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

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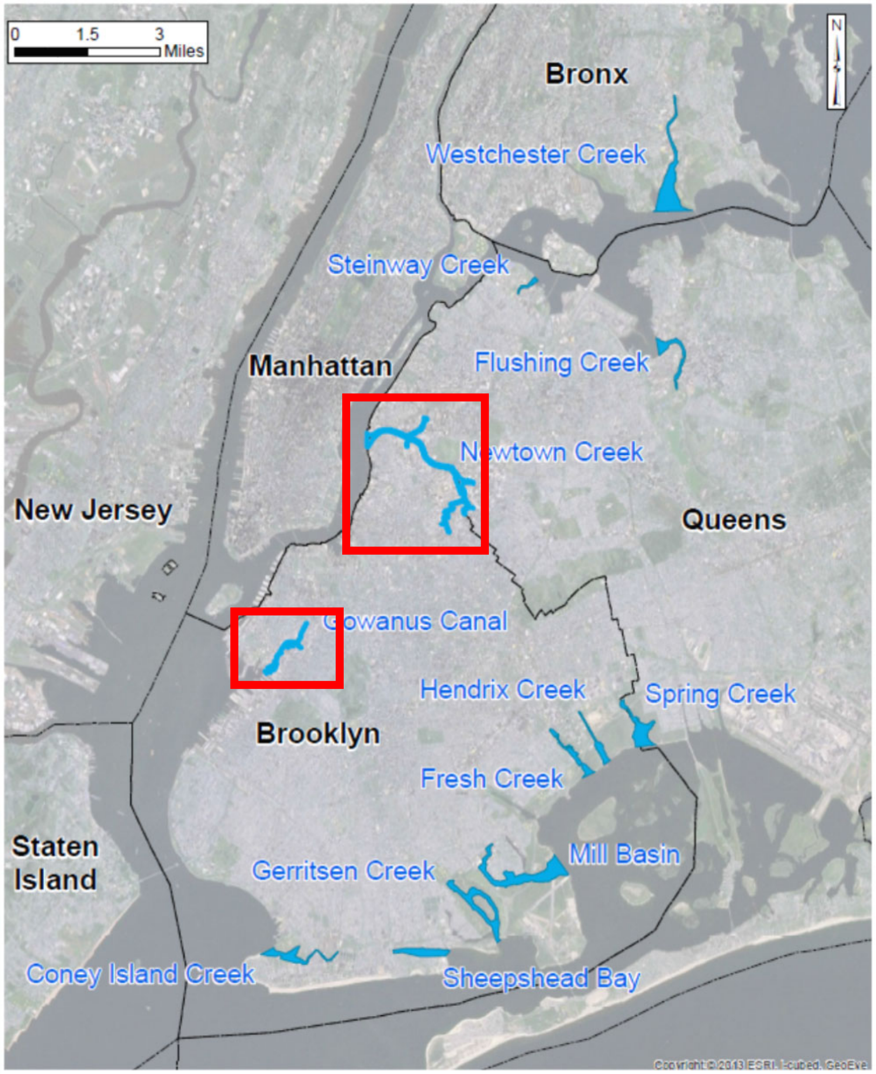
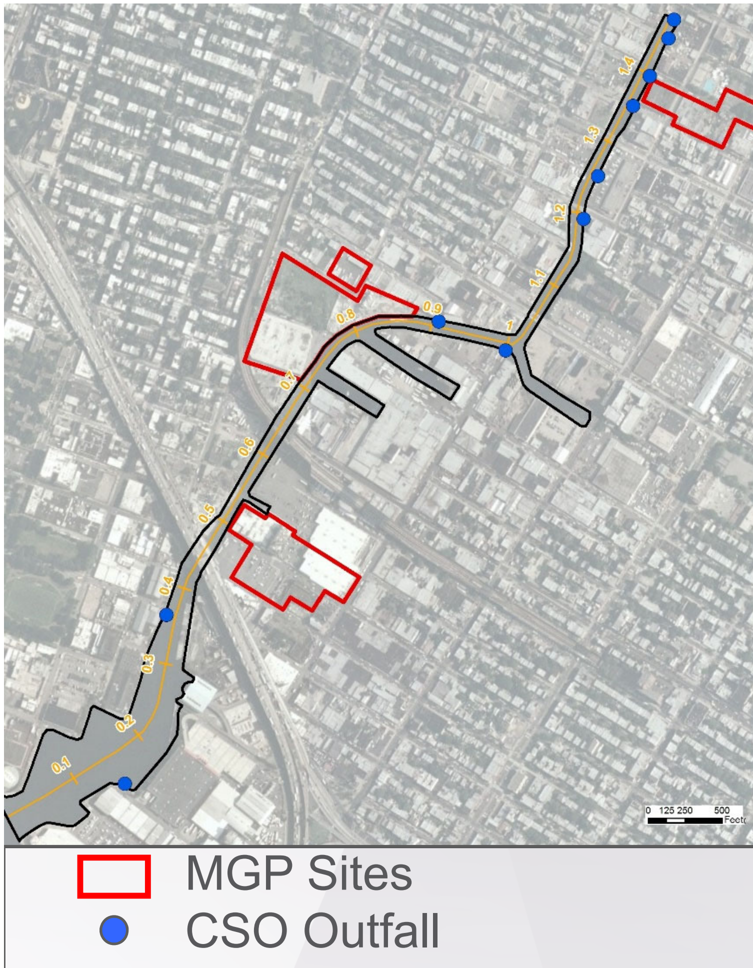


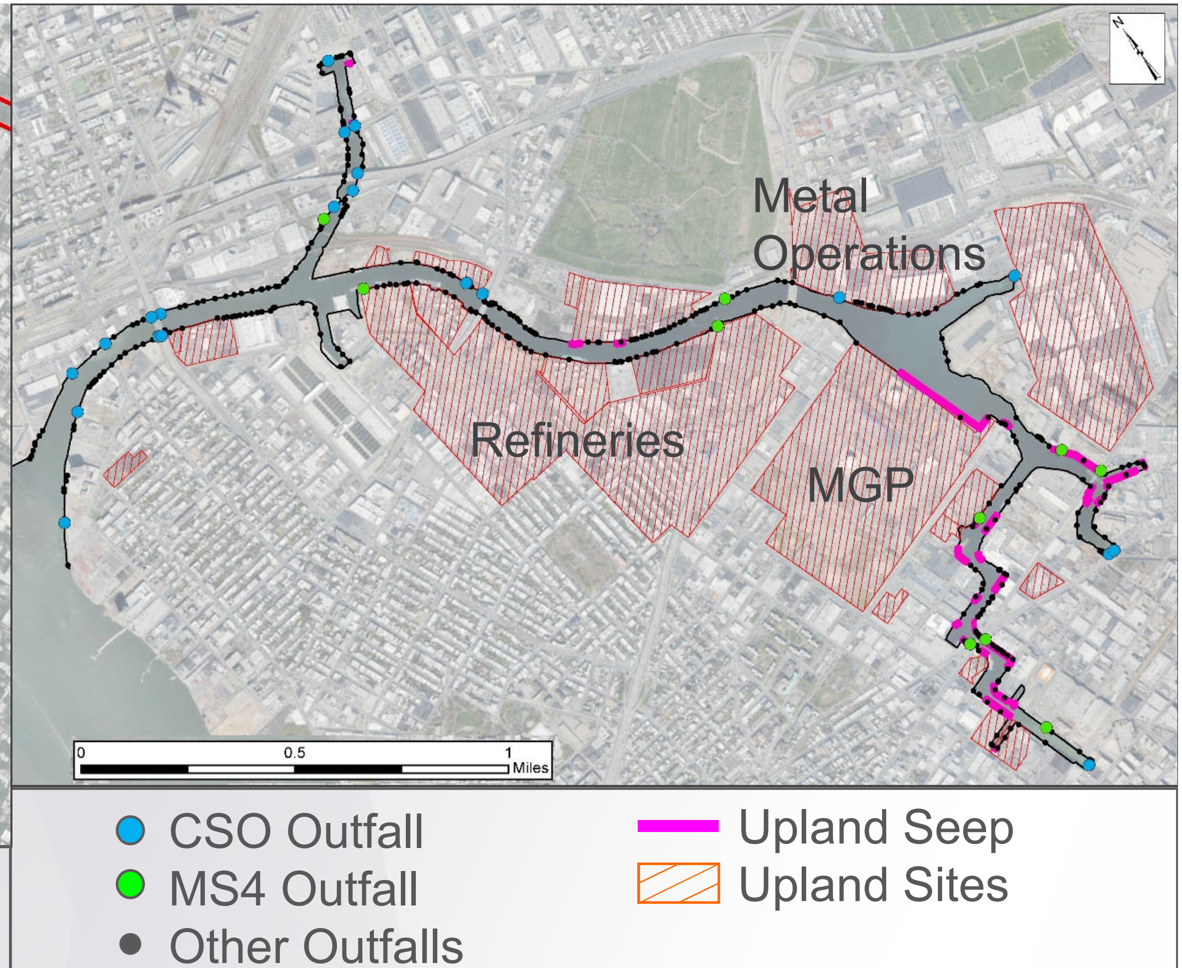
❖ 16 Urban Tidal Waterbodies
- 2 Superfund
- 14 Represent Regional Background

