Sources and Reference Concentrations of PAHs in Surface Soil at Eielson Air Force Base

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Introduction

- Investigation of the sources and concentrations of PAHs distributed in surface soil across Eielson Air Force Base
- Conducted on behalf of the U.S. Air Force Civil Engineer Center, in support of on-base site remediation efforts.
- Performed in consultation with the U.S. EPA and Alaska Department of Environmental Conservation.

Disclaimer: The inclusion of information and images representing the Department of the Air Force, Eielson Air Force Base, and the Air Force Civil Engineer Center do not imply endorsement.

Outline

- Background
- Objective
- Sampling Design
- Analytical Design
- Data Analysis
  - Forensics Analysis
  - Statistical Analysis of Reference PAH Concentrations
- Proposed Applications for Remedial Decisions
- Summary/Conclusions

Background

- PAHs often exceed human health cleanup levels in surface soil in areas without specific sources.
- Potential PAH sources:
  - Emissions from combustion of diesel, gasoline, jet fuel, and coal
  - Coal and coal dust
  - Asphalt
  - Petroleum releases
  - Biomass
  - Forest fires
- Critical to determine if detected PAHs are site-related or from emissions and other widely distributed impacts.

Objective

- The objective of the study was to characterize PAHs in surface soils on and in proximity to the base, using forensic techniques and statistical methods, to provide lines of evidence that can be used in evaluating whether PAHs detected in soil are derived from site-specific activities.

Sampling Design

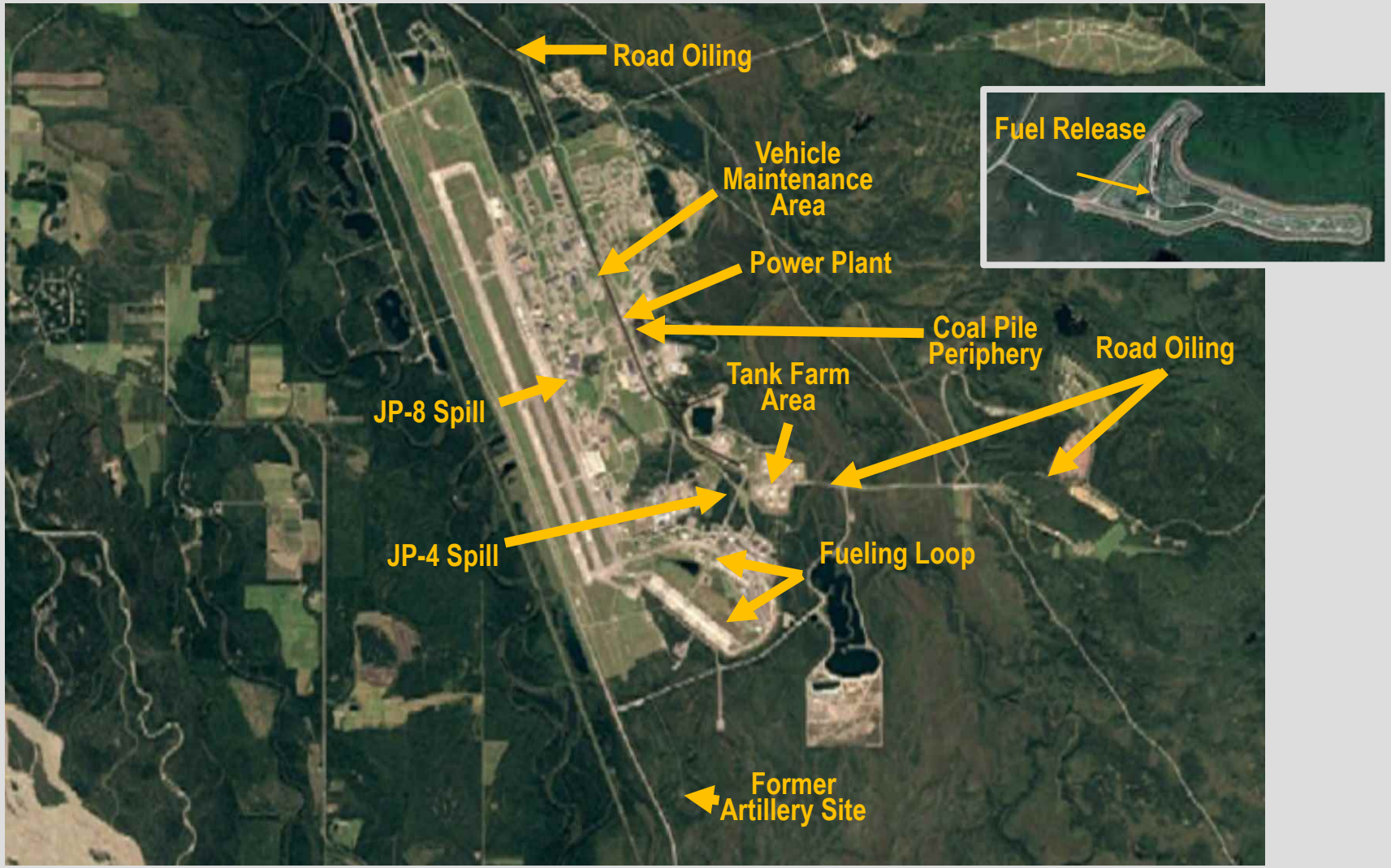
200 PAH “reference samples”

- Surface soil samples collected from 20 areas without site-specific PAH sources to evaluate reference concentrations.
- Sampling areas were categorized based on characteristics expected to impact PAH signatures and concentrations:
  - Land use (developed or undeveloped)
  - Distance to pavement (10-30 ft or more than 30 ft)

Sampling Design

30 site-specific source samples:

- Surface soil samples collected from sites with known PAH contamination, for comparison to reference samples

