PAH FINGERPRINT ANALYSIS OF THE SYDNEY TAR PONDS, SYDNEY HARBOUR AND THE SURROUNDING AREA

Devin MacAskill
Verschuren Centre
Cape Breton University
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Purpose/Hypothesis

Purpose – confirm correlation between Polycyclic Aromatic Hydrocarbons (PAHs) in the Sydney Tar Ponds with PAHs in the shallow sediments of the Sydney Harbour.

Hypothesis – If PAH Fingerprinting Techniques confirm similarities between PAH Fingerprints in shallow sediments of Sydney Harbour and the PAH Fingerprints in the Sydney Tar Ponds, then these PAH impacts share the same source of contamination.

Study Background

- The Sydney Tar Ponds contained an estimated 700,000 tonnes of contaminated sediments. Remediation by Solidification/Stabilization was completed 2009-2013.

- The Coke Ovens, part of the former Sydney Steel Plant, is considered the primary contributor of contamination to the Muggah Creek Watershed (later named the Tar Ponds).

- Polycyclic Aromatic Hydrocarbons (PAHs) are considered the primary contaminant of concern (COC) in the Sydney Tar Ponds.

- The study area includes the Sydney Tar Ponds, Coke Ovens, Sydney Harbour and off-site background locations.

Sydney Steel and Coke Ovens

- C. 1960s
- Coke is produced by thermal treatment of coal and had several uses at the plant.
- Coking process creates coal tar as one of many by-products.
- Coal tar was discharged into Coke Ovens Brook, flowing into the Muggah Creek estuary.

Sydney Tar Ponds 2008

Sydney Tar Ponds 2012

- 2 of 3 phases of remediation completed.
- Solidification/ Stabilization using cement to immobilize contaminants in place.

STPA Environmental Effects Monitoring (EEM) Program – Dillon Consulting

- Environmental monitoring during remediation 2009-2013 to assess environmental impacts due to the remediation (e.g., impacts to Sydney Harbour).

- Scope did not include source apportionment study, so we could not confirm that PAHs in found in the Harbour were from the Tar Ponds. This became the driver for this study.

- Results from the EEM used in this study include
  - Sydney Harbour Sediments
  - Upstream Tributary Sediments
  - Coal Pier Sediments

Historic and Reference Data

Previous studies were referenced for:

- Tar Ponds Sediment (North and South Pond)
- Off-site Urban Shallow Soil

ASTM regulatory publication:

- Coal Tar Standard PAH Reference Material

Study Data Set

- 52 soil and sediment sample results with 19 PAH parameters for each sample.

Acenaphthene
Acenaphthylene
Anthracene
Benzo[a]anthracene
Benzo[a]pyrene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[ghi]perylene
Chrysene
Dibenzo[a,h]anthracene
Fluoranthene
Fluorene
Indeno[1,2,3-cd]pyrene
1-Methylnaphthalene
2-Methylnaphthalene
Naphthalene
Perylene
Phenanthrene
Pyrene

- Predominantly detectable PAH concentrations;
- Temporal and spatial coverage;
- Upstream Sediments, Urban Background Soils, Tar Ponds Sediments, Harbour Sediments, Coal Sediments.

Use of Non-Detect Data

- Some results include some PAH parameter concentrations below laboratory detection limits (e.g. <0.01 µg/g).
- A detailed assessment of the non-detect data was conducted using the Robust Method (Helsel, 1990).

Mean Concentrations	Cadmium	Chromium	Copper	Lead	Zinc	Acenaphthene	Acenaphthylene	Anthracene
Robust Method	0.57	39.14	367.30	34.02	444.50	0.049	0.031	0.037
ND=1/2 RDL	0.56	39.14	365.67	33.96	441.25	0.049	0.031	0.037
Exclude NDs	0.83	52.87	428.09	58.28	500.37	0.052	0.038	0.044
ND=Zero	0.53	38.01	364.41	31.79	438.34	0.048	0.030	0.036
ND=RDL	0.59	40.26	366.49	36.14	444.16	0.049	0.032	0.038

Data Normalization

Data normalized to remove bias due to varying concentrations.

In order to consider how the molecular weights of PAH parameters can affect the distributions, Molar Fractions (% of Total Moles) for each PAH result were calculated.

Molar Fraction is how much of the total moles of PAH is contributed by a given PAH (e.g., 69% of the total PAH moles is Napthalene).

All PAH results become relative numbers between 0.0 and 1.0, as relative contributions to the Total PAH in a sample.

Fingerprint Methods

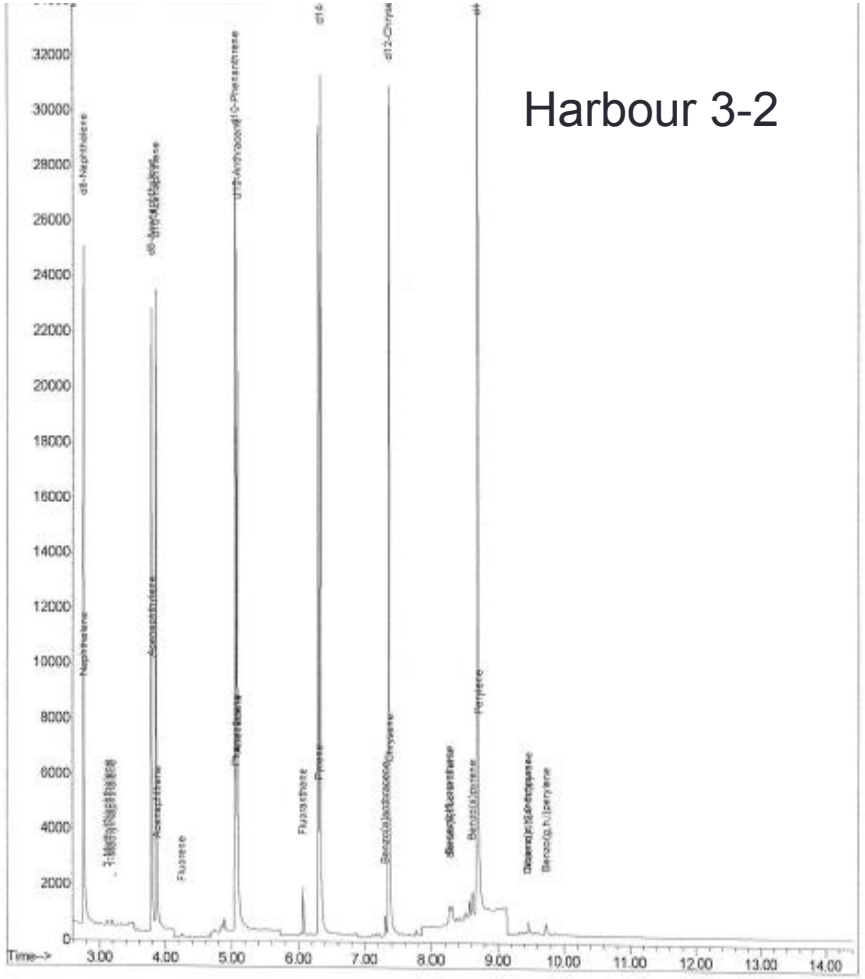
- Chromatograms
- Histograms
- Pearson Correlation Analysis
- Principal Component Analysis
- Diagnostic Ratios
- Mann-Whitney Non-Parametric Test

Results

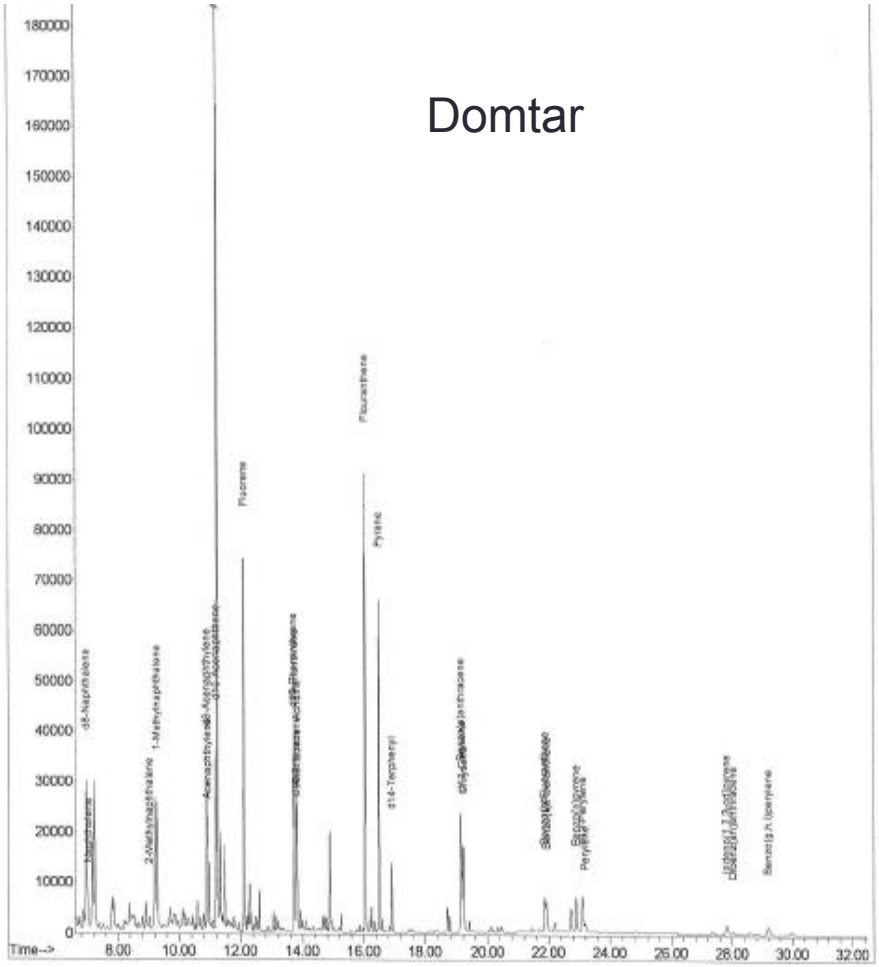
Chromatograms

Note: Chromatograms were not available for historical data.