Superfund

Waterbodies in NYC



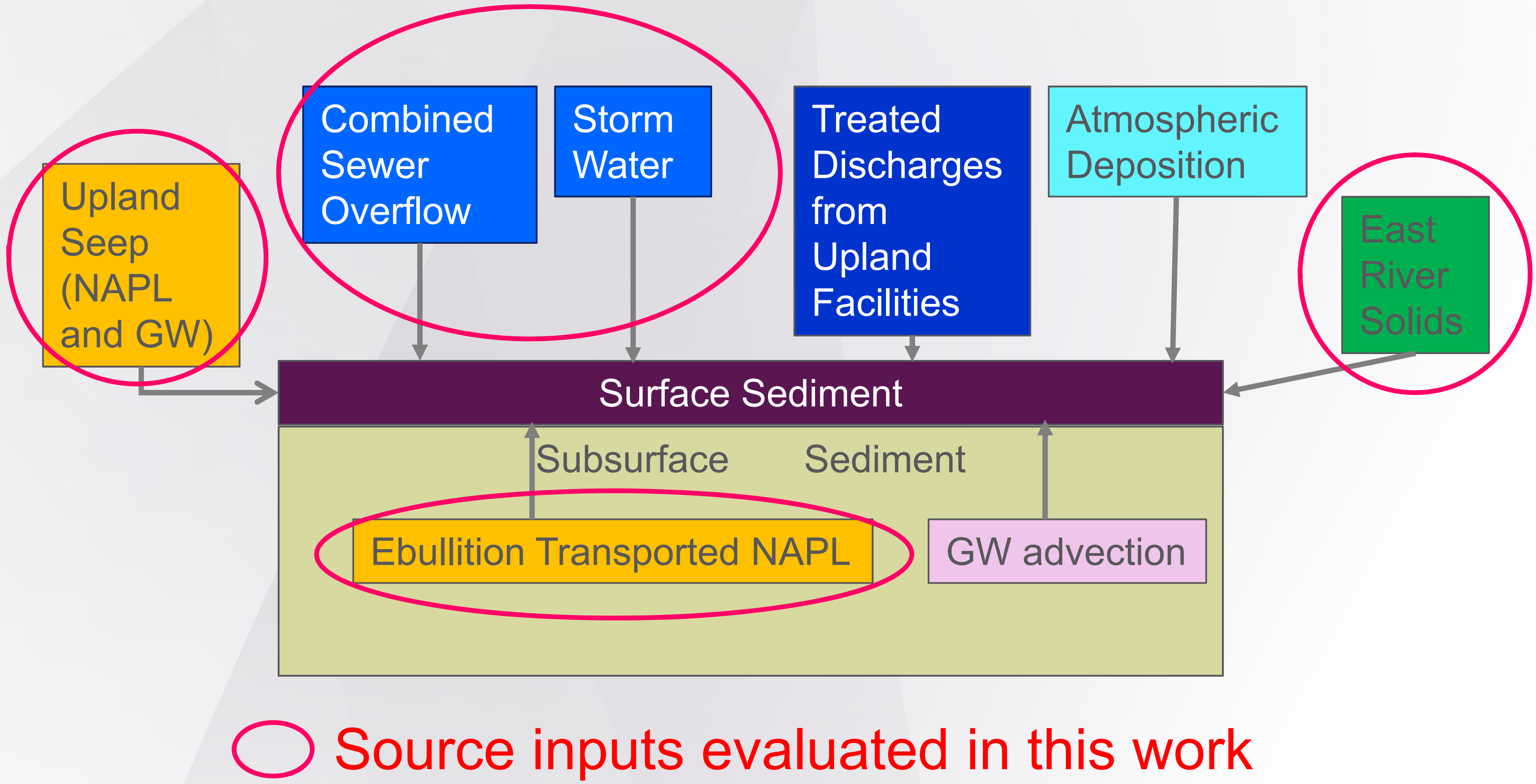
Gowanus Canal Map



Newtown Creek Map

NAPL Migration Due to Ebullition

NAPL Migration from Upland Sites



Conceptual Site Model

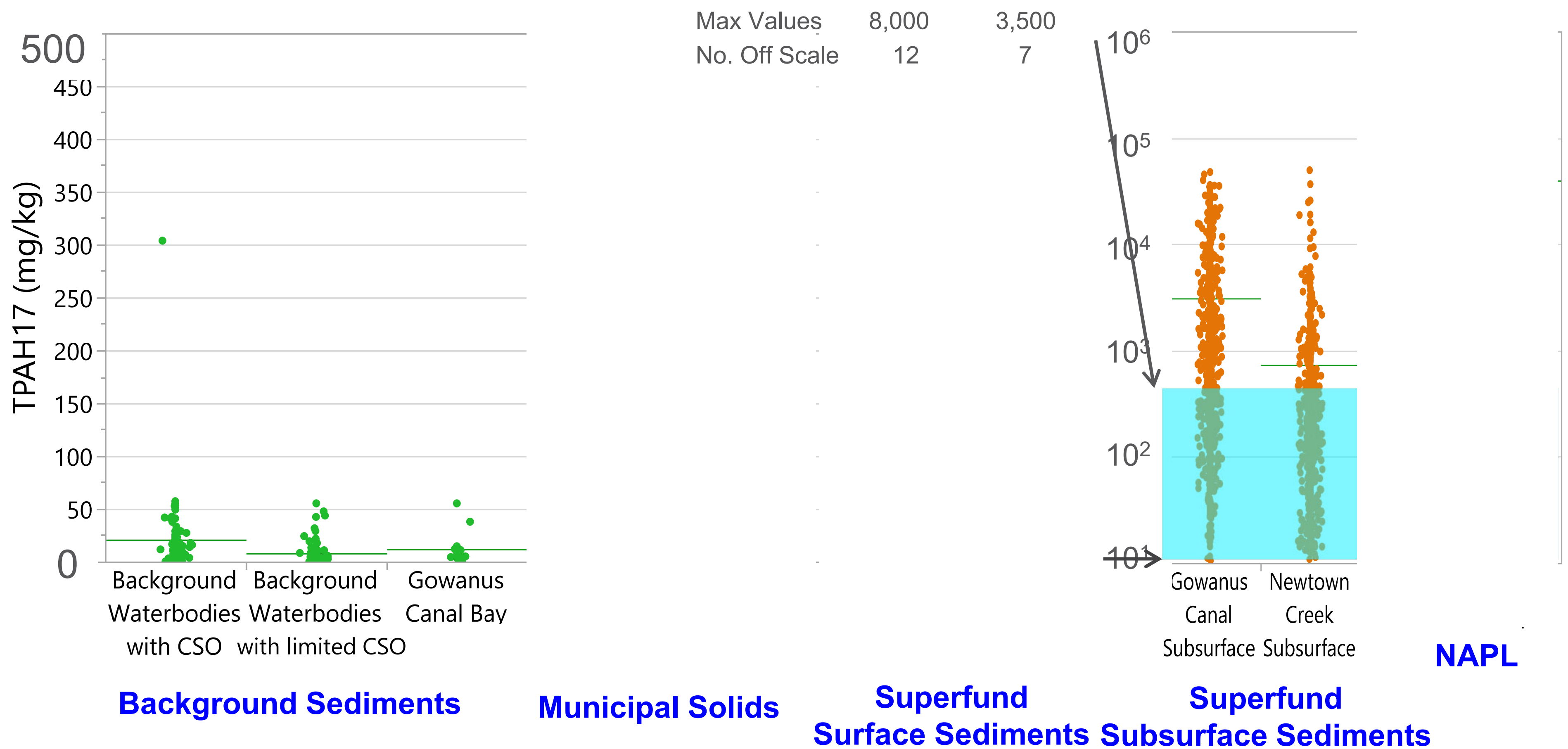
Approach

- Concentration
- Mass Fraction Pattern
- Source Ratio
- Principal Component Analysis
- Other Source Indicators

Name	Abbrev	Ring	MW	Name	Abbrev	Ring	MW
Naphthalene	**N0**	2	128	C3-Phenanthrenes/Anthracenes	PA3	3	220
C1-Naphthalenes	N1	2	142	C4-Phenanthrenes/Anthracenes	PA4	3	234
C2-Naphthalenes	N2	2	156	**Fluoranthene**	**FL0**	4	202
C3-Naphthalenes	N3	2	170	**Pyrene**	**PY0**	4	202
C4-Naphthalenes	N4	2	184	C1-Fluoranthenes/Pyrenes	FP1	4	216
Acenaphthylene	**AY**	3	152	**Benz[a]anthracene**	**BA0**	4	228
Acenaphthene	**AE**	3	154	**Chrysene**	**C0**	4	228
Fluorene	**F0**	3	166	C1-Benz[a]anthracenes/Chrysenes	BAC1	4	242
C1-Fluorenes	F1	3	180	C2-Benz[a]anthracenes/Chrysenes	BAC2	4	256
C2-Fluorenes	F2	3	194	C3-Benz[a]anthracenes/Chrysenes	BAC3	4	270
C3-Fluorenes	F3	3	208	C4-Benz[a]anthracenes/Chrysenes	BAC4	4	284
