



Analysis of Petroleum Coke for Polycyclic Aromatic Hydrocarbon Signatures

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U.S. EPA Region 5

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for

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U.S. Environmental Protection Agency

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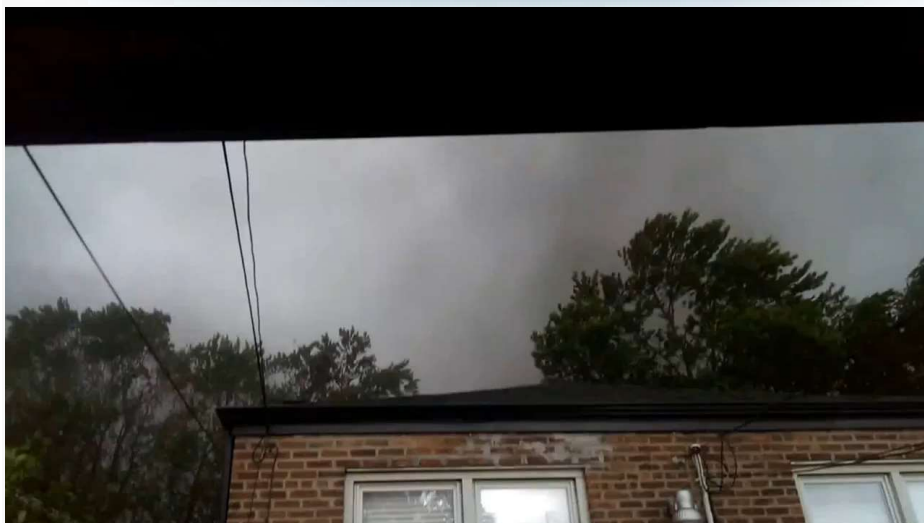
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Nuisance?



Near Chicago

David Windycity



Near Detroit

3860remerson



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What was the problem?



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What was the problem?

Are the piles associated with nuisance dust?

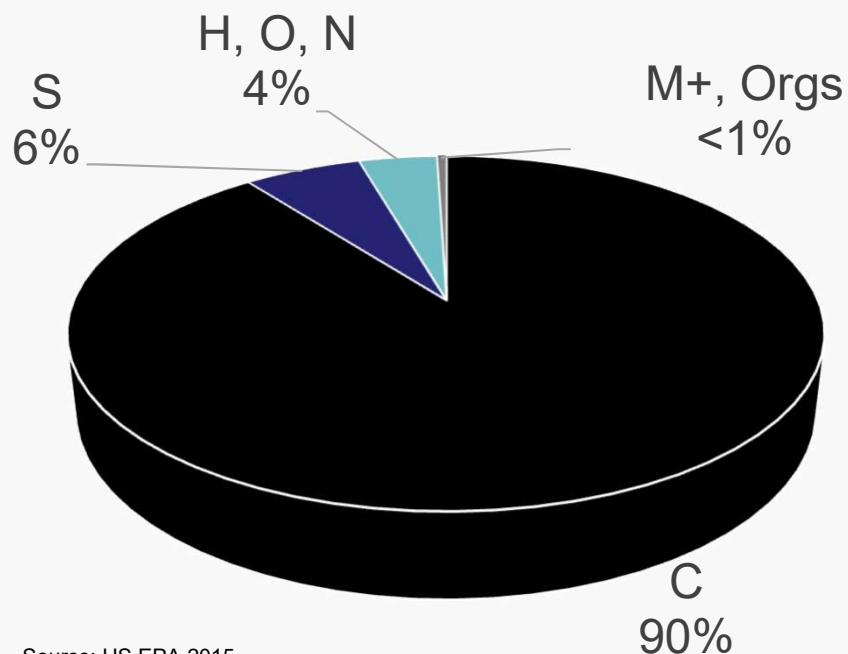


Petcoke Material

Stable, non-reactive

US: In 2012, 56M tonnes, 80% exported.

(CRS 2013)



Source: US EPA 2015

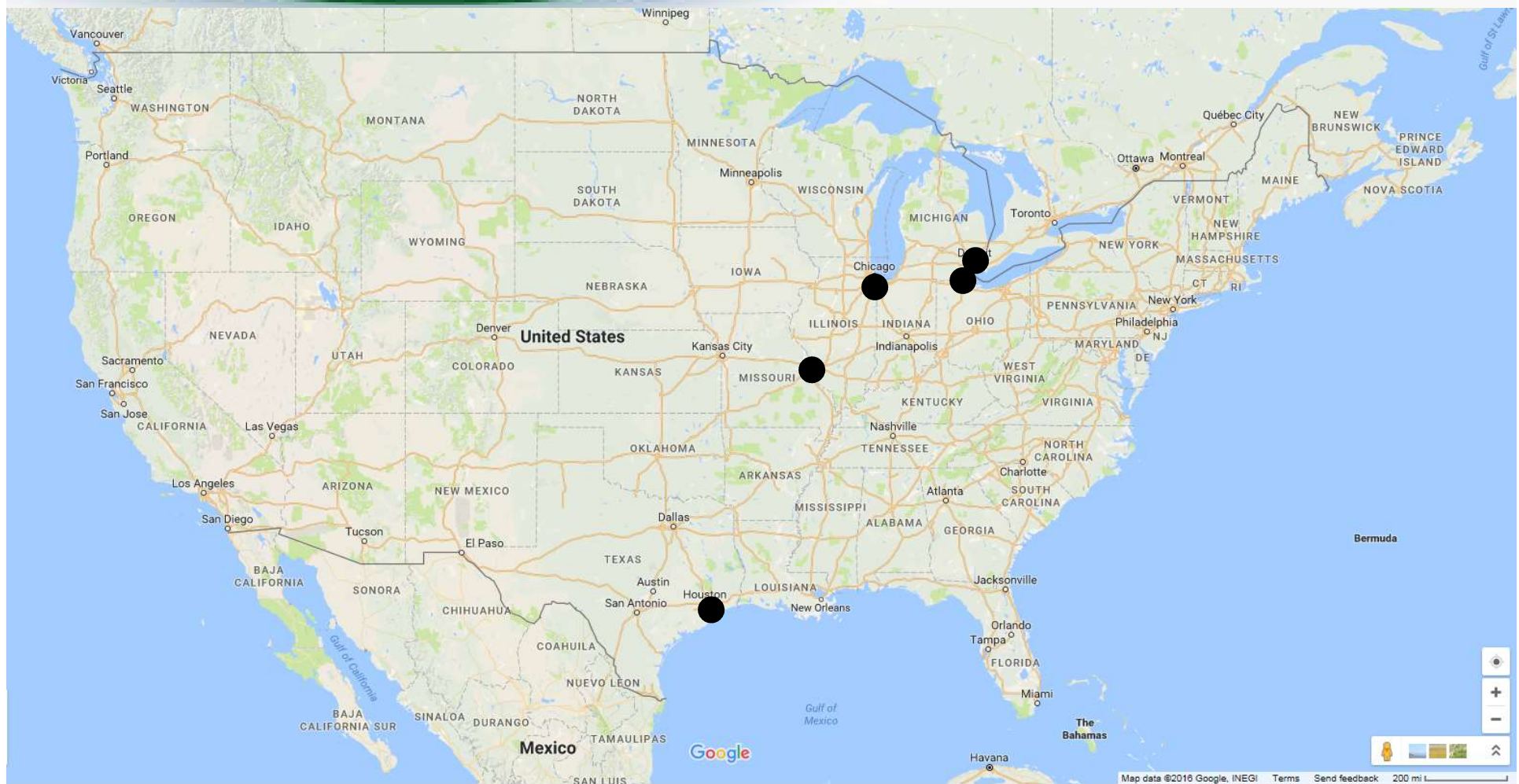
$d=1.4-1.6 \text{ g/cm}^3$



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Where was the problem?