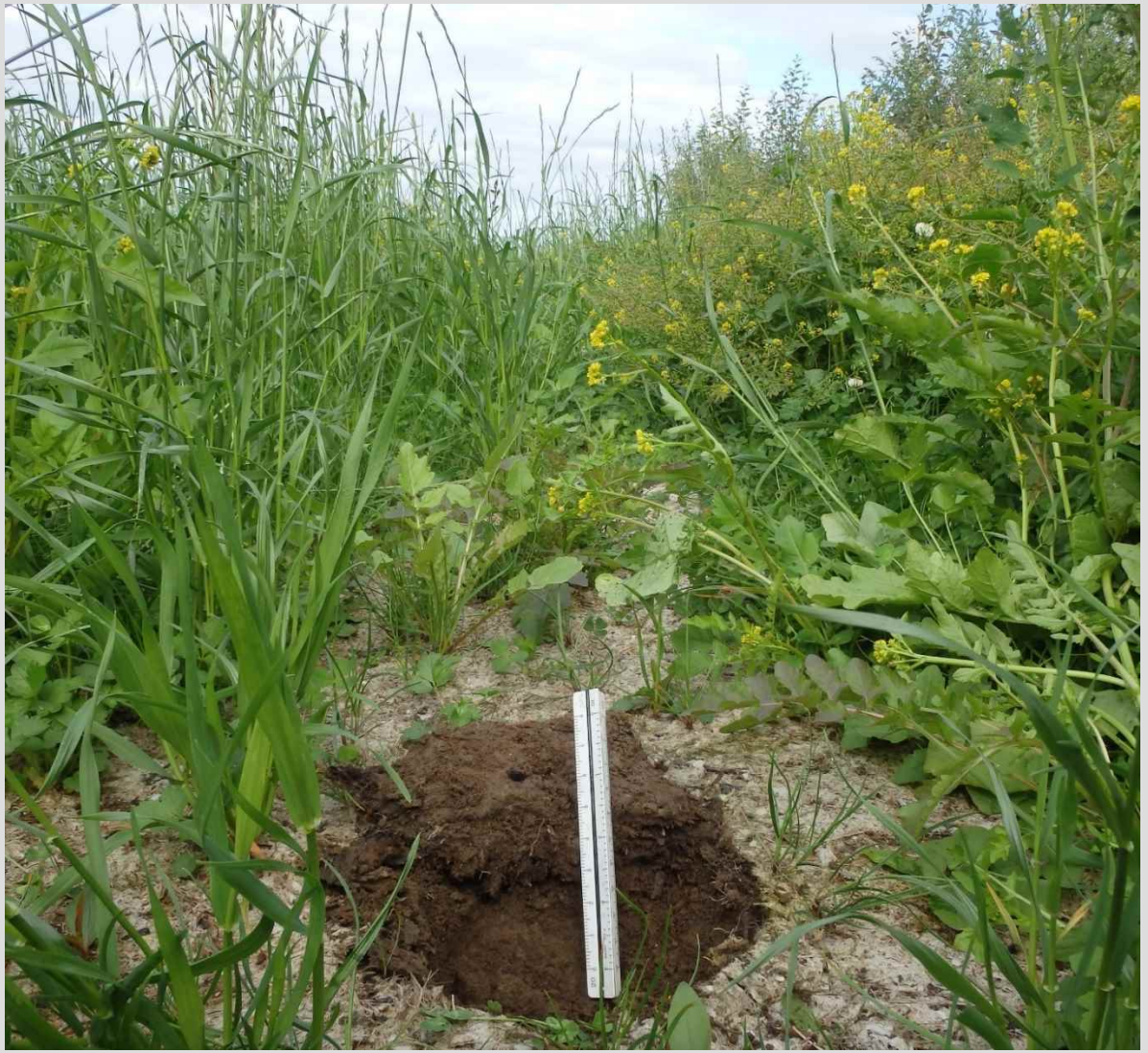


Analytical Design

- Samples were analyzed at an off-site laboratory as follows:
  - Expanded list of PAHs and related analytes (decalins, benzothiophenes) by SW-846 8270 SIM Modified
  - Hydrocarbon fingerprinting by SW-846 8015D Modified.

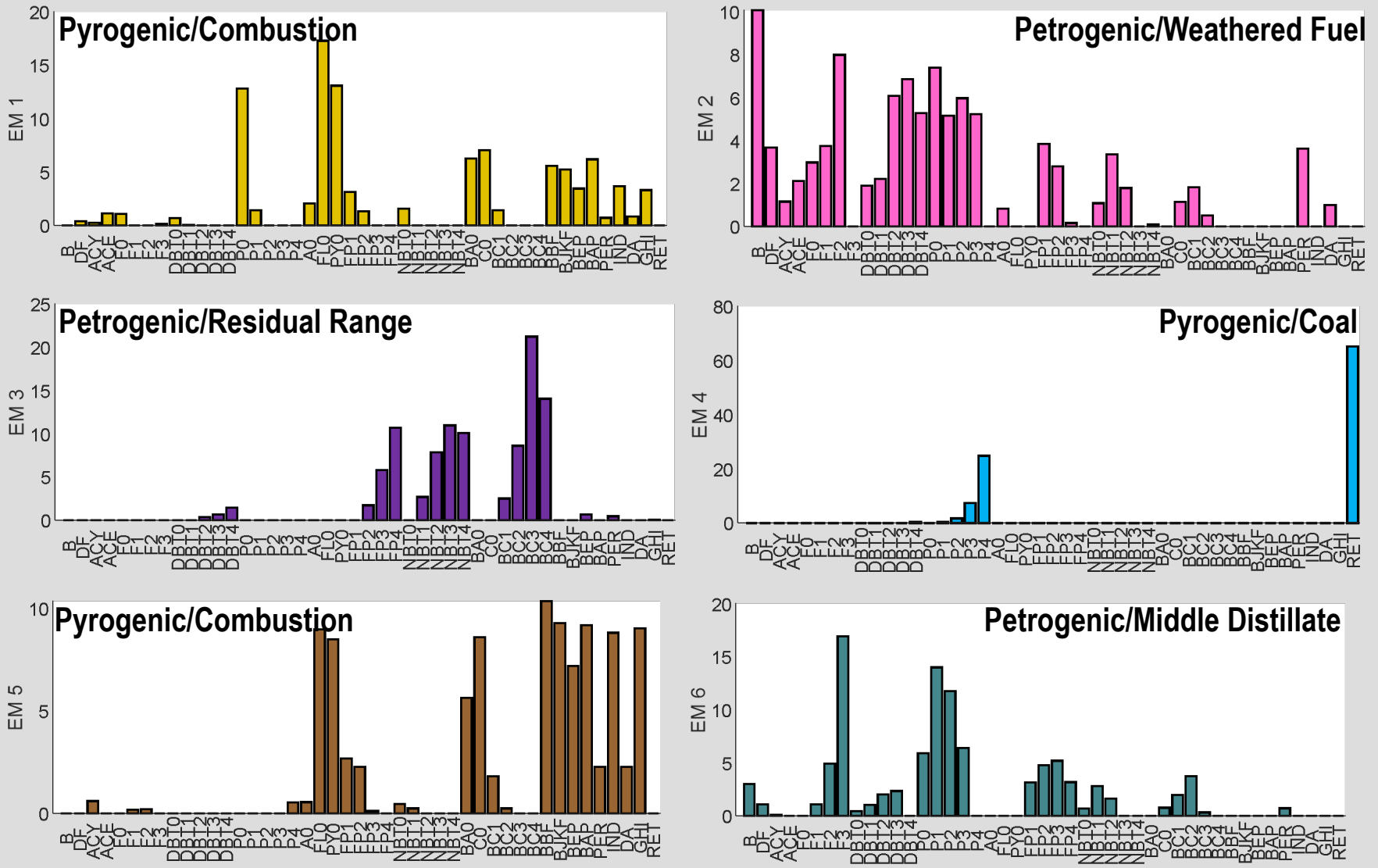
Data Analysis

- Forensic source evaluation to characterize PAH composition in surface soils, using two approaches:
  - Multivariate analysis, specifically polytopic vector analysis (PVA) and t-Distributed Stochastic Neighbor Embedding (t-SNE)
  - Diagnostic PAH source ratio analysis
- Statistical analysis of reference PAH concentrations in surface soil by location type and grouping (based on land use, distance from pavement)

