



DISTINGUISHING PYROGENIC PAH SOURCES IN SEDIMENT FROM MGP AND OTHER TAR SOURCES USING EXPLORATORY DATA ANALYSIS

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Objectives and Approach: Tar v. PICs

- Focus is on pyrogenic PAHs
 - I assume that a Pyro – Petro assessment is done and most of the PAH mass is pyrogenic
- Identify PAH formation variables that determine PAH patterns
- Develop smallest PAH target list that accounts for maximum variability





Data Set

- **Background surface soil samples**
 - 418 samples from 5 States
 - Analyzed for PAHs/alkylated PAHs and hydrocarbon fingerprint
- **SRMs**
 - 8 samples urban dust, diesel exhaust, etc.
 - Data from Certificates
- **MGPs and other tars**
 - 233 samples (including some duplicates)
 - Includes coke oven tars, creosote, MGP coal tars, MGP CWG tars, and unknowns
 - Analyzed for PAHs/alkylated PAHs and hydrocarbon fingerprints
 - Data from several labs



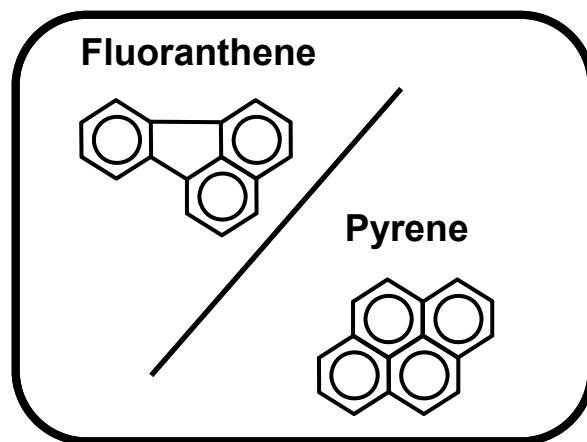
Discrimination by Composition – Tar or PICs

- **450 compounds identified**
 - Coal Tar Data Book, 1965
- **Butane – Coronene+**
- **Includes many classes of organic compounds**
- **Principal constituents are MAHs and PAHs, but also:**
 - Phenols, organic acids
 - Nitrogen, sulfur, oxygen heterocyclics
 - Alkanes, alkenes, naphthenes
 - others

There's gotta
be a
combination
that works

Structures Sensitive to Formation Conditions

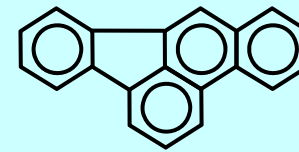
- Peri-condensed and kata-annellated;
alternate and non-alternate forms
 - Sensitive to formation conditions



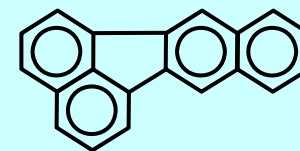
There are many combinations of PAHs – some have discriminating power; some don't