Dibenzothiophene	DBT0	3	184	**Benzo[b]fluoranthene**	**BBF**	5	252
C1-Dibenzothiophenes	DBT1	3	198	**Benzo[jk]fluoranthene**	**BJKF**	5	252
C2-Dibenzothiophenes	DBT2	3	212	Benzo[e]pyrene	BEP	5	252
C3-Dibenzothiophenes	DBT3	3	226	**Benzo[a]pyrene**	**BAP**	5	252
C4-Dibenzothiophenes	DBT4	3	240	Perylene	PER	5	252
Phenanthrene	**P0**	3	178	**Indeno[1,2,3-cd]pyrene**	**IND**	6	276
Anthracene	**A0**	3	178	**Dibenz[a,h]anthracene**	**DA**	5	278
C1-Phenanthrenes/Anthracenes	PA1	3	192	**Benzo[g,h,i]perylene**	**GHI**	6	276
C2-Phenanthrenes/Anthracenes	PA2	3	206				

PAH Compounds

PAH Concentrations



Comparison of Concentrations - $tPAH_{17}$

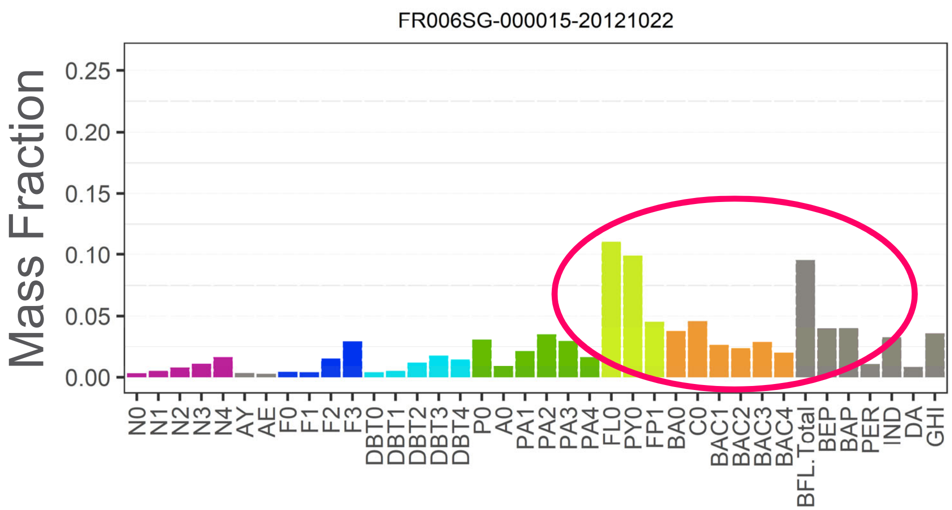
	Number of Rings Per Molecule		Molar Fraction
Naphthalene	2	×	0.7
		+	
Fluoranthene	4	×	0.3
		=	
		2.8	

Number of Rings Per Molecule for a PAH Mixture

PAH Mass Fraction Patterns

Background Surface Sediments

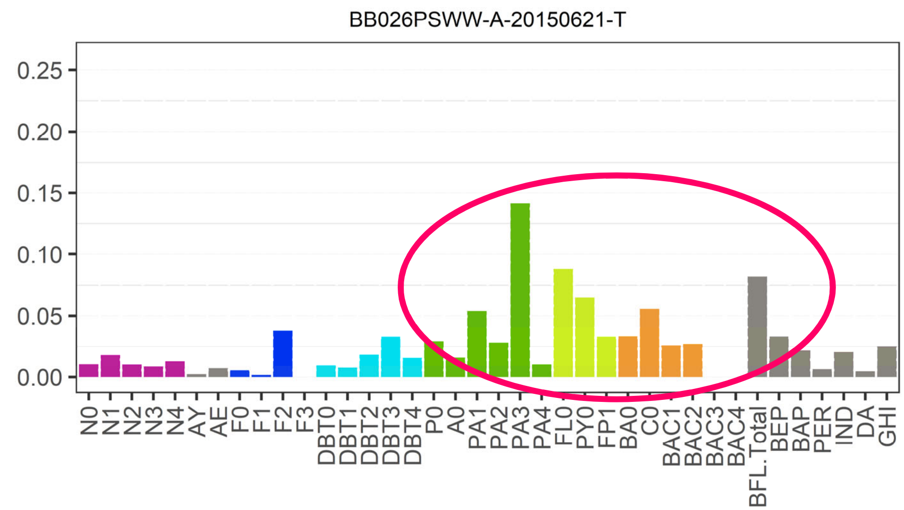
No. of Rings per Molecule = 3.9
PAH_{17} = 33 mg/kg



PAH Compound
Parent and Methylated Daughter
(Increasing Number of Rings and MW →)

