Apportioning variability of polycyclic aromatic hydrocarbons (PAHs) in the ambient air in the Memphis Tri-State Area, USA

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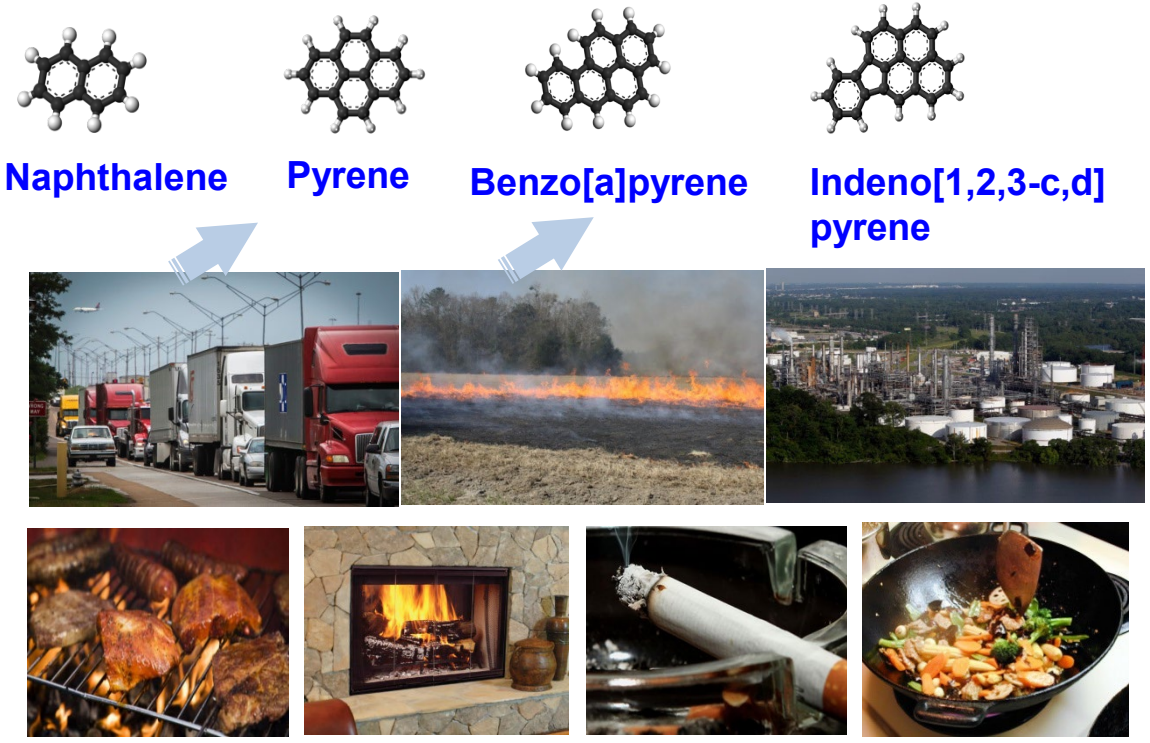
Outline

1. Background
2. Study objectives
3. Sampling and analytical methods
4. Results
5. Conclusions and implications

Background

- Polycyclic Aromatic Hydrocarbons (PAHs)
  - Over 100 PAHs
  - Formed in combustion of any organic materials
  - Existed in air as gases and in particles
- Health Effects
  - Asthma
  - Bronchitis
  - Heart disease
  - Low birth weight
  - IQ decrease
  - Cancers