Other Candidates

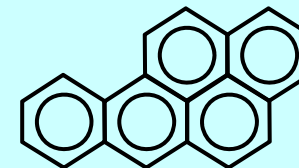
Benzo(b)fluoranthene



Benzo(k)fluoranthene

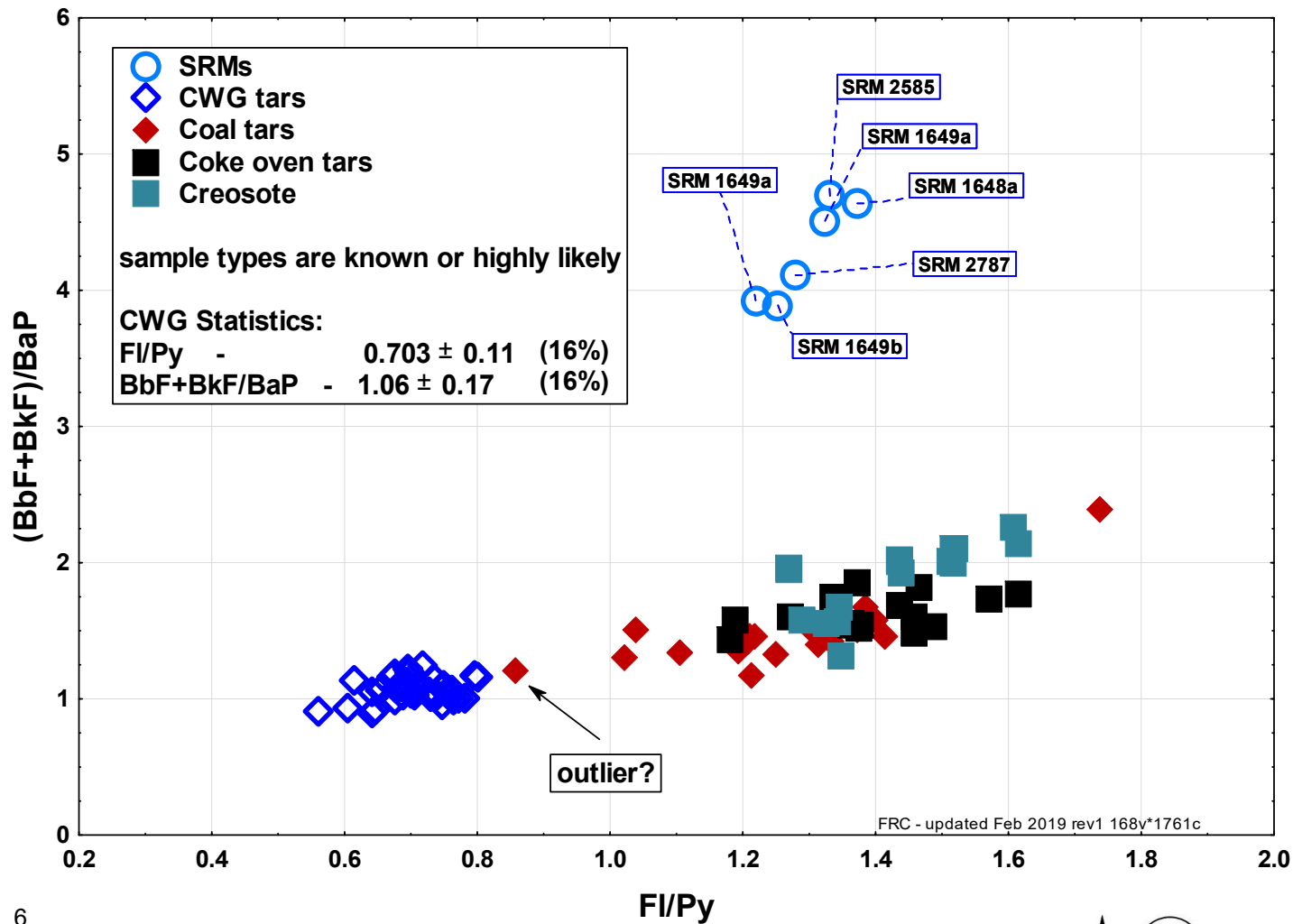