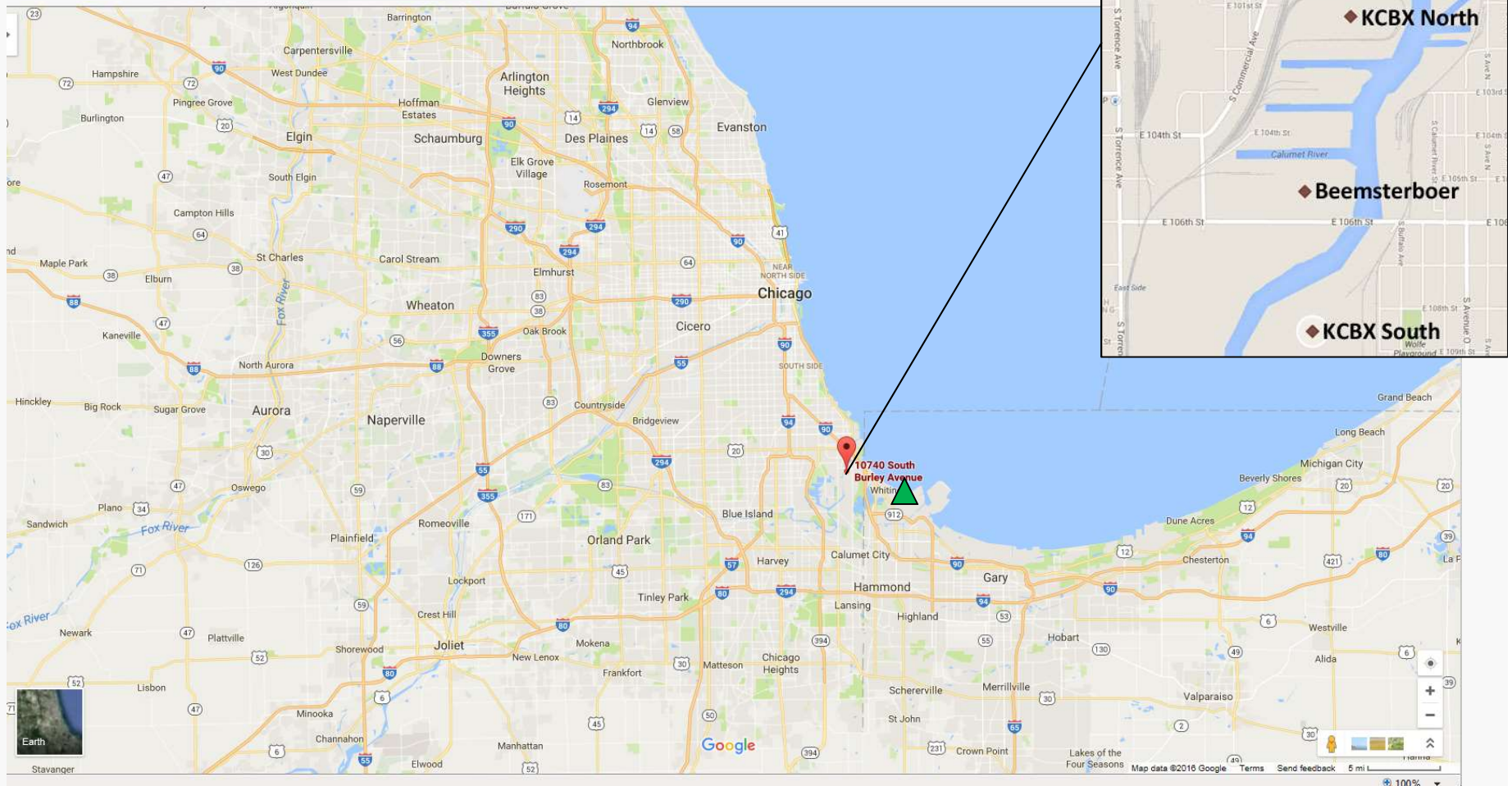


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Where was the problem?



Site



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Where was the problem?



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Why was there a problem?



PM₁₀

Particulate matter less than 10 microns



Inhalation

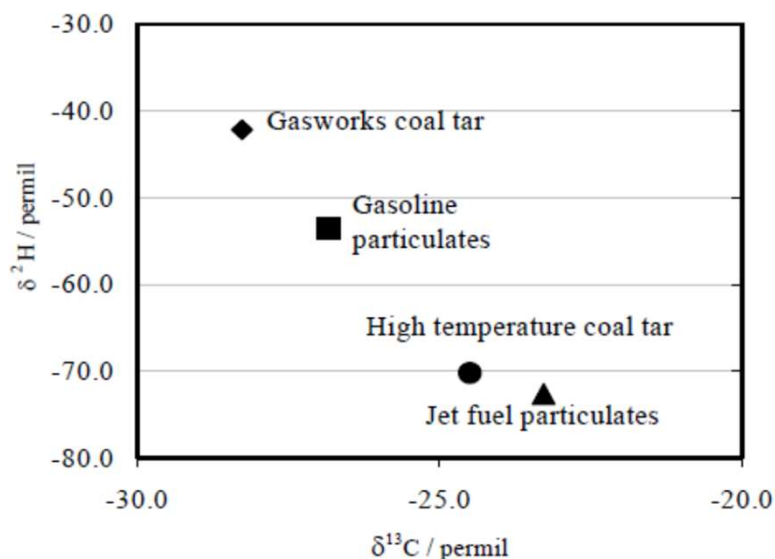
Assessing the Problem

Are the piles associated with residential dust?

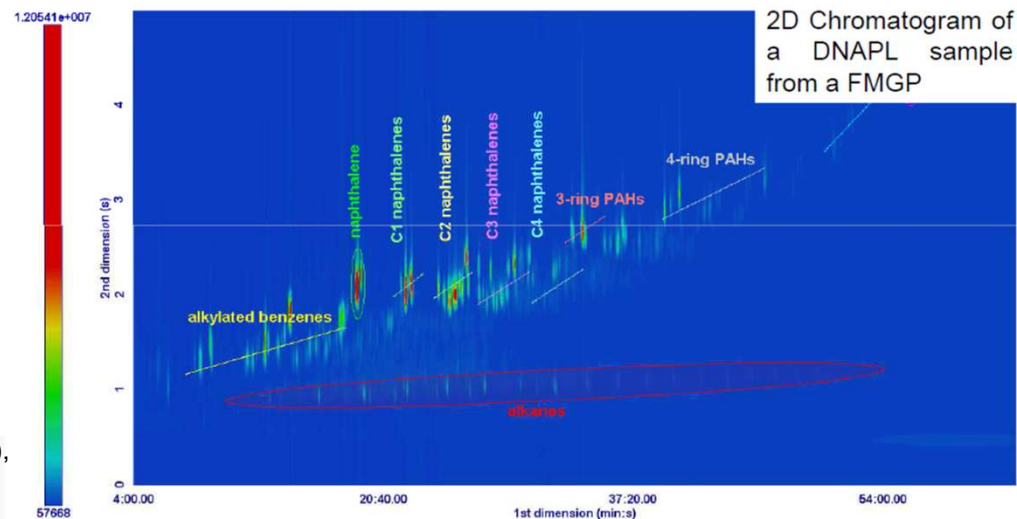


- CSIA ($\delta^{13}\text{C}$) or GCxGC not readily available
- Abundance “fingerprinting” PAH accessible

GCxGC contour plot



Sun et al., Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. **2003**, 48(2), 761



Robert M. Kalin U of Strathclyde Engineering

Simple plan: collect samples from piles and wipes to look at the PAH fingerprints.