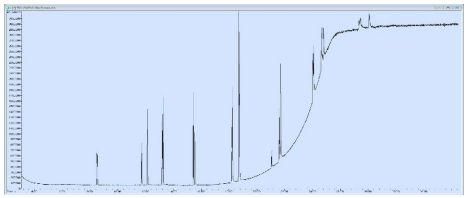
Burden in PAH monitoring

High-vol PUF Sampler, Filter and Sorbents

Extraction

Concentration

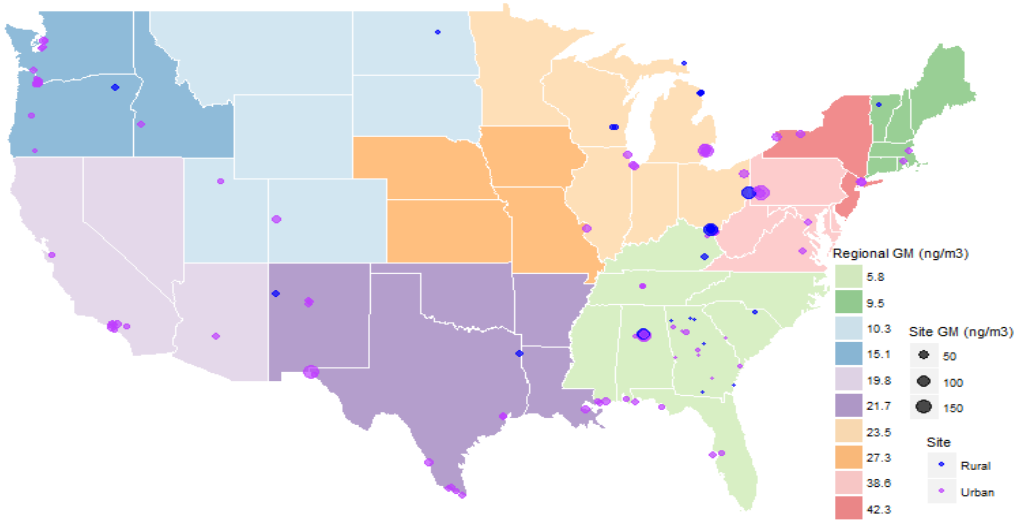
GC/MS Analysis



Data Analysis

Centralized monitoring

- Current air monitoring practice uses centralized monitoring stations.
  - Assumption: air quality measured at a central location can represent that in a large area.
  - The representativeness is often criticized.
  - Miss important emission sources.
  - Cannot address environmental justice (EJ) issues.
- Question:
  - Can centralized monitoring of PAHs represent the pollution level in a large area?