Benzo(a)pyrene



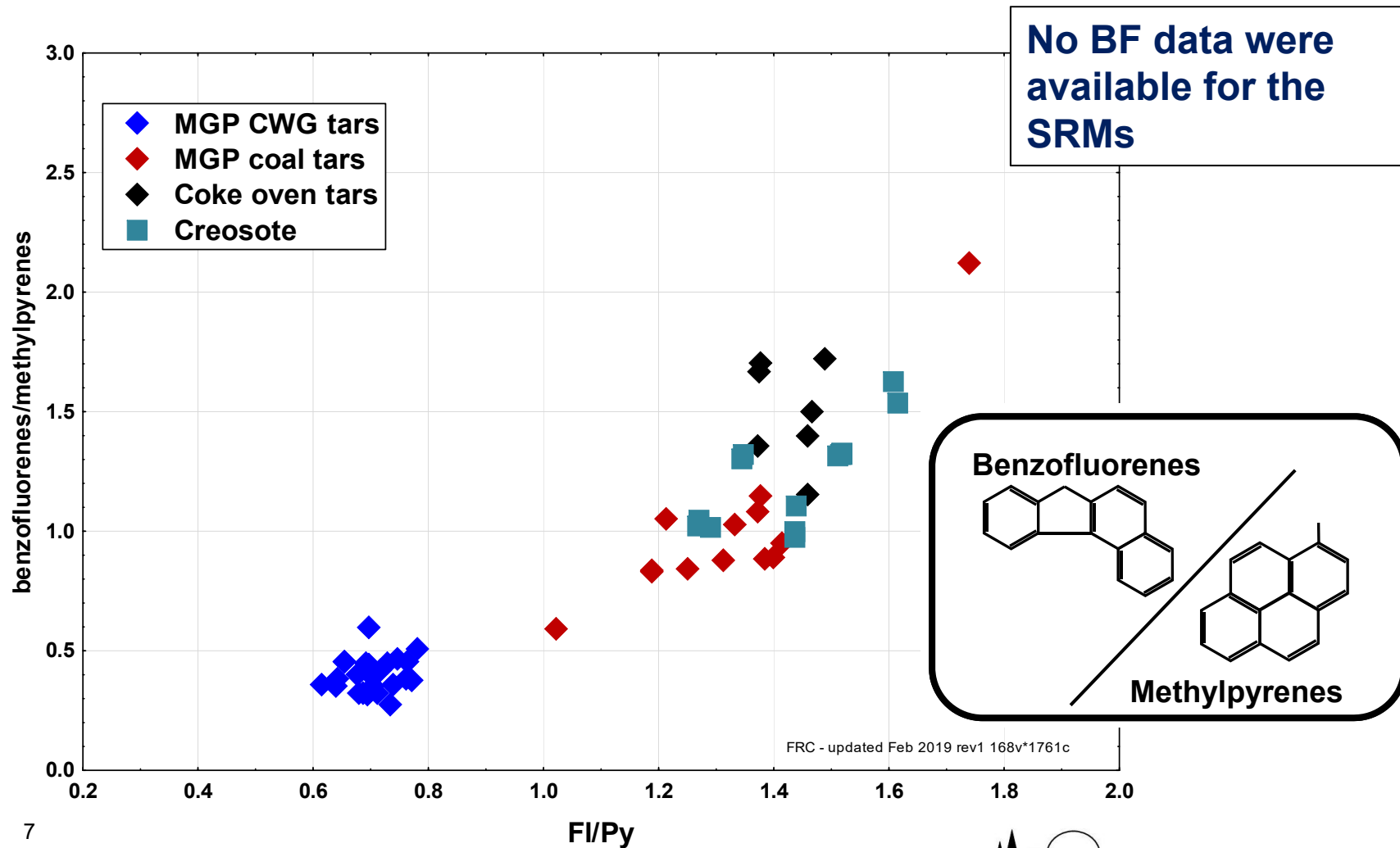


2 Structure-Sensitive PAH Ratios (*sample types are known or highly likely*)