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Figure 1. Petcoke Sampling Locations at South Terminal

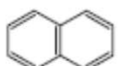
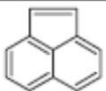
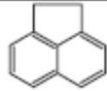
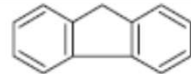
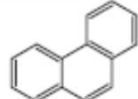
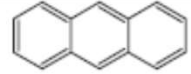
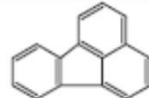

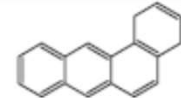
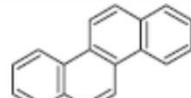
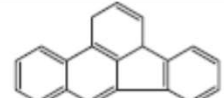
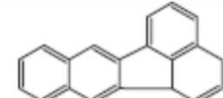
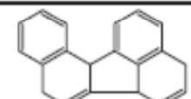
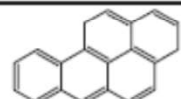
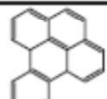
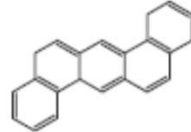

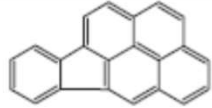


Blue line is approximate KCBX property boundary

Figure 2. Petcoke Sampling Locations at North Terminal



Blue line is approximate KCBX property boundary

 <i>naphthalene</i> * $C_{10}H_8$	 <i>acenaphthylene</i> (D) $C_{12}H_8$	 <i>acenaphthene</i> $C_{12}H_{10}$
 <i>fluorene</i> (D) $C_{13}H_{10}$	 <i>phenanthrene</i> (D) $C_{14}H_{10}$	 <i>anthracene</i> (D) $C_{14}H_{10}$
 <i>fluoranthene</i> (D) $C_{16}H_{10}$	 <i>pyrene</i> (D) $C_{16}H_{10}$	 <i>benzo[a]anthracene</i> (B2) $C_{18}H_{12}$
 <i>chrysene</i> (B2) $C_{18}H_{12}$	 <i>benzo[b]fluoranthene</i> (B2) $C_{20}H_{12}$	 <i>benzo[k]fluoranthene</i> $C_{20}H_{12}$
 <i>benzo[j]fluoranthene</i> $C_{20}H_{12}$	 <i>benzo[a]pyrene</i> (B2) $C_{20}H_{12}$	 <i>benzo[e]pyrene</i> $C_{20}H_{12}$
 <i>dibenz[a,h]anthracene</i> (B2) $C_{22}H_{14}$	 <i>benzo[g,h,i]perylene</i> (D) $C_{22}H_{12}$	 <i>indeno[1,2,3-c,d]pyrene</i> (B2) $C_{22}H_{12}$



- X benz(a)anthracene
- X benzo(a)pyrene
- X benzo(b)fluoranthene
- X benzo(k)fluoranthene
- X chrysene
- X dibenz(a,h)anthracene
- X indeno(1,2,3-c,d)pyrene.

Assessing the Problem



ANALYTE	REPORTING LIMIT (µg/kg)
Naphthalene	3.3
2-Methylnaphthalene	3.3
1-Methylnaphthalene	3.3
Acenaphthylene	0.67
Acenaphthene	3.3
Fluorene	3.3
Phenanthrene	3.3
Anthracene	0.67
Fluoranthene	3.3
Pyrene	3.3
Benzo (a) anthracene	0.67
Chrysene	0.67
Benzo(b)fluoranthene	0.67
Benzo(k)fluoranthene	0.67
Benzo (e) pyrene	0.67
Benzo(a)pyrene	0.67
Perylene	0.67
Indeno(1,2,3-cd)pyrene	0.67
Dibenz(a,h)anthracene	0.67
Benzo(g,h,i)perylene	0.67

13 Waste, 14 Wipes



Assessing the Problem



Figure 2. Shot Coke
Partially Crushed



Source: John D. Elliott, Shot Coke: Design & Operations, http://www.fwc.com/publications/tech_papers/oil_gas/shotcoke.pdf.

Congressional Research Service, 2013

Assessing the Problem



Prep: Pressurized fluid extraction (EPA 3545A; $\text{C}_3\text{H}_6\text{O}$, CH_2Cl_2 (one to one)), 30 g sample size, 22 mL cell

Drying (Na_2SO_4)

Concentration to 1 mL with N_2

Assessing the Problem



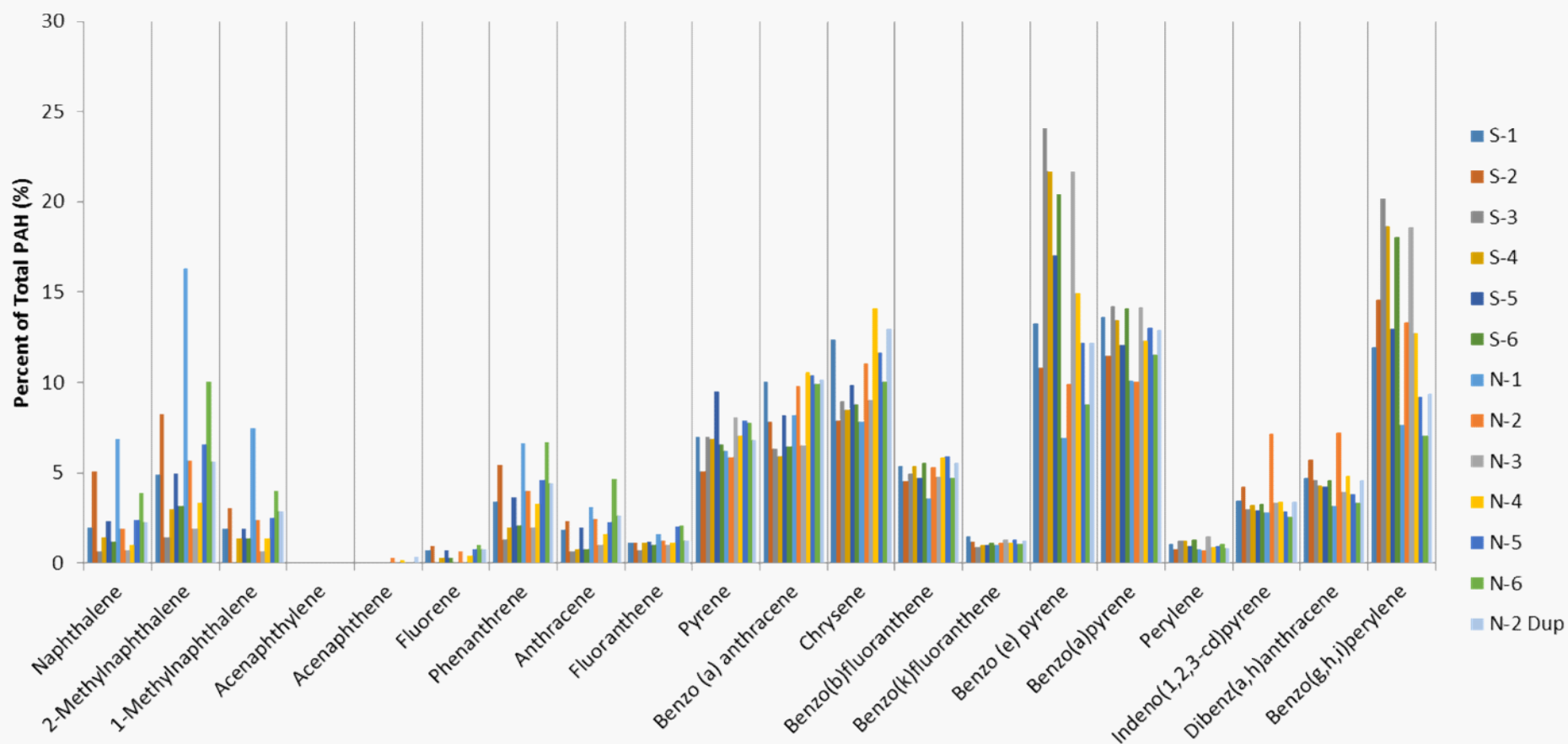
Analysis:
GC/MS in SIM mode (EPA 8270D)