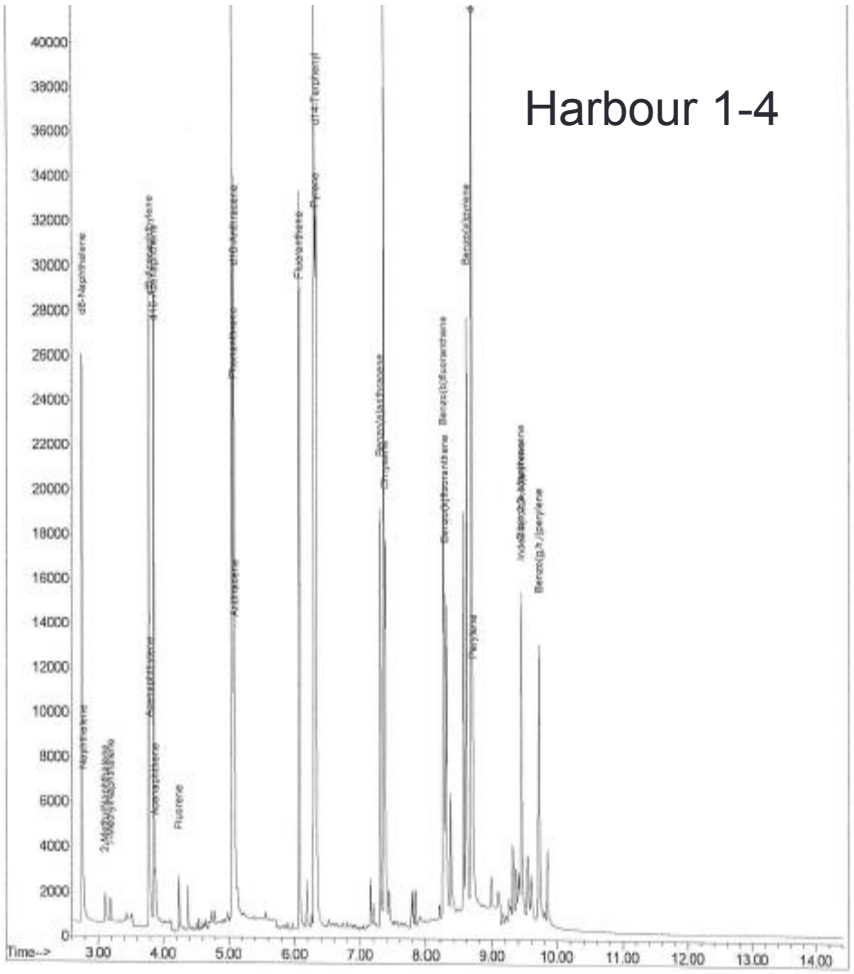
Harbour 3-2

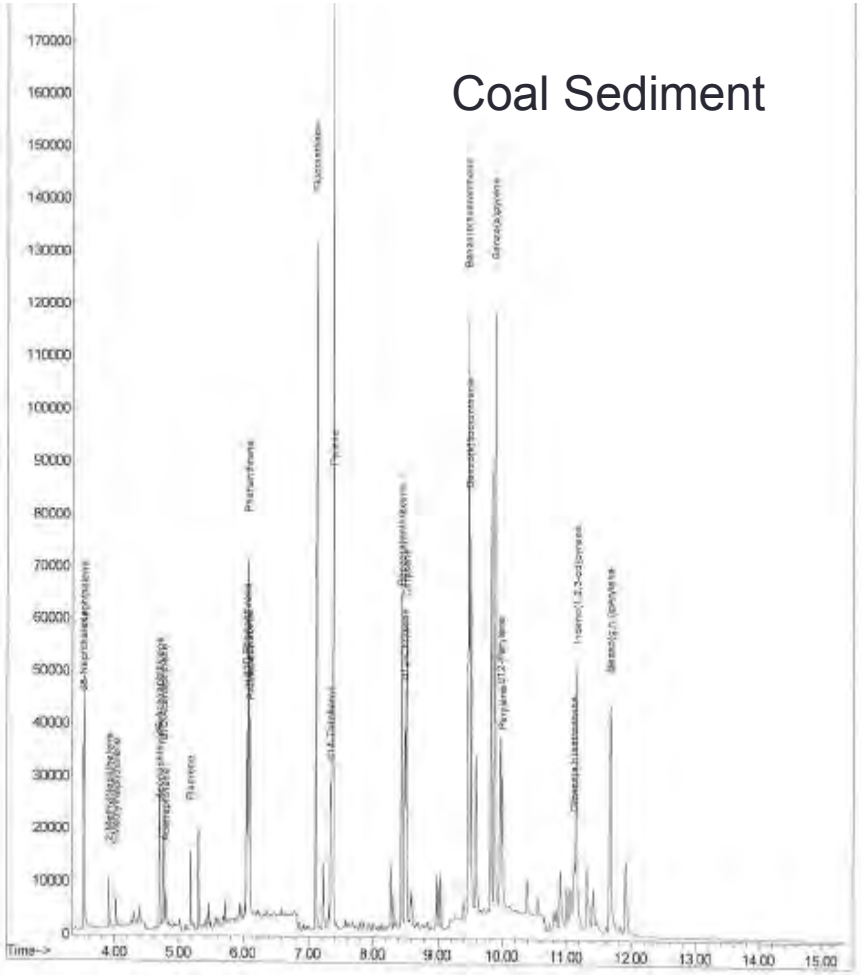


Domtar

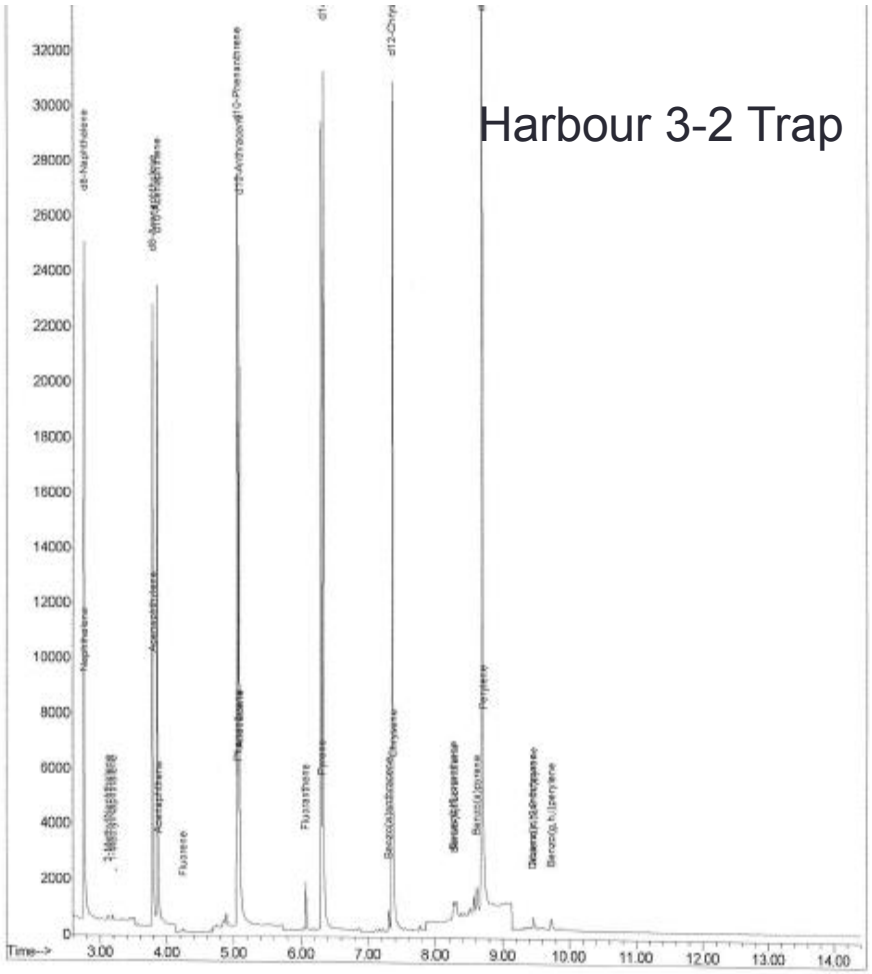


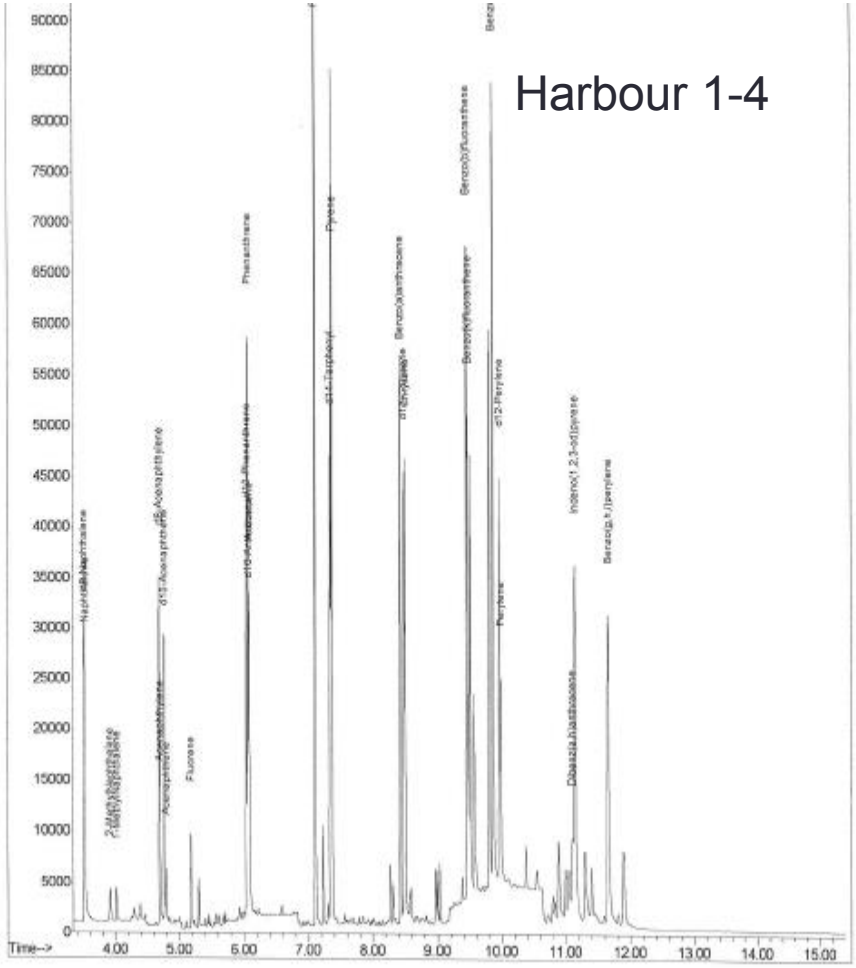