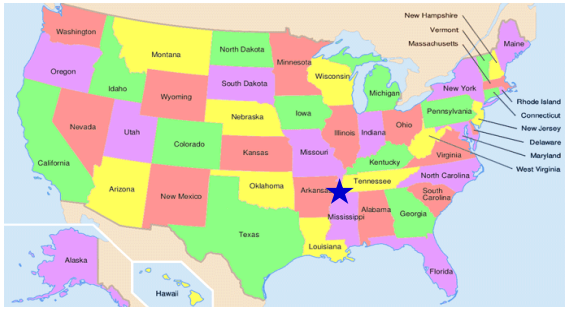
Study objective

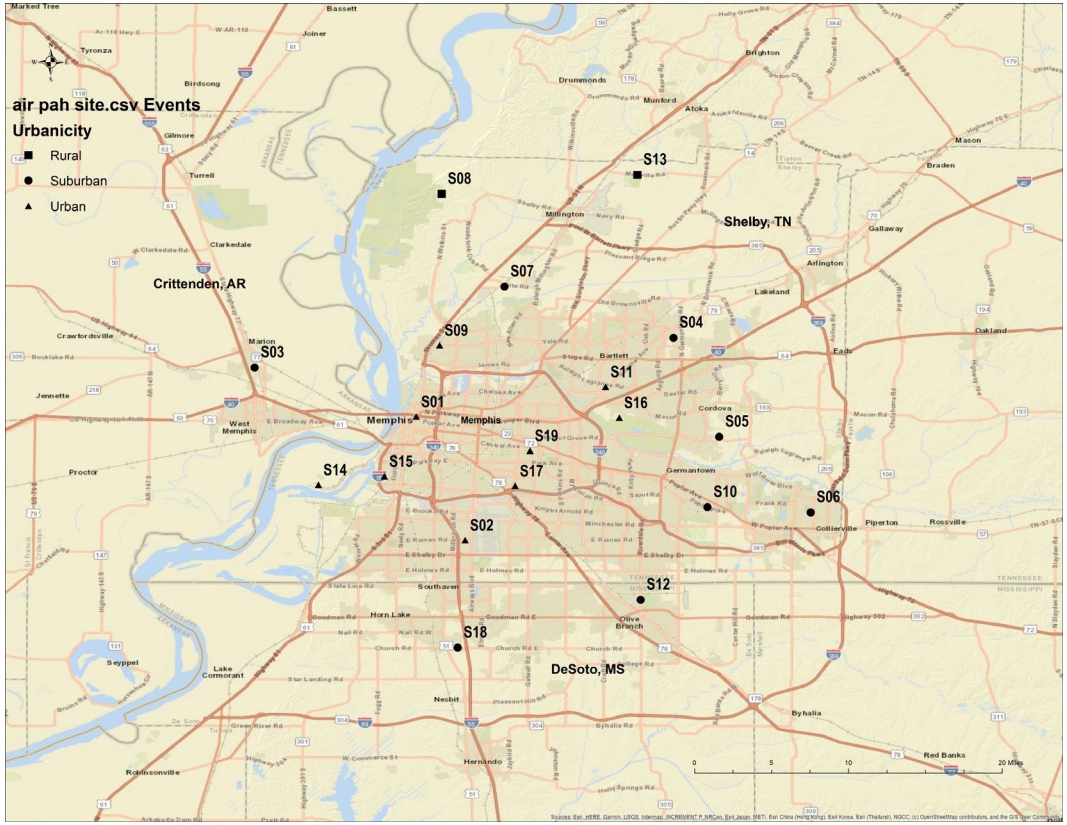
- For any air monitoring program, we want to
  - maximize the spatial and temporal variability
  - minimize the measurement uncertainty
- Previous studies have addressed criteria pollutants and volatile organic compounds.
- Overall objective: to understand the variability in PAH concentrations in the ambient air in a metropolitan area in the Mid-South USA.

Study design

- The Memphis tri-state area: Shelby County, TN, DeSoto County, MS, and Crittenden County, AR.
  - 19 sites
  - 24-hour sampling
  - Every 12 days
  - 14-month:

    Mar 2018 - May 2019





Monitoring sites

Urban background

Near-road

Community setting

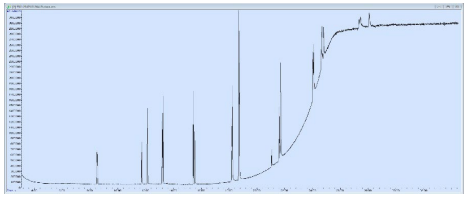
Sampling and analytical methods

Filter and Sorbent

Extraction

Concentration

GC/MS Analysis



Data Analysis

Data quality

- **Completeness:** 120%
- **Field blanks:** very low levels of some 3-ring and 4-ring PAHs, but most are ≤0.1ng.
- **Duplicate precision:** mostly within 25%.
- **Recovery:** 60-120%

Surrogates	N	Mean	Min	Median	Max
Fluorene-d10	162	67	45	67	105
Fluoranthene-d10	162	79	60	80	120
Pyrene-d10	162	80	61	80	97
Benzo(a)pyrene-d12	162	79	60	77	115

Meet the data quality objectives!

