



Assessing the Contribution of Coal Tar Sealants to the Polycyclic Aromatic Hydrocarbons of Urban Sediments: A Forensic Chemist's Perspective

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Background

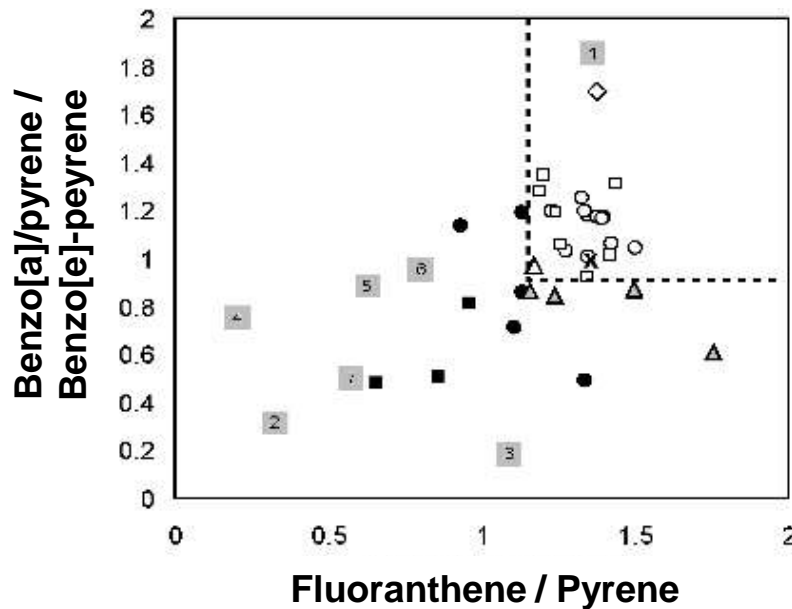
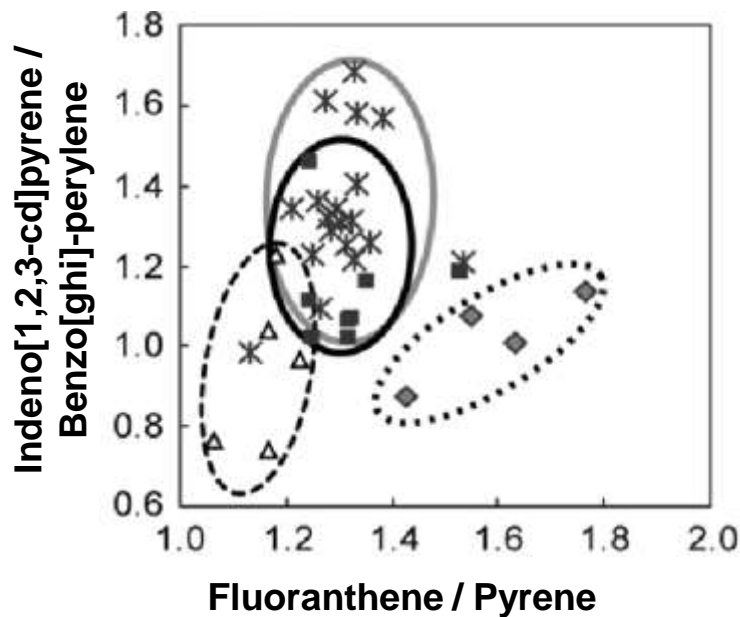
■ Traditional hypothesis

- In the absence of a localized source, atmospheric deposition in a watershed is a primary source of PAHs in urban sediments

■ Recent hypotheses

- *Parking lot sealcoat may dominate loading of PAHs to urban water bodies (Mahler et al. 2005)*
- *PAH loading to lakes in central and eastern U.S. cities includes a substantial contribution from coal tar sealcoat (Van Metre et al. 2009)*

Published Evidence to Support New Hypothesis



Samples and ellipse approximate distribution of:

- ◻ Coal-tar sealed parking lots
- ◊ Asphalt sealed parking lots
- △ Unsealed asphalt and cement parking lots
- ✱ Urban stream sediment

Pavement dust

- ◊ Sealcoated, central and eastern
- Sealcoated, western
- △ Austin, coal-tar-base sealcoat
- ▲ Austin, asphalt-base sealcoat

Lake sediment

- ◻ Central and eastern
- Western

Parking lot runoff

- ✱ Coal-tar-sealed lots, Austin (mean) (9)