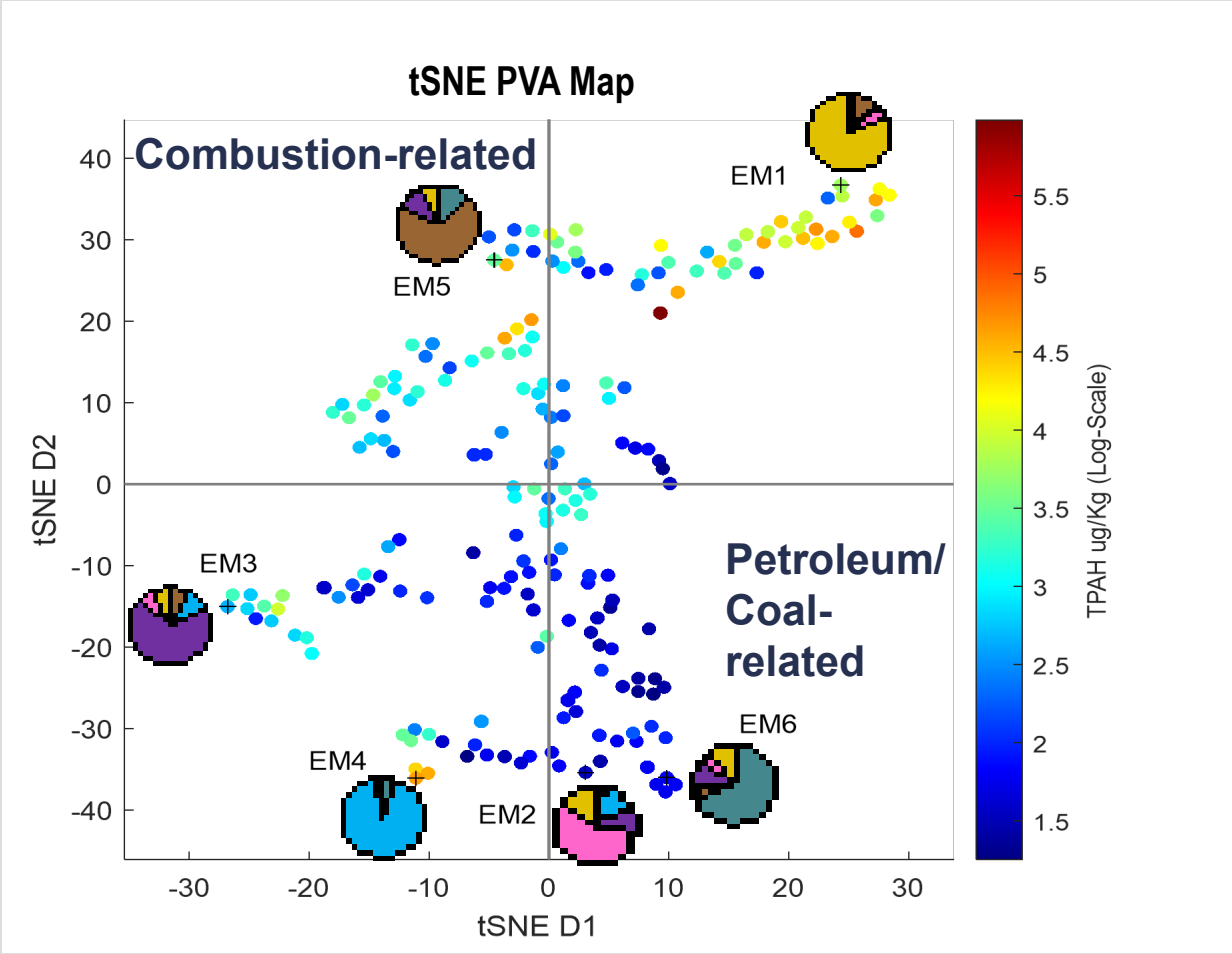


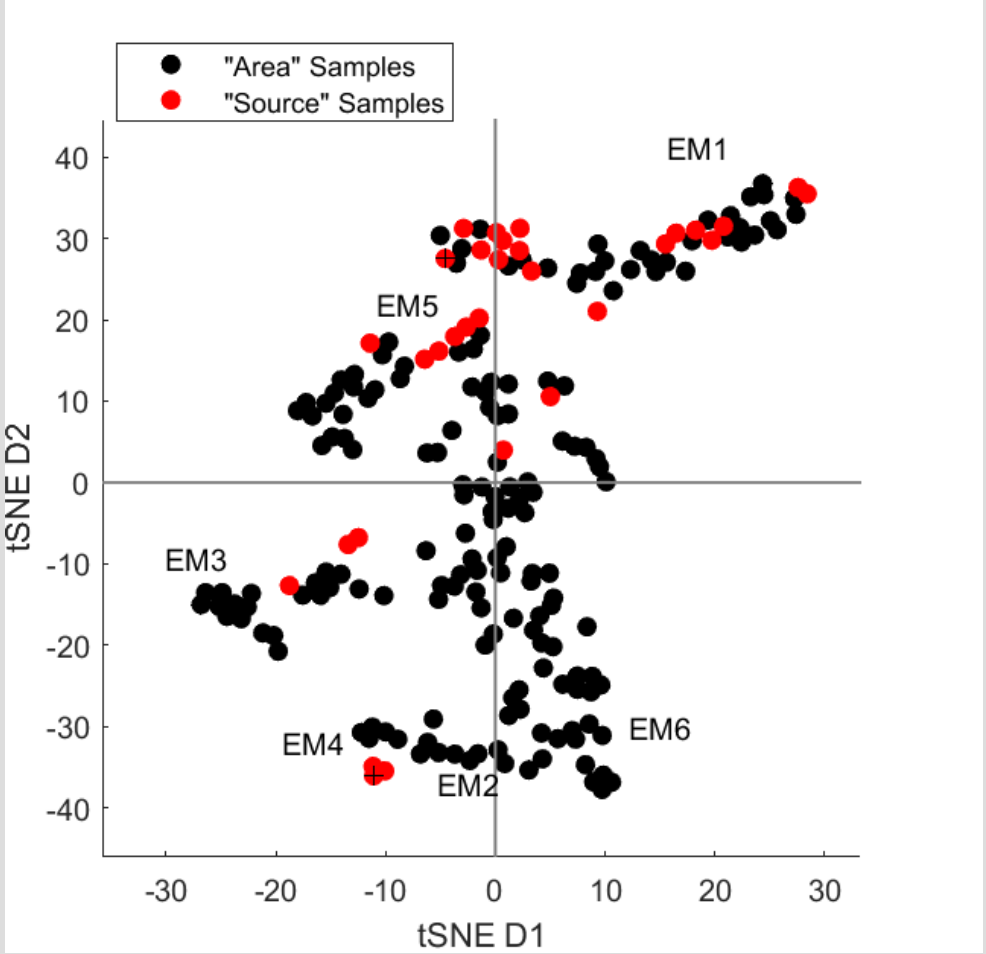
Forensics: Multivariate Analysis

- Six distinct, statistically derived end members were identified to describe the PAH composition of the samples collected.
  - 2 Pyrogenic (combustion)
  - 3 Petrogenic (petroleum)
  - 1 Coal-Related



Forensics: Multivariate Analysis





Generally, higher Total PAH (TPAH) concentrations were associated with combustion-related (pyrogenic) fingerprints and lower TPAH concentrations were associated with fuel (petrogenic) fingerprints.