Major PAHs in MTA vs National

PAHs	Abbr.	MTA (n=663)				National (n=649−1,911)			
		DF (%)	Mean	SD	Max	DF(%)	Mean	SD	Max
Naphthalene	NAP	100	26.9	45.8	992	99	44.1	52.4	1,040
Acenaphthylene	ACY	91	0.40	0.80	12.9	70	0.64	1.34	11.8
Acenaphthene	ACP	100	5.73	8.24	114	82	4.40	8.56	108
Fluorene	FLR	100	7.80	17.0	363	97	4.26	7.42	157
Phenanthrene	PHE	98	12.9	17.2	100	98	7.87	13.1	195
Anthracene	ANT	100	4.15	6.74	53.9	68	0.39	0.76	11.5
Fluoranthene	FLT	100	3.44	5.03	29.3	93	2.19	3.58	51.7
Pyrene	PYR	100	2.67	3.34	20.3	88	1.25	1.68	22.5
Benz(a)vanthracene	BaA	99	0.47	1.18	14.9	71	0.11	0.22	3.85
Chrysene	CHR	87	0.18	0.23	3.04	76	0.23	0.31	5.53
Benzo(b,j,k)fluoranthene	BbjkF	50	0.07	0.12	1.79	98*	1.34*	2.33*	9.96*
Benzo(a)pyrene	BaP	29	0.04	0.07	1.01	34	0.12	0.21	2.09
Indeno[1,2,3-c,d]pyrene	IcP	16	0.04	0.05	0.52	73	0.23	0.73	12.7
Dibenz[a,h]anthracene	DhANT	6.9	0.02	0.02	0.22	39	0.03	0.06	0.73
Benzo(g,h,i)perylene	BgP	31	0.03	0.06	0.88	69	0.15	0.22	3.02
ΣLMW			64.6	74.8	1,116		63.5	76.7	1,279
ΣHMW			0.16	0.27	3.05		1.32	2.24	21.3
Σ16PAHs			64.7	77.8	1,122		64.5	76.7	1,277

Apportioning variability

❑ Variance components of the total variance of the measurements were apportioned using mixed models for individual PAHs and sum PAHs.

- ***Model 1: Spatial and temporal variations***

  Var(total) = Var(site) + Var(visit)

- ***Model 2: Variation by urbanicity, site, season, and visit***

  Var(total) = Var(urbanicity) + Var(site) + Var(season) + Var(visit)

- ***Model3: Sampling and Analytical uncertainty***

  Var(total) = Var(site) + Var(visit) + Var(DupSam)+Var(DupAna)

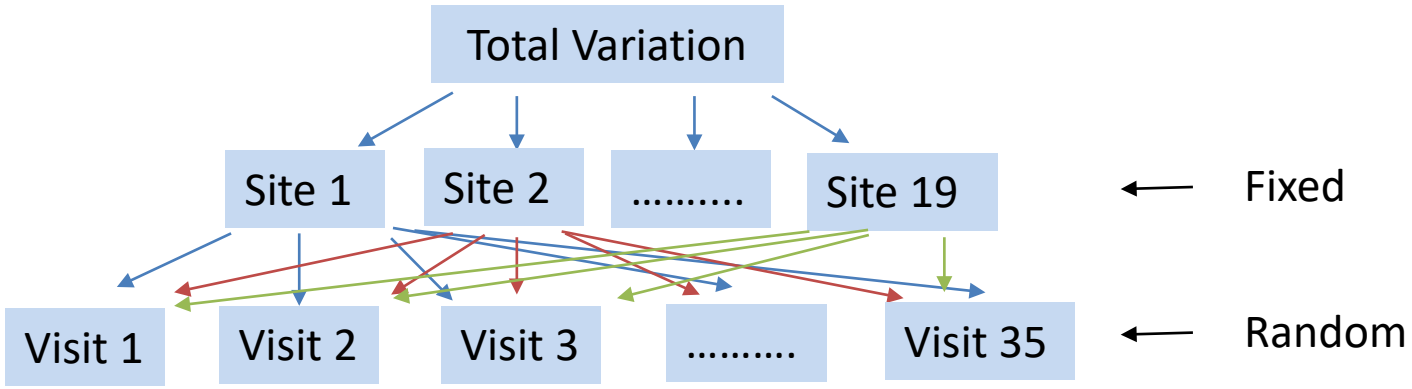
❑ SAS programs:

- ➢ Proc mixed
- ➢ Proc nested

Model 1: Spatial and temporal var

- ***Model 1: Spatial and temporal variations***

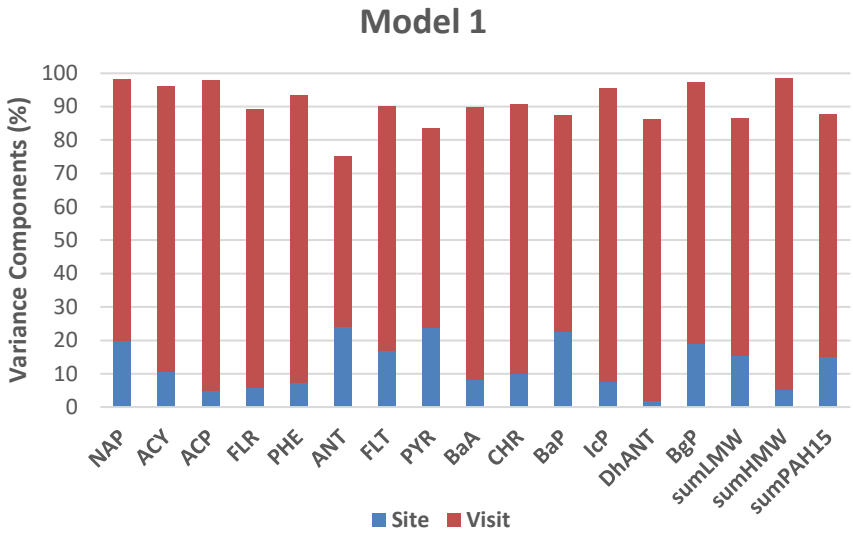
  $y = \beta_0 + \beta_1 (site) + \Upsilon(visit) + \varepsilon$



Model 1 Results

PAHs	Model_1, Var Per(%)	
	Site	Visit
Naphthalene	19.9	78.4
Acenaphthylene	10.6	85.5
Acenaphthene	5.00	93.1
Fluorene	5.80	83.3
Phenanthrene	7.30	86.1
Anthracene	24.2	51.0
Fluoranthene	17.0	73.3
Pyrene	23.7	59.9
Benz(a)anthracene	8.10	81.6
Chrysene	10.0	80.8
Benzo(a)pyrene	22.6	64.8
Indeno[1,2,3-c,d]pyrene	7.80	87.8
Dibenz[a,h]anthracene	1.80	84.4
Benzo(g,h,i)perylene	19.0	78.3
sumLMW	15.4	71.1
sumHMW	5.30	93.2
sumPAH15	15.3	72.6
sumPAH30	13.8	76.8

