Use of Chemometrics in Support of PAH Allocation in Sediments at Former MGP Sites

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Summary

In most cases, the allocation of remediation costs for polycyclic aromatic hydrocarbons (PAHs) in urban sediment is at least partially based on identification of PAH sources and estimates of the contribution of each source at each location. This is frequently attempted using one of several source apportionment models. However, urban sediment is complex and PAH allocation can be difficult to achieve with confidence. Regardless, for sites with mixed impacts, such as urban sediments near former MGP sites, the ultimate goal is always to determine the amount of each source in each sample with some known level of confidence.

Principal components analysis (PCA) was performed using data from a former MGP site and adjacent sediment samples. The effects of PAH weathering and laboratory biases on the estimated numbers of sources was examined. Subsequently, the PAH composition of the underlying sources and the percent contribution of each source were estimated using polytopic vector analysis (PVA).

Site Conditions and Methods

- MGP site in an urban area near a canal
- Small upstream tar storage and refining plant (short-lived)
- NAPL seeps observed in the shoreline near the MGP
- PAHs detected upstream, downstream, and adjacent to the MGP
- Other potential PAH sources identified including petroleum storage, various commercial operations, and storm water discharges

> - 3 NAPL samples from monitoring wells at the MGP
> - 17 sediment samples from canal
> - 28 soil samples from MGP site and tar processing site
> - Samples were analyzed for:
>   - GC/FID fingerprint
>   - PAHs/Alkylated PAHs by GC/MS

The samples were shipped to META Environmental, Inc. in Watertown, MA for environmental forensic testing to determine the nature and possible source(s) of hydrocarbons in the various sample matrices; including wide range hydrocarbon fingerprinting by GC/FID and extended PAH profiles (EPPs), including parent and alkylated PAHs, by GC/MS/SIM. Table 1 shows the compounds measured.

Table 1. Target Compound List

META Extended PAH profiles by GC/MS/SIM		
Benzene	Naphthalene	C3-Phenanthrene/anthracenes
Toluene	C1-Naphthalenes	C2-Phenanthrene/anthracenes
Ethylbenzene	C2-Naphthalenes	C3-Phenanthrene/anthracenes
m/p-Xylenes	C3-Naphthalenes	C4-Phenanthrene/anthracenes
o-Xylenes	C4-Naphthalenes	Fluoranthene
Styrene	1-Methylnaphthalene	Pyrene
Isopropylbenzene	2-Methylnaphthalene	C1-Fluoranthene/pyrenes
n-Propylbenzene	Acenaphthylene	C2-Fluoranthene/pyrenes
1,3,5-Trimethylbenzene	Acenaphthene	C3-Fluoranthene/pyrenes
1,2,4-Trimethylbenzene	Dibenzofuran	Benz(a)anthracene
t-Butylbenzene	Fluorene	Chrysene
p-Isopropyltoluene	C1-Fluorenes	C1-Chrysenes
n-Butylbenzene	C2-Fluorenes	C2-Chrysenes
C1-Benzene	C3-Fluorenes	C3-Chrysenes
C2-Benzene	Dibenzothiophene	C4-Chrysenes
C3-Benzene	C1-Dibenzothiophenes	Benzo(b)fluoranthene
C4-Benzene	C2-Dibenzothiophenes	Benzo(k)fluoranthene
C5-Benzene	C3-Dibenzothiophenes	Benzo(e)pyrene
trans-Decalin	Phenanthrene	Benzo(a)pyrene
cis-Decalin	Anthracene	Indeno(1,2,3-c,d)pyrene
Biphenyl		Dibenz(a,h)anthracene
		Benzo,g,h,i)perylene
heptadecane		Perylene
pristane		Retene
octadecane		Benzo(b/c)fluorenes
phytane		2-Methylpyrene
2,6,10-trimethyldodecane		4-Methylpyrene
2,6,10-trimethyltridecane		1-Methylpyrene
norpristane		Benzo(b)naphtho(2,1-d)thiophene

> PCA is a statistical procedure that takes multiple, correlated variables (such as chemicals in a sample) and reduces the data to a few uncorrelated variables. Polytopic vector analysis (PVA) is a related method that takes the output from a PCA and estimates the number of contributing sources, the composition of each source, and the percent of each source in each sample.
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> PCA was done with Statistica v10 (Statsoft, Norman OK). PVA was done with software provided by Dr. Robert Ehrlich.

Figure 1. Environmental weathering changes the PAH profiles for many of the target compounds; and must be accounted for in the PCA and PVA.

NAPL from MGP (unweathered)

Sediment upstream of MGP

Soil from tar processing site
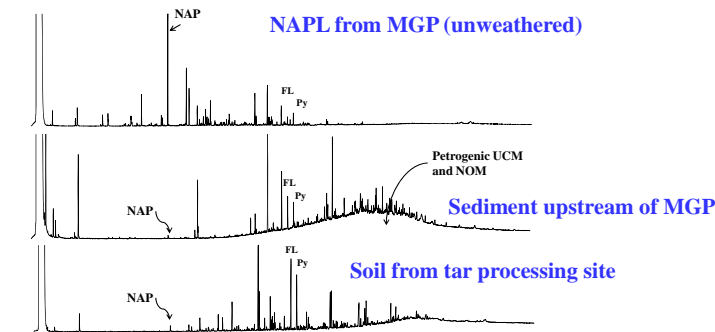
> At various locations, GC/FID fingerprinting of the sediment samples showed light and/or heavy petroleum products, 2 or more tar-like patterns, low concentrations of high molecular weight PAHs (HPAHs), a range of PAH ratios, a range of degrees of degradation, and natural organic matter.
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> The complexity of the sediment chemistry is reflected in the PCA results (Figure 2)