Chromatograms





Chromatograms



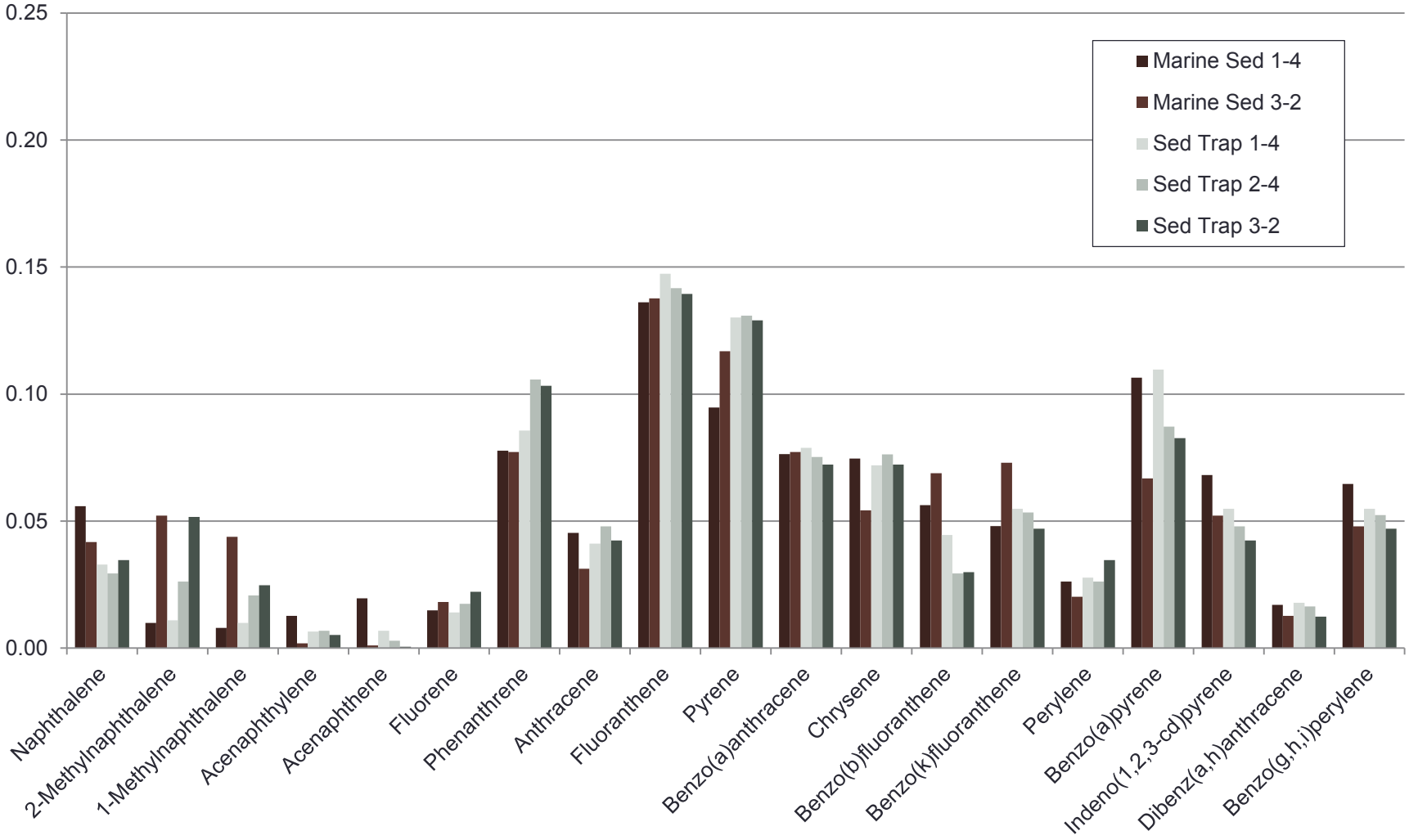


Histograms

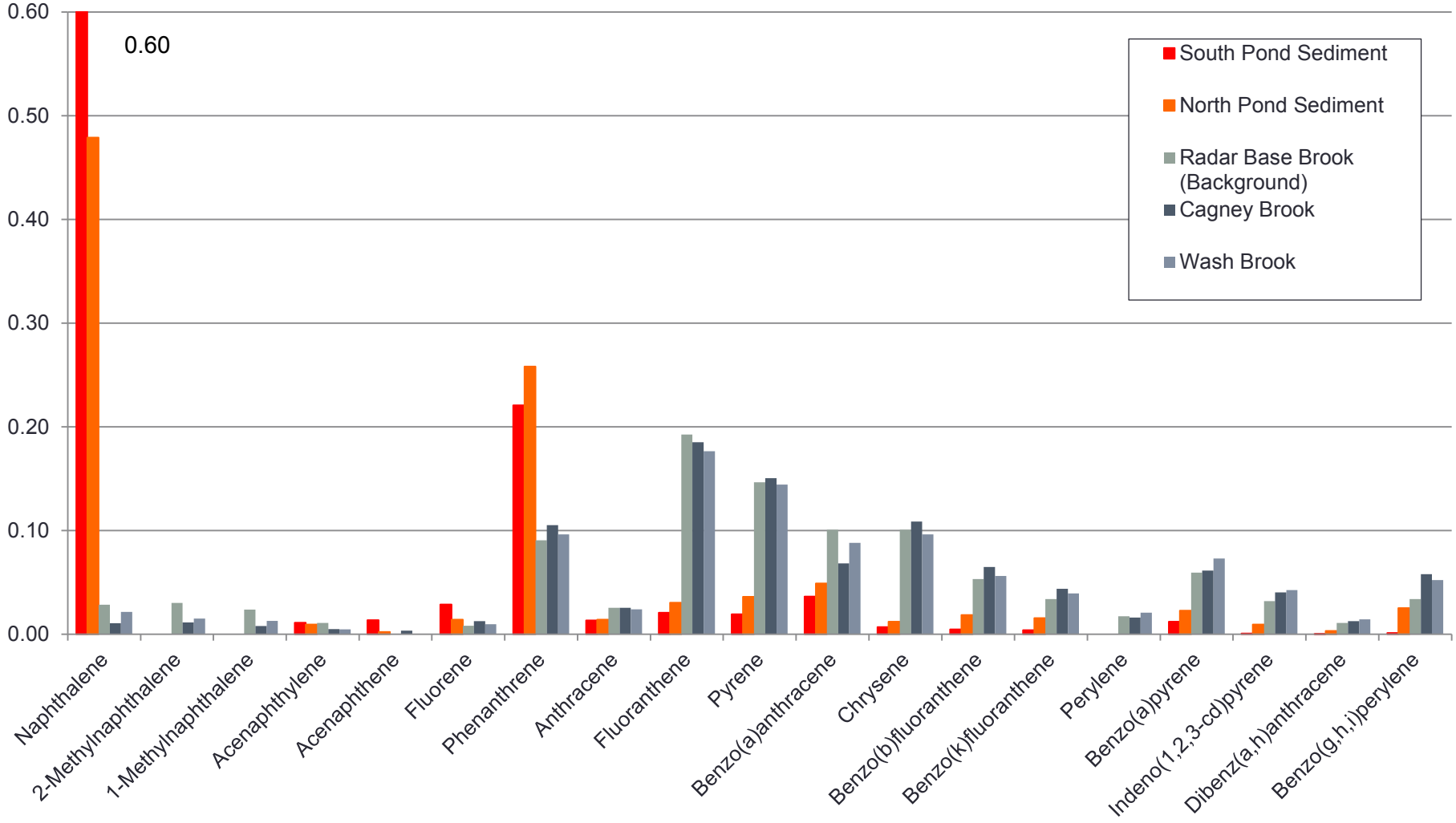
The following histograms have been prepared in several combinations:

- Tar Ponds Sediment vs. Upstream Tributaries
- Tar Ponds Sediment vs. Harbour Sediment
- Harbour Sediments vs. Sediment Traps
- Tar Ponds Sediment vs. Coal Sediment
- Coal Sediments vs. Harbour Sediments

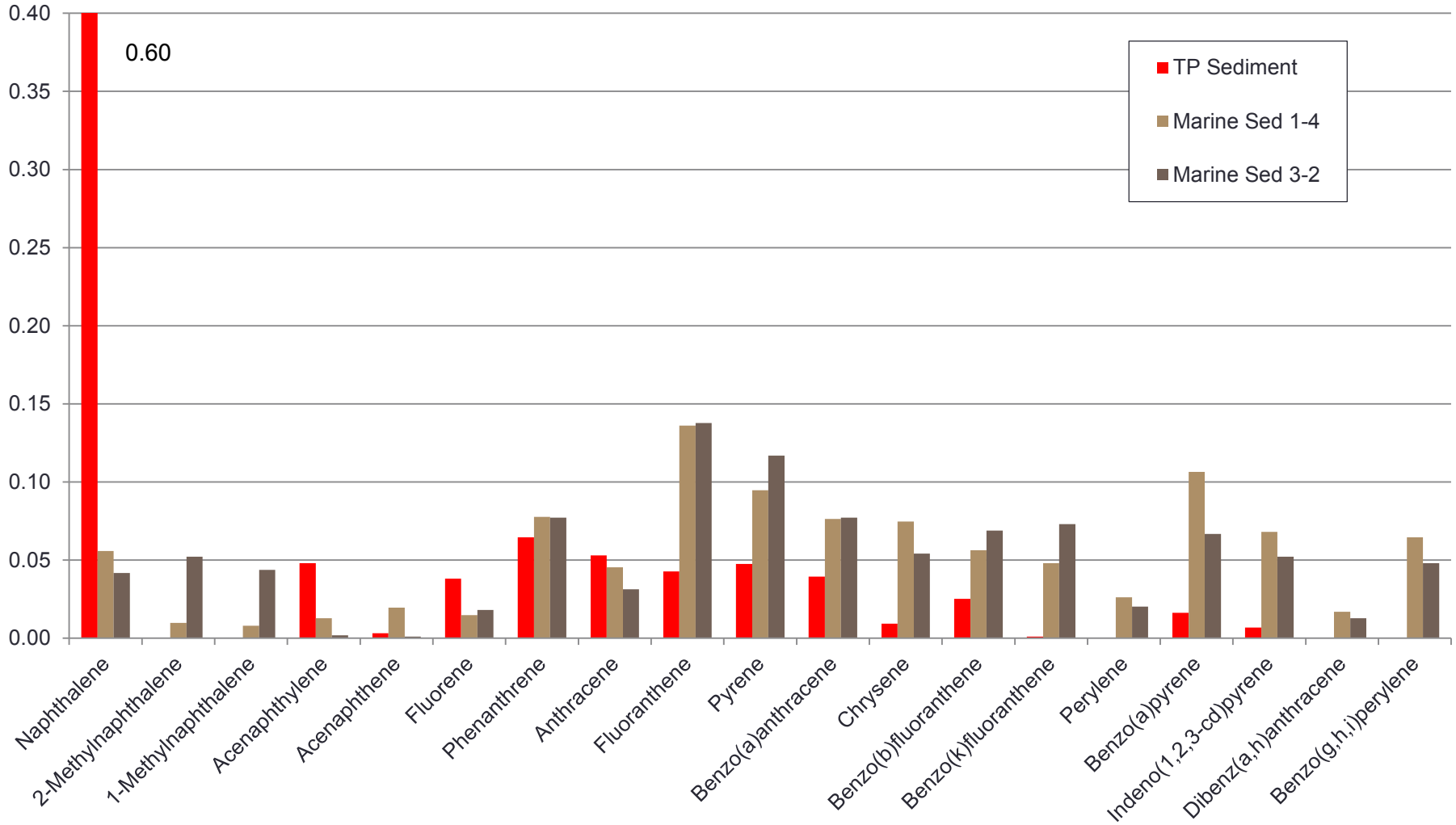
Harbour Sediment vs Sediment Traps



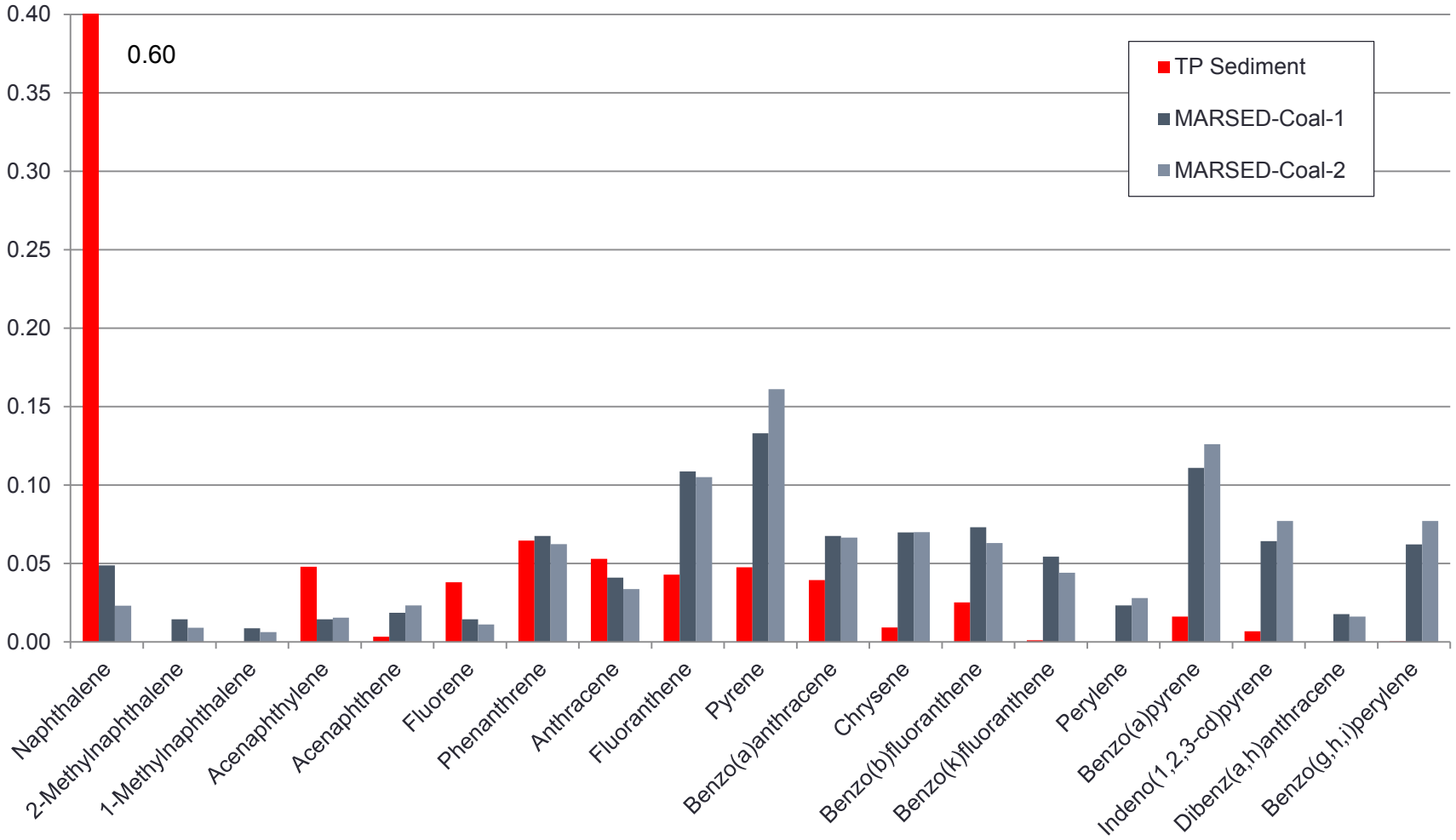
Tar Ponds vs Upstream Sediment



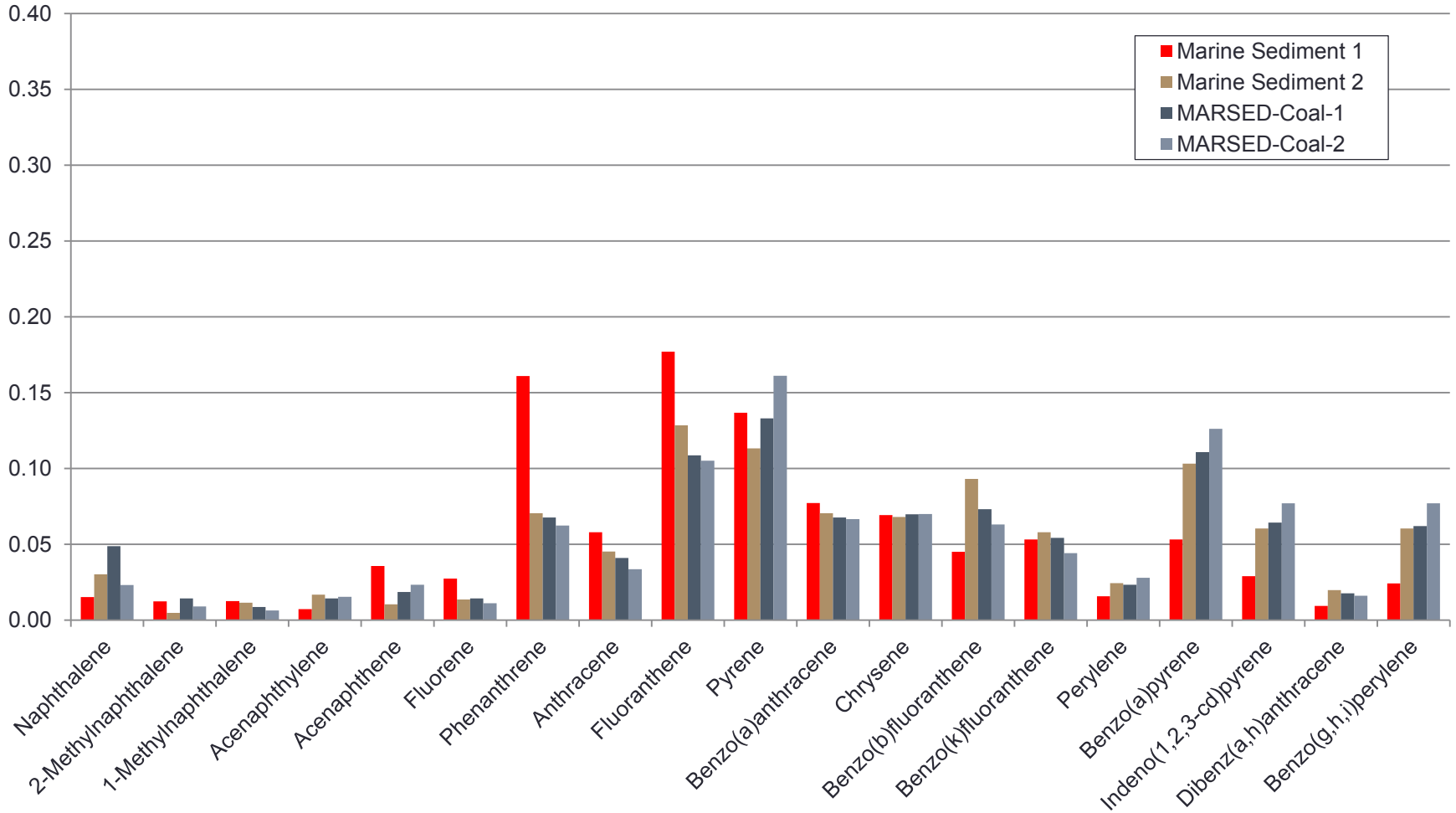
Tar Ponds vs. Harbour Sediments



Tar Ponds vs. Coal Pier Sediment



Coal Sediment vs. Harbor Sediment



Correlation Analysis

PAH Fingerprint relationships exhibiting high (>0.8) Pearson correlation coefficients (r):

- Tar Ponds Sediments (homogeneous)
- Harbour Sediments (homogeneous)
- Tar Pond Sediment / Standard Reference Material, confirming Coal Tar source of PAHs

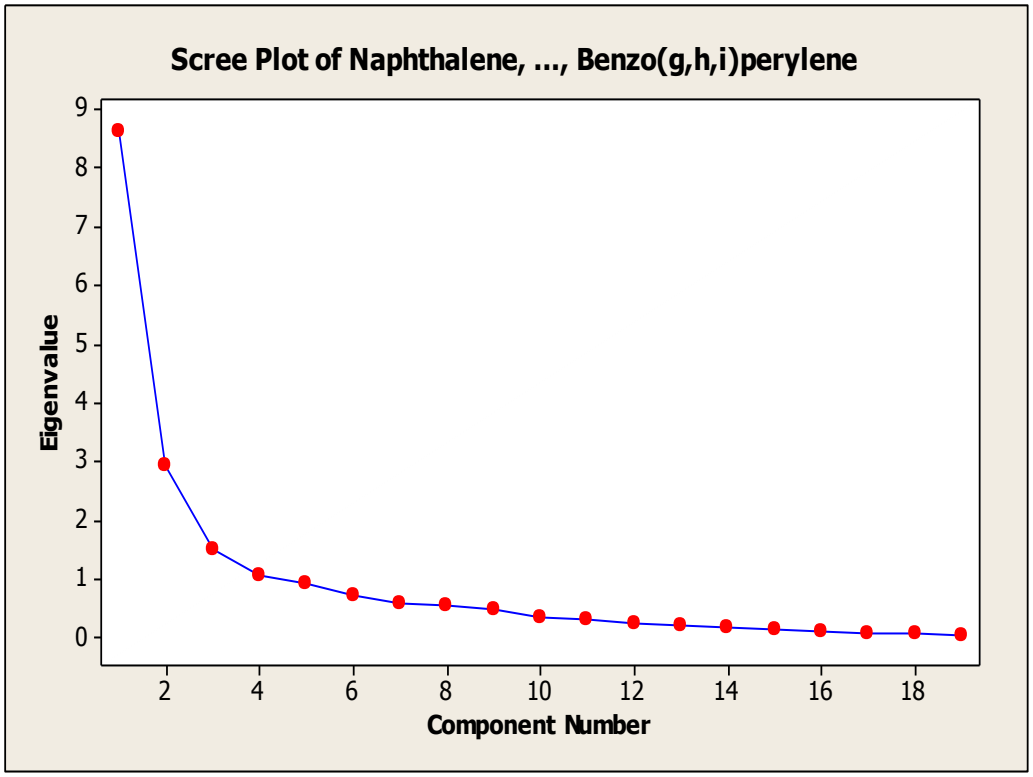
Relationships exhibiting very low correlation (<0.3) include:

- Coal Sediment / Coal Tar Standard Reference Material (PAHs in coal sediments are not derived from Coal Tar).
- Harbour Sediment / Tar Pond Sediment (PAHs in Harbour Sediments are not derived from they Sydney Tar Ponds).

Principal Component Analysis

- Transforms potentially correlated data into smaller, uncorrelated “principal components” for analyzing the structure of the data sets;
- Goal is to explain the maximum amount of variance with the fewest number of principal components (e.g., approx. 90% of variance);
- PCA identifies variables that express target conditions (e.g. similar PAH behaviour) and PCA may uncover unsuspected relationships.
- This PCA analysis included the 19 PAH parameters as the variables (X) with the 52 sample locations as predictors (Y).