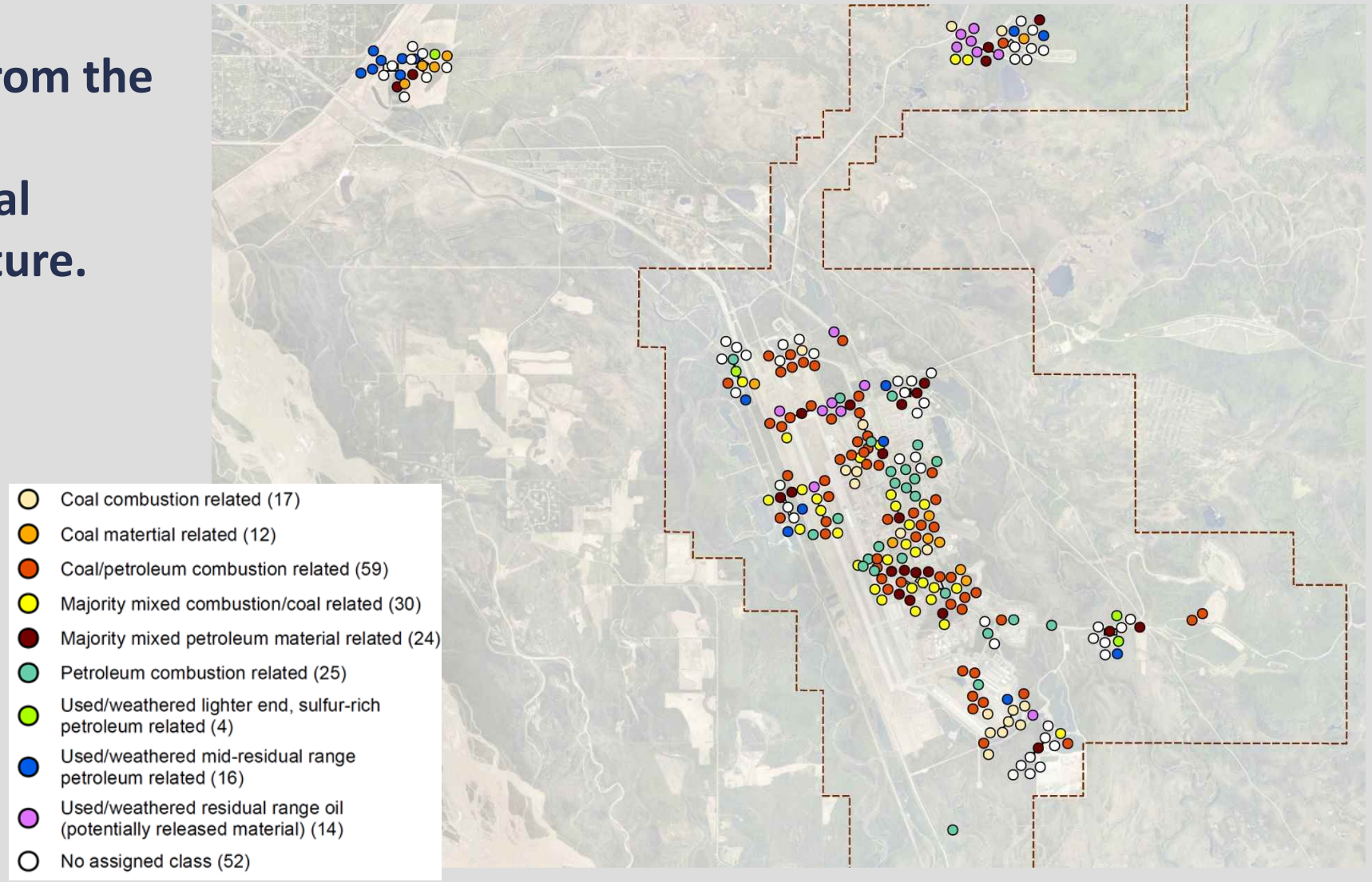
Forensics: Classification of Samples

Sample classification scheme based on end-member (EM) compositions.

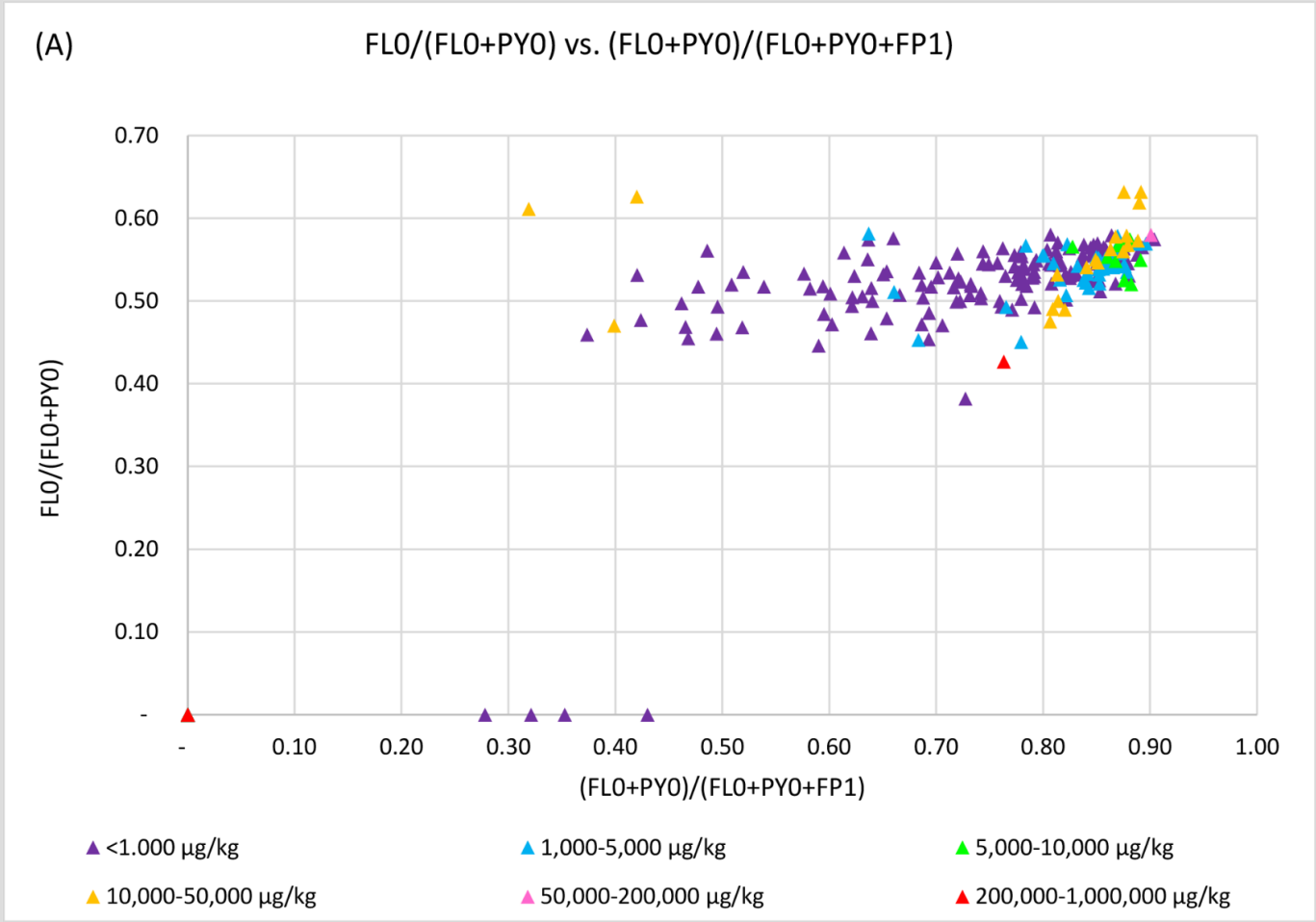
EM compositions	Sample classification
EM1 ≥40%	Coal combustion related
EM5 ≥40%	Petroleum combustion related
EM1+EM5 ≥60%	Coal/petroleum combustion related
EM4 ≥40%	Coal material related
EM3 ≥40%	Used/weathered residual range oil (potentially released material)
EM2 ≥30%	Used/weathered lighter end, sulfur-rich petroleum related
EM6 ≥40%	Used/weathered mid-residual range petroleum related
EM3+EM2+EM6 >50%	Majority mixed petroleum material related
EM1+EM5+EM4 >50%	Majority mixed combustion/coal related

Forensics: Distribution of Samples by Category

- Most of the samples from the main base area had a combustion and/or coal material related signature.