Municipal Solids

No. of Rings per Molecule = 3.6
PAH_{17} = 32 mg/kg

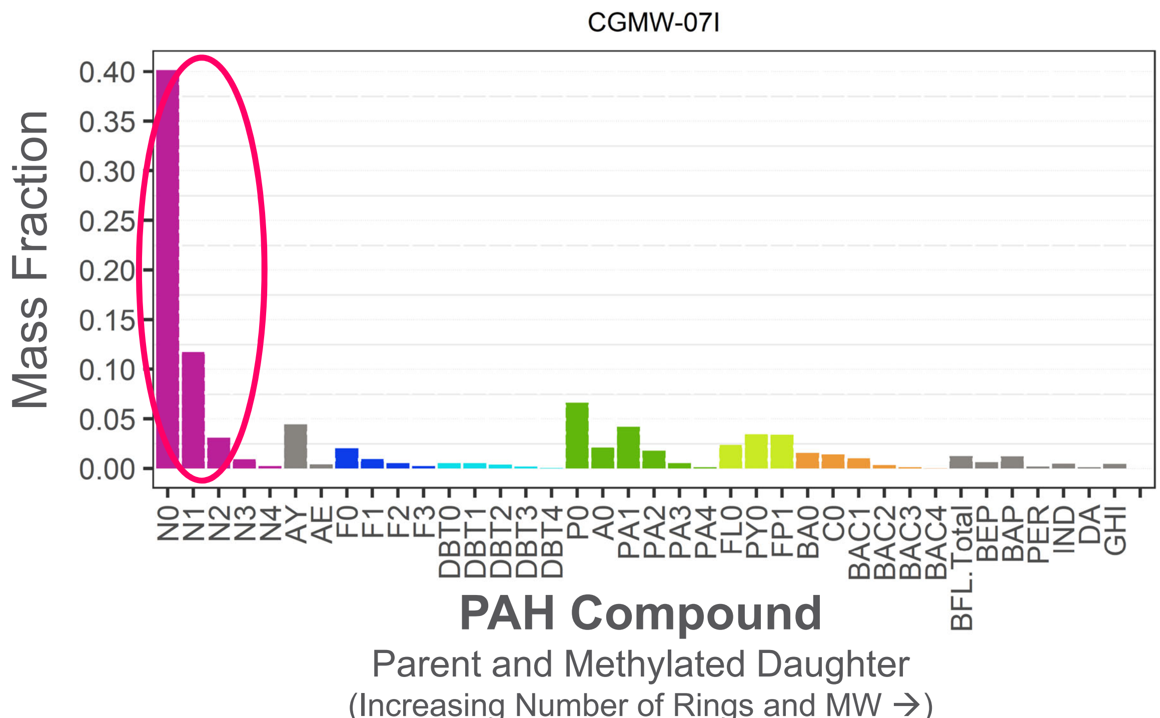


PAH Compound
Parent and Methylated Daughter
(Increasing Number of Rings and MW →)

PAH Patterns

MGP Tar

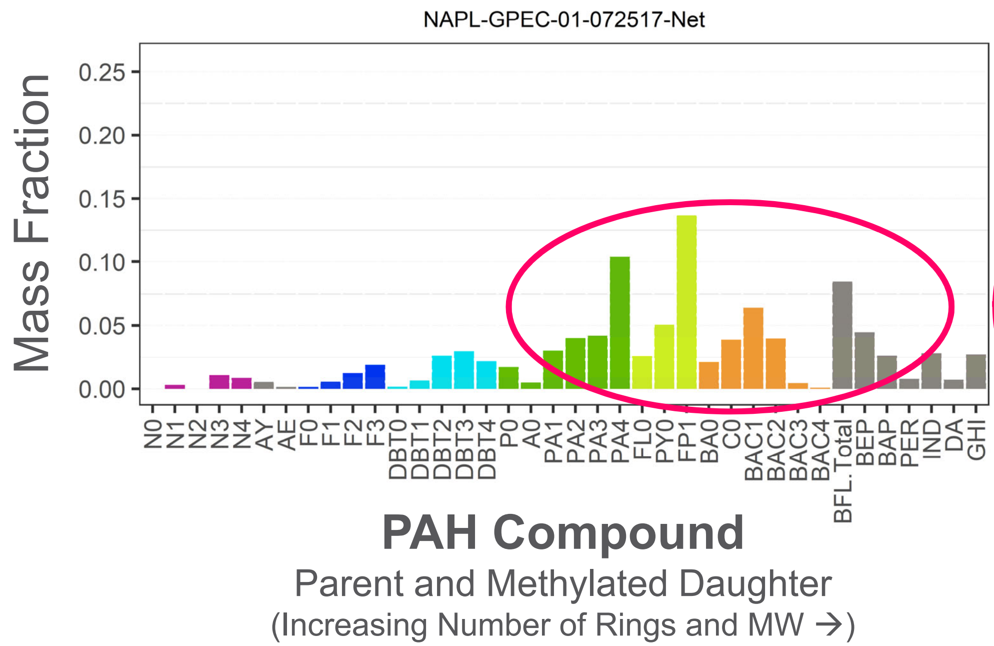
No. of Rings per Molecule = 2.5
PAH_{17} = 180,000 mg/kg



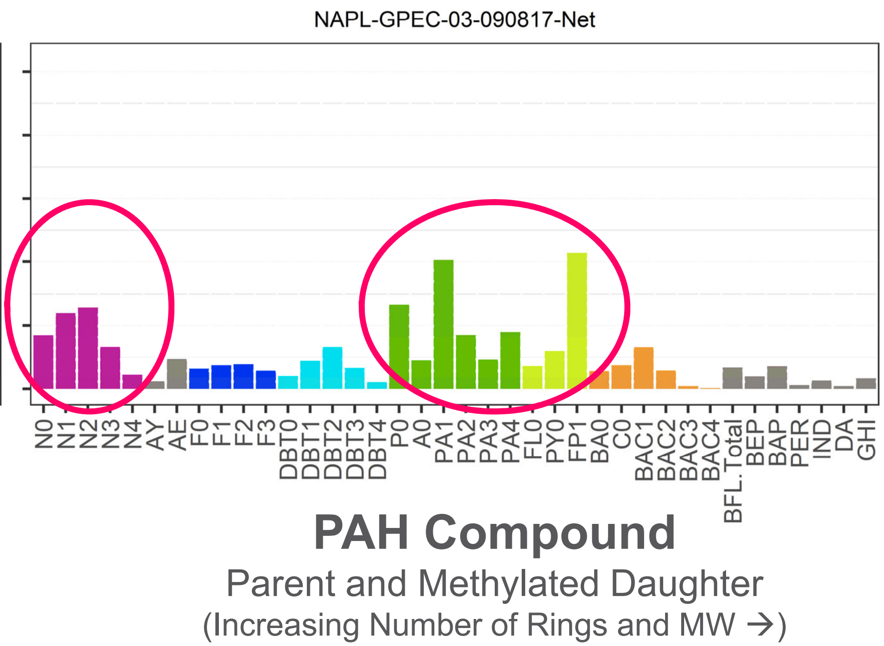
PAH Patterns

Oil Seep from an Upland Site

No. of Rings per Molecule = 3.8
PAH_{17} = 900 mg/kg



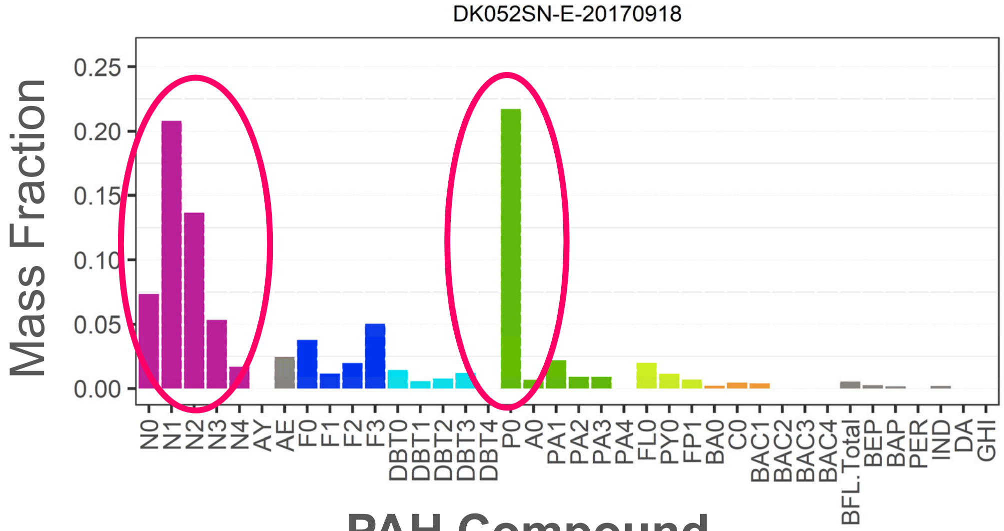
No. of Rings per Molecule = 3.0
PAH_{17}=53,000 mg/kg