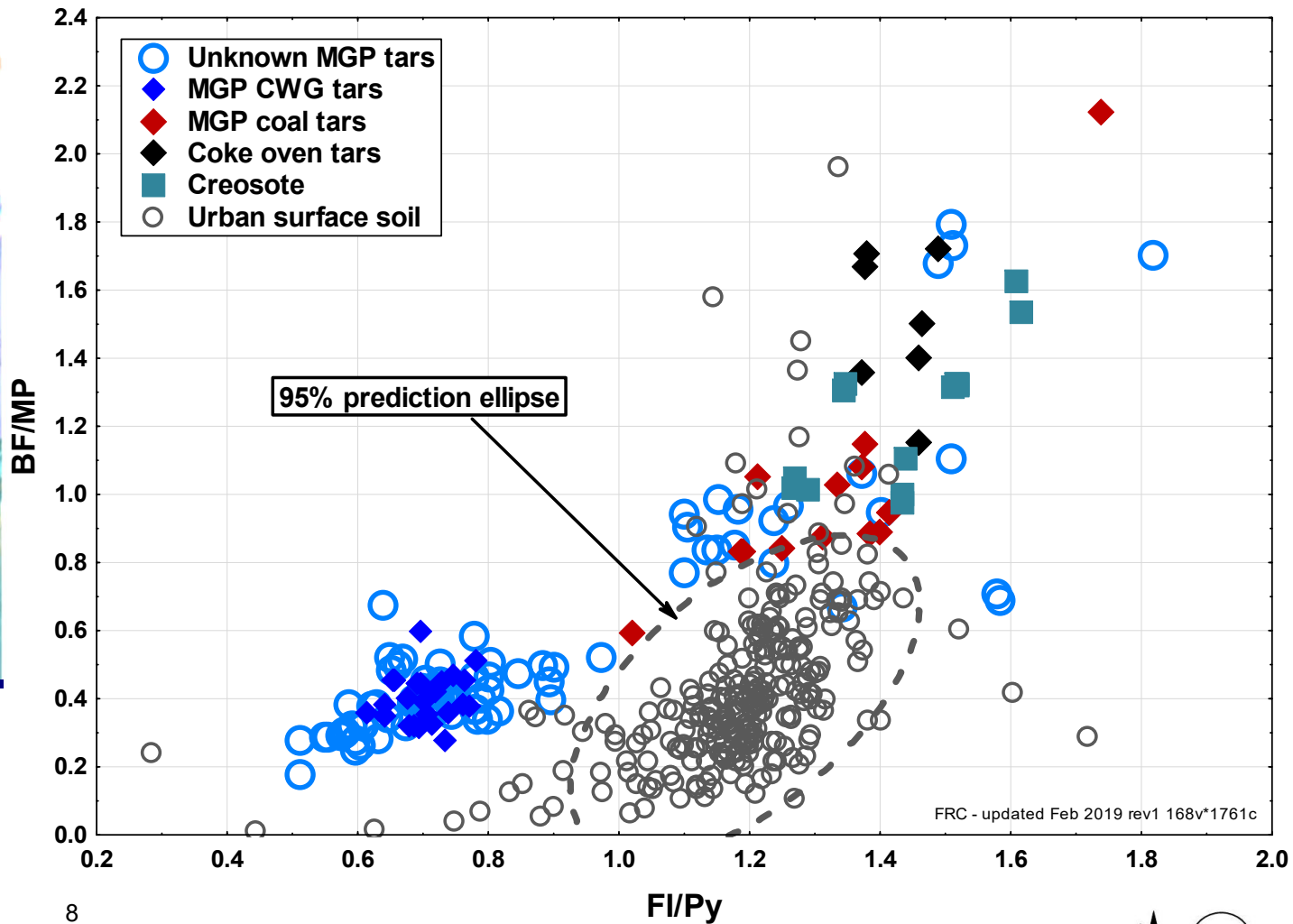




Another Structure-Sensitive Ratio (*sample types are know or highly likely*)