Results

Relative Abundances



Relative PAH Abundances in Petcoke

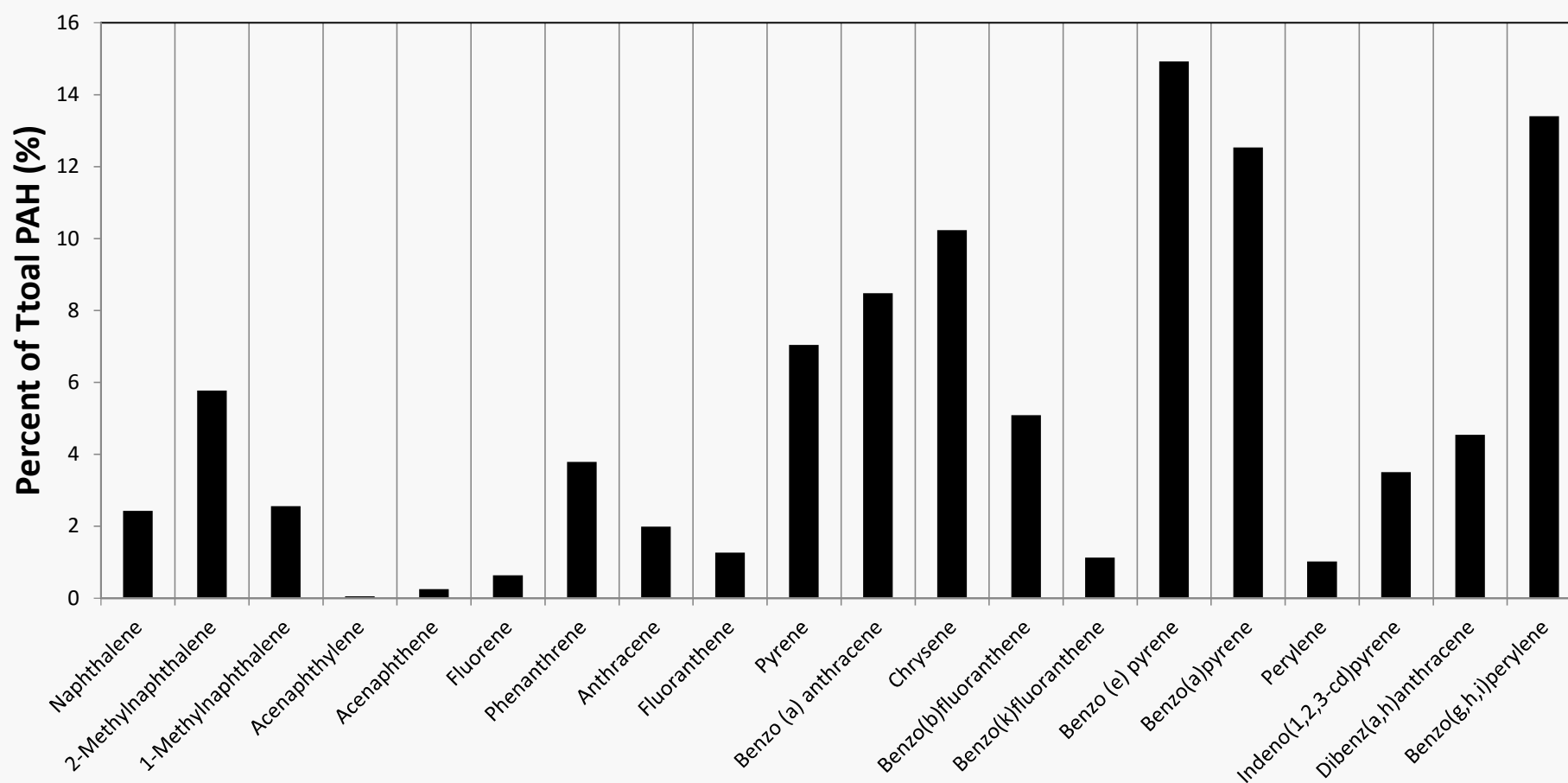


Results

Relative Abundances



Mean Relative PAH Abundances in Petcoke



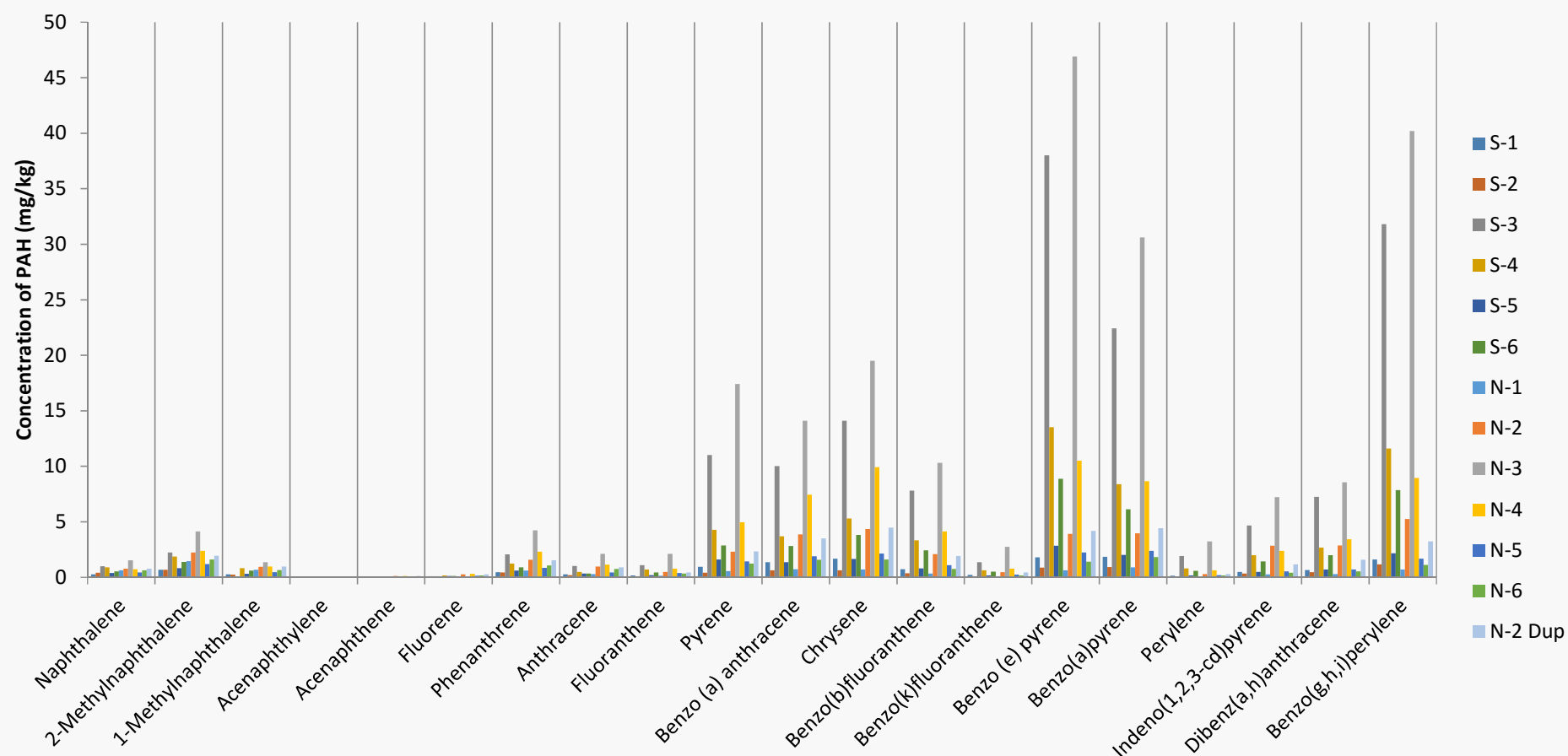
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Results