Figure 2. A PCA of all target compounds and all samples suggested 10 or more PAH sources with weathering (i.e., loss of low molecular weight compounds) the most significant variable. The degree of petrogenic character was the second most significant variable
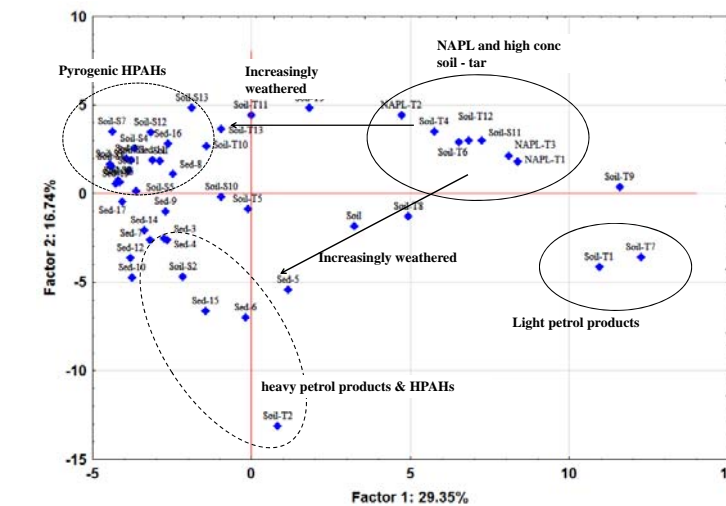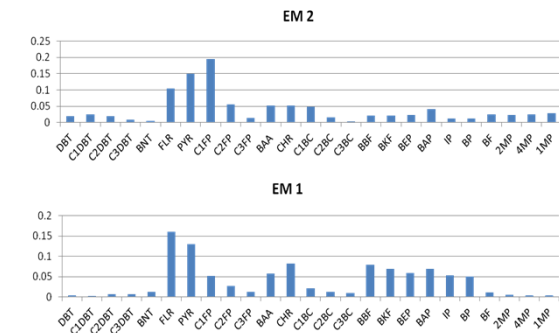

The data set was conditioned to simplify the PCA and PVA:
- Removed compounds prone to weathering (e.g., naphthalene)
  - Except, retained dibenzothiophenes (sulfur)
- Removed cmpds prone to detection limit and other analytical issues
  - E.g., C4-DBT, C4-BAA/CHR, dibenz(a,h,)anthracene, coronene
- Removed perylene (natural source)
- Removed redundant samples
  - Averaged 3 MGP NAPLs
  - Averaged groups of similar land-side soil sample results
  - Removed lab and field duplicates
- Removed samples contributing minimal HPAHs
  - E.g., samples identified as light petroleum products by GC/FID
- Removed SoilT14, SoilS2 – analytical issues

Results

Number of potential sources (end members) was reduced to between 4 and 6; a 4-end member solution was chosen as most representative.

A clean PVA solution was not obtained but reasonable end members and mixing trends were observed

MGP NAPL (carbureted water gas (CWG) pattern

Upstream and far downstream sediment
Mostly pyrogenic; low concentration

PVA Results: % of each source in each sample (rounded and normalized)

Sample	EM 1	EM 2 MGP NAPL	EM 3 bkgd	EM 4 MGP soil2	
NAPL-ave	0.0%	100.0%	0.0%	0.0%	— CWG-like tar
SoilTave1	0.0%	51.9%	0.0%	48.1%	
SoilTave2	0.0%	0.0%	0.0%	100.0%	— CC-like pattern
SoilSave	48.6%	0.0%	0.0%	51.4%	— Tar processing site soil
Sed1	56.0%	12.6%	0.0%	31.4%	⎤
Sed2	27.5%	6.0%	6.6%	60.0%	⎟ NAPL Seep Area
Sed3	42.9%	0.0%	31.8%	25.4%	⎦
Sed4	100.0%	0.0%	0.0%	0.0%	— *Pyrogenic background*
Sed5	69.6%	2.8%	9.4%	18.2%	
Sed6	49.7%	0.0%	41.1%	9.2%	
Sed7	45.6%	0.0%	15.1%	39.4%	— Far Downstream
Sed8	53.5%	0.0%	0.0%	46.5%	
Sed9	90.9%	0.0%	3.4%	5.7%	
Sed10	66.3%	0.0%	33.7%	0.0%	— Upstream
Sed11	52.5%	0.0%	0.0%	47.5%	
Sed12	84.9%	0.0%	6.4%	8.7%	— Upstream
Sed13	53.6%	0.0%	0.0%	46.4%	
Sed14	71.4%	0.0%	0.0%	28.6%	— *Far Upstream*
Sed15	0.0%	0.0%	100.0%	0.0%	— *Far Upstream*
Sed16	14.4%	30.2%	0.0%	55.4%	— NAPL Seep Area
Sed17	68.1%	0.0%	0.0%	31.9%	

Conclusions

- Focus on HPAHs and other weathering-resistant compounds reduced the number of potential sources substantially – to 4 or 5
- MGP CWG NAPL – little to no contribution to sediments even though present in on-site wells
- NAPL seep area impacted by coal tar plus substantial portion of pyrogenic background
- Petrogenic PAHs contributed little, except far upstream and in a few other locations (based on contributions of alkylated PAHs)
- Tar processing site soil was similar to NAPL seep area and some sediment locations.
- PVA generated reasonable estimates of PAH source contributions that were consistent with PAH ratios, concentrations, location, and other indicators.