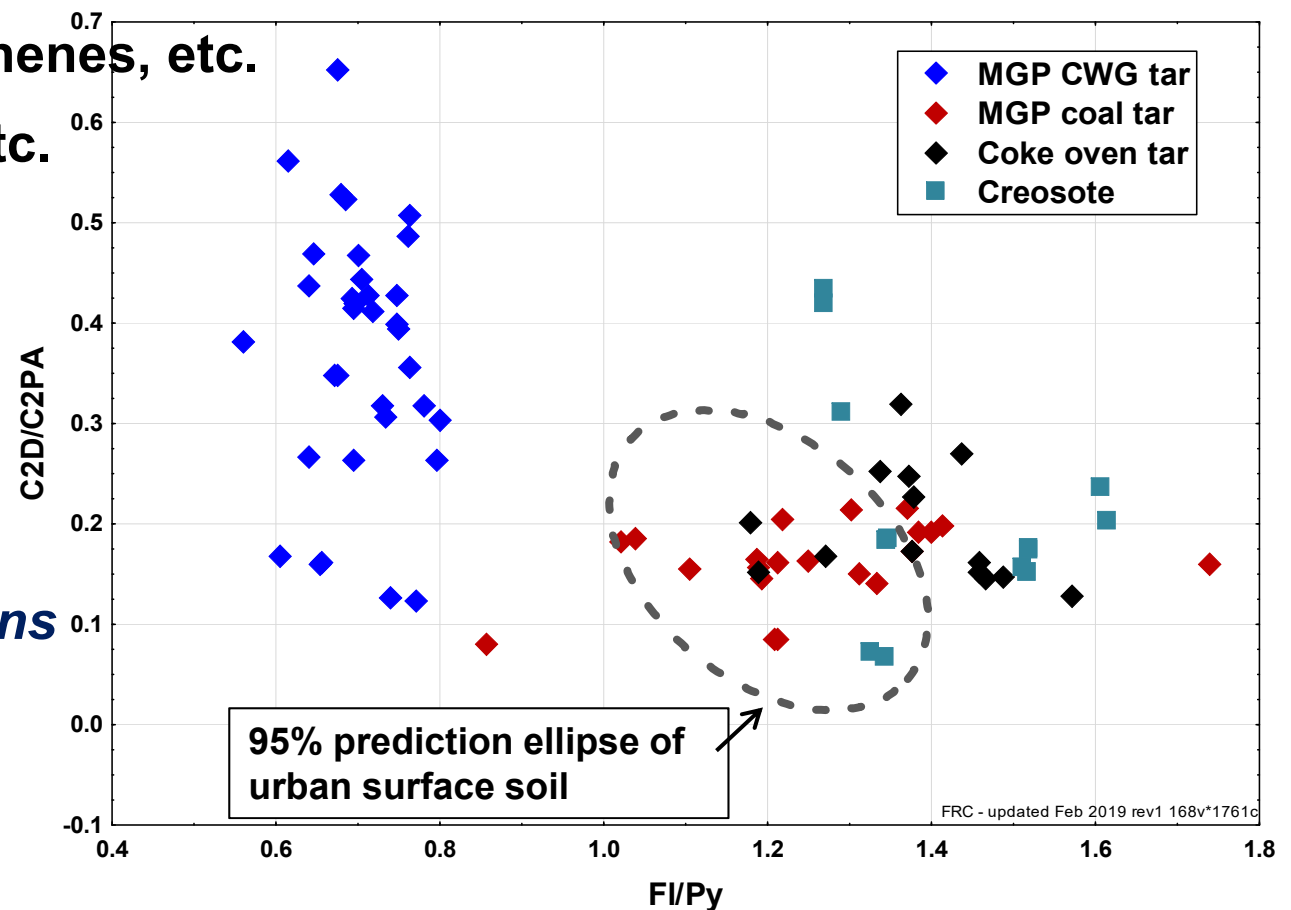
Add more MGP tars and urban background samples



Heteroatom-containing Compounds: oxygen, sulfur, nitrogen

- Dibenzofurans, phenols, etc.
- Dibenzothiophenes, etc.
- Carbazoles, etc.