PAH Patterns

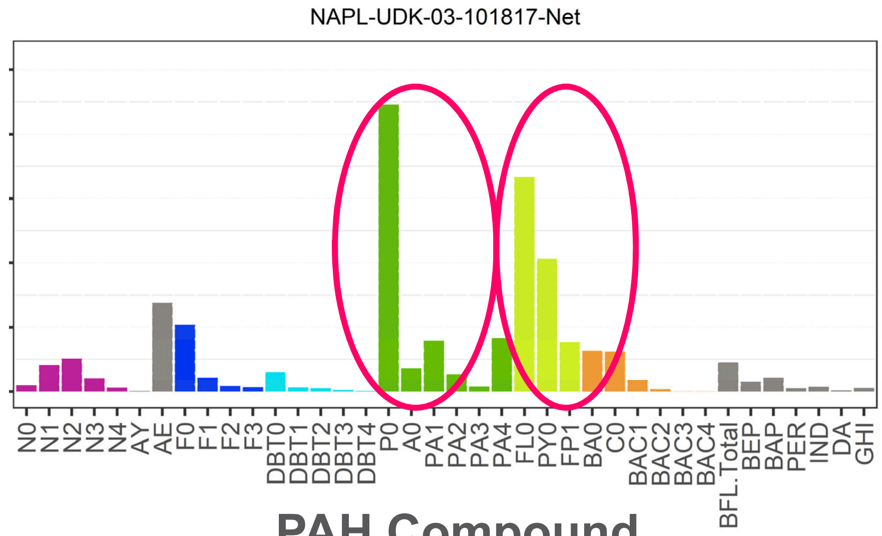
NAPL Migration Due to Ebullition
Newtown Creek Tributary – Dutch Kills

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



PAH Compound
Parent and Methylated Daughter
(Increasing Number of Rings and MW →)

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



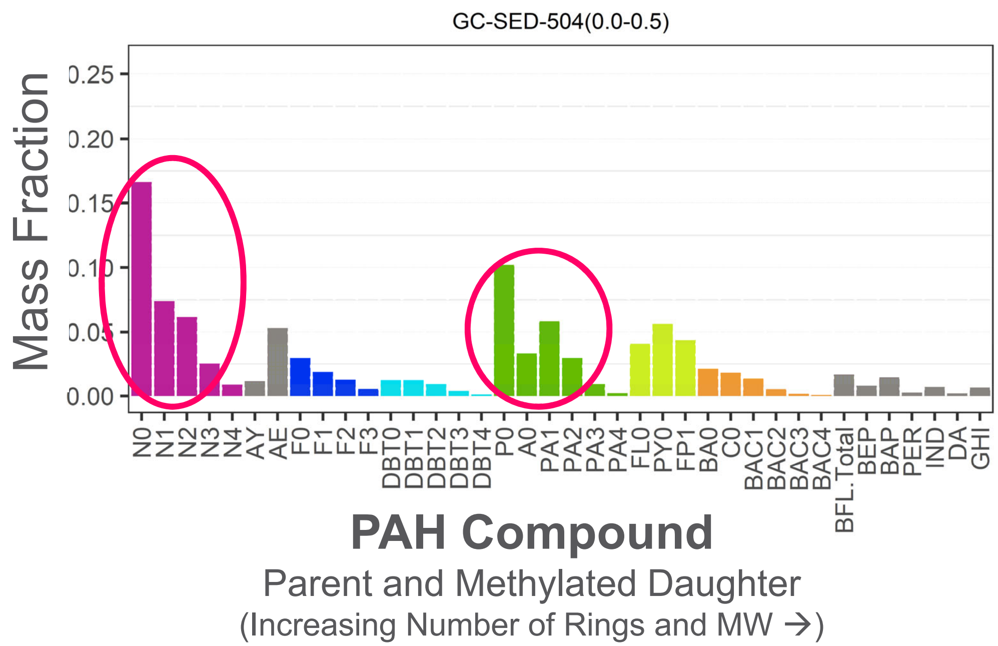
PAH Compound
Parent and Methylated Daughter
(Increasing Number of Rings and MW →)