Raw Concentrations



PAH Concentraitons in Petcoke



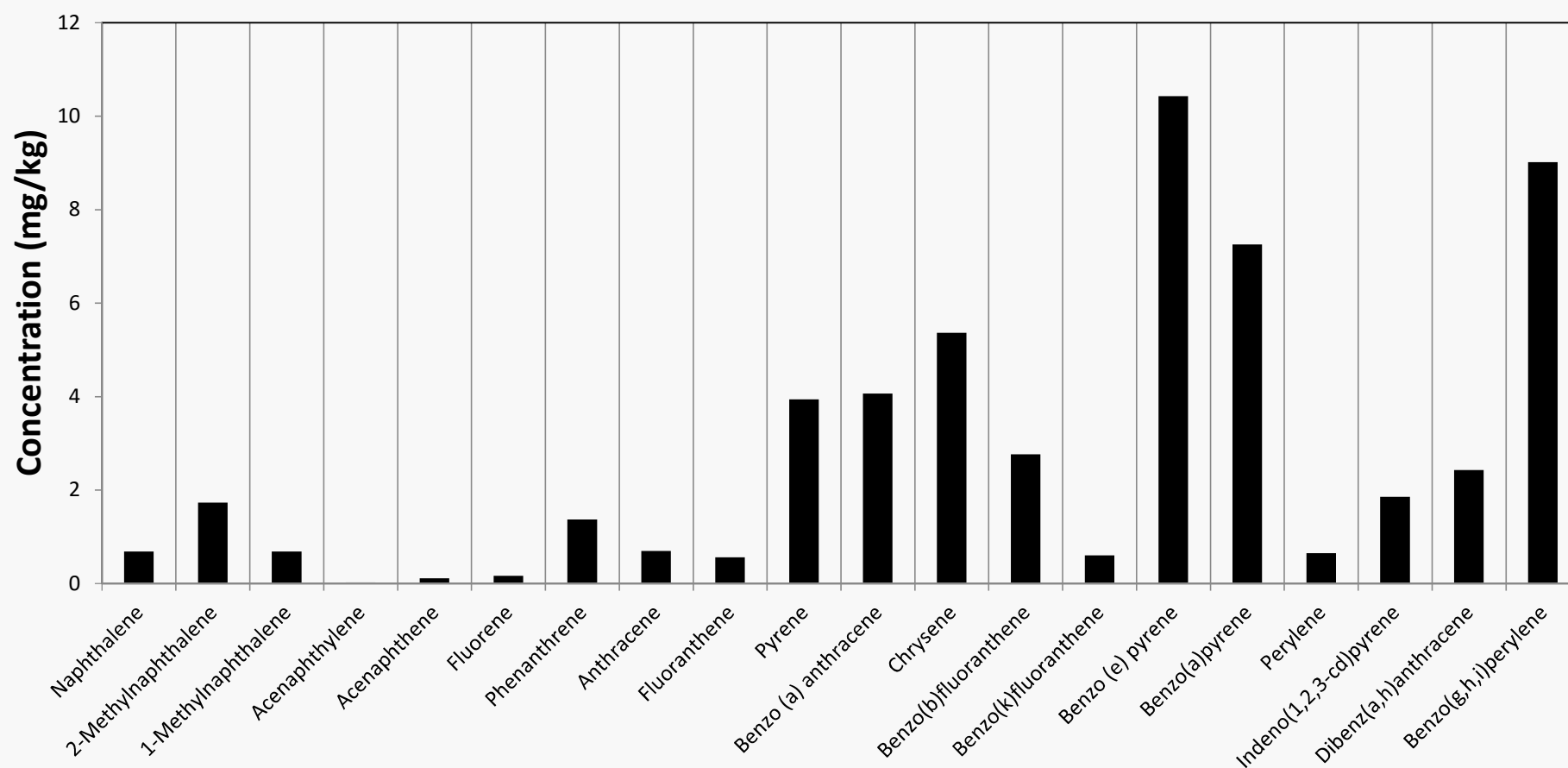
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Results

Raw Concentrations



Mean Concentration PAH in Petcoke



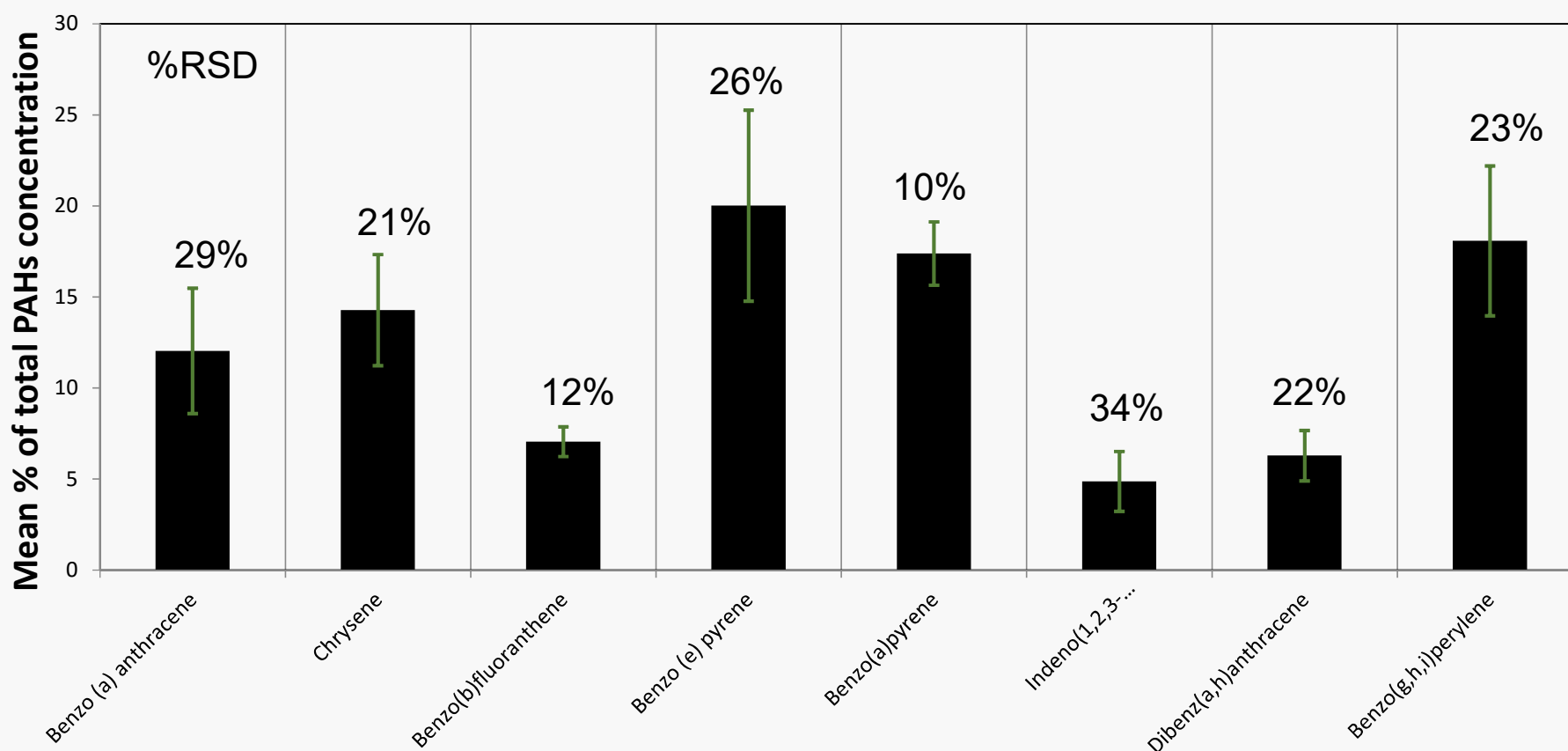
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Results