Note: all the p-values <0.0001

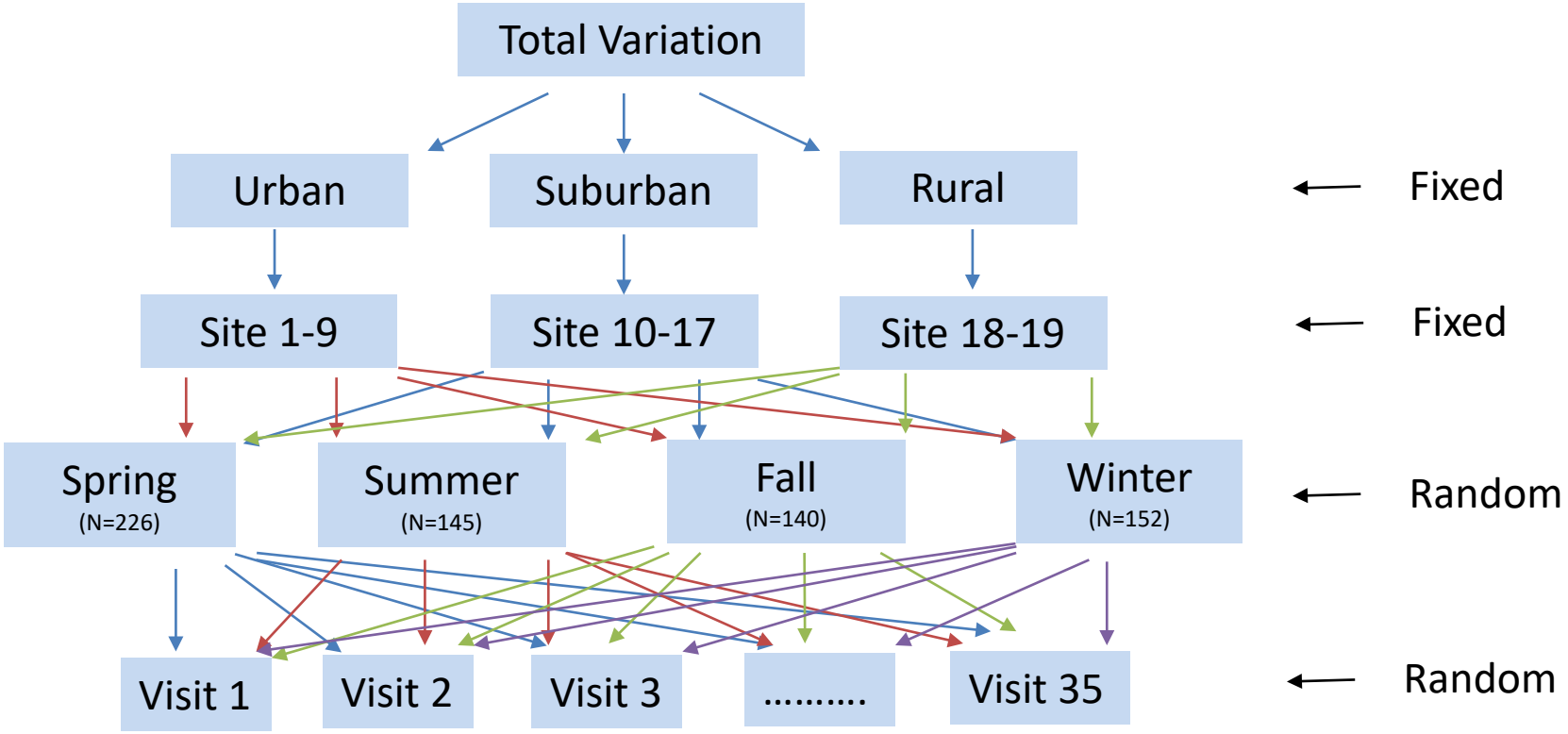


- Ambient PAHs have much larger temporal variability than spatial variability.
  - Spatial variability: 14%
  - Temporal variability: 77%

Model 2: urbanicity, site, season, visit

- ***Model 2: Variation by urbanicity, site, season, and visit***

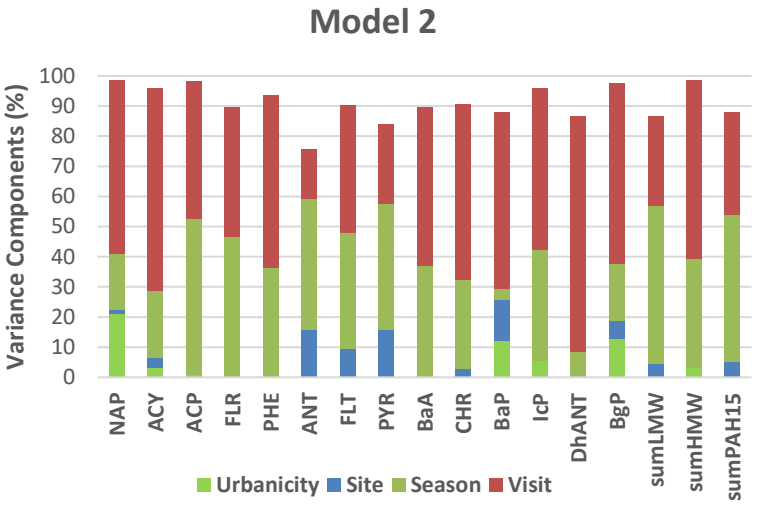
$$y = \beta_0 + \beta_1 (\text{urbanicity}) + \beta_2 (\text{site}) + \beta_3 (\text{site*urbanicity}) + \Upsilon_1 (\text{season}) + \Upsilon_2 (\text{visit}) + \varepsilon$$