PAH Patterns

PAH Patterns

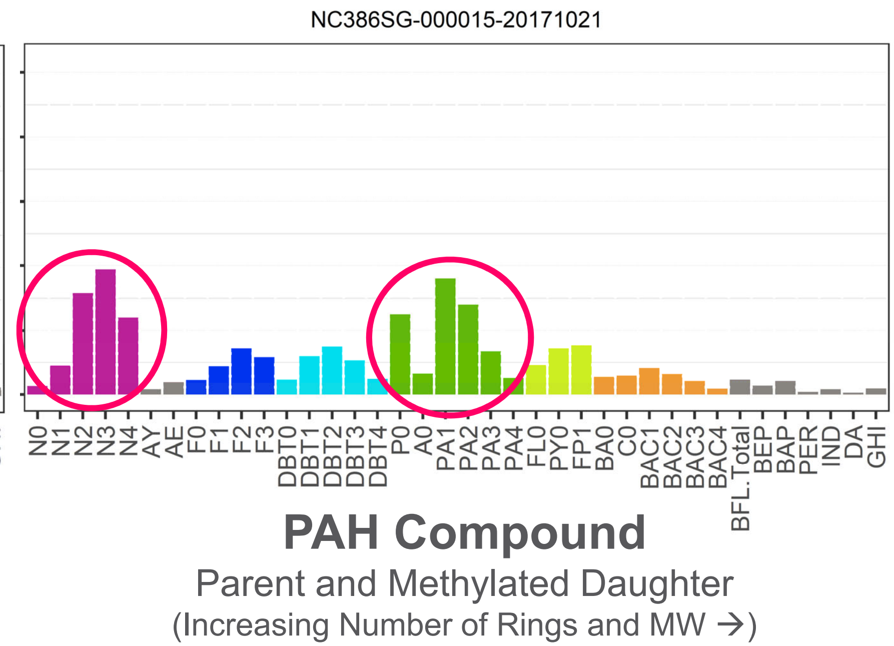
Gowanus Canal Surface Sediments

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

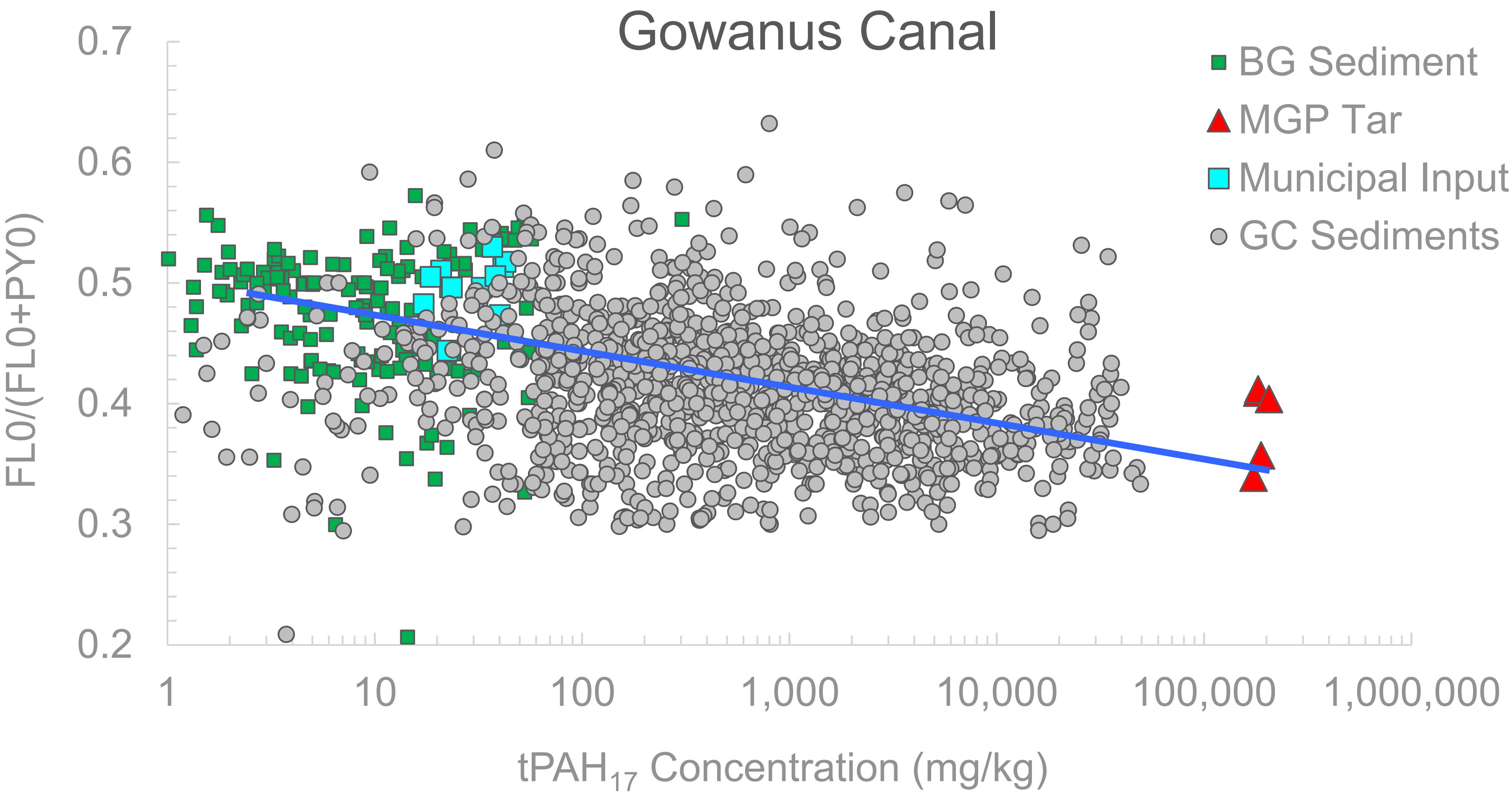


Newtown Creek Surface Sediments

No. of Rings per Molecule = 2.9
PAH_{17} = 1,400 mg/kg

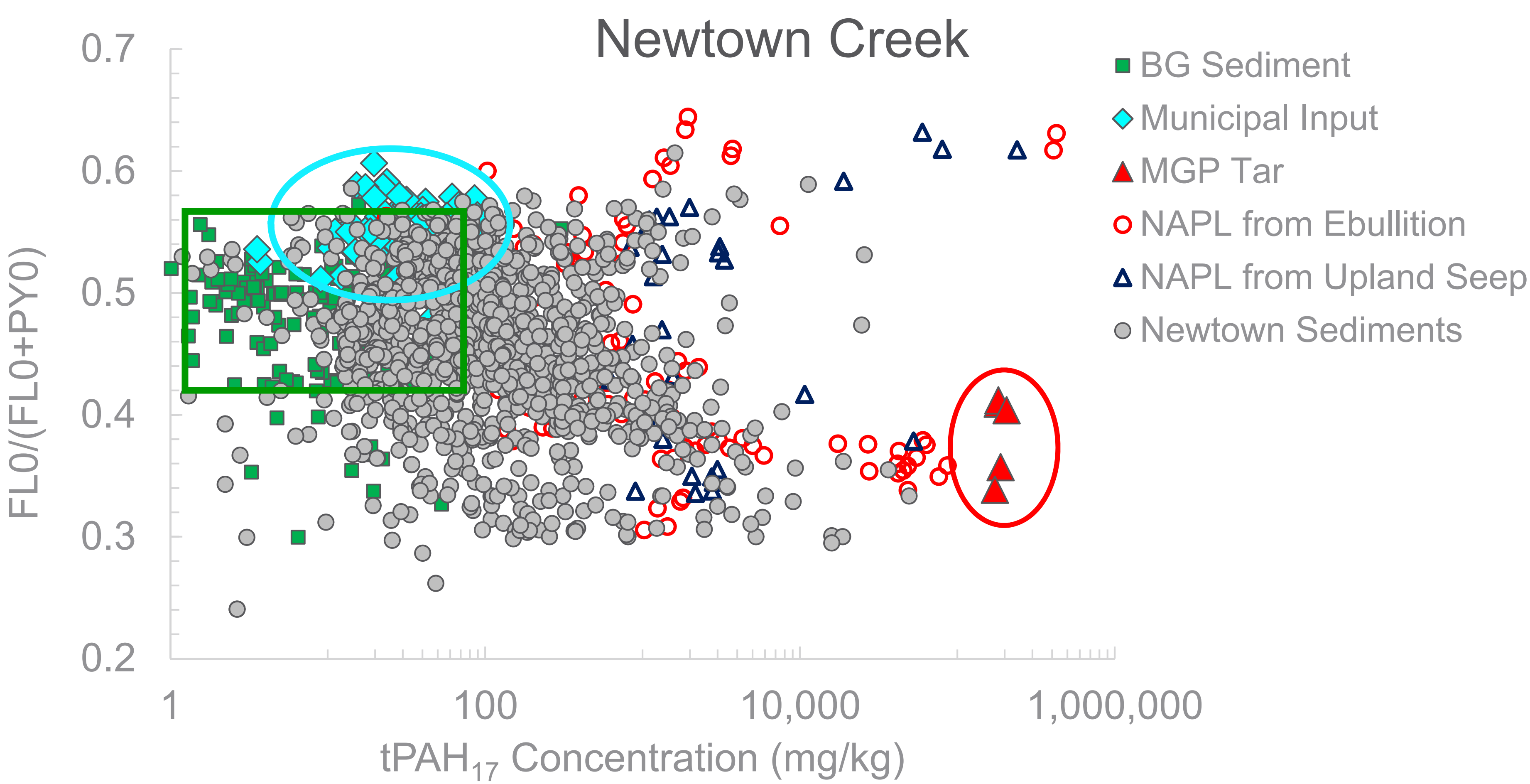


PAH Source Ratio



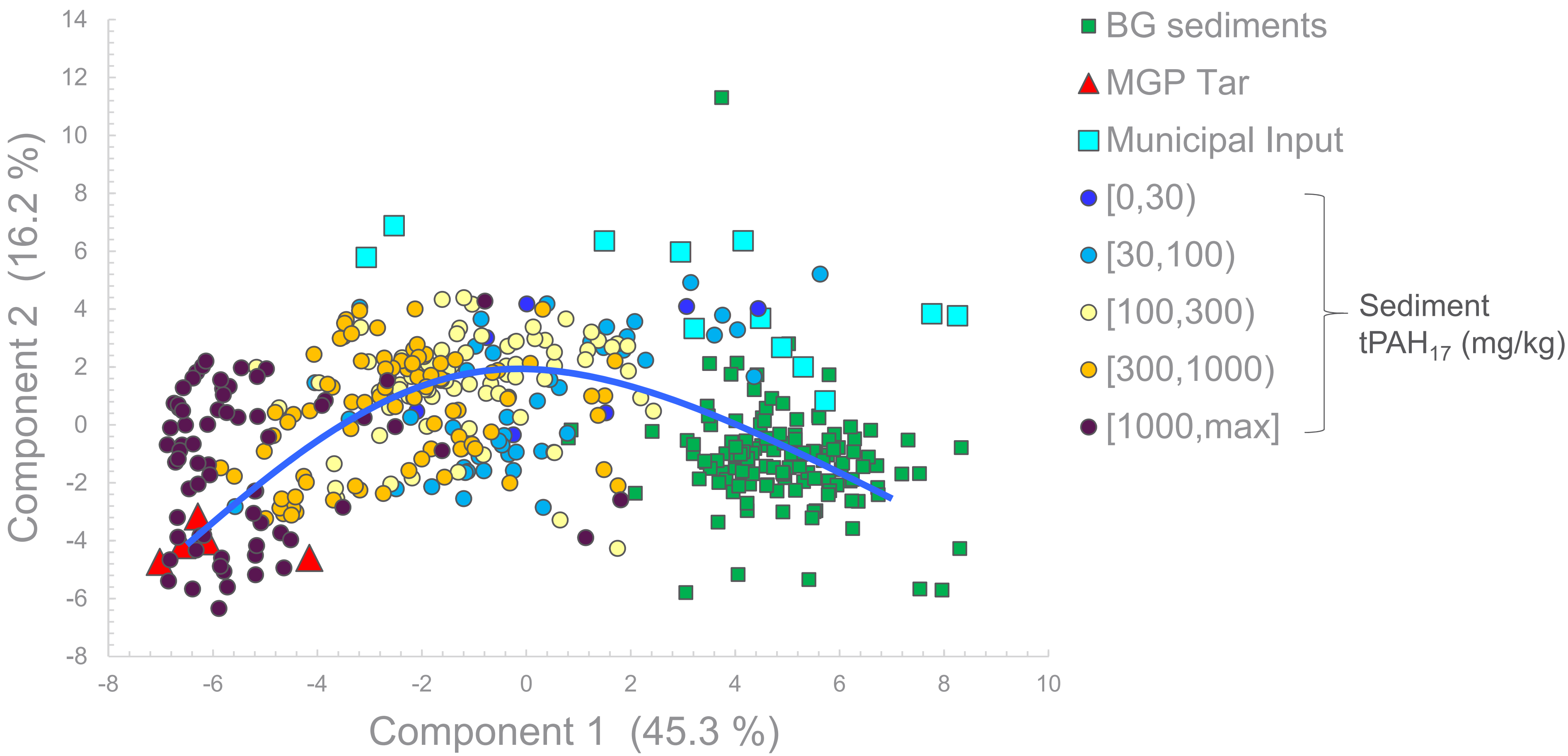
Gowanus Canal
BG Sediment