Principal Component Analysis Scree Plot



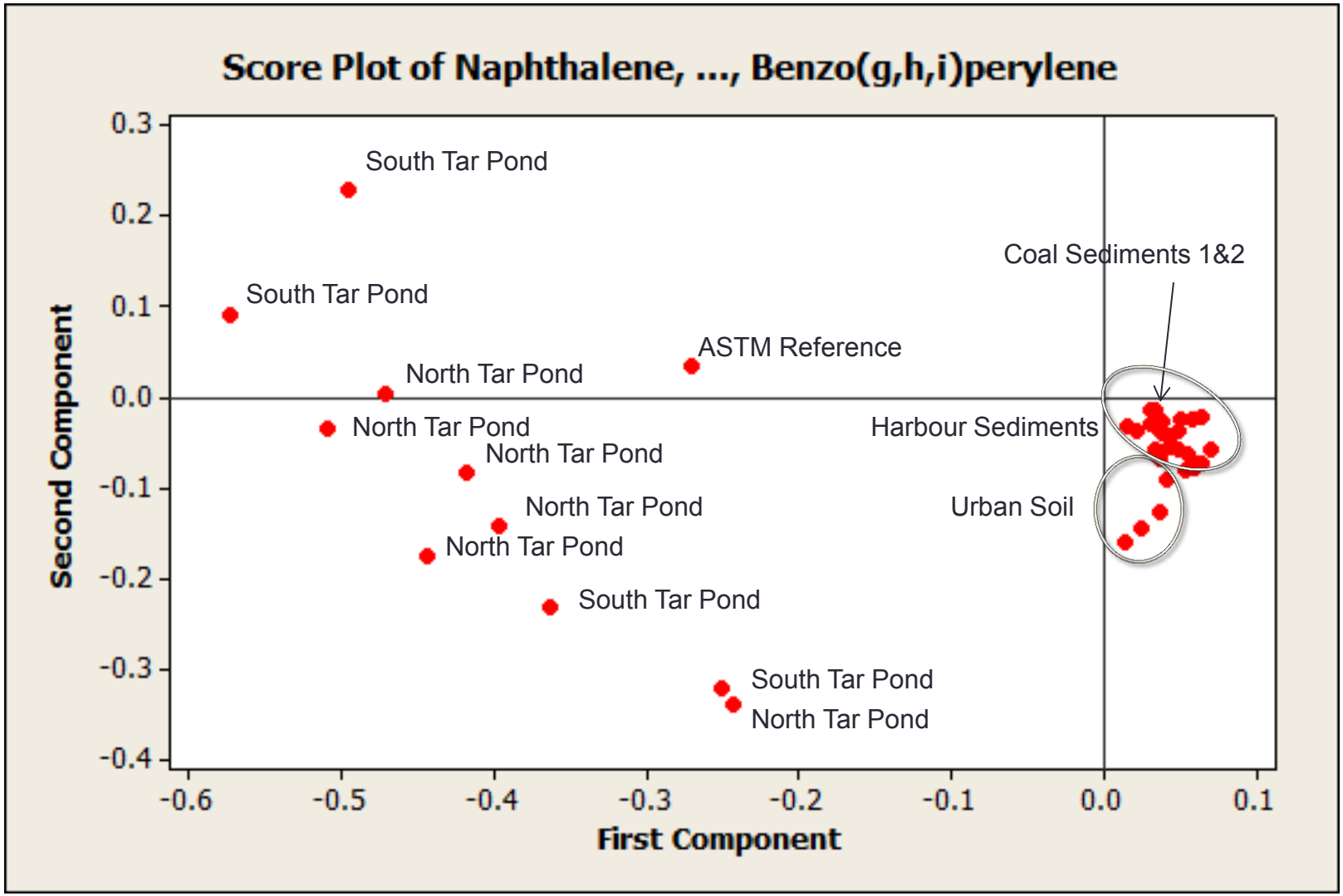
- 19 PAH parameters resulting in 19 PCs.
- The first two PCs account for 89% of the variance so these two PCs become the focus.

Principal Component Analysis Variable Loading

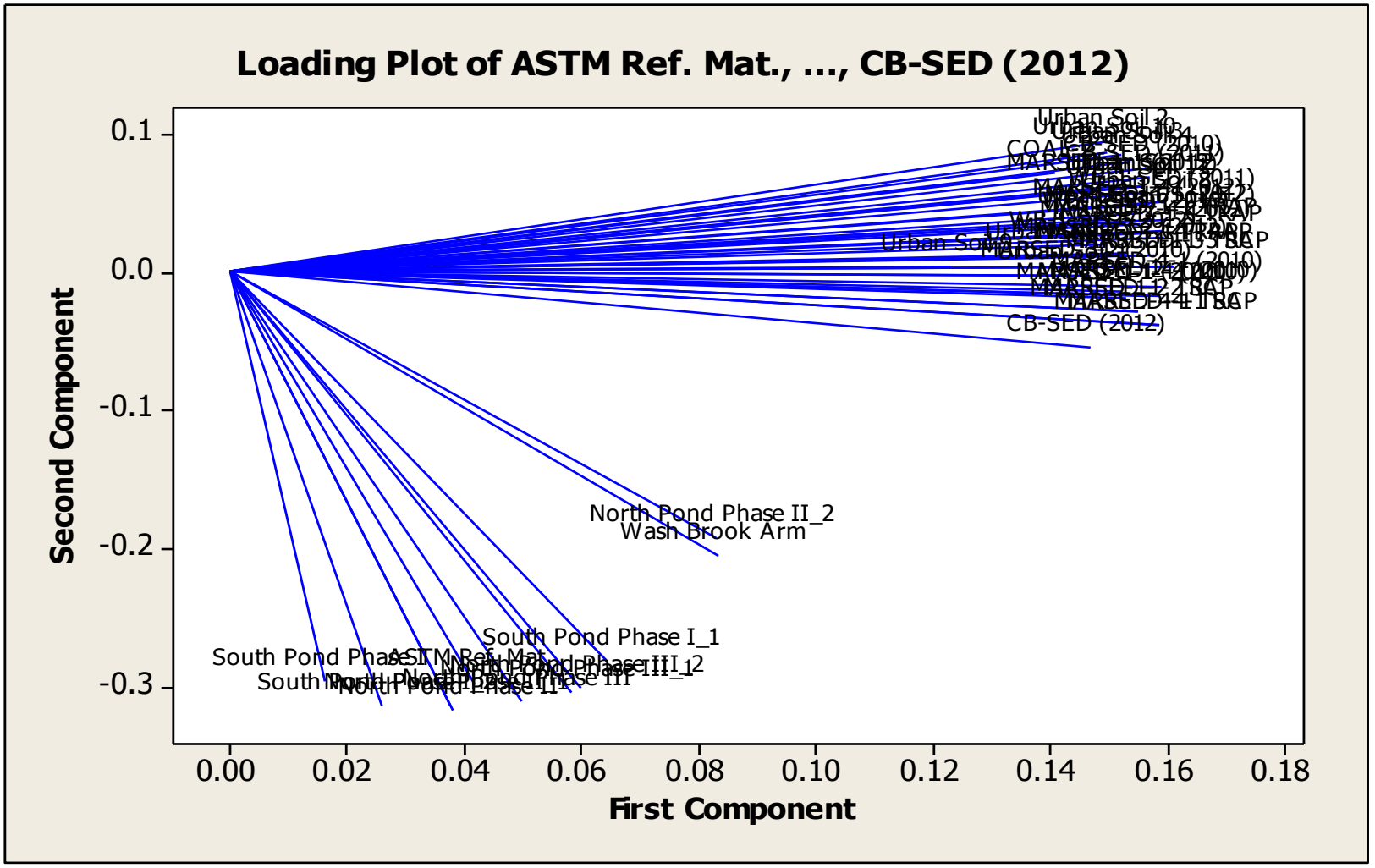
- PC1 is influenced primarily by samples other than Tar Ponds Sediments.
- PC2 is influenced primarily by Tar Ponds Sediments