Variability



Variability in relative concentrations of select PAHs in petcoke samples



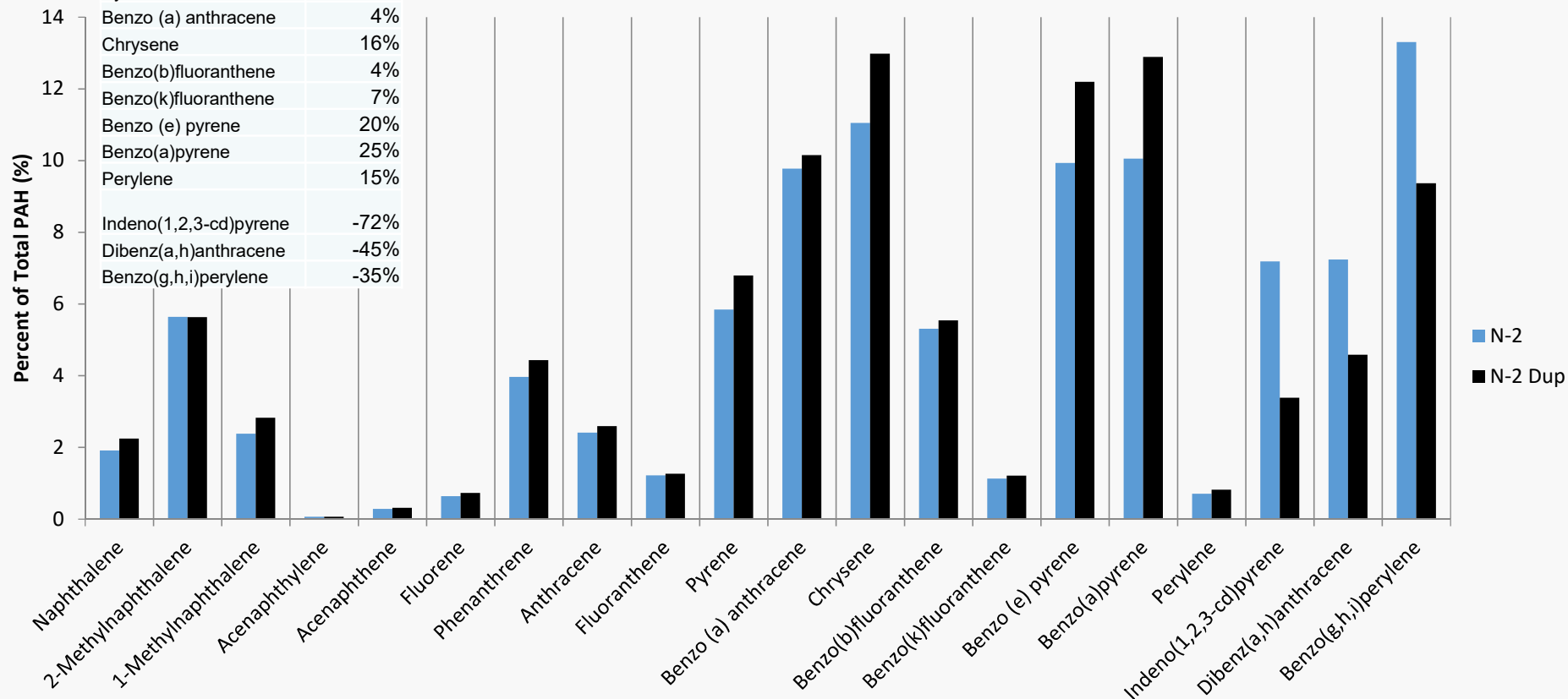
Results

Variability



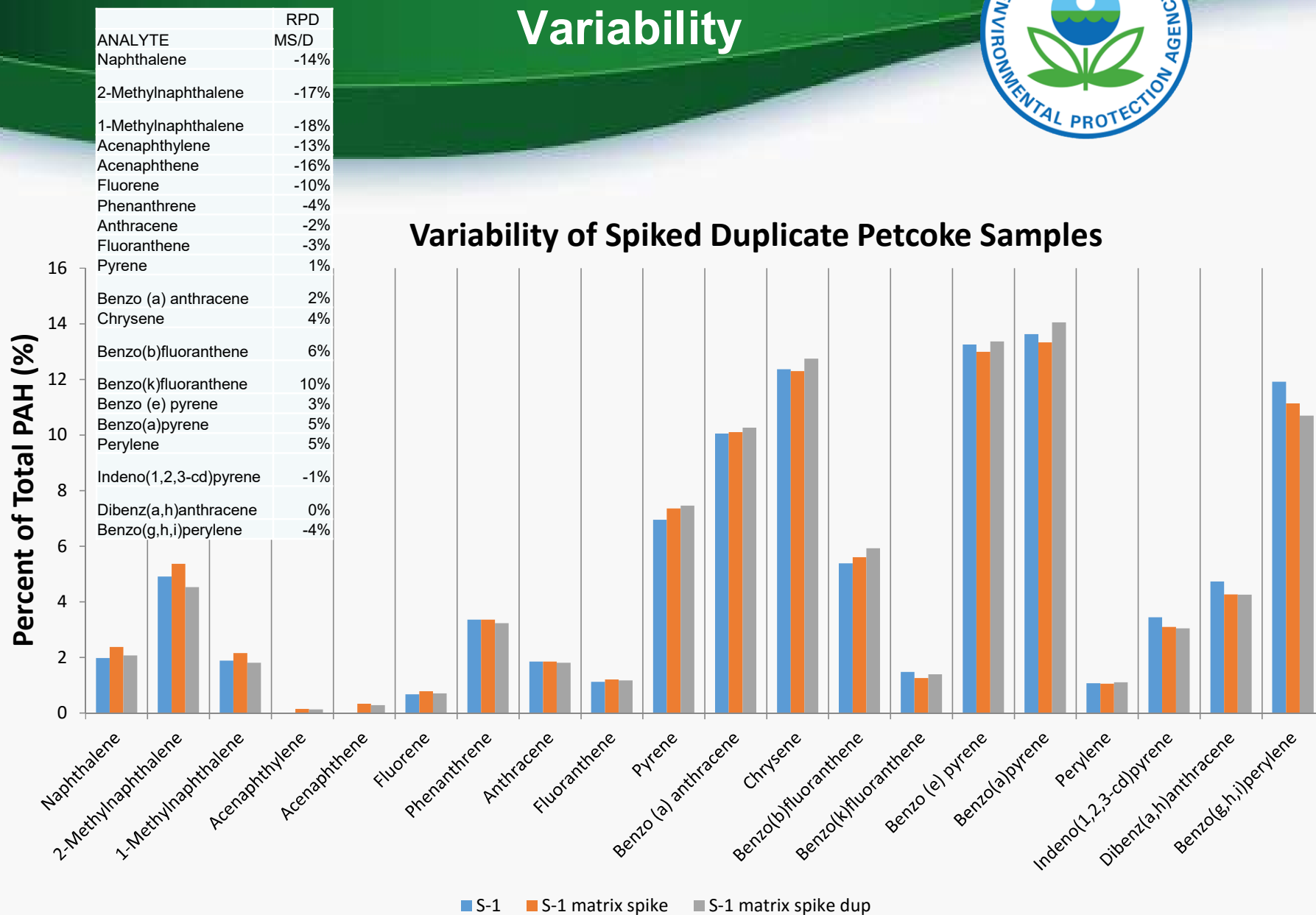
ANALYTE	RPD N2-DUP
Naphthalene	16%
2-Methylnaphthalene	0%
1-Methylnaphthalene	17%
Acenaphthylene	-3%
Acenaphthene	12%
Fluorene	13%
Phenanthrene	11%
Anthracene	7%
Fluoranthene	4%
Pyrene	15%
Benzo (a) anthracene	4%
Chrysene	16%
Benzo(b)fluoranthene	4%
Benzo(k)fluoranthene	7%
Benzo (e) pyrene	20%
Benzo(a)pyrene	25%
Perylene	15%
Indeno(1,2,3-cd)pyrene	-72%
Dibenz(a,h)anthracene	-45%
Benzo(g,h,i)perylene	-35%