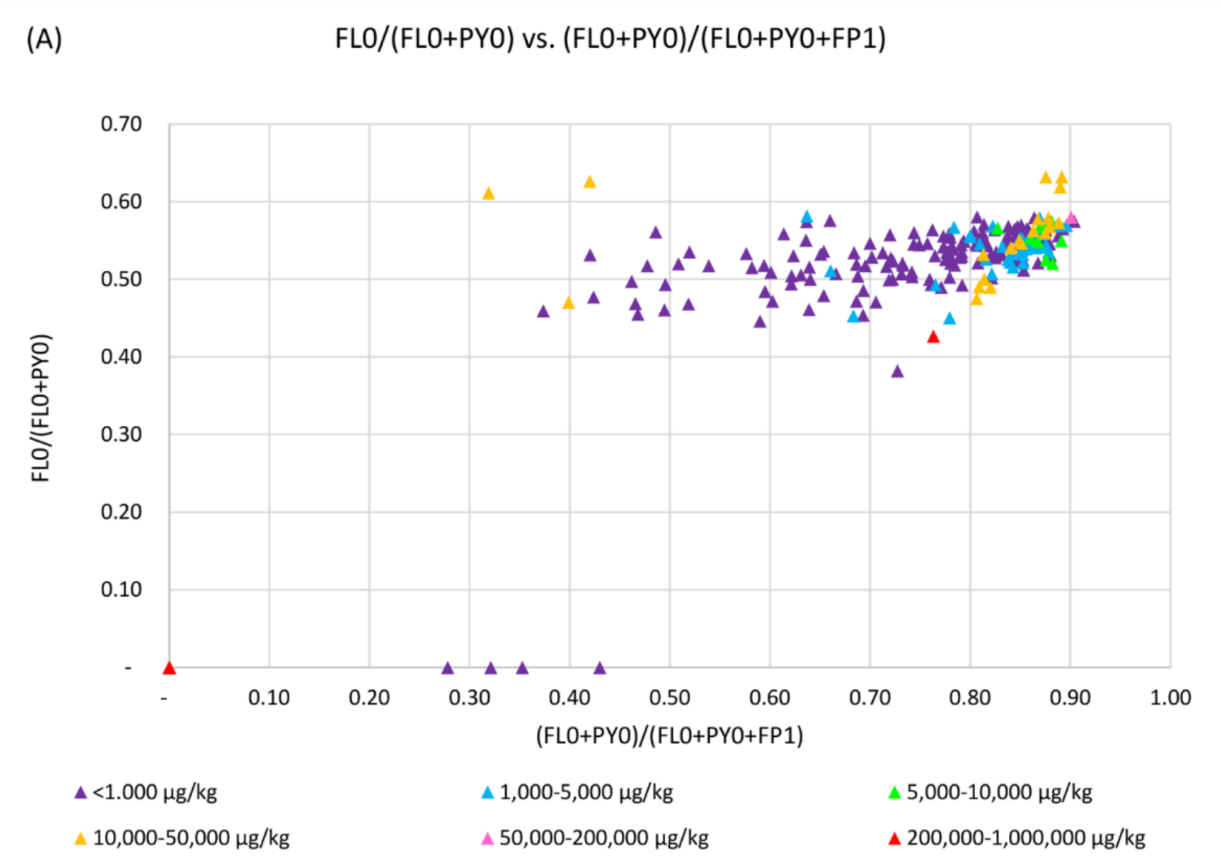


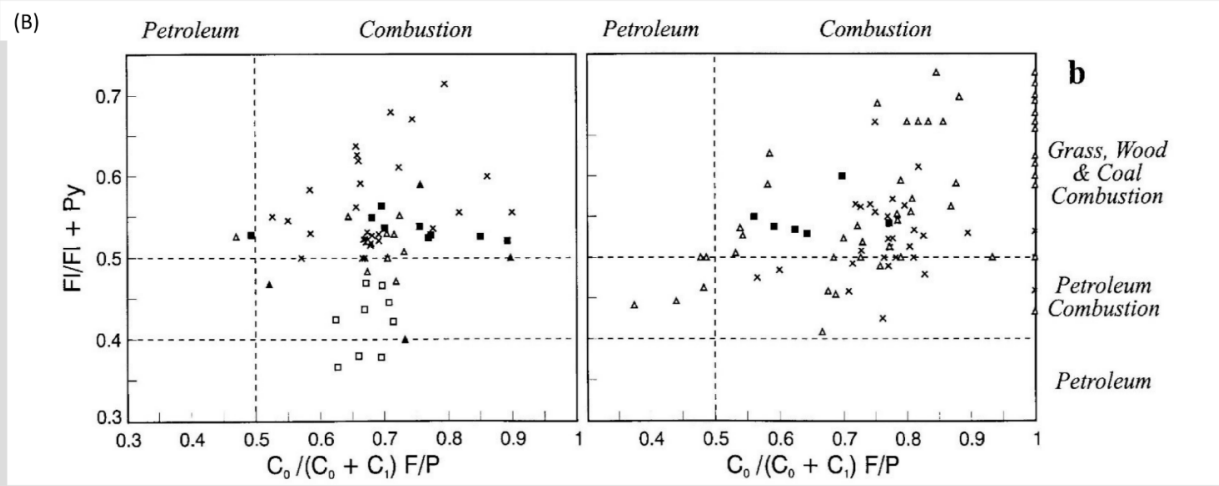
Forensics: Diagnostic PAH Ratio Evaluation



$$\frac{\text{Fluoranthene}}{\text{Fluoranthene+Pyrene}} \text{ vs. } \frac{\text{Fluoranthene+Pyrene}}{\text{Fluoranthene+Pyrene+C1–Fluoranthenes+Pyrenes}}$$

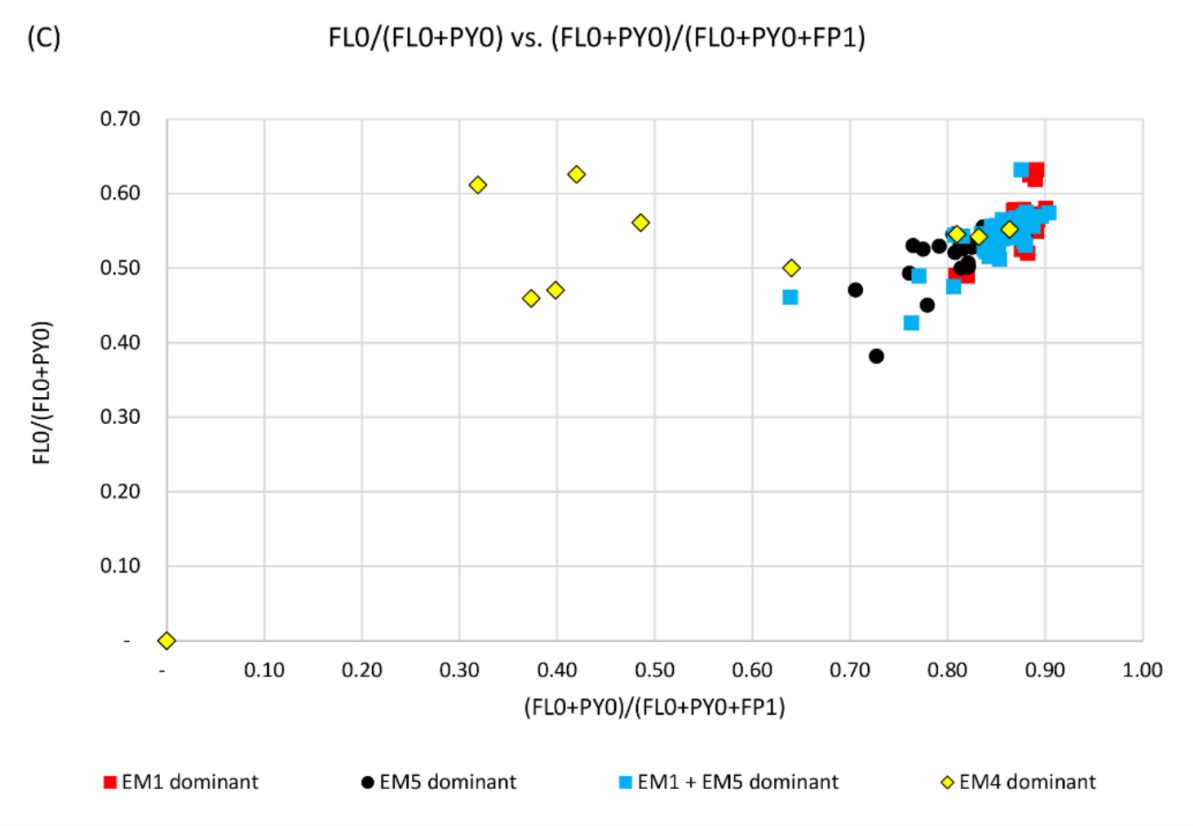
Forensics: Diagnostic PAH Ratio Evaluation