Variable	PC1	PC2	PC3	PC4
ASTM Ref. Mat.	0.042	-0.297	-0.111	-0.034
Wash Brook Arm	0.083	-0.205	0.343	0.035
South Pond Phase I	0.016	-0.296	-0.218	0.031
South Pond Phase I_1	0.064	-0.283	0.189	0.030
South Pond Phase I_2	0.026	-0.314	-0.122	0.015
North Pond Phase II	0.038	-0.317	-0.036	0.016
North Pond Phase II_1	0.038	-0.315	-0.076	0.021
North Pond Phase II_2	0.083	-0.193	0.360	0.038
North Pond Phase III	0.050	-0.312	0.003	0.023
North Pond Phase III_1	0.058	-0.304	0.065	0.025
North Pond Phase III_2	0.060	-0.302	0.086	0.006
Urban Soil 1	0.143	-0.003	0.289	-0.004
Urban Soil 2	0.150	0.094	0.049	0.059
Urban Soil 3	0.152	0.085	0.016	-0.034
Urban Soil 4	0.154	0.081	0.018	-0.019
Urban Soil 5	0.160	0.038	0.016	0.047
Urban Soil 6	0.149	0.038	0.214	-0.025
Urban Soil 7	0.141	0.011	0.302	-0.035
Urban Soil 8	0.157	0.049	0.076	-0.051
Urban Soil 9	0.123	0.004	-0.176	-0.508
Urban Soil 10	0.150	0.087	0.061	0.074
Urban Soil 11	0.156	0.058	0.133	-0.011
Urban Soil 12	0.156	0.062	0.057	-0.083
Urban Soil 13	0.155	0.062	0.103	-0.022
MARSED-1-1 TRAP	0.159	0.030	-0.002	0.135
MARSED-1-2 TRAP	0.155	-0.029	-0.167	0.096
MARSED-1-3 TRAP	0.161	0.004	-0.106	0.048
MARSED-1-4 TRAP	0.159	0.025	-0.051	0.132
MARSED-2-4 TRAP	0.158	0.012	0.031	-0.025
MARSED-3-1 TRAP	0.155	0.012	-0.074	-0.243
MARSED-4-1 TRAP	0.159	-0.039	-0.057	-0.041
MARSED-1-1 (2010)	0.153	-0.018	-0.187	0.085
MARSED-1-1 (2012)	0.151	0.062	-0.107	0.236
MARSED 1-4 (2010)	0.156	-0.018	-0.129	0.089
MARSED-1-4 (2012)	0.156	0.043	-0.096	0.222
MARSED 2-4 (2010)	0.158	-0.016	-0.105	-0.103
MARSED-2-4 (2012)	0.157	0.028	0.067	0.112
MARSED-3-2 (2010)	0.147	-0.002	-0.110	-0.389
MARSED-3-2 (2012)	0.153	0.014	0.026	-0.131
MARSED-4-1 (2010)	0.159	-0.010	-0.132	0.000
MARSED-4-1 (2012)	0.158	0.038	-0.059	0.150
COAL-1	0.152	-0.014	-0.157	0.207
COAL-2	0.141	0.072	-0.112	0.255
MARSED-4-1 SC	0.159	-0.039	-0.057	-0.041
MARSED-1-3 SC	0.161	0.004	-0.106	0.048
MARSED-1-2 SC	0.155	-0.029	-0.167	0.096
WB-1-SED (2010)	0.155	0.035	0.092	-0.206
WB-1-SED (2011)	0.160	0.051	0.005	-0.037
WB-1-SED (2012)	0.150	0.020	0.226	0.017
CB-SED (2010)	0.157	0.075	0.046	0.041
CB-SED (2011)	0.157	0.069	0.046	-0.020
CB-SED (2012)	0.147	-0.055	-0.109	-0.316

Principal Component Analysis Score Plot



Principal Component Analysis Loading Plot



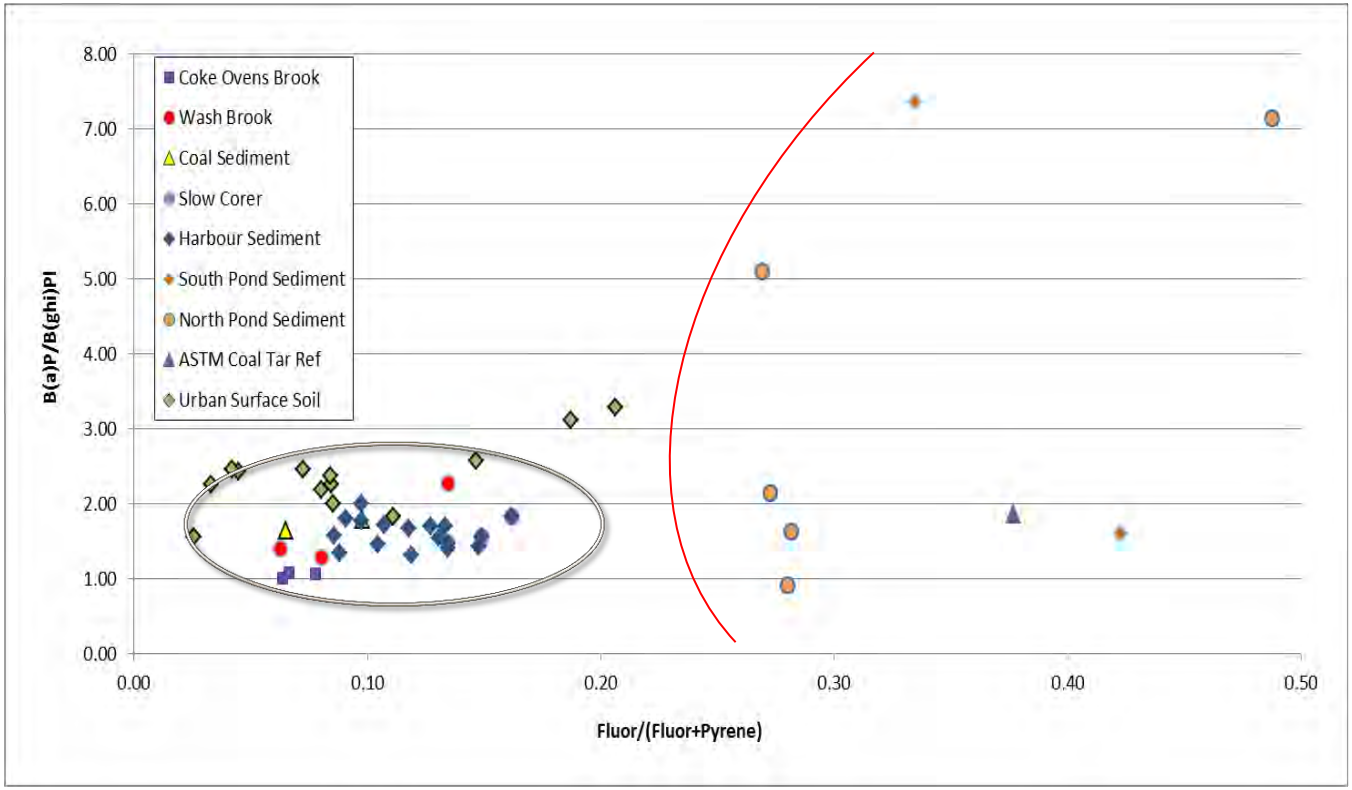
Diagnostic Ratios

- The following diagnostic ratios of PAH parameters were used to assess sample characteristics and relationships:
  - B(a)P/Benzo(g,h,i)perylene vs. Flour/(Fluor/Pyrene)
  - Flour/(Fluor/Pyrene) vs. (Ideno(1,2,3)/(Ideno(1,2,3)+ Benzo(g,h,i)perylene)
  - Fluoranthene/Pyrene vs. B(a)A / B(a)P
  - Fluoranthene/Pyrene vs. B(a)A / Chrysene
  - Fluoranthene/Pyrene vs. Chrysene / B(a)P
  - Anthracene/(Anthracene+Phenanthrene) vs. B(a)A/(B(a)A+Chrysene)
  - Fluoranthene / Pyrene vs. Phenanthrene / Anthracene

Diagnostic Ratios

- Tar Ponds Sediments and Coal Tar Reference Material are clearly higher in Fluoranthene / (Fluoranthene + Pyrene) ratios. This ratio suggests potential pyrogenic (combustion-related) sources for these PAH fingerprints.

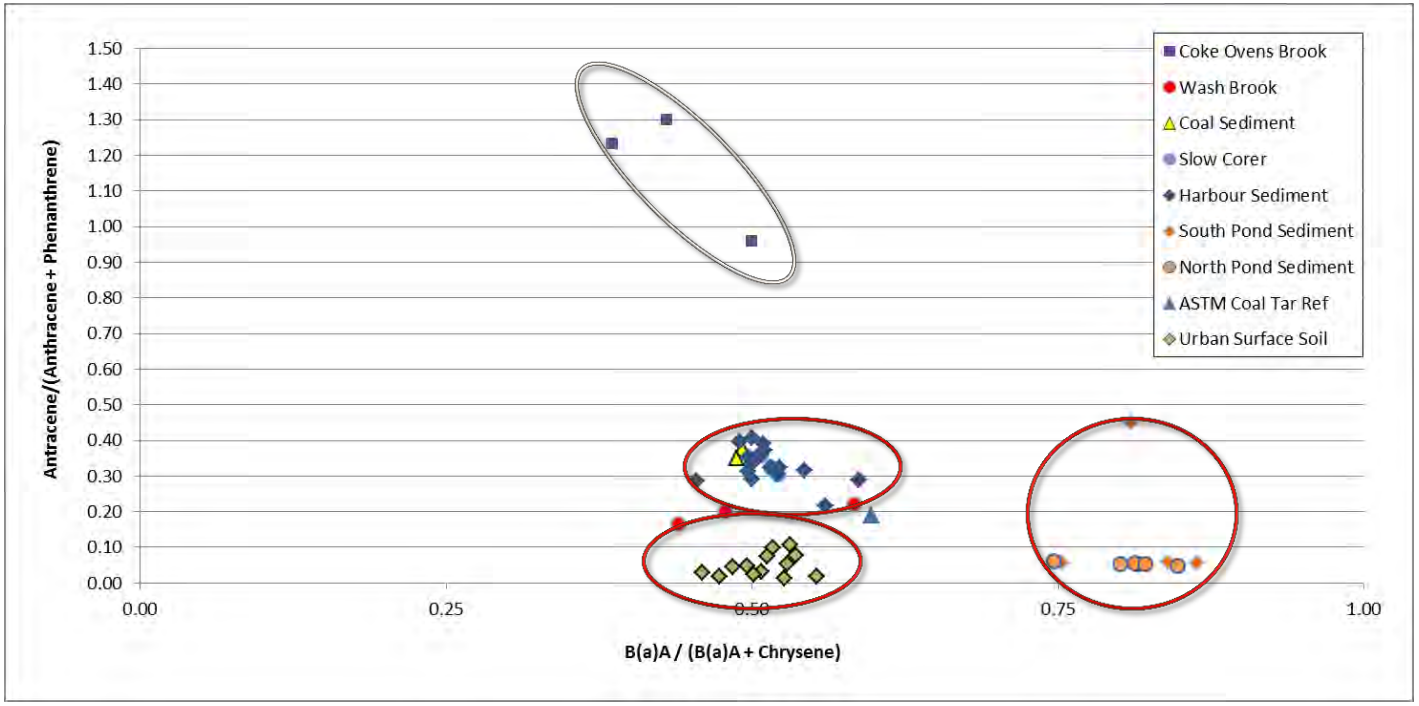
- Harbour Sediments, Urban Surface Soil and Coal Sediments are clearly clustered, suggesting a similar source for these PAH Fingerprints.