Variability of Field Duplicate Petcoke Samples



Results

Variability

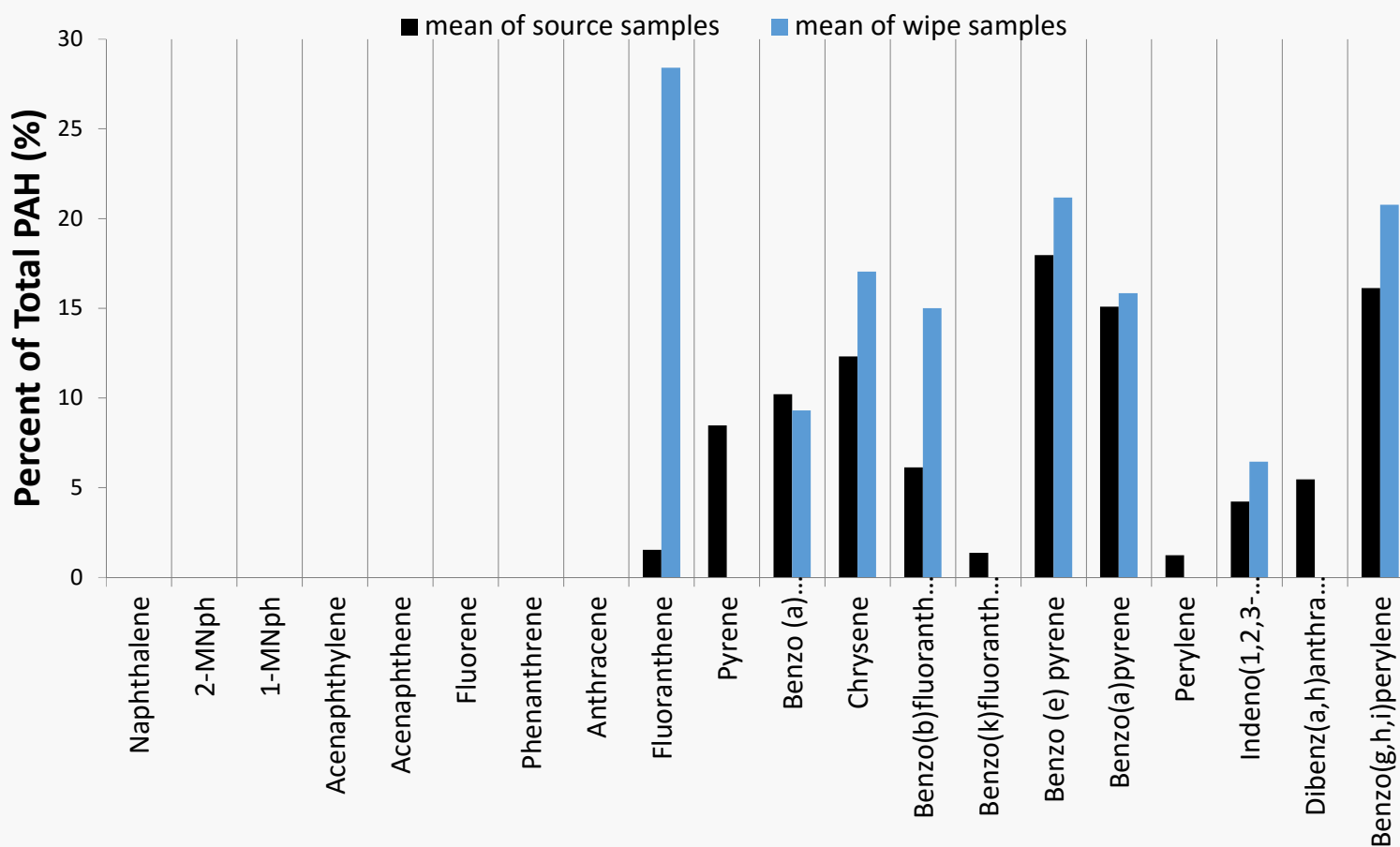


Results

Matrices

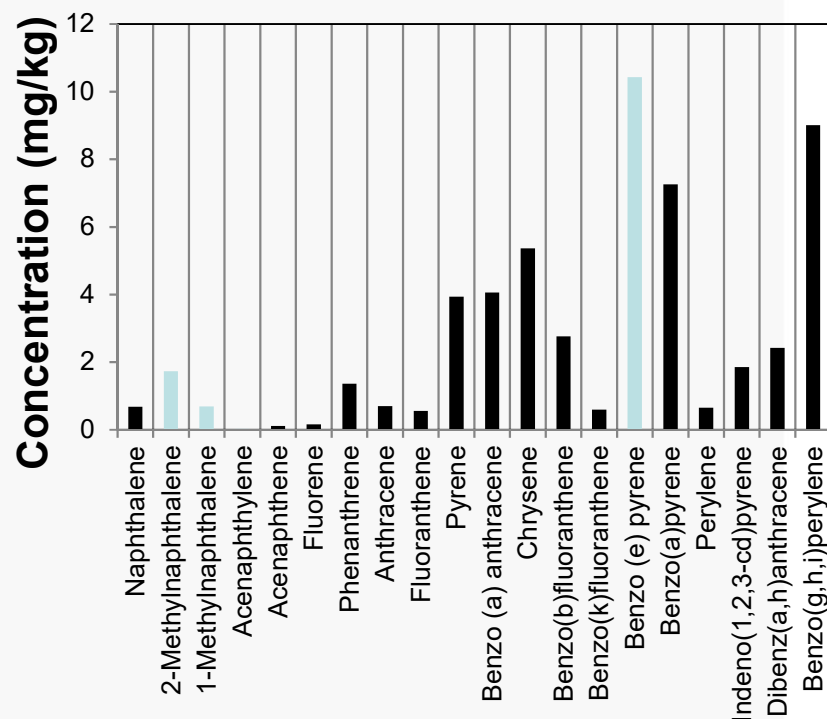


Comparison of Relative Concentrations of PAHs in Wipes and Petcoke Source Samples