Potential urban PAH sources

- 1 Coal tar, NIST standard 1597a (22)
- 2 Petroleum crude oil, NIST standard 1582 (23)
- 3 Diesel particulate matter, NIST standard 1650b (24)
- 4 Tire-wear particles (7)
- 5 Brake-lining particles (7)
- 6 Automobile exhaust (25)
- 7 Diesel truck exhaust (25)

Project Goal

- **Use environmental forensic methods to evaluate the hypothesis that coal tar sealants are a significant source of PAHs in urban sediments**

Sources of PAHs and Sediment Solids Evaluated

- **Data for over 140 samples compiled from peer-reviewed articles and agency reports with individual sample results**
 - Atmospheric particles
 - Roof dust
 - Coal tar (CT) sealed parking lots
 - Highway runoff
 - Soils
 - Urban pond sediments

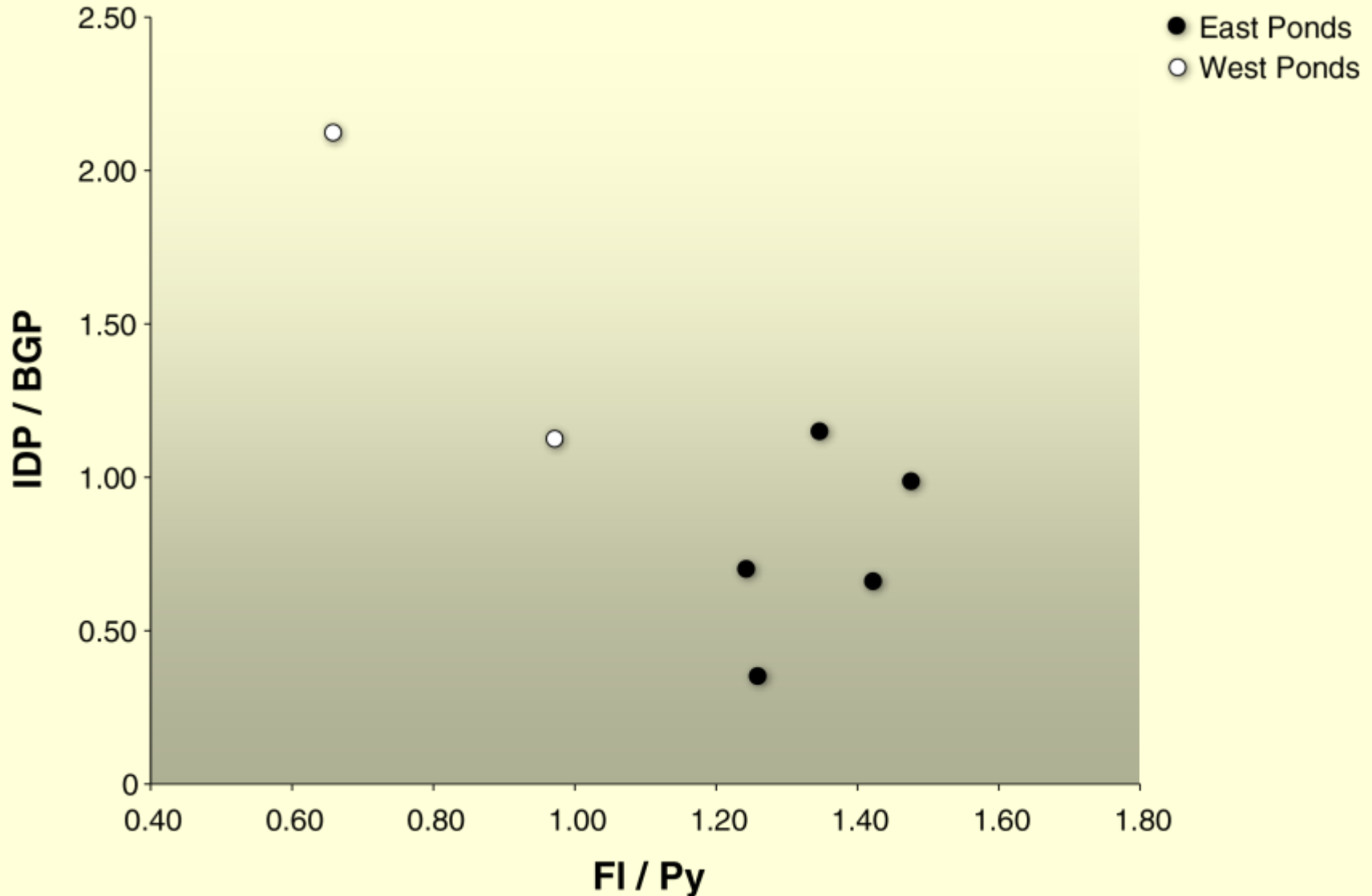
Forensic Methods

- **Concentration histograms**
- **PAH double ratios**
- **Pearson correlation**
- **Principal component analysis**