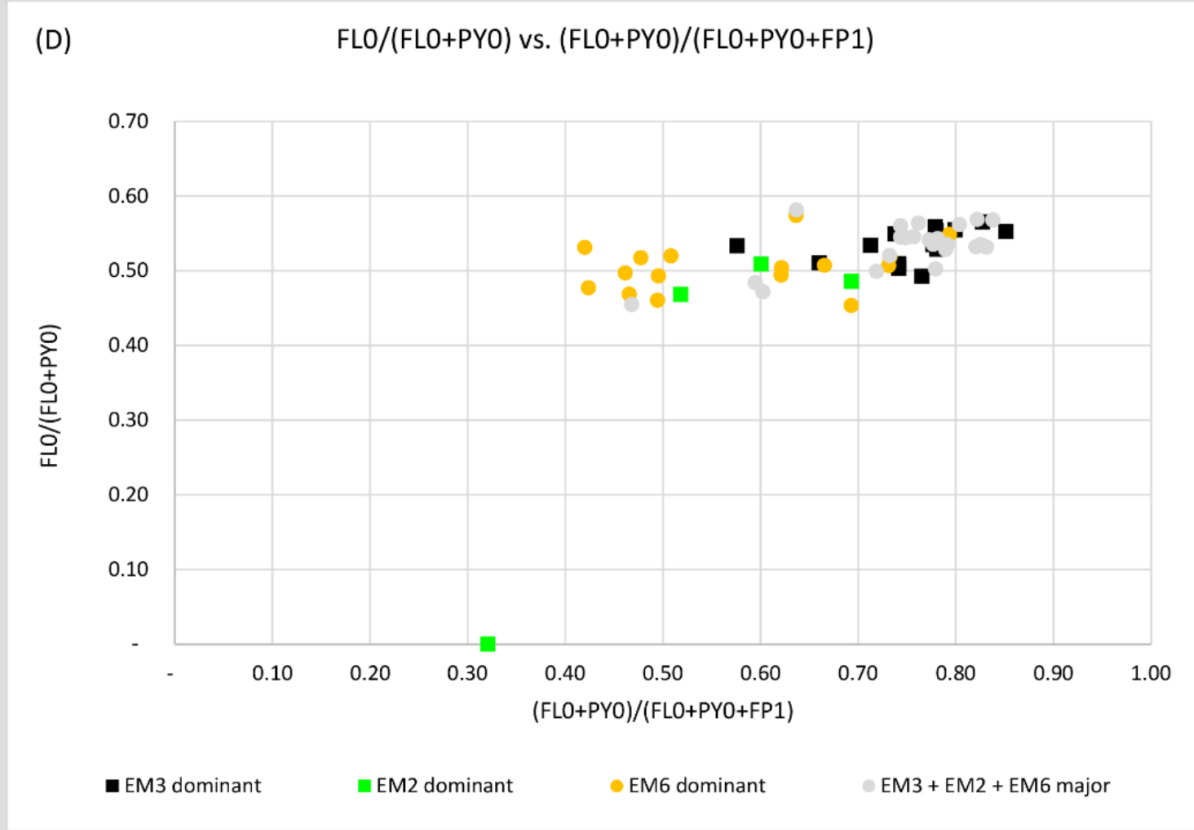




From Yunker et al. 2002 (Figure 4b).

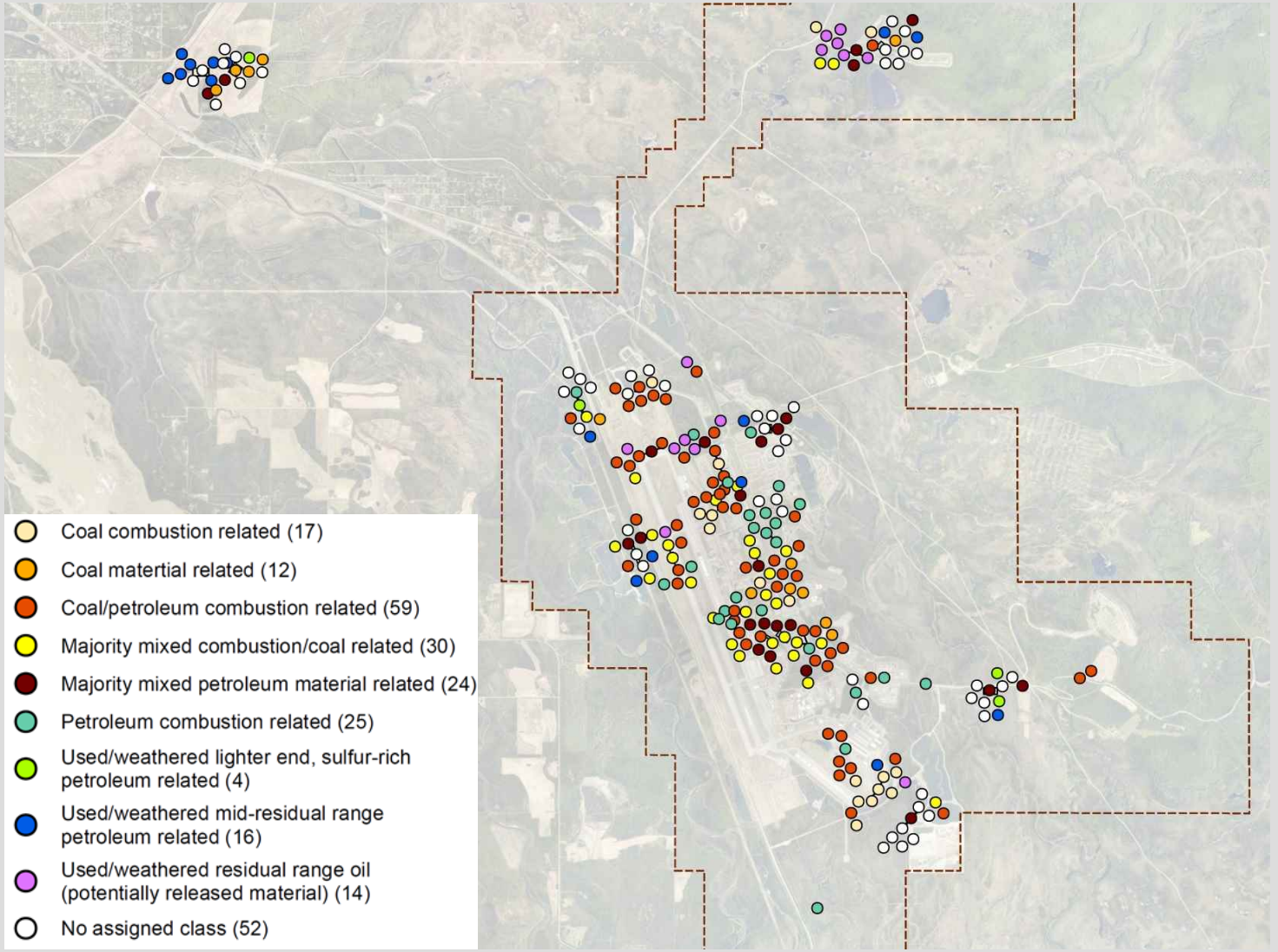
Forensics: Diagnostic PAH Ratio + Multivariate Analysis