Diagnostic Ratios

- Tar Ponds sediments are higher in the B(a)A/(B(a)A + Chrysene) ratios, a good indicator of pyrogenic sources of PAH. Coke Ovens Brook sediments were noticeably higher in the Ant/(Ant+Phe) ratios, suggesting potential impacts of the municipal waste facility upstream not seen in other samples.

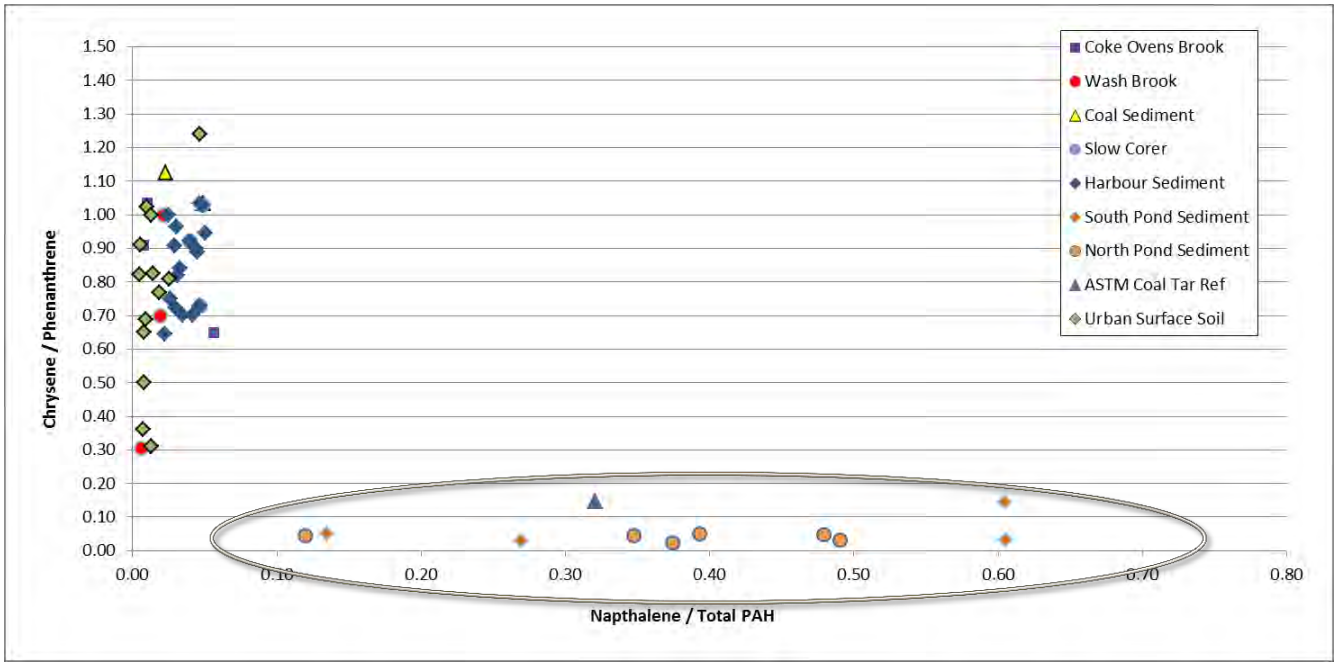
- Urban Soils and Harbour Sediments are closely clustered, with Coal Sediments plotted within Harbour Sediment results. This plotting indicates similar sources for the PAHs.



Diagnostic Ratios

- Chry / Phen ratios can be used as a weathering indicator. Here, Tar Ponds Sediments have lower values suggesting that the PAH in the Tar Ponds may be less weathered than the PAH found in other locations. This may be due to sampling techniques.

- Napthalene / Total PAH ratios vary widely in Tar Ponds Sediments samples, as compared to the small range of ratio values elsewhere in the study area. This suggests a predominance of light molecular weight PAHs in the Tar Ponds Sediments.



Non-Parametric Tests

The Mann-Whitney Non-Parametric Test determines if two population medians are equal. This would indicate similarities between sample PAH Fingerprints.

Non-parametric tests do not require populations (sample results) to maintain a normal distribution, but the test does include two assumptions:

- Populations of data have the same shape (e.g., we are looking for similar PAH parameter distributions); and,
- Populations are independent (e.g., the study sample data was collected across a large study area).

Mann-Whitney Results

Mann-Whitney Test and Tar Pond Sediment (North Pond), and Upstream Sediment (Wash Brook):

	N	Median
North Pond Phase II	19	0.0101
WB-1-SED	19	0.0314

Point estimate for ETA1-ETA2 is -0.0189
95.3 Percent CI for ETA1-ETA2 is (-0.0396,-0.0025)
W = 285.5
Test of ETA1 = ETA2 vs ETA1 not = ETA2 is significant at 0.0136
The test is significant at 0.0136 (adjusted for ties)

In this test, p<alpha(0.05). So I reject Ho and consider the populations (PAH Fingerprints) as significantly different.

Mann-Whitney Results

Harbour Sediments vs. Harbour Sediments

The MW test conducted between extreme locations (N and S) showed that the population medians are equal, meaning very similar PAH Fingerprints. This confirms a homogeneity in Harbour Sediments.

Tar Ponds Sediments vs. Coal Sediments

Four MW tests showed that the population medians (and PAH Fingerprints) were significantly different.

Harbour Sediment vs. Coal Sediments

Four MW tests were conducted using shallow sediment samples from throughout Sydney Harbour. Results were the same, the population medians were found to be equal, indicating similar PAH Fingerprints for the Harbour Sediments and Coal Sediments.

Conclusions

- Chromatograms
  - Difficult to compare and overall, inconclusive.
- Histograms
  - PAH profiles similar throughout Harbour Sediments.
  - PAHs in they Sydney Tar Ponds are derived from Coal Tar.
  - Harbour Sediments profile very similar to Coal Sediment profile and other samples that may have been impacted by coal.

Conclusions

- Correlation Analysis
  - Confirm homogeneity of Tar Ponds and Harbour Sediments.
  - Tar Ponds Sediments did not correlate with any other samples.
  - Harbour Sediments highly correlated (>0.8) with Coal Sediments.
- Principal Component Analysis
  - No single sample dominates loadings.
  - PC2 is dominated by Tar Ponds Sediment variables.
  - PC1 is dominated by all other environmental samples.
  - Loading patterns indicate relationships between all samples except the Tar Ponds.

Conclusions

- Diagnostic Ratios
  - Harbour Sediments clustered with Coal Sediments, Upstream Sediments and Urban Soils.
  - Tar Ponds Sediment ratios plot separately from Harbour Sediments suggesting another source of these PAHs (i.e. coal).
- Mann-Whitney Non-Parametric Test
  - Similar Fingerprints were identified for Upstream Sediments, Coal Sediments and Harbour Sediments.
  - Dissimilar Fingerprints were identified for Tar Ponds Sediments and all other samples (with the exception of the Reference Material).

Discussion

Results suggest PAHs found in shallow Sydney Harbour Sediments are not derived from the same source as the Sydney Tar Ponds Sediments.

This means that PAHs deposited in Sydney Harbour during the remediation of the Sydney Tar Ponds are not related to releases from the remediation project site.

Based on this analysis of PAH Fingerprints, coal related sediments are the source of PAHs in shallow Sydney Harbour Sediments.

Continuing Research

- Identify distinct coal types handled in the vicinity of the project site (e.g., domestic and foreign), conduct a PAH Fingerprint Analysis and compare the results to this study.
- Explore the potential effects of PAH weathering on this type of study.
- Conduct the same Fingerprint Analyses using groundwater and surface water to identify relationships.

Acknowledgements

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Thank you

Devin MacAskill
Verschuren Centre
Cape Breton University
devin_macaskill@cbu.ca
(902)563-1386