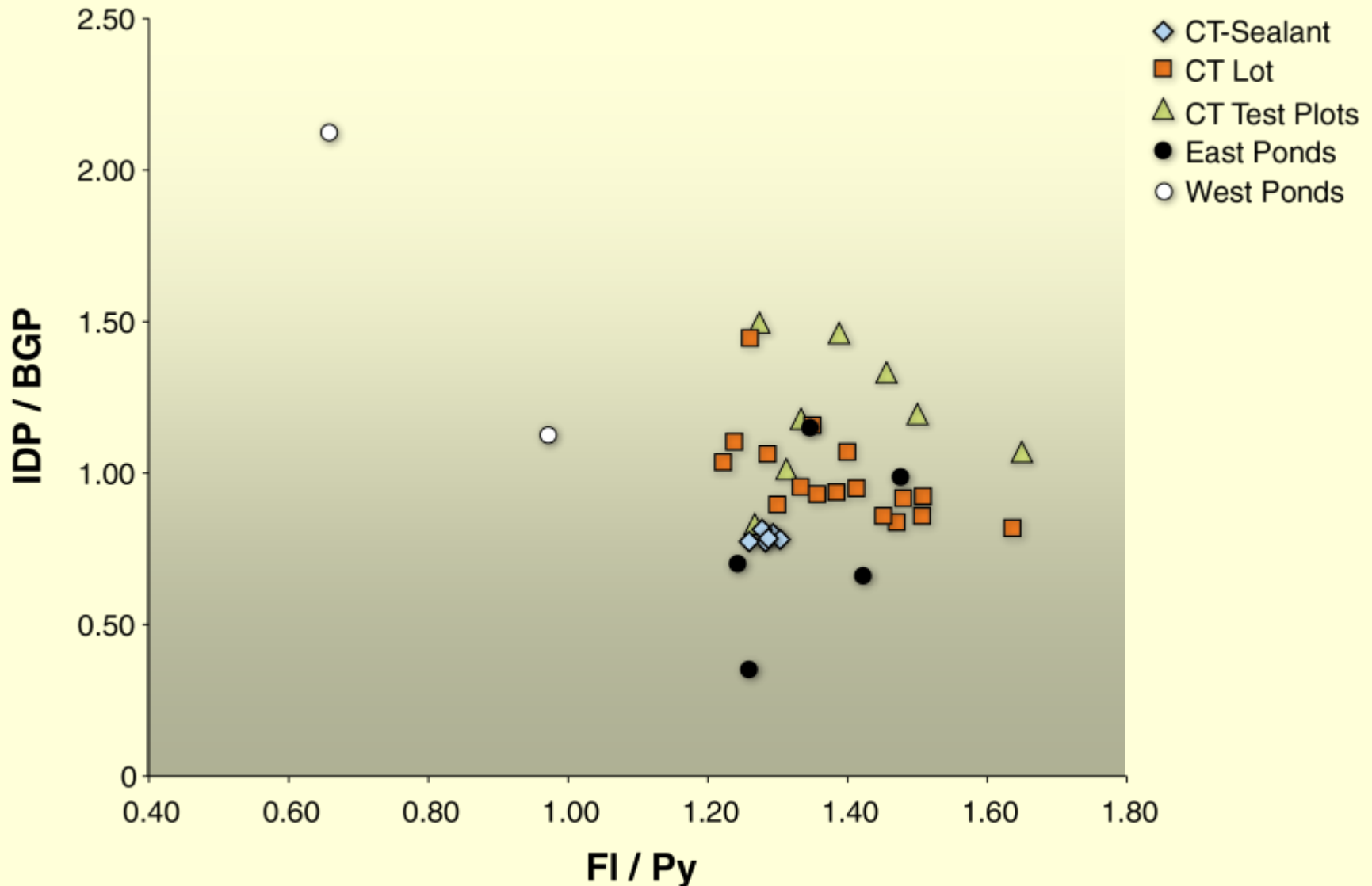
PAH Double Ratio Plots

- Can be useful for distinguishing differences among sources and sample types
- Less useful for differentiating among similar sources
- Focused on: Fluoranthene/pyrene (FI/PY) and indeno[1,2,3-cd]pyrene/benzo[ghi]perylene (IDP/BGP) ratios based on Mahler et al. (2005)