MGP Tar
Municipal Input
GC Sediments
0.7
0.6
0.5
0.4
0.3
0.2
FL0/(FL0+PY0)
1
10
100
1,000
10,000
100,000
1,000,000
tPAH17 Concentration (mg/kg)

FL0/(FL0+PY0)

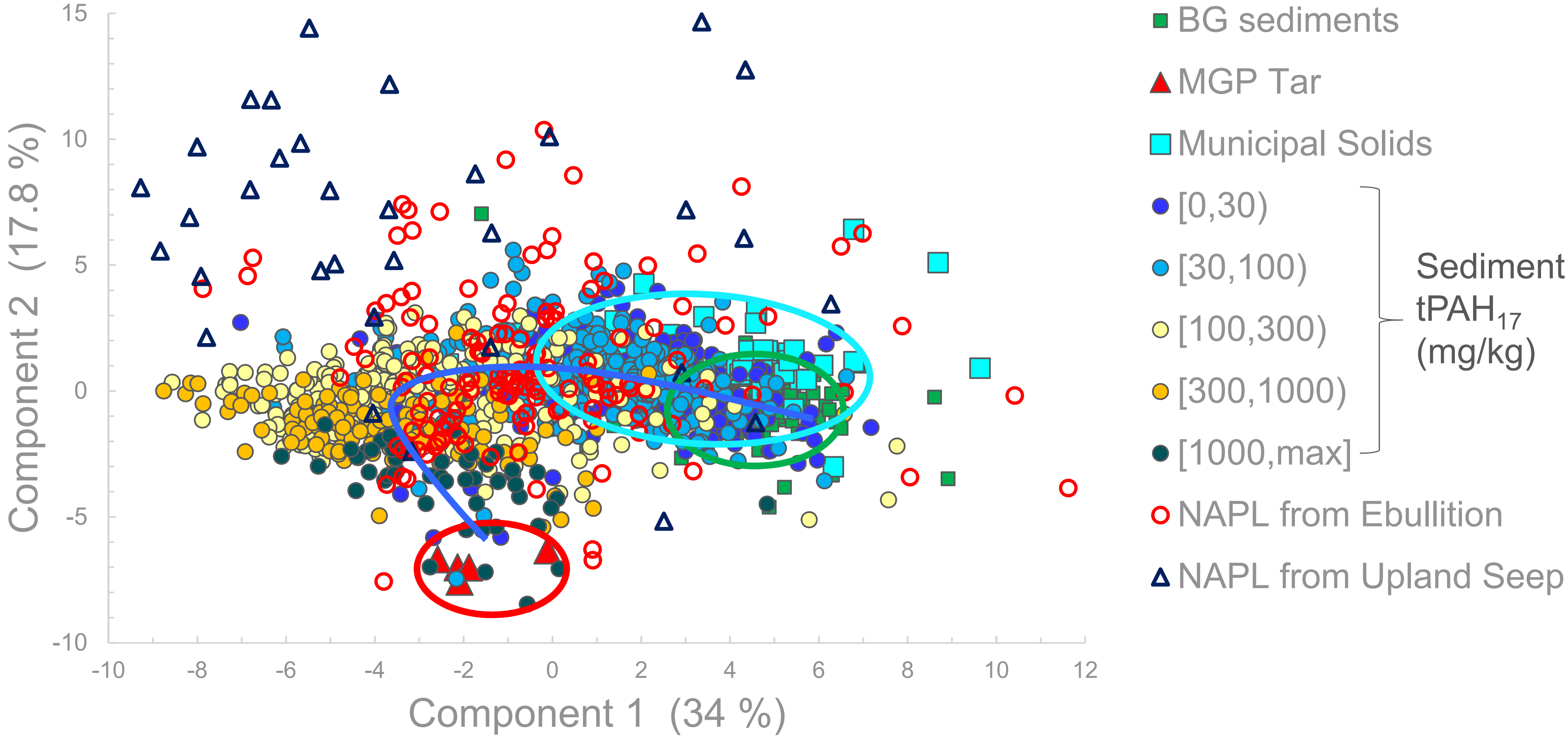

Newtown Creek
0.7
0.6
0.5
0.4
0.3
0.2
FL0/(FL0+PY0)
1
100
10,000
1,000,000
tPAH17 Concentration (mg/kg)
BG Sediment
Municipal Input
MGP Tar
NAPL from Ebullition
NAPL from Upland Seep
Newtown Sediments

FL0/(FL0+PY0)