Results

Mean PAH Concentration in Petcoke

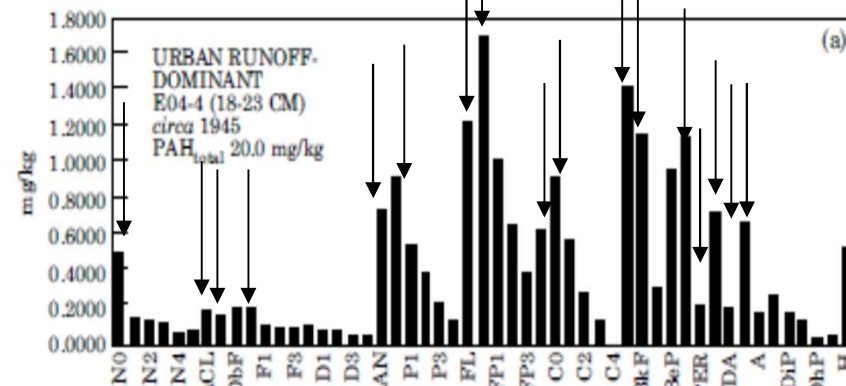


0.11

N=13

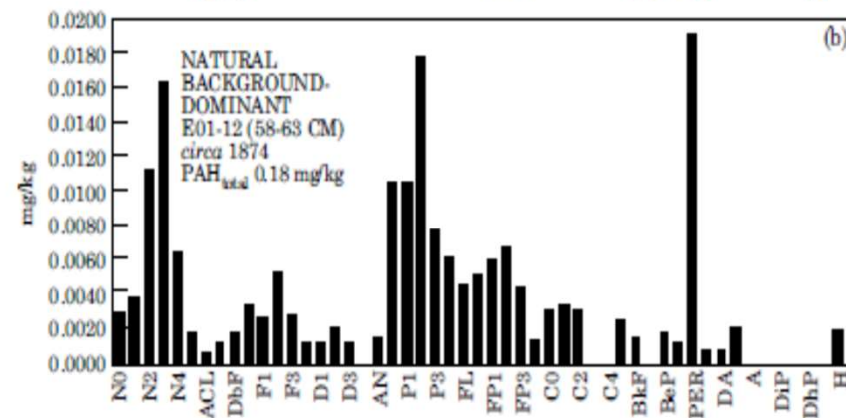
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S. A. Stout *et al.*

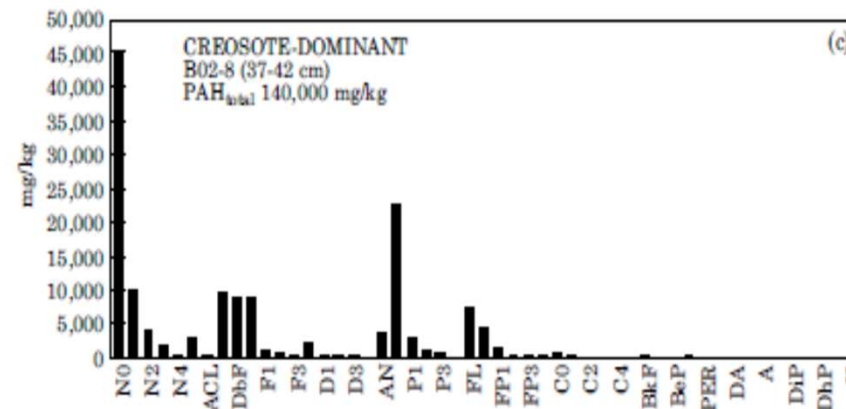


Ring
Ratios

0.25
n=29



0.98
n=15



3.18
n=23

Figure 9. PAH histograms for the three sediment samples selected from the apices of the "trends" shown in Figure 7. See Table 2 for the PAH list and abbreviations.

Assessing the Problem



Results

- Pyrogenic indicators
- Abundances distant from the source might not be the same for air transport as fluid transport
- Variability (between matrices, within duplicates) and Matching

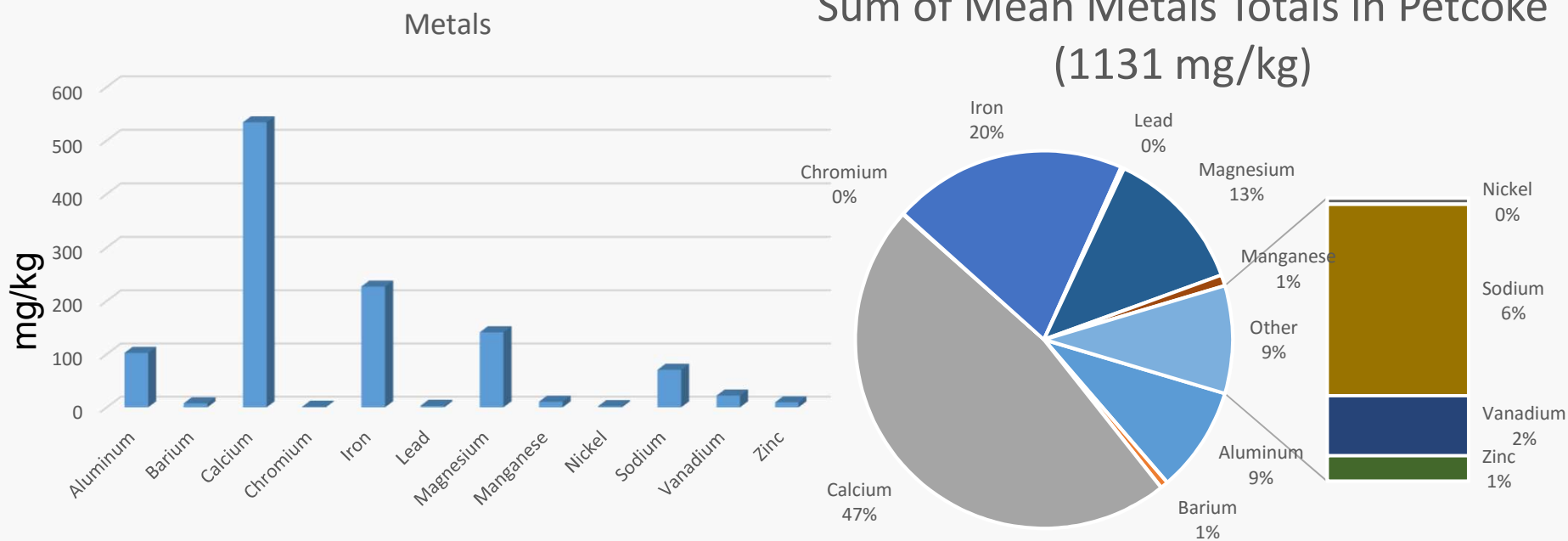
Assessing the Problem



Metals

Mean V:Ni	Petcoke	Wipe
Chicago	9.0	1.2

Sum of Mean Metals Totals in Petcoke
(1131 mg/kg)



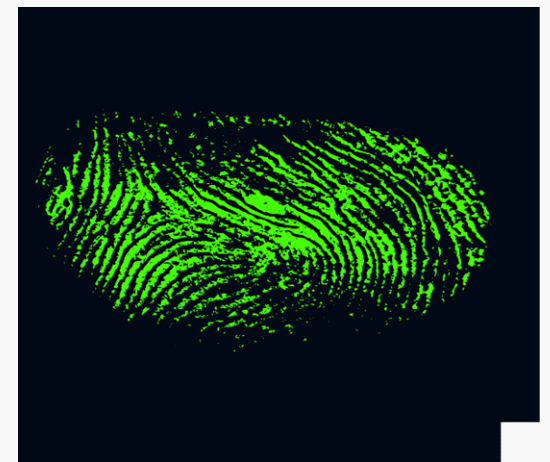
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Assessing the Problem



Summary (+/-)

- Expected type of PAH histogram
- Including alkylated groups
- **Qualitative** matching for lines of evidence
- Accessible technique, especially with source available



Problem Resolution



Summary

- Monitoring network
- NAAQS PM₁₀ NOV 4/2015
- Containment ordinance
- Piles removed



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Questions?

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Thank You!

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