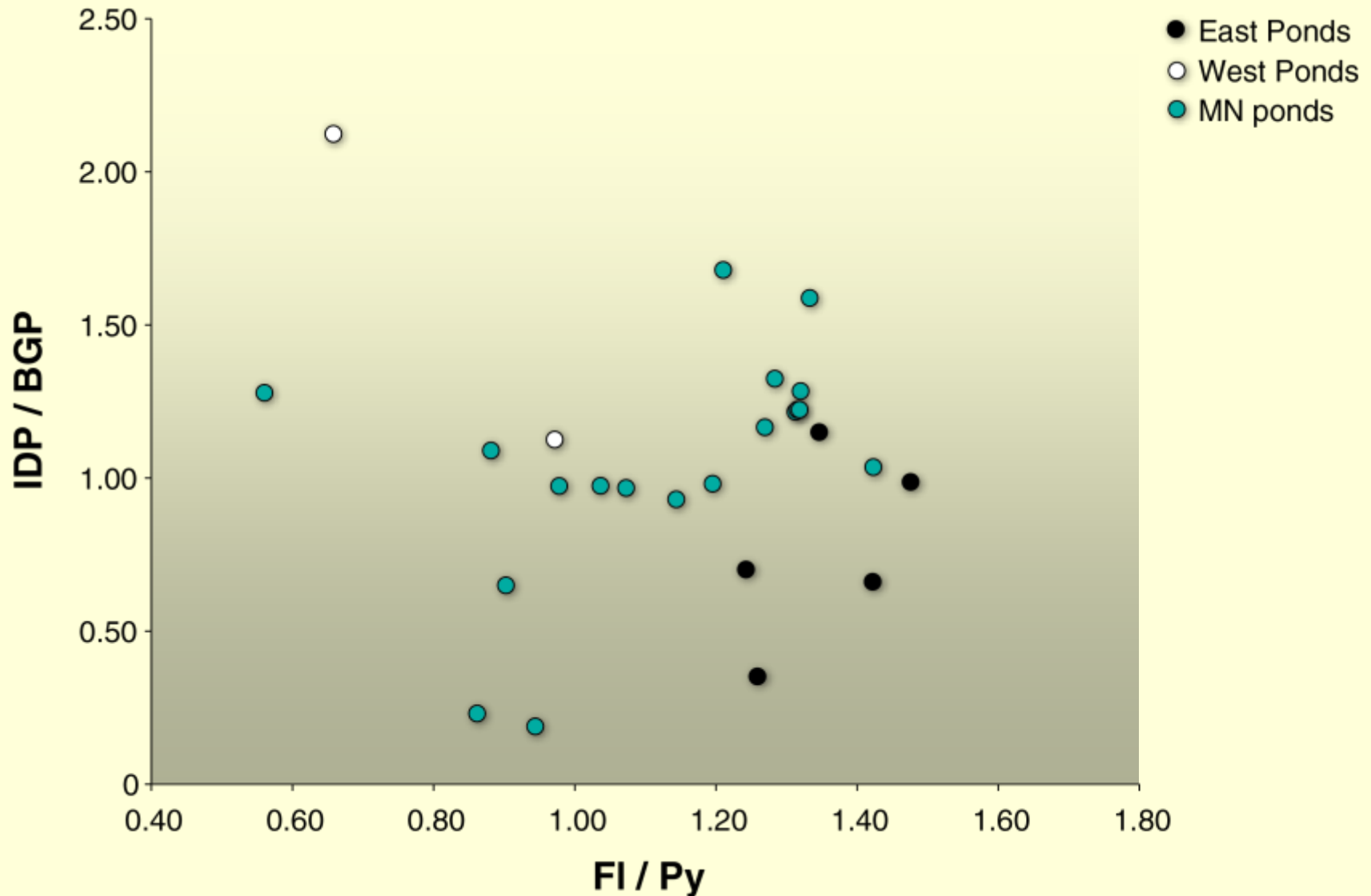
Data from Van Metre et al. (2009) Suggests Regional Differences in Urban Sediment Chemistry Potentially Linked to Differences in Sealant Usage



