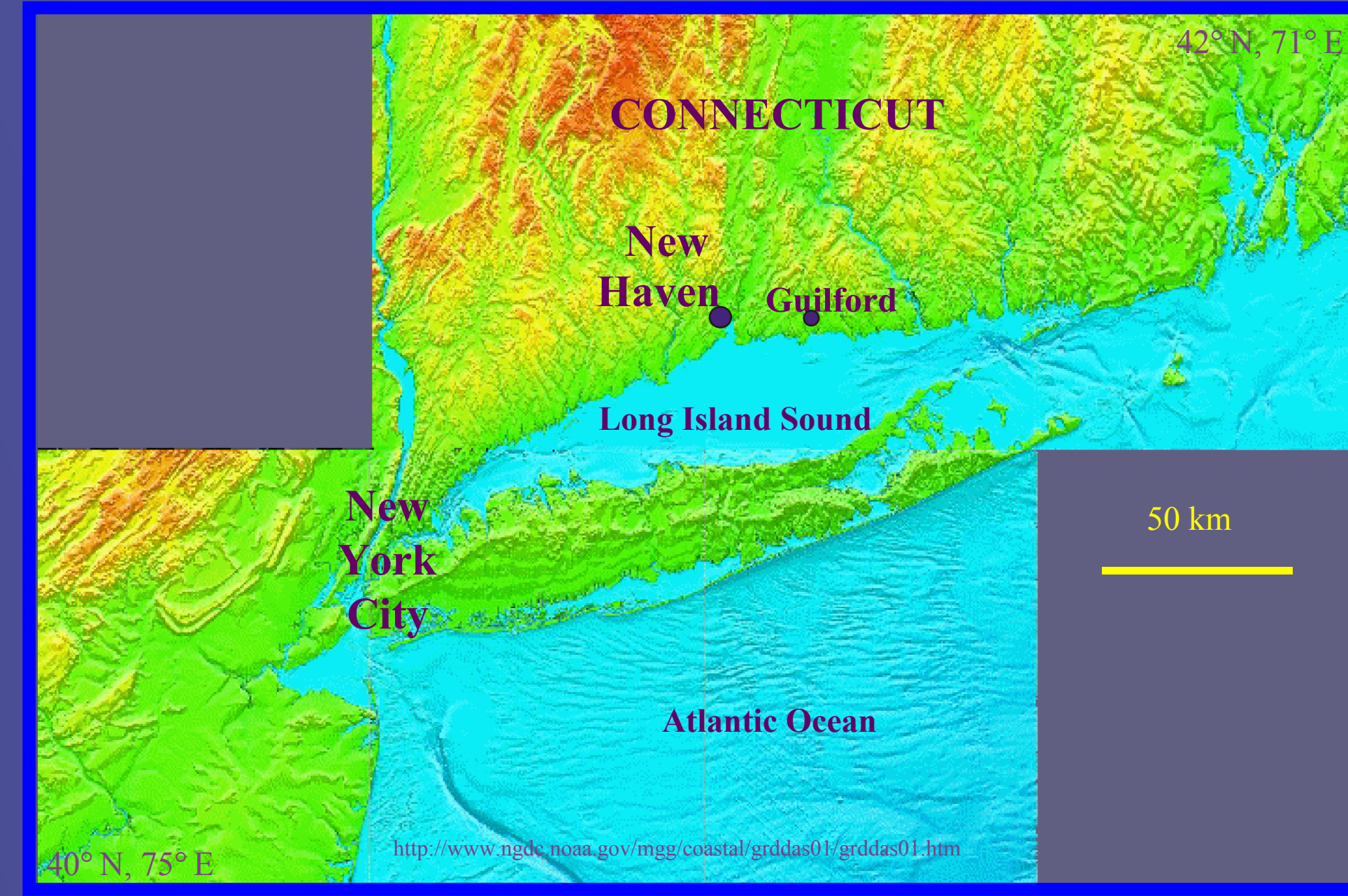
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The urbanized shore areas of Long Island Sound in the vicinity of New Haven, Connecticut (USA) have a long history of exposure to point and non-point sources of pollution, New Haven having been one of the birthplaces of the industrial revolution. As an unintended consequence of such activities, the region's sedimentary systems have incorporated a complex mixture of organic and inorganic contaminants. With its long and varied pollution history and the multiplicity of sedimentary environments (fluvial, estuarine, intertidal, marsh, etc.) present in a compact geographical area, the region is ideal natural laboratory for field testing new contamination assessment techniques. The residents of this densely-populated region continue to exploit the local waterways for recreation and economic benefit, including the harvest of seafood. A comprehensive, systematic evaluation of organic and inorganic contamination thus also addresses public health concerns.

