Characterization of Contaminant and Biomass-Derived Organic Matter in Sediments from the Lower Passaic River, New Jersey, USA

Nicole M. Bujalski
Michael A. Kruge
Earth and Environmental Studies Department, Montclair State University, New Jersey, USA
Project Goals

• Understand the processes involved in legacy and ongoing contaminant patterns in the lower Passaic River using an environmental forensics approach

• Distinctive molecular fingerprints

• Relation to sediment and contaminant transport
We previously reported at PRS:

Importance and characteristics of sedimentary biomass land plant, algal, bacterial, sewage

PAH and petroleum contamination orders of magnitude greater than dioxin

Possible subsurface migration of coal tar (MGP?) into deep PR sediments
Methods

High resolution sub-sampling of four long (4-7 m) sediment cores from the Lower Passaic River

Sediment grain size distribution

Molecular organic geochemistry (Pyrolysis-GC/MS)
  Polycyclic aromatic compounds
  Petroleum biomarker compounds
  Biomass pyrolysis products

Principal components analysis

Integration of results with existing LPRRP data set

Chemostratigraphy
Sediment Core Locations – Detail

**Core 9A**

**Core 10A**

**Core 7A**

**Core 5A**

**Diamond Alkali Chemical Plant**

**Former Manufactured Gas Plant**
Radiometric Age Estimation

$^{137}\text{Cs (pCi/g)}$ \hspace{5mm} $\log^{210}\text{Po excess}$

Data: LPRRP, 2008
Radiometric Age Estimation – Stratigraphic Zonation

$^{137}$Cs (pCi/g)  log $^{210}$Po excess  PCBs (mg/kg)  2,3,7,8-TCDD (μg/kg)

Data: LPRRP, 2008
Radiometric Age Estimation – Stratigraphic Zonation

$^{137}$Cs (pCi/g)  log $^{210}$Po excess  PCBs (mg/kg)  2,3,7,8-TCDD (μg/kg)

Data: LPRRP, 2008
Age Estimation & Zonation: Core 5A

Data: LPRRP, 2008
Age Estimation & Zonation: Core 10A

Data: LPRRP, 2008
Mean Sediment Grain Size (log 2, μm)

(Fraction < 2 mm, Mastersizer 2000)
Total Organic Carbon (%)

Increase Upstream

Data: LPRRP, 2008
**Molecular Organic Analysis**

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

- **Pyrolysis** – 610°C
- **Sediment Prep** – Dry at 40°C
- **Advantages:**
  - milligram quantities of dry sediment
  - minimal sample preparation
  - no solvents needed - "green chemistry"
  - rapid procedure suitable for sediment screening
  - robust, reproducible, semi-quantitative

*Similar to EPA Method 8275a*
Pyrolysis vs. EPA Method 8270

EPA Method 8270 Data: LPRRP, 2008
Molecular Fingerprints

Core 7A

Sediment Depth (meters)

- Sample 01 (Upper)
  - mud, light brown
- Sample 25 (Mid)
  - mud, medium brown
- Sample 37 (Lower)
  - silt with pebbles, dark
  - sand with pebbles, reddish
Py-GC/MS Raw Data (TIC)
3 Representative Samples
Core 7A
Origin of PAHs in Core Sediments

Graphic after Yunker et al., 2002
Marker for PAH Contamination in Core Sediments
Markers for Petroleum Contamination

C29 + C30 Hopanes Estimated (mg/kg)

(Red ovals: elevated PAH contamination)
What about the biomass present in the river sediments?
Vinyl Guaiacol and Indole (VGI) Ratio

Vinyl Guaiacol

\[ m/z: 124, 138, 150, 164, 152, 166 \]

Lignin (Land Plant Derivation)

\[ \text{VGI} = \frac{\text{VG}}{[\text{I} + \text{VG}]} \]

Protein (Aquatic Biomass)

\[ m/z: 117 \]

Pyrolysis – GC/MS
Core 7A: Sample 1 (0-7.5 cm)
VGI Ratio

(Higher: more land plant biomass; Lower: More aquatic biomass)
Summary of Molecular Results (Pyrolysis)
All 4 Cores

"Combustion"
Phenanthrene + Pyrene

"Petroleum"
C29 + C30 Hopanes

"Biomass"
Indole + Vinlyguaiacol
Conclusions

Recognition of 3 chemostratigraphic zones in all 4 cores

PAH contamination ranges from "serious" to "extreme"
  Notable in lower zone – "pyrogenic signature"
  Associated with sandy lens in Core 7 (near former MGP)

Petroleum contamination distinctive
  Notable in middle zone

Biomass relatively more abundant in upper zone
  Aquatic signature closer to river mouth – tidal influence
  Land plant signature upstream – fluvial influence
Consider -

*PR sediments are very organic-rich:*

- Hydrocarbon contamination & biomass
  - Approaching fuel-grade
  - Something like Canada's Athabasca tar sands

*Alternate solution to disposal of dredged materials:*

- Advanced fluidized bed reactor
  - Energy generation (electricity, steam)
  - Clean residual sediment for beneficial reuse
  - Eliminates vexing disposal issues
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