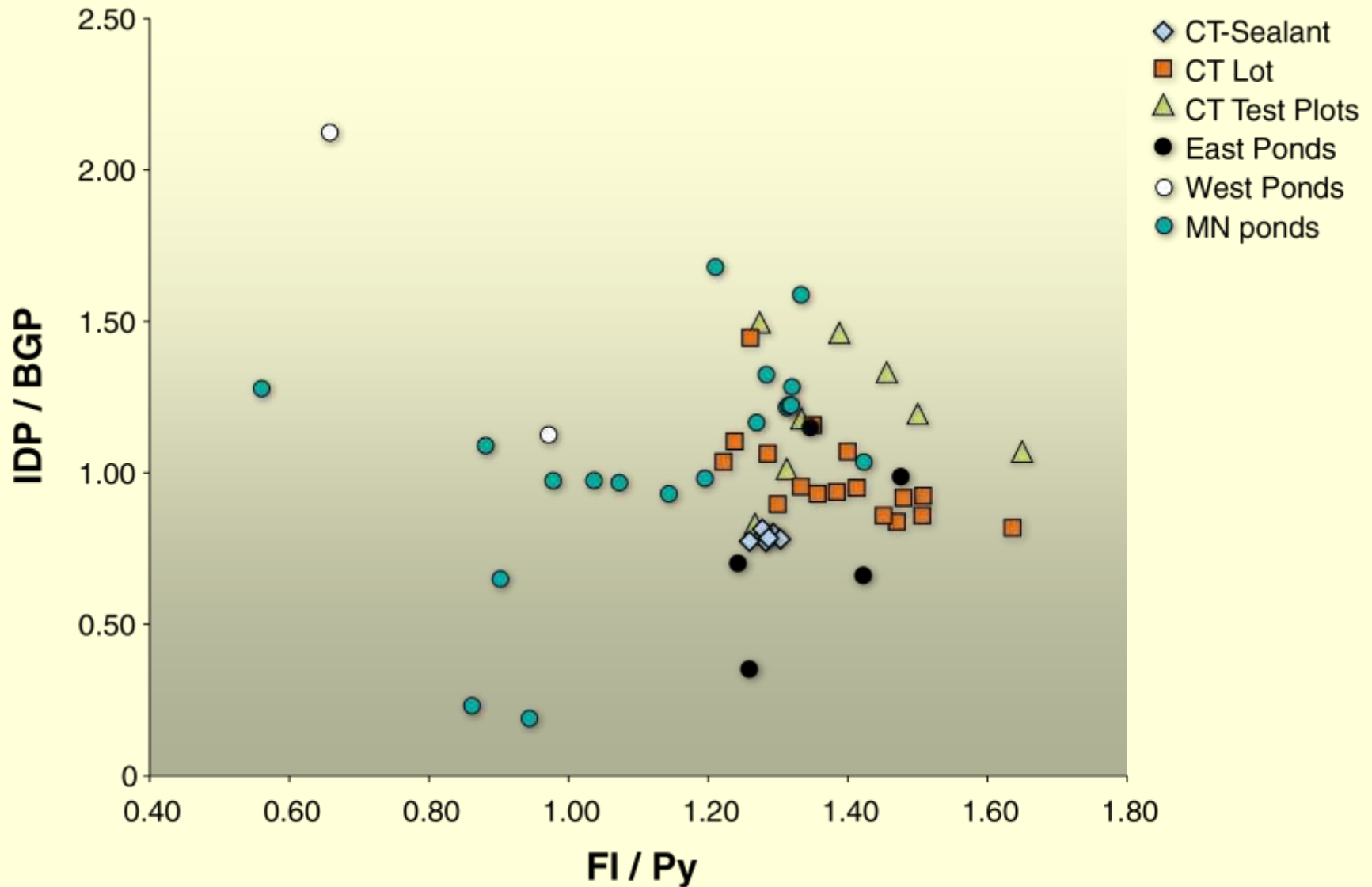
PAH Ratios of Eastern Ponds in this Data Set Are More Similar to Those of Sealant than Pond Samples from the West