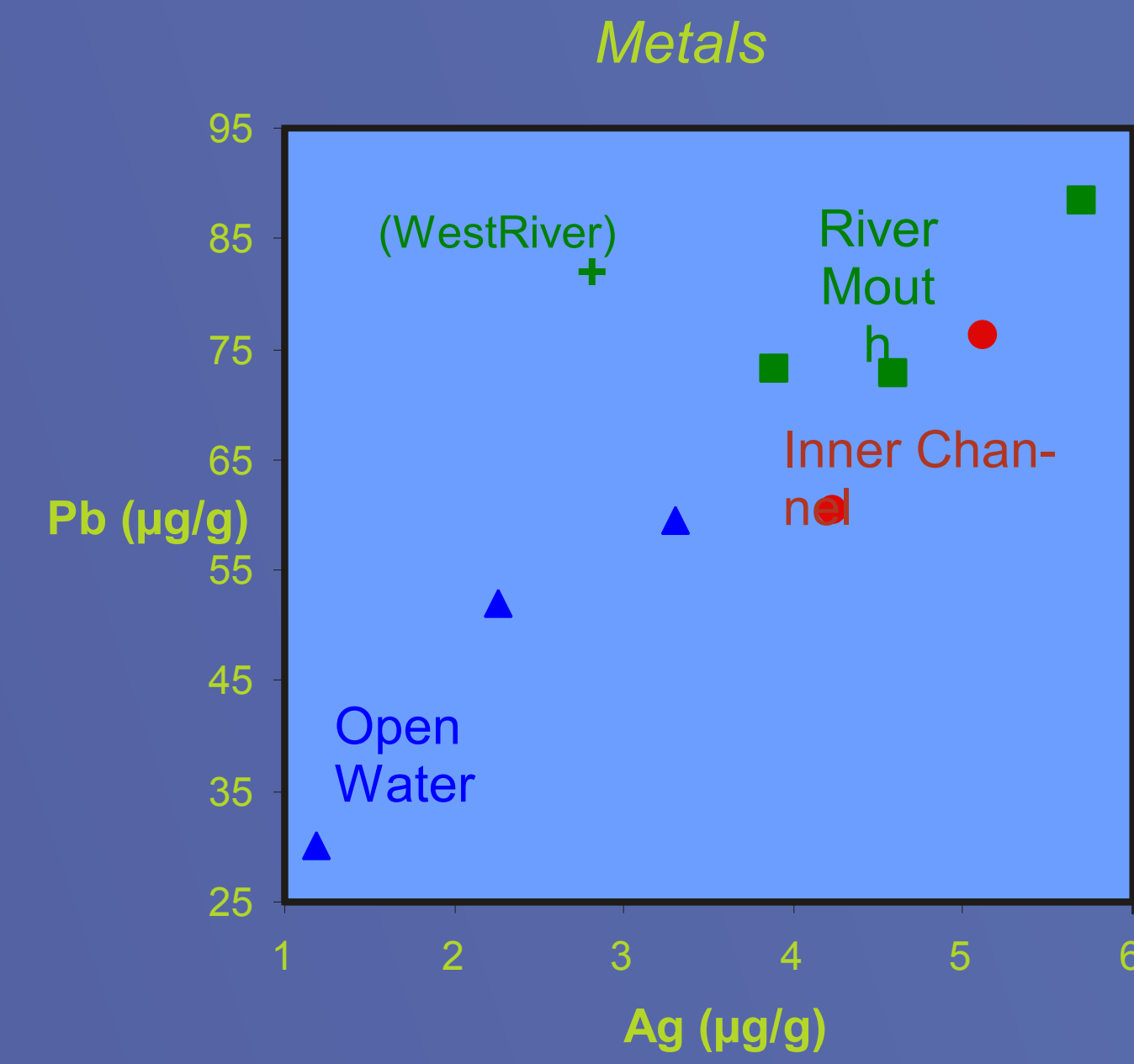
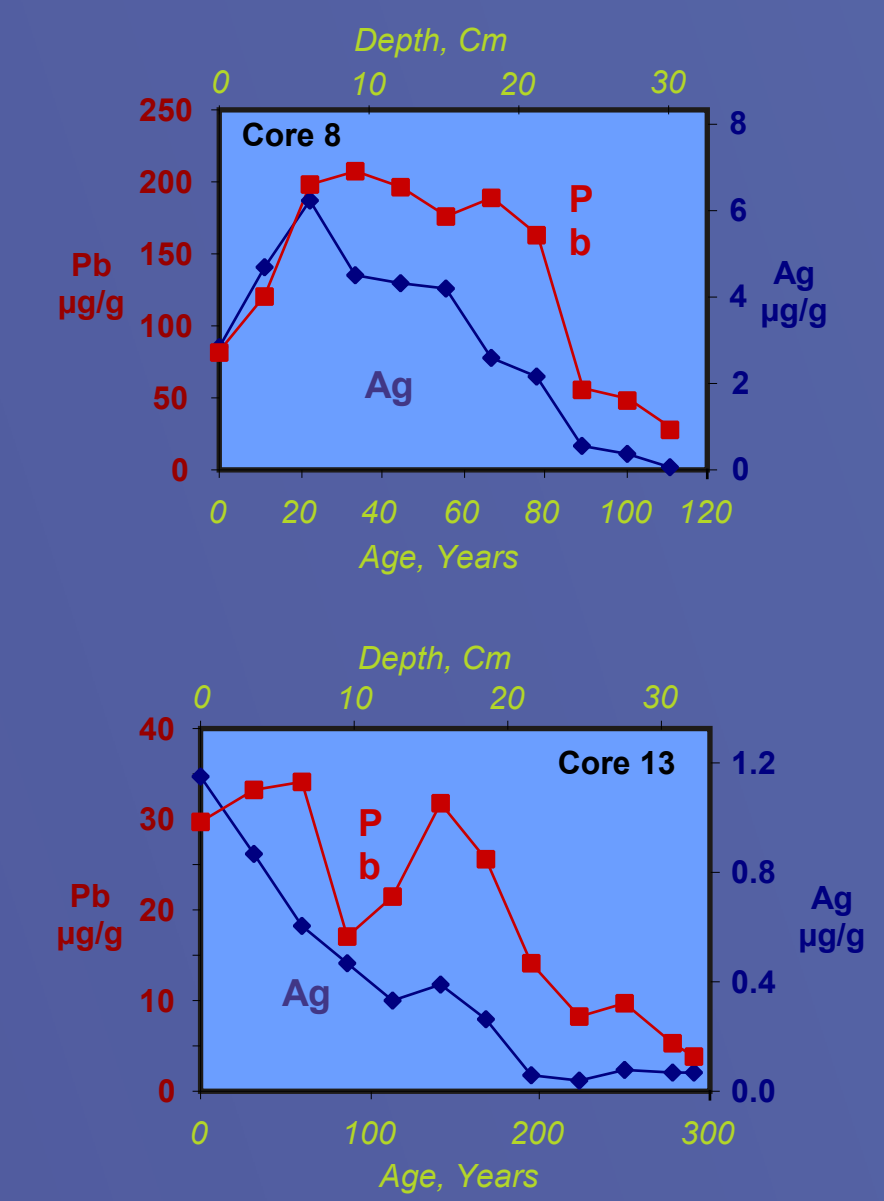
New Haven harbor, an embayment approximately 3 by 5 km, is an active terminus for international marine cargo. The tidally-influenced Quinnipiac, Mill and West Rivers empty into the harbor, the shoreline of which is the site of docking facilities, a petroleum tank farm, a power generation station, sewage treatment facilities, a busy interstate highway, housing and park land. The shipping channel leading into the inner harbor is maintained by periodic dredging. A series of shallow core samples were taken in open water, in the shipping channel, in the inner harbor and at the river mouths. For comparative purposes, several additional sediment samples were taken in waters near Guilford, a residential suburb of New Haven with low density housing and a pleasure boat marina.