Model 2 Results

PAHs	Model_2 Var Per(%)			
	Urbanicity	Site	Season	Visit
Naphthalene	21.2	1.33	18.4	57.6
Acenaphthylene	3.35	3.07	22.4	67.3
Acenaphthene	0.86	0.00	51.6	45.7
Fluorene	0.00*	0.00	46.7	43.0
Phenanthrene	0.00*	0.00	36.4	57.1
Anthracene	0.00*	15.8	43.4	16.6
Fluoranthene	0.00*	9.46	38.7	42.2
Pyrene	0.00*	15.8	41.8	26.4
Benz(a)anthracene	0.00*	0.00	37.0	52.7
Chrysene	0.22	2.73	29.4	58.4
Benzo(a)pyrene	12.2	13.4	3.54	58.7
Indeno[1,2,3-c,d]pyrene	5.76	0.00	36.5	53.7
Dibenz[a,h]anthracene	0.00*	0.00	8.40	78.1
Benzo(g,h,i)perylene	12.9	5.96	18.8	59.9
sumLMW	0.00*	4.39	52.6	29.6
sumHMW	3.20	0.00	36.1	59.3
sumPAH15	0.00*	5.16	48.7	34.1
sumPAH30	0.79	2.09	46.4	41.3

Note: all the p-values <0.0001, except for the numbers with *

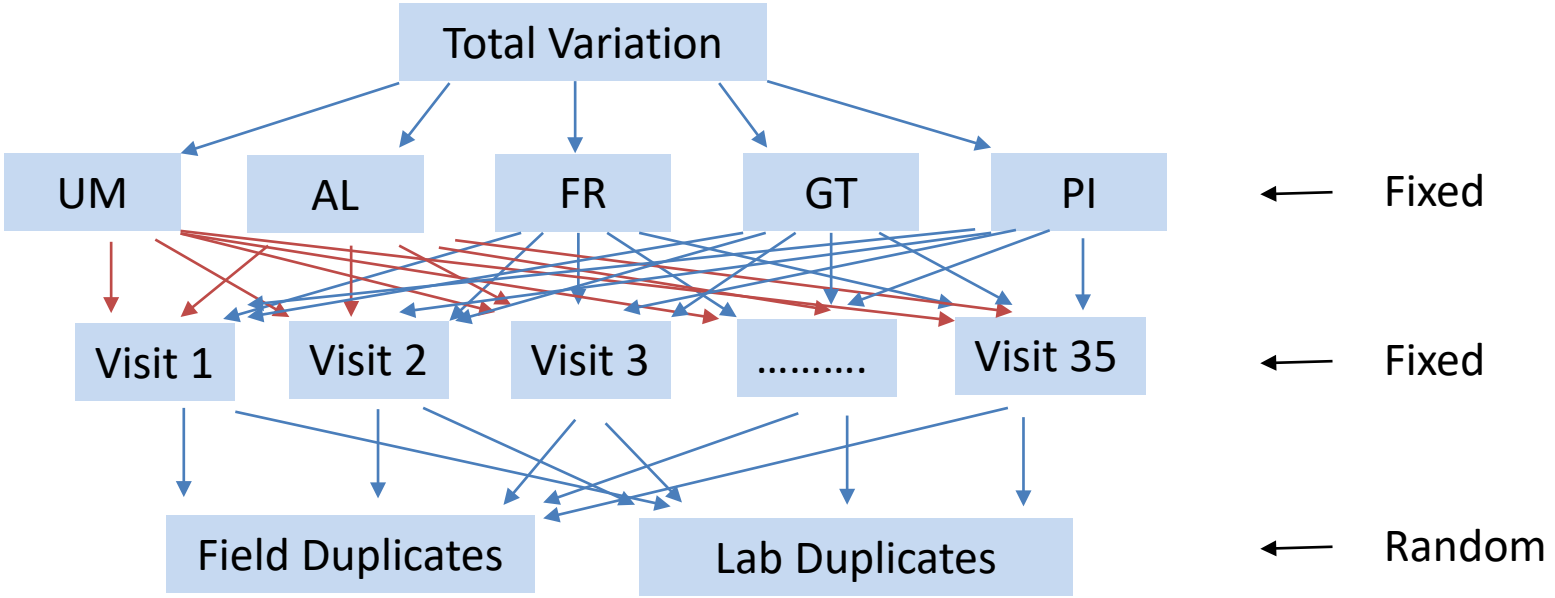


- ❑ Negligible urbanicity effect
- ❑ Small between-site variability
- ❑ Seasonal variability: 46%
- ❑ Between-visit variability: 41%