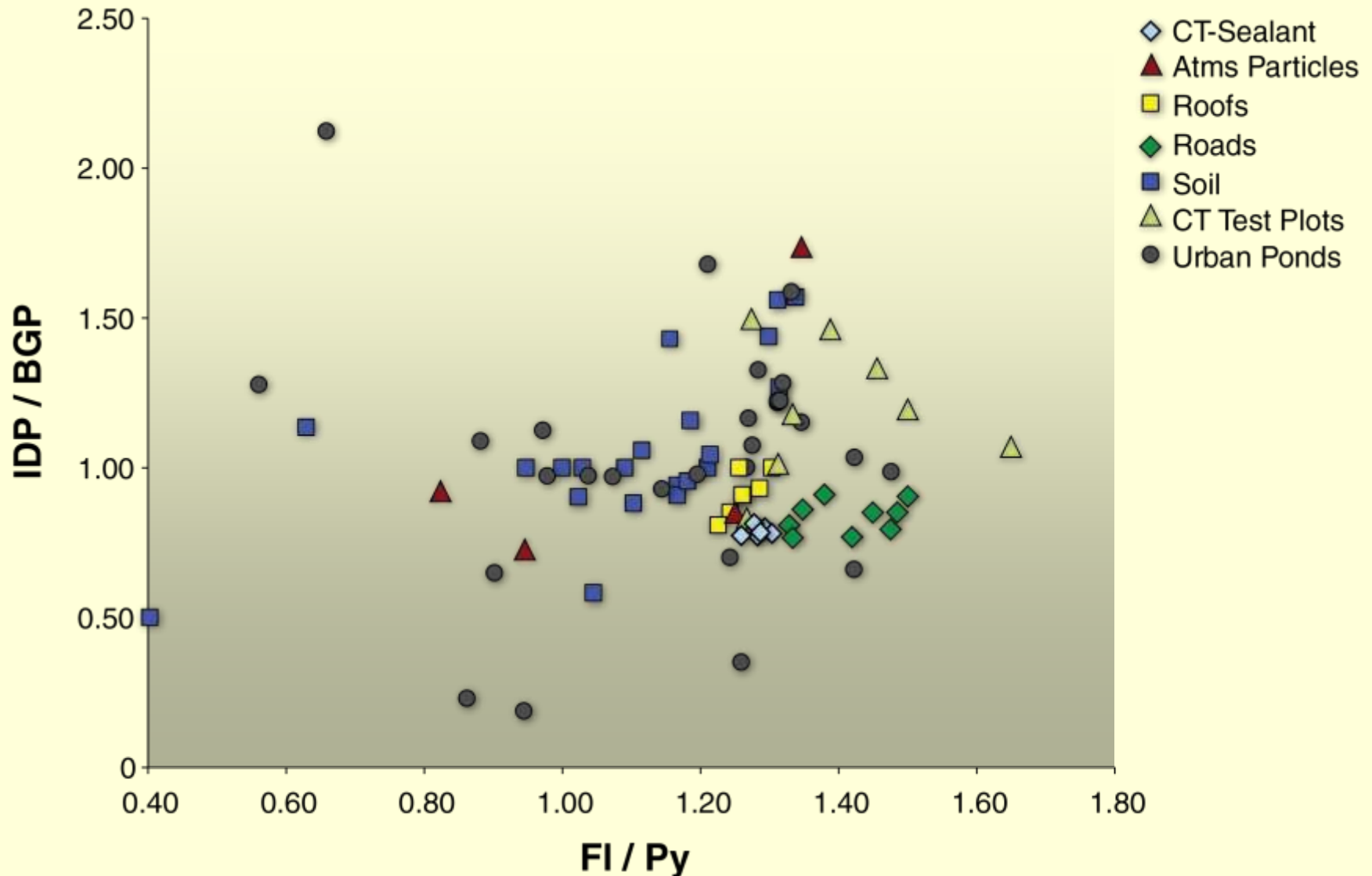
An Evaluation of Multiple Ponds within a Single Urban Area (Polta et al. 2005) Indicates a Broad Range of PAH Ratios