For molecular organic analysis, we employed pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), using milligram quantities of dry, whole sediment. The compounds thus detected form a complex mixture of thermally extractable components, plus the products of the thermal decomposition of (bio)polymers present in the sample. The Py-GC/MS technique as used here offers a practical alternative to high cost, time-consuming standard analytical procedures, particularly in a regional survey employing a large number of specimens. The New Haven harbor samples were also analyzed for trace metals.

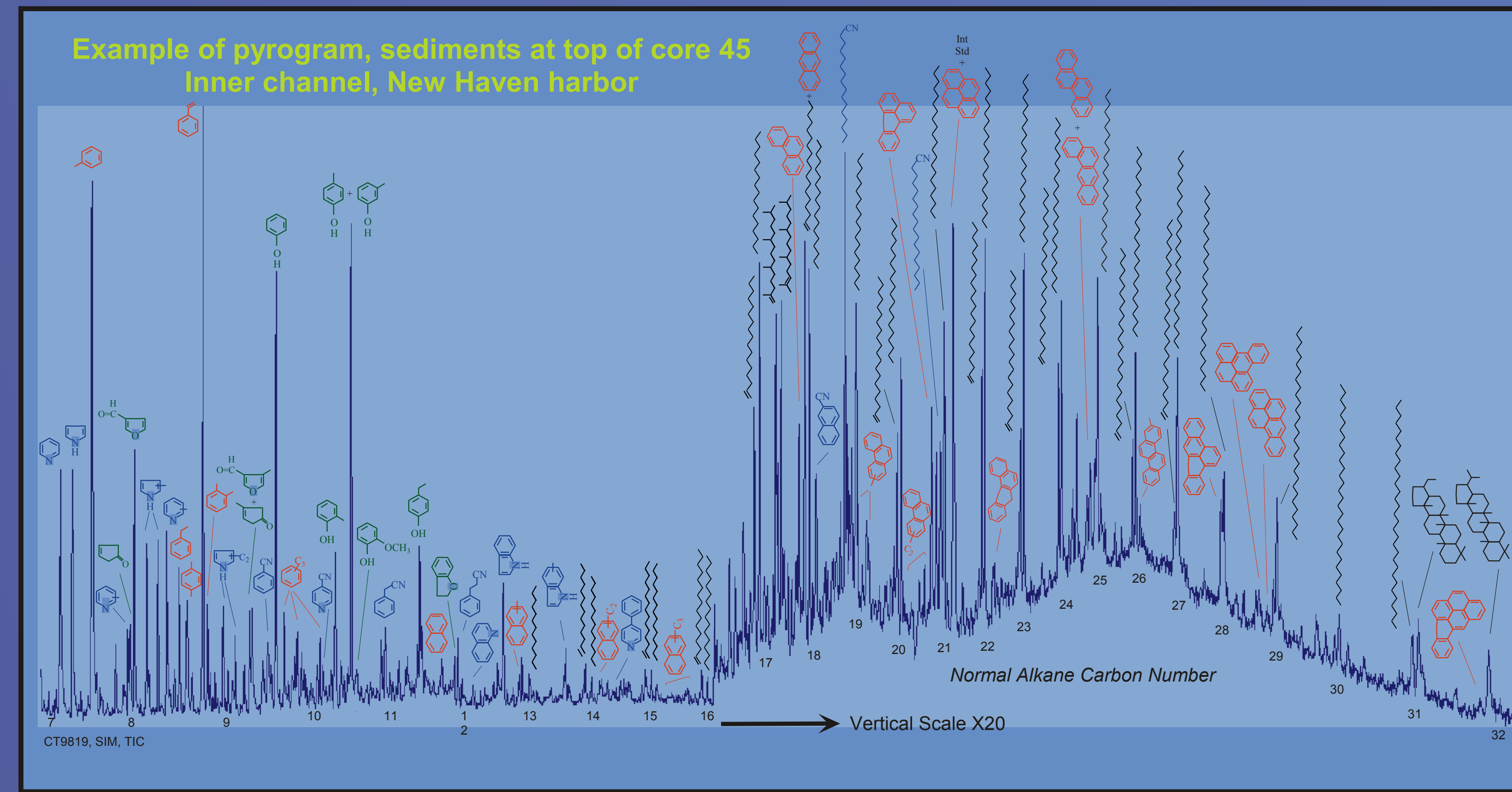
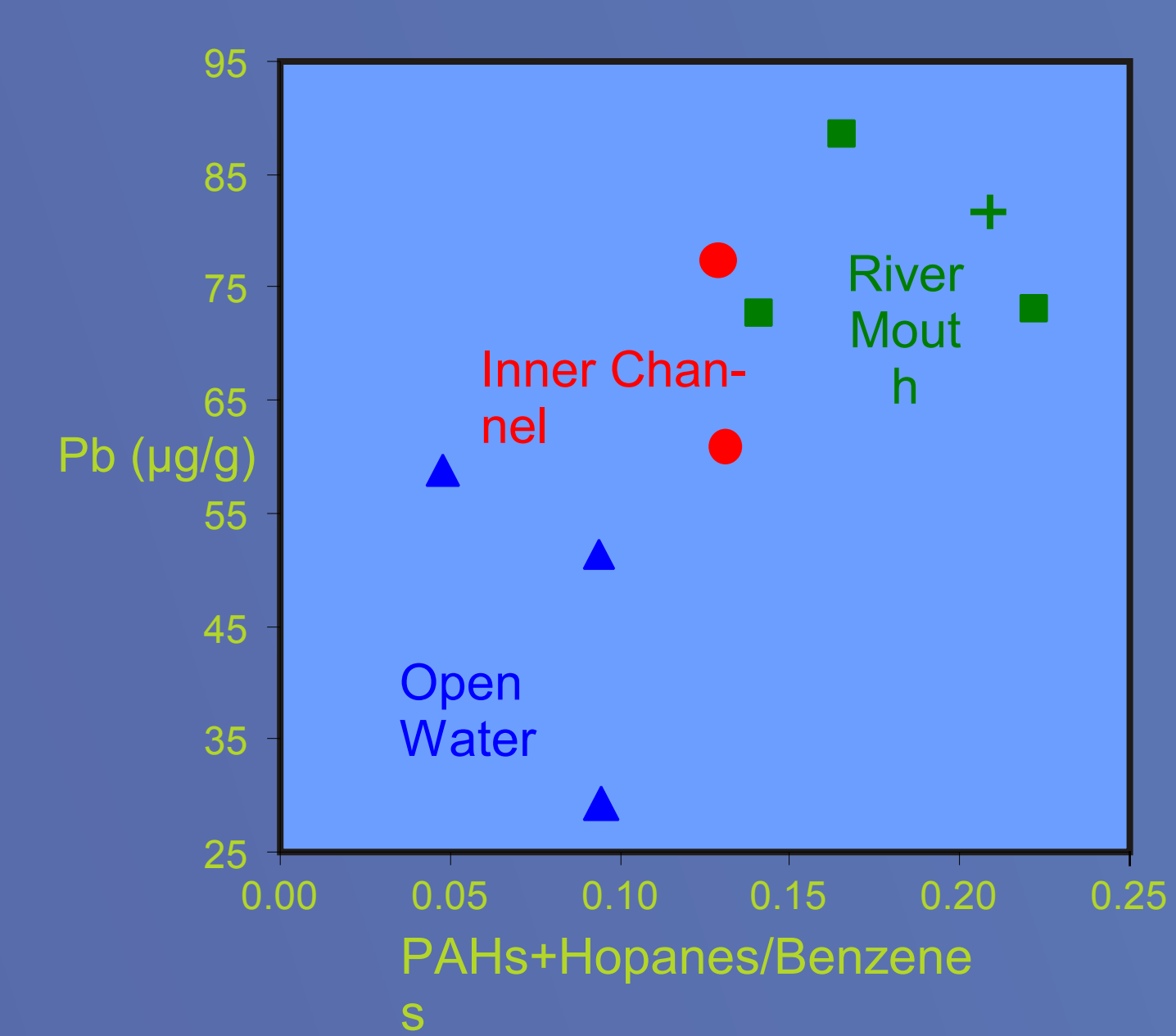
The Py-GC/MS results indicate a predominance of aquatic organic matter (OM) in the open water sediment samples at both sites, as evidenced by the relatively high abundance of nitrogen compounds in the pyrolyzate, including pyrroles, pyridines and indoles. These compounds are characteristic pyrolysis products of proteins and degraded proteinaceous matter, in this case largely from marine algae and bacteria. In contrast, estuarine samples show a larger terrestrial OM component, including the phenolic pyrolysis products of lignin and thermally-extracted long chain, odd carbon-numbered normal alkanes. A subset of the samples (from the river mouths and, to a lesser extent, from the inner harbor in New Haven) shows significantly higher relative concentrations of thermally-extractable polycyclic aromatic hydrocarbons (PAHs) and petroleum-derived hopanes. The Guilford and open water New Haven harbor samples appear relatively uncontaminated by PAHs. Our analytical approach permits the recognition of biogeochemical differences indicative of the parent OM and the depositional environment, as well as potentially hazardous anthropogenic contributions to the sediment.