Model 3: monitoring uncertainty

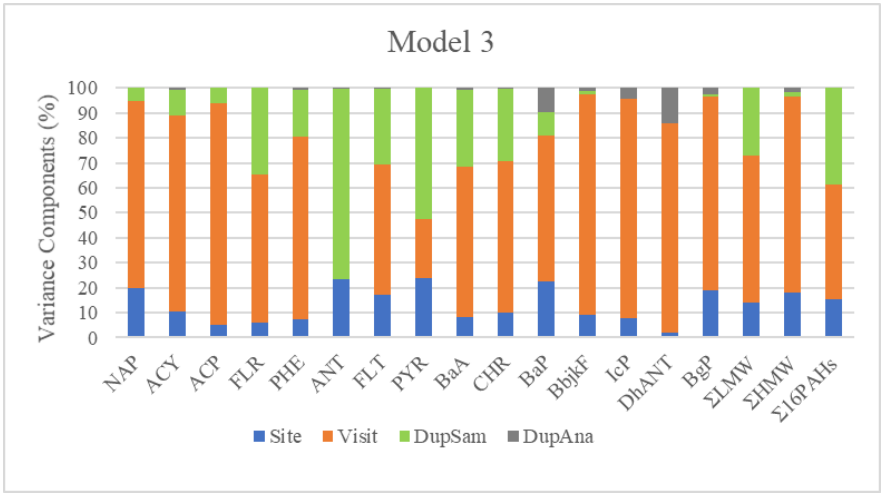
- ***Model3: Sampling and Analytical uncertainty***

$$y = \beta_0 + \beta_1 (site) + \beta_2 (visit) + \beta_3 (visit*site) + \Upsilon_1(DupSam) + \Upsilon_2(DupAna) + \varepsilon$$



Model 3 Results

PAHs	Model_3 Var Per(%)			
	Site	Visit	DupSam	DupAna
Naphthalene	19.9	74.7	5.38	0.03
Acenaphthylene	10.6	78.3	10.5	0.69
Acenaphthene	4.99	88.9	6.05	0.04
Fluorene	5.84	59.6	34.5	0.03
Phenanthrene	7.34	73.4	18.6	0.73
Anthracene	23.4	0.00	76.4	0.18
Fluoranthene	17.0	52.5	30.3	0.29
Pyrene	23.7	23.9	52.3	0.07
Benz(a)anthracene	8.12	60.4	30.9	0.62
Chrysene	9.96	60.8	29.0	0.15
Benzo(a)pyrene	22.6	58.2	9.54	9.67
Indeno[1,2,3-c,d]pyrene	7.81	87.7	0.12	4.35
Dibenz[a,h]anthracene	1.81	84.1	0.00	14.1
Benzo(g,h,i)perylene	19.0	77.6	1.03	2.37
sumLMW	15.4	41.3	43.4	0.01
sumHMW	5.28	91.8	2.01	0.90
sumPAH15	15.3	45.9	38.9	0.01
sumPAH30	13.8	56.1	30.1	0.01



- ❑ Small spatial variability (14%)
- ❑ Large temporal variability (56%)
- ❑ Sizable sampling uncertainty (30%)
- ❑ Negligible analytical uncertainty

Conclusions

- Spatial variability of PAHs was small (14%);
- Temporal variability was large (77%):
  - Both seasonal (46%) and within-season (41%) variations were significant.
- Sampling uncertainty was significant (30%), but analytical uncertainty was negligible.

Implications for PAH monitoring

- Provides evidence that centralized monitoring can represent a large area.
- Suggests the need for repeated samples to capture temporal variability
  - Sampling in all seasons, and
  - Sampling at multiple time points within a season
- Suggests the need to improve field sample collection quality.

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EPA United States Environmental Protection Agency