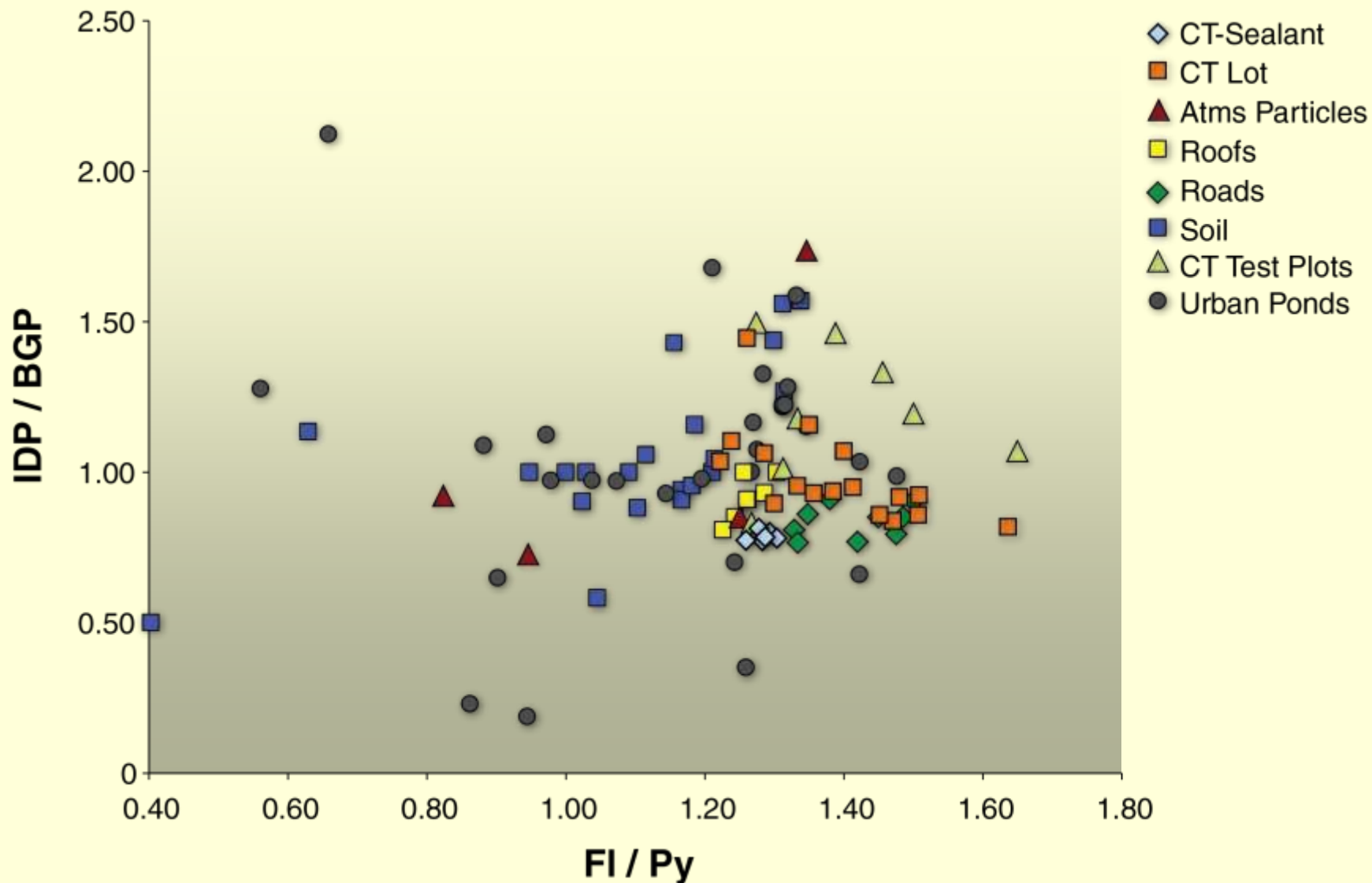
There Are Overlaps in PAH Ratios between Some Urban Ponds Sediment and Sealant Samples



There Are Overlaps in PAH Ratios between Urban Ponds Sediments and Non-Sealant-Related Sources



Ratio Analysis Does Not Demonstrate That Sealants Are a Unique Source of PAHs to Pond Sediments



Application of Pearson Coefficient to Make Sample-to-Sample Comparisons

- **A statistical approach for assessing the similarity of sources and sample types that utilizes the results of all measured analytes, not just several ratios**
- **Used to:**
 - Evaluate similarities within and between sources and sample types
 - Compare individual sediment samples to potential sources

Pearson Coefficient between Six Sample Types and Urban Sediments from Nine States

	OR	WA	UT	TX	MN	IL	MI	DC	CT
Fresh sealant	0.58	0.43	0.61	0.23	0.38	0.51	0.53	0.71	0.50
Sealed lot (TX)	0.94	0.95	0.81	0.92	0.93	0.96	0.83	0.93	0.92
Sealed lot (WI)	0.91	0.88	0.79	0.77	0.87	0.94	0.75	0.94	0.86
Atm. part. (IL)	0.89	0.88	0.77	0.88	0.90	0.91	0.74	0.87	0.83
Roof dust	0.92	0.91	0.78	0.78	0.90	0.94	0.75	0.88	0.86
Soil	0.90	0.97	0.75	0.96	0.97	0.97	0.87	0.88	0.95
Highway	0.91	0.95	0.76	0.88	0.94	0.97	0.75	0.87	0.88