*META has shown
several combinations
that discriminate*



FRC - updated Feb 2019 rev1 168v*1761c



Other Considerations for Compound List

- Availability of data
- Likely quality of data
- Weathering effects

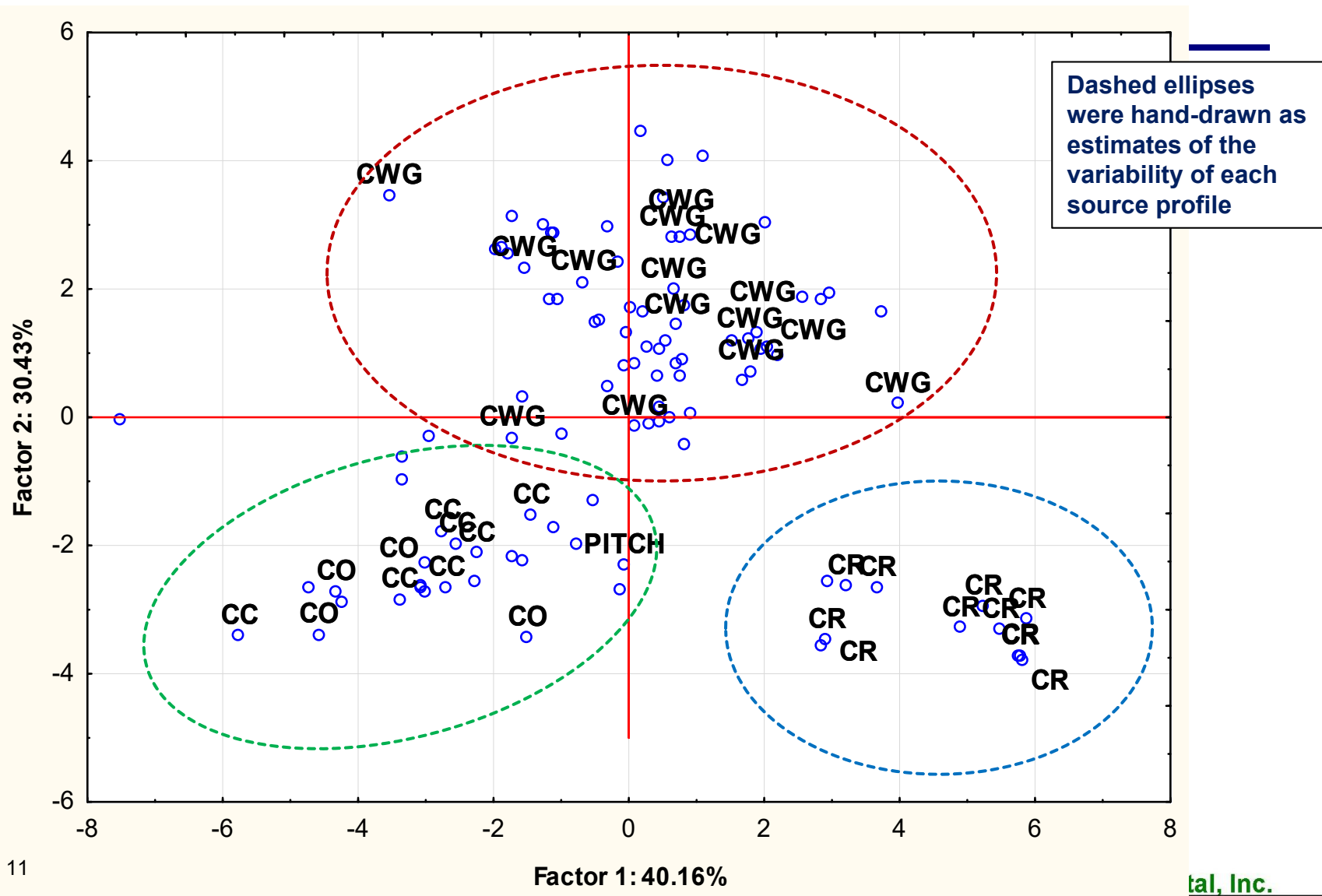
Final this study

Dibenzofuran
Fluorene
Phenanthrene
Anthracene
Dibenzothiophene
Fluoranthene
Pyrene
Benzo[b]fluoranthene
Benzo[j/k]fluoranthene
Benzo(e)pyrene
Benzo[a]pyrene
Indeno[1,2,3-cd]pyrene
Benzo[g,h,i]perylene
Benzo(b/c)fluorenes
2-Methylpyrene
4-Methylpyrene
1-Methylpyrene