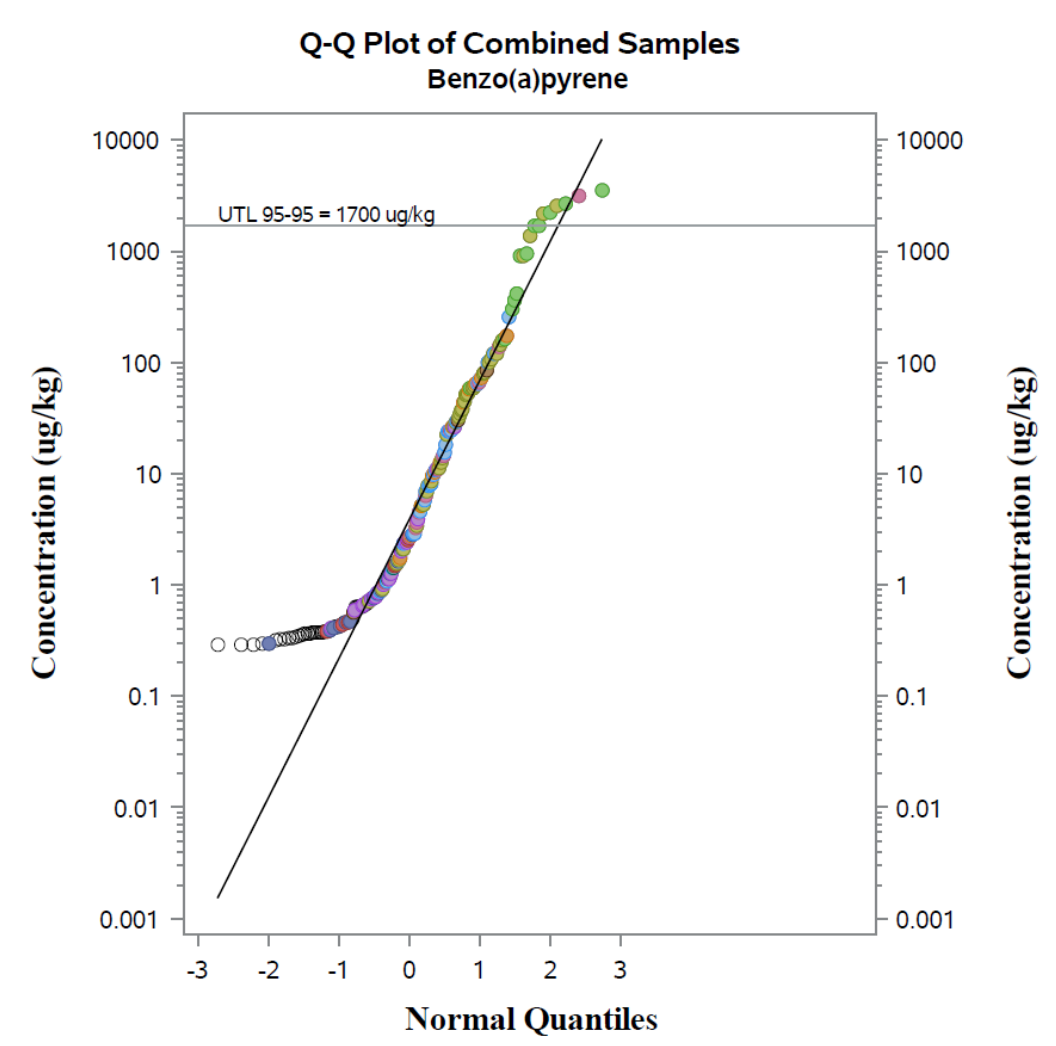


Forensics: Conclusions

- Significant spatial trends.
- Main base:
  - PAHs from combustion-related and coal-related sources
  - Higher TPAH concentrations.
- Other areas:
  - More petrogenic sources
  - Lower TPAH concentrations
- Overall, surface soil in the main base area contains elevated concentrations of pyrogenic PAHs.



Statistical Analysis of Reference PAH Concentrations

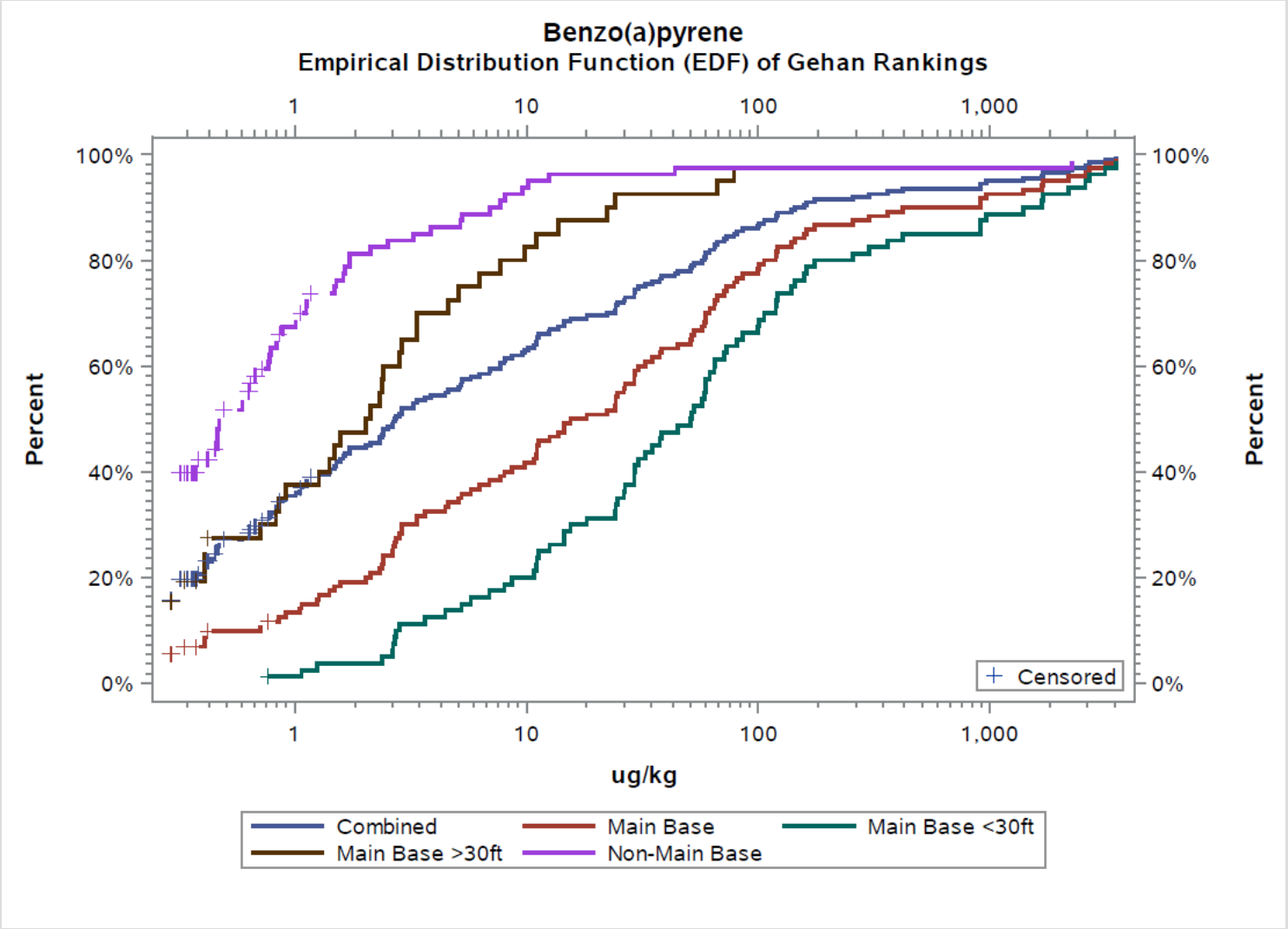


- Q-Q plots of individual PAHs in reference soil data used to evaluate the data distribution and identify potential outliers.
- No outliers were removed from calculations.