r>0.90

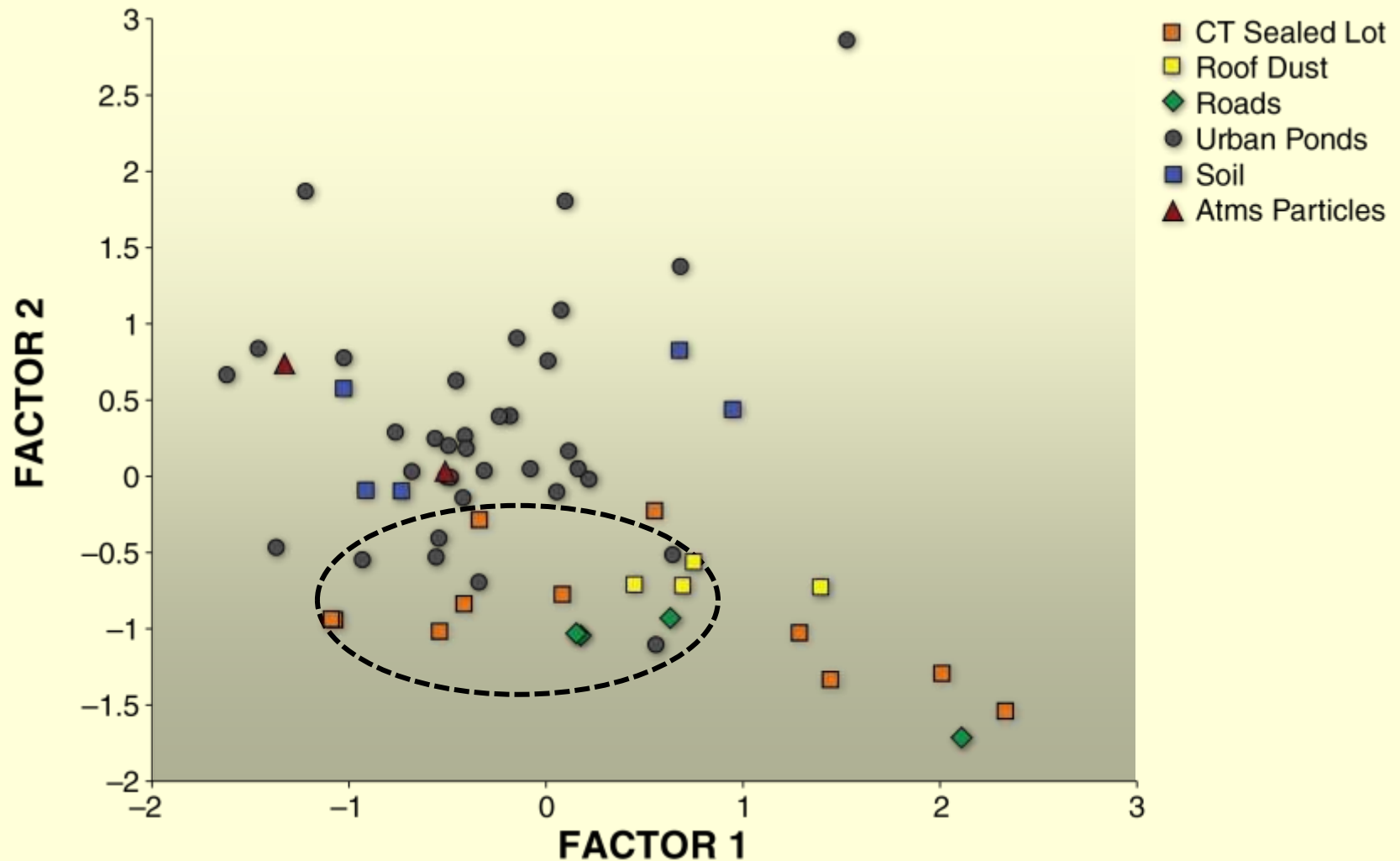
r>0.95

- No regional trends
- Correlation to sealant is similar to that with other sample types

Application of Principal Component Analysis

- **A multivariate statistical method that uses normalized PAH data to group samples with similar chemical characteristics**
- **Commonly used in forensic analysis to identify and distinguish among sources**

Principal Component Analysis



- Limited overlap between sealant and sediment samples
- Similar results with other environmental sample types

Conclusion: A Forensic Chemist's Perspective

- A forensic assessment is strengthened by including a range of source and sample types
- Multiple forensic methods are required to examine relationships and to distinguish among similar pyrogenic samples
- The results presented here do not support the hypothesis that sealants are a unique source that *“dominate loading of PAHs to urban water bodies”*
- The results do not eliminate sealants as a potential PAH source in some locations

Acknowledgment

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