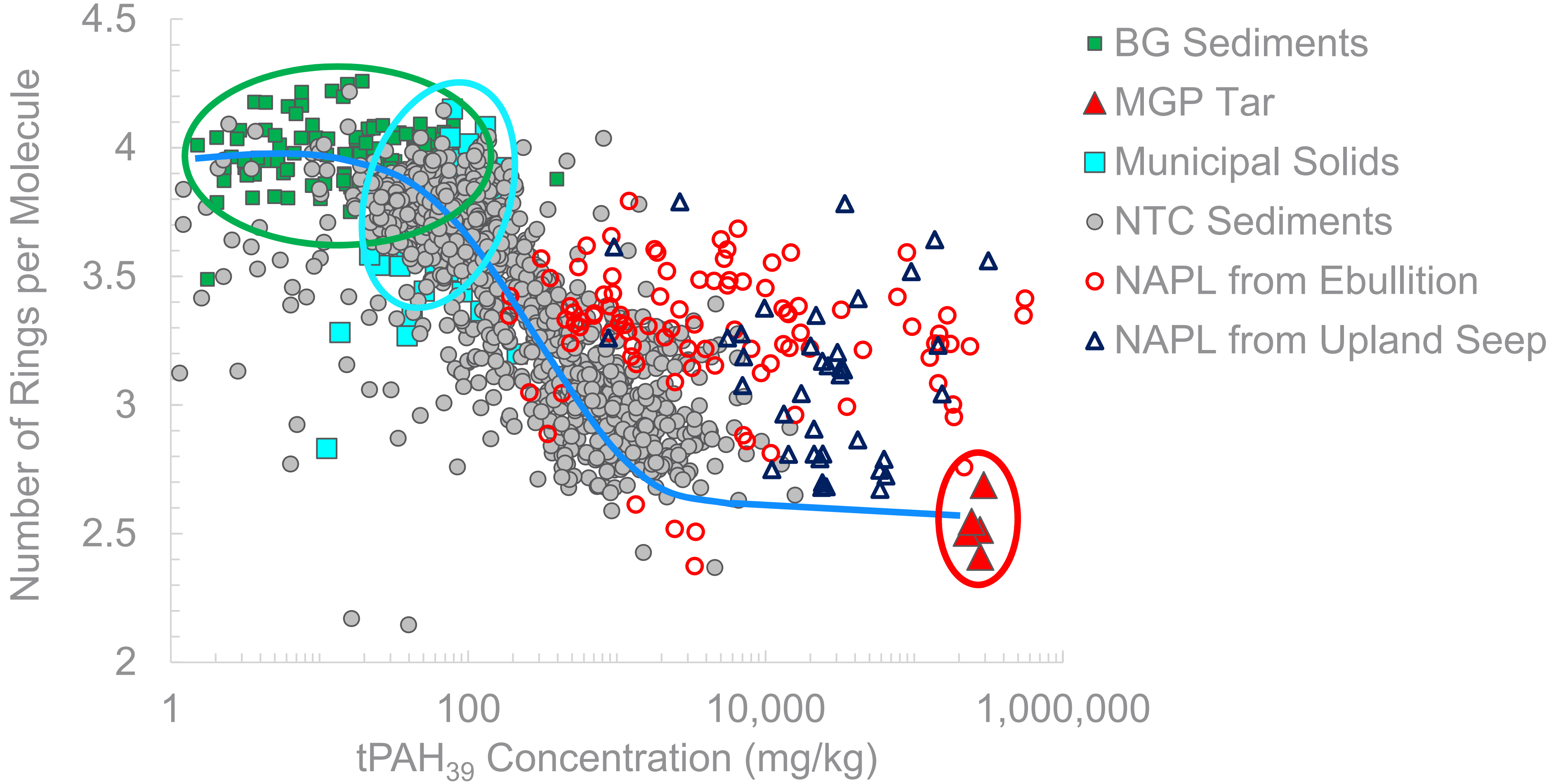
Principal Component Analysis



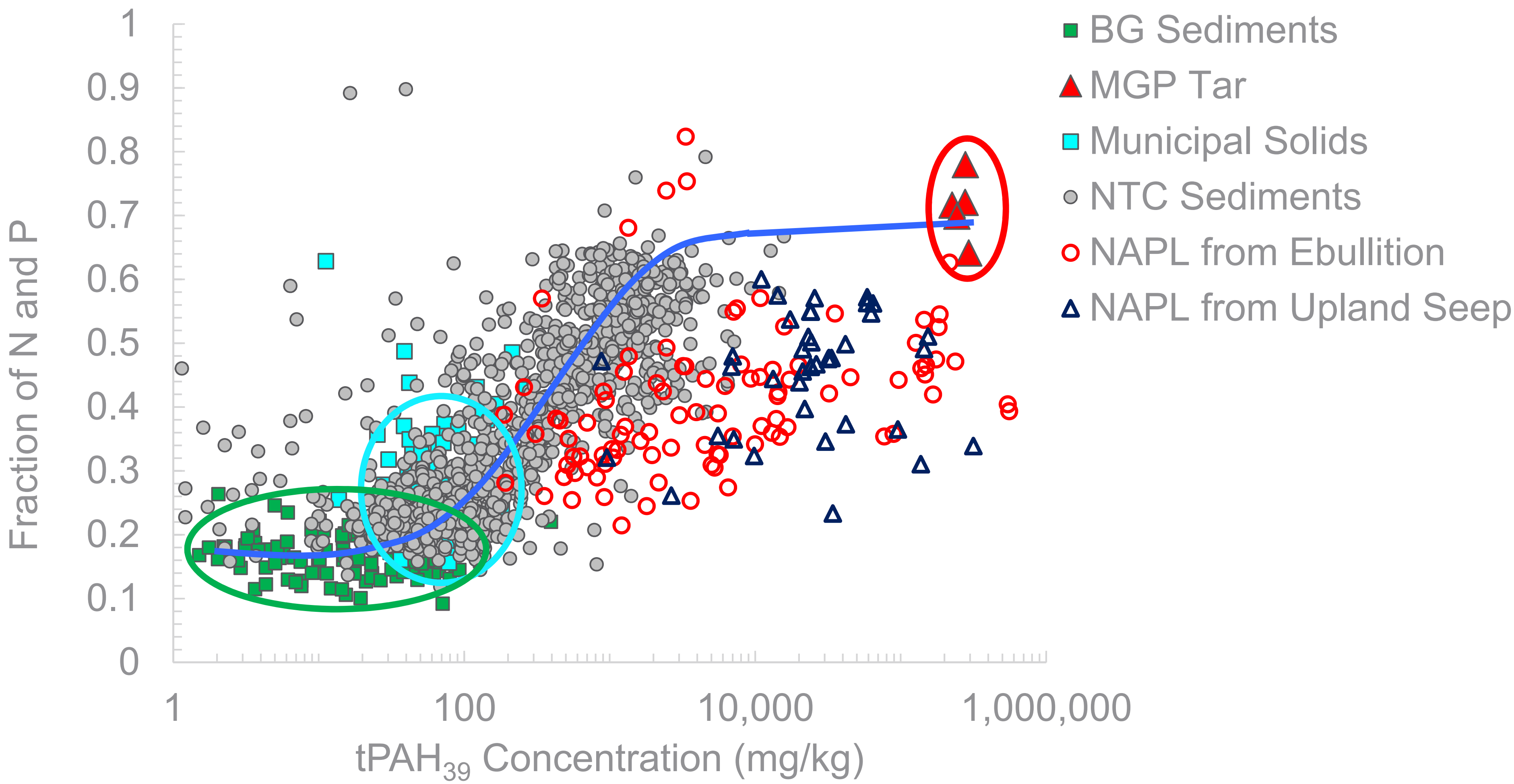
PCA Score Plot – Gowanus Canal



PCA Score Plot – Newtown Creek



PAH Composition vs. Concentration - Newtown



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.

Conclusions