Influx of metals over time Eastern New Haven Harbor



Correspondence between organic and inorganic contaminants



Methods

Sediment cores (ca. 30 cm) and grab samples

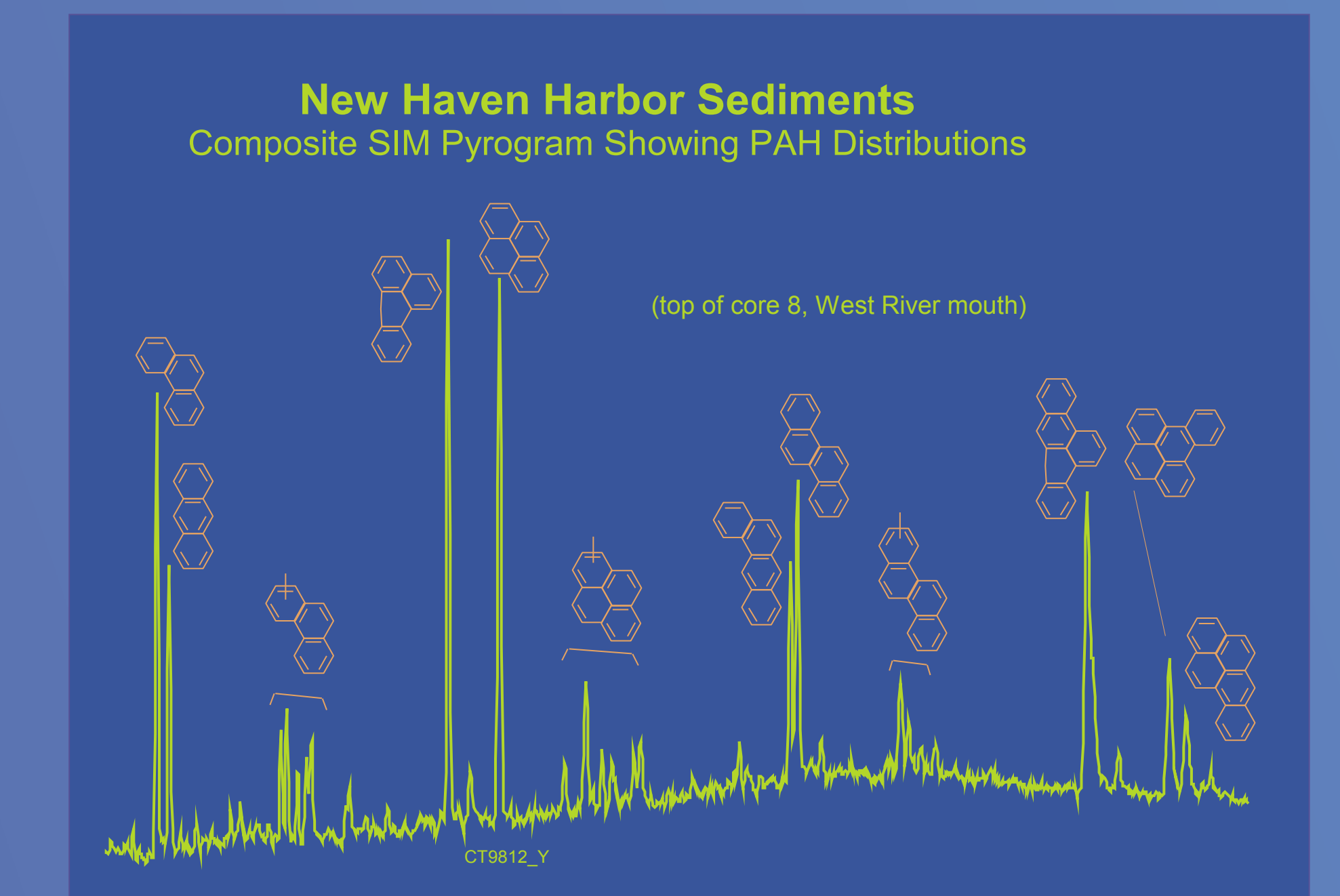
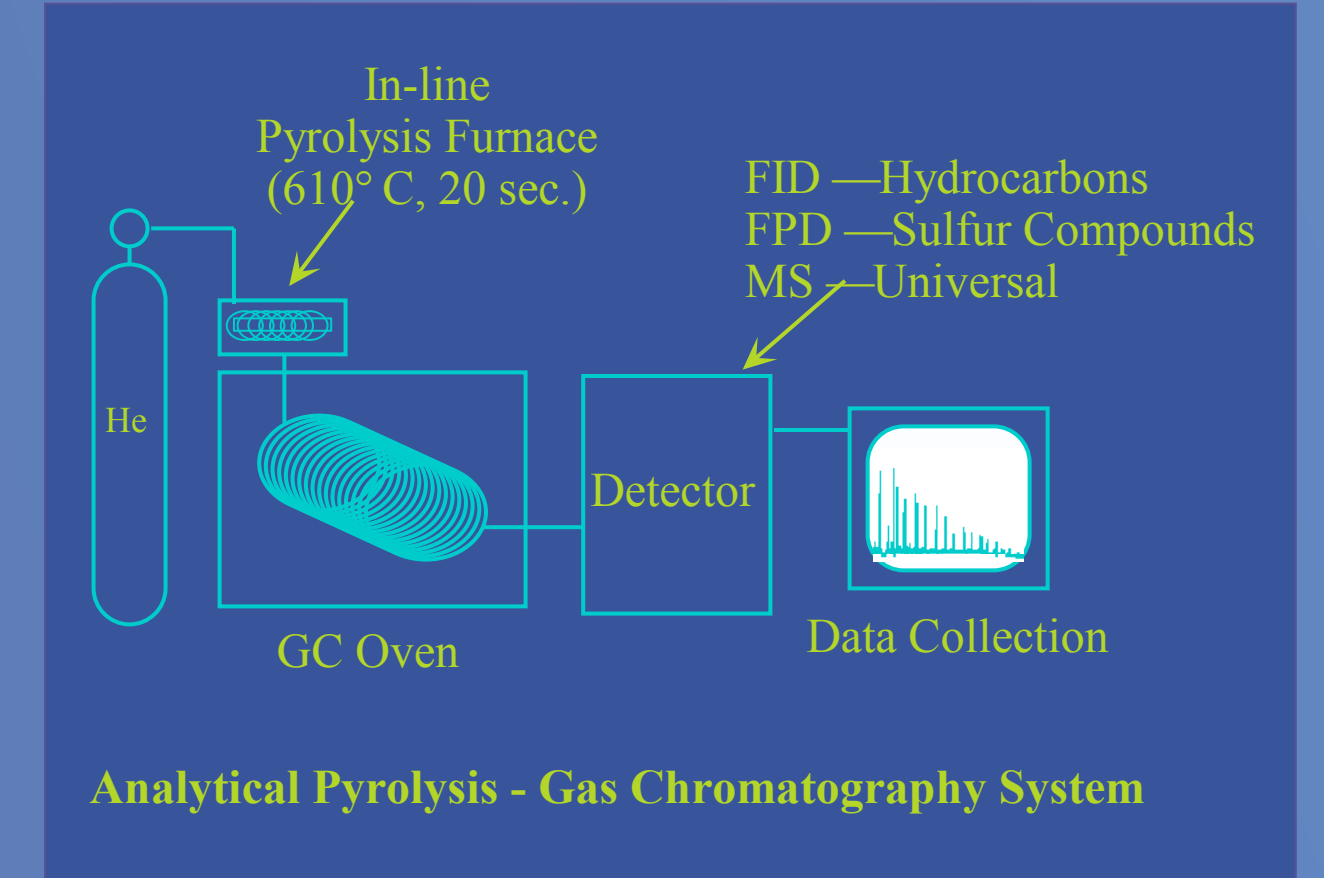
Major and minor elements, ²¹⁰Pb, ¹³⁷Cs (cores only)

Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS) of whole, dry sediment samples (Core tops and grab samples only)

Target organic analytes:
 Normal and isoprenoid hydrocarbons
 Hopanoids
 Aromatic hydrocarbons (1 to 6 ring)
 Cyclic nitrogen compounds
 Thiophenes

Multivariate analysis of Py-GC/MS results

GIS



CONCLUSIONS

Predominance of aquatic OM in the open water sediment samples:
 —Abundant nitrogen compounds in the pyrolyzate.
 —Pyrolysis products of proteins and degraded proteinaceous matter >>> marine algae and bacteria.

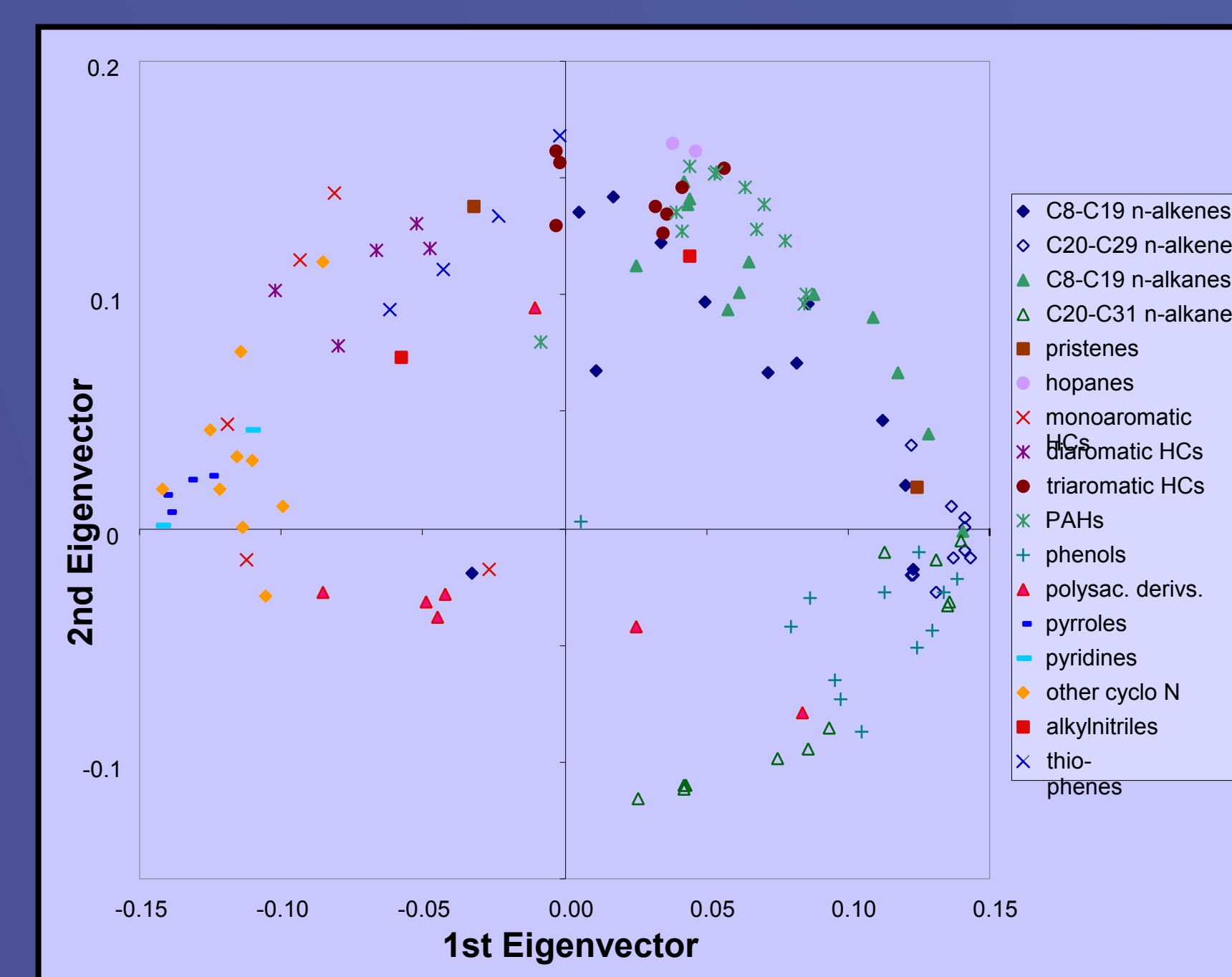
Estuarine samples >>> larger terrestrial OM component:
 —Phenolic pyrolysis products of lignin
 —Long chain, Codd n-alkanes.

