Use of Forensic Methods to Identify Sources of Elevated PAH Concentrations in Sediments from Urban Tidal Waterbodies

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Waterbodies in NYC

- 16 Urban Tidal Waterbodies
  - 2 Superfund
  - 14 Represent Regional Background

Waterbodies in NYC
NAPL Migration Due to Ebullition
NAPL Migration from Upland Sites
Source inputs evaluated in this work

Conceptual Site Model
Approach

- Concentration
- Mass Fraction Pattern
- Source Ratio
- Principal Component Analysis
- Other Source Indicators
<table>
<thead>
<tr>
<th>Name</th>
<th>Abbrev</th>
<th>Ring</th>
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Comparison of Concentrations - tPAH$_{17}$

- **Background Sediments**
  - Waterbodies with CSO
  - Waterbodies with limited CSO
  - Gowanus Canal Bay

- **Municipal Solids**

- **Superfund**
  - Surface Sediments
  - Subsurface Sediments

<table>
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<tr>
<th>Location</th>
<th>Max Values (mg/kg)</th>
<th>No. Off Scale</th>
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<td>12</td>
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<tr>
<td>Subsurface</td>
<td>3,500</td>
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NAPL
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<tr>
<th>Molecule</th>
<th>Rings Per Molecule</th>
<th>Molar Fraction</th>
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<td>Naphthalene</td>
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<td>Fluoranthene</td>
<td>4</td>
<td>0.3</td>
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\[ \text{Number of Rings Per Molecule for a PAH Mixture} = N_1 F_1 + N_2 F_2 = 2 \times 0.7 + 4 \times 0.3 = 2.8 \]
PAH Mass Fraction Patterns
Background Surface Sediments

No. of Rings per Molecule = 3.9
PAH$_{17} = 33$ mg/kg

Municipal Solids

No. of Rings per Molecule = 3.6
PAH$_{17} = 32$ mg/kg
MGP Tar

No. of Rings per Molecule = 2.5
PAH$_{17}$ = 180,000 mg/kg
Oil Seep from an Upland Site

No. of Rings per Molecule = 3.8
PAH$_{17}$ = 900 mg/kg

No. of Rings per Molecule = 3.0
PAH$_{17}$=53,000 mg/kg
NAPL Migration Due to Ebullition
Newtown Creek Tributary – Dutch Kills

No. of Rings per Molecule = 2.5
PAH$_{17}$ = 1,900 mg/kg

No. of Rings per Molecule = 3.3
PAH$_{17}$ = 410,000 mg/kg

PAH Patterns
PAH Patterns

Gowanus Canal Surface Sediments

No. of Rings per Molecule = 2.8
PAH$_{17}$ = 1,200 mg/kg

Newtown Creek Surface Sediments

No. of Rings per Molecule = 2.9
PAH$_{17}$ = 1,400 mg/kg
PAH Source Ratio
Newtown Creek

- FL0/(FL0+PY0)

Concentration (mg/kg)

- BG Sediment
- Municipal Input
- MGP Tar
- NAPL from Ebullition
- NAPL from Upland Seep
- Newtown Sediments
BAC4 was excluded in the PCA due to high percentage of non-detect observations (12%). Samples with more than 10 non-detect PAH compounds were excluded from the PCA analysis. The non-detect values were replaced by a random number between zero and the minimum detected value for each PAH compound. Exclude samples which were analyzed by 8270 method (non-SIM method). Concentration data were first normalized to the total concentration of 38 PAHs to obtain the proportion data. Centered log-ratios were obtained by dividing each proportion by the geometric mean of all proportions across a specific sample (Howell, 2007; Yunker, 2012):

\[ \text{Where, } i \text{ represents variable, } j \text{ represents sample, } d \text{ is number of variables included in PCA, } p \text{ indicates proportion data} \]

PCA was then derived from the correlation matrix of the centered log-ratios of proportions.

PCA Score Plot – Gowanus Canal

Component 1 (45.3 %)

Component 2 (16.2 %)

Sediment tPAH$_{17}$ (mg/kg)

- BG sediments
- MGP Tar
- Municipal Input

- [0,30)
- [30,100)
- [100,300)
- [300,1000)
- [1000,max]
PAH Composition vs. Concentration - Newtown
Municipal discharges are not a significant source of PAHs in Superfund Sediments:

- Municipal discharges have not resulted in elevated PAH concentrations in sediments in the receiving background waterbodies.
- Sediments in Superfund waterbodies contain PAH levels which are greater than those on municipal solids.
- Superfund sediments with elevated PAH concentrations show a different PAH composition from that on municipal solids.

Coal tar and other NAPL are likely sources:

- Coal tar, ebullition-transported NAPL and NAPL seep from upland sites contain PAHs at levels several orders of magnitude greater than municipal solids.
- Sediments with high PAH concentrations exhibit a composition that is more similar to coal tar.
- NAPL samples show a large variability in PAH concentration and composition. These variabilities can be attributed to both different sources and degree of weathering. Additional characterization of these NAPL sources is required to understand their contribution to PAH in sediments.