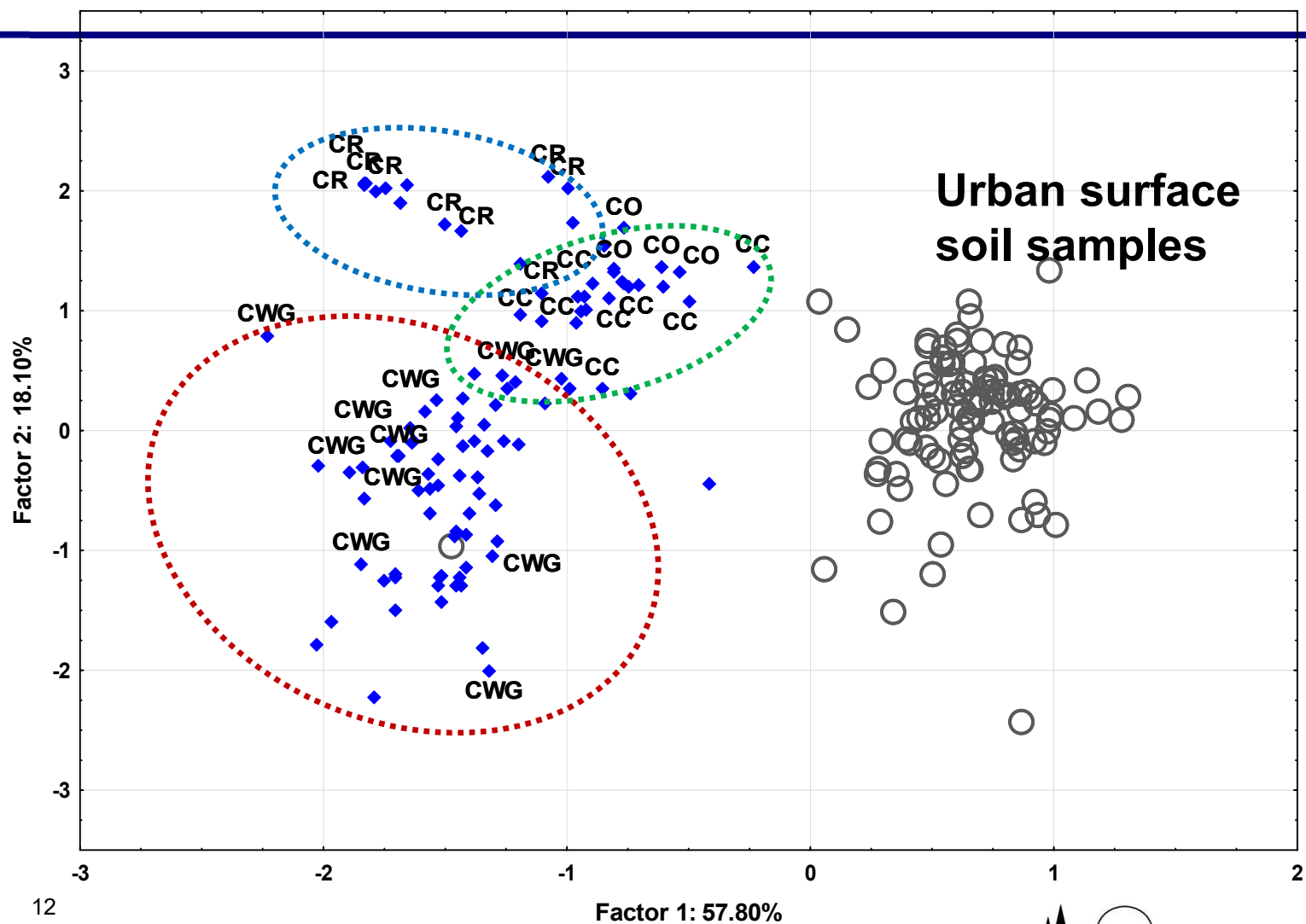
PCA of Tar Reference Samples

Samples from known or suspected sources have been labeled





PCA of Ambient Surface Soil Samples and Tar Reference Samples





Conclusions

- **PAH formation conditions and resulting composition provide source-specific characteristics**
 - Tars v PICs
- **Ratios work – but not always**
- **The full compound list (PAHs, alkylated PAHs, biomarkers) often isn't needed for exploratory analysis**
- **Source ID should always be supported by multiple indicators and lines of evidence**



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