New Haven river mouth (and inner harbor) samples show higher relative concentrations of:
 —Thermally-extractable PAHs
 —Petroleum-derived hopanes
 —Heavy metals

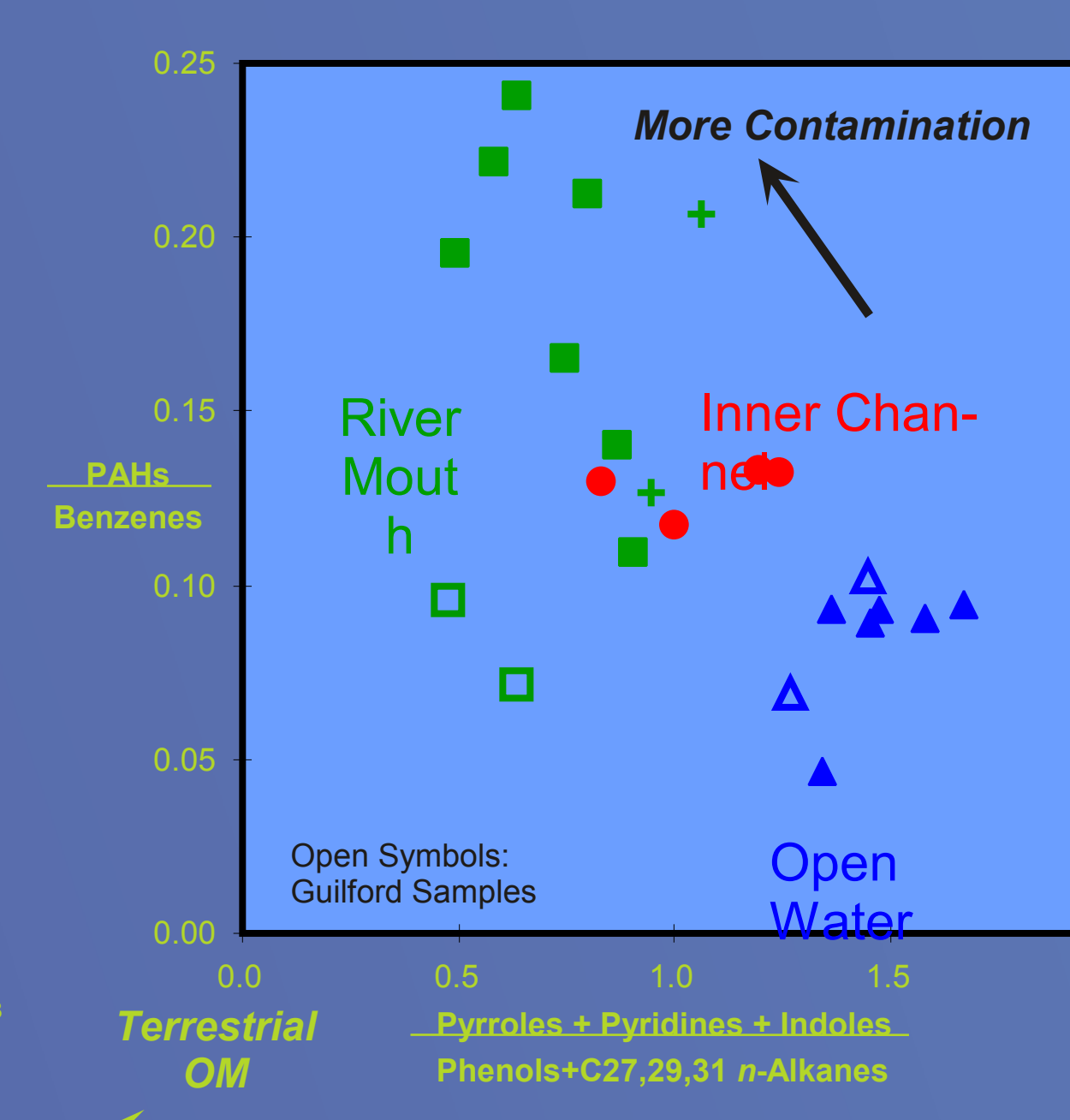
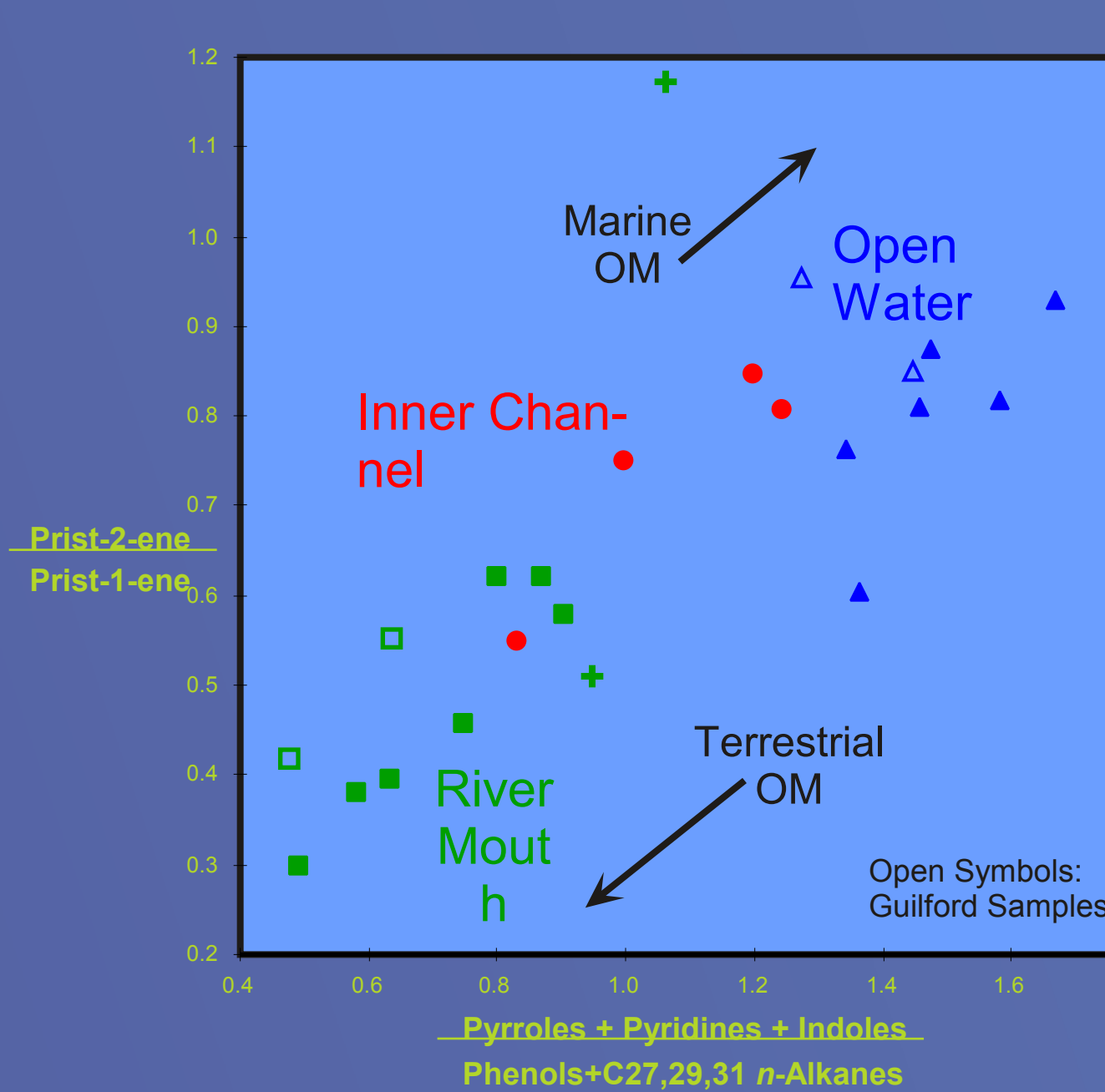
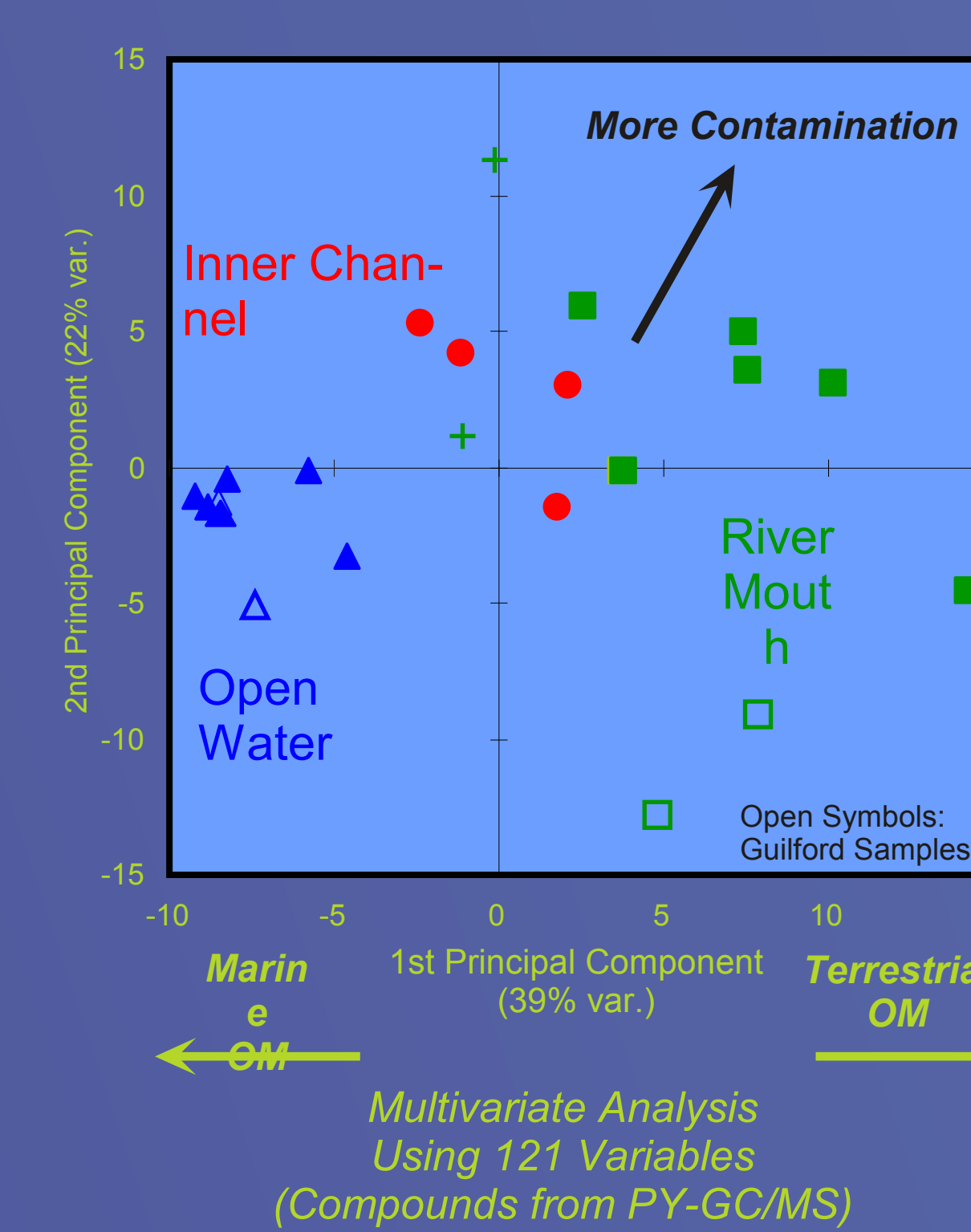
The Guilford and open water New Haven harbor samples appear relatively uncontaminated.

Our thanks to Carl Harvey and George Wheeler for contributing sediment samples.

Results of multivariate analysis, showing relationships between compounds detected by Py-GC/MS.



Organic Indicators of Sedimentary Environment



Multivariate Analysis Using 121 Variables (Compounds from PY-GC/MS)