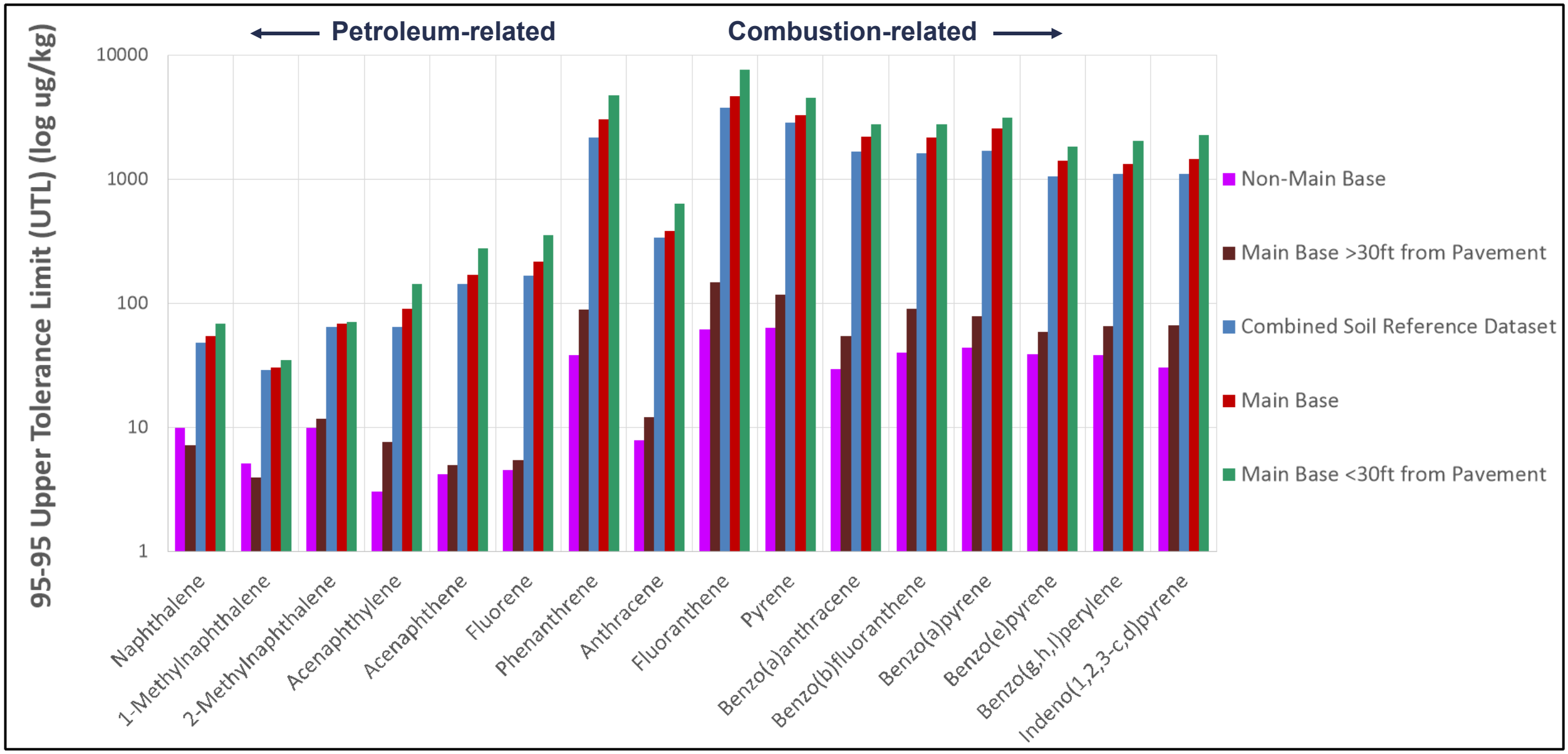
CLASS
- No assigned class
- Used/weathered mid-residual range petroleum related
- Used/weathered lighter end, sulfur-rich petroleum related
- Coal material related
- Majority mixed petroleum material related
- Coal/petroleum combustion related
- Majority mixed combustion/coal related
- Petroleum combustion related
- Used/weathered residual range oil (potentially released material)
- Coal combustion related

Statistical Analysis of Reference PAH Concentrations

- EDF Plots were created to provide visual comparison of the data sets for different soil reference sample groupings



Statistical Analysis of Reference PAH Concentrations



Proposed Applications for Remedial Decisions

Suggested approaches for analyzing PAH surface soil from specific sites to provide lines of evidence as to whether the PAHs are site-related or consistent with the reference PAH signature at Eielson:

- **Compare a site-specific PAH data set of 10 or more samples to 95-95UTLs using a single-sample hypothesis test.**
- **Compare a site-specific PAH data set of 20 or more samples to 95-95UTLs, with data considered consistent with the PAH reference values if fewer than 5% of results exceed the 95-95UTL.**
- **Compare site-specific and reference PAH data sets using hypothesis testing.**
- **Compare site-specific PAH datasets of fewer than 10 samples to the percentile and maximum concentrations from the reference data set.**

Summary/Conclusions

- ✓ Combustion-related PAHs are widely distributed in surface soils at Eielson AFB, with UTL95-95 reference concentrations exceeding 1,000 µg/kg, or 1 mg/kg.
- ✓ Forensics analysis indicates that most of the mass of PAHs present in soils on the developed portion of the base is derived from coal and petroleum combustion.
- ✓ PAH concentrations in soil farther from the base power plant, flightline, and roadways are substantially lower.
- ✓ EPA and Alaska Department of Environmental Conservation approved the findings for use as appropriate to evaluate surface soil PAH data for sites at Eielson AFB and guide remedial decisions.

Thank You!

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BACKUP SLIDES

Analytes

PAHs and Related Analytes Reported by Method SW-846 8270 MOD:

Acenaphthene*	Pyrene*
Acenaphthylene*	Perylene*
Anthracene*	Retene*
Benzo(a)pyrene*	1-Methylnaphthalene
Benzo(a)anthracene*	2-Methylnaphthalene
Benzo(b)fluoranthene*	2,6-Dimethylnaphthalene
Benzo(j+k)fluoranthene*	2,3,5-Trimethylnaphthalene
Benzo(e)pyrene*	1-, 2-, 3-, and 9/4-Methylphenanthrene
Benzo(g,h,i)perylene*	2-Methylanthracene
Biphenyl*	1-, 2-, and 4-Methylpyrenes

Chrysene/Triphenylene*	1-, 2/3-, and 4-Methyldibenzothiophenes
Cis/trans-Decalin*	C1-, C2-, C3-, C4-Benzo(b)thiophenes
Dibenz(a,h)+(a,c)anthracene*	C1-, C2-, C3-, C4-Chrysenes*
Dibenzofuran*	C1-, C2-, C3-, C4-Decalins*
Dibenzothiophene*	C1-, C2-, C3-, C4-Dibenzothiophenes*
Fluoranthene*	C1-, C2-, C3-, C4-Fluoranthenes+pyrenes*
Fluorene*	C1-, C2-, C3-Fluorenes*
Indeno(1,2,3-cd)pyrene*	C1-, C2-, C3-, C4-Naphthalenes*
Naphthalene*	C1-, C2-, C3-, C4-Naphthobenzothiophenes*
Phenanthrene*	C1-, C2-, C3-, C4-Phenanthrenes+anthracenes*

*Asterisks indicate analytes used in forensic evaluation