Organic Speciation for Source Apportionment in DEARS

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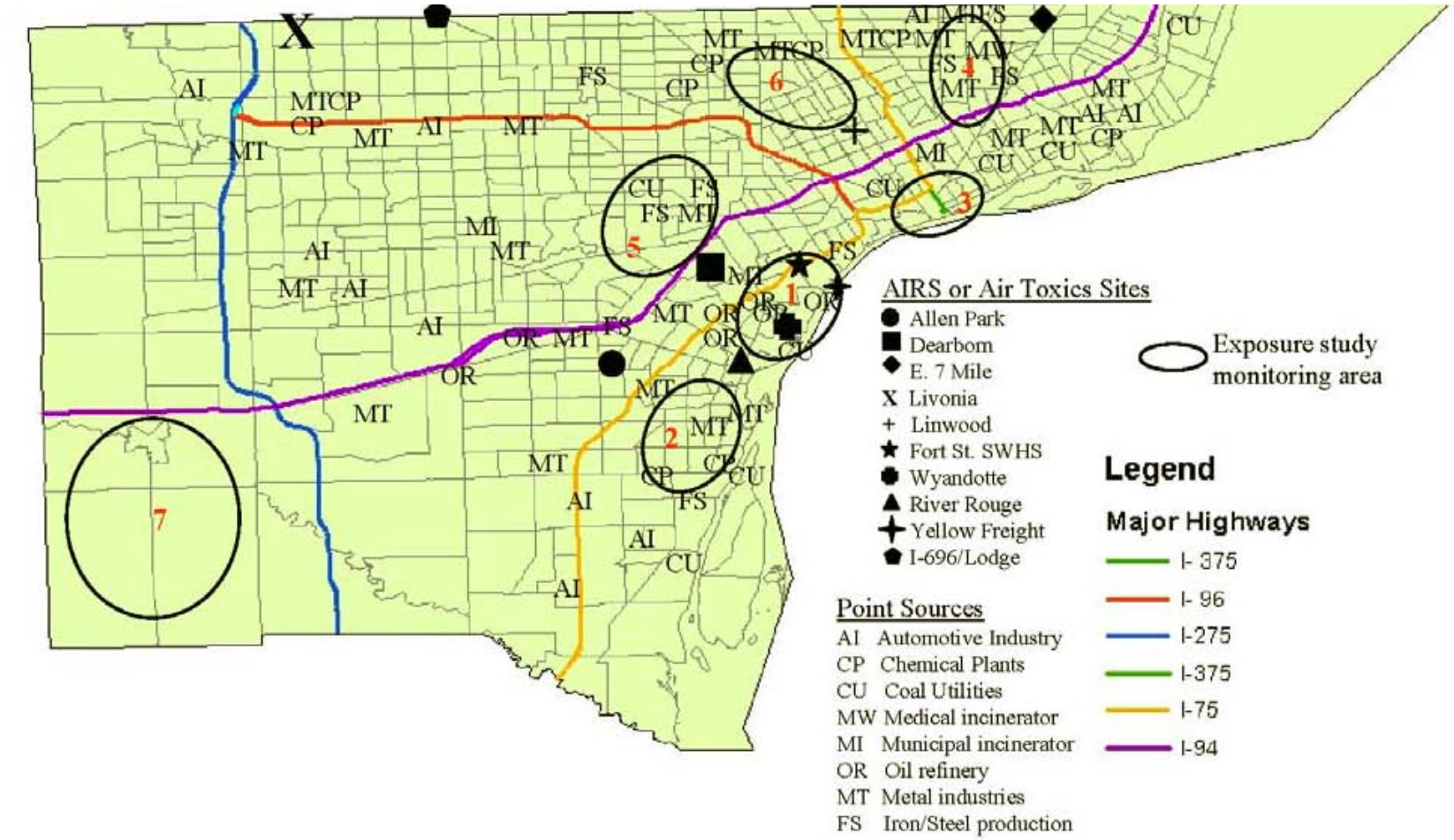
DEARS Objective #1:

(1) To determine the associations between concentrations measured at central site monitors and outdoor residential, indoor residential and personal exposures for selected air toxics, PM constituents, ***and PM from specific sources***.

Source: www.epa.gov/dears

DEARS Study Design



Sampling

Central Site

Residential Monitor

Sampling & Analysis Methods

- Allen Park community air monitoring station in Detroit, MI
- From July 13, 2004 to August 28, 2004
- 34 high-volume (113 liters/minute) PM2.5 samples

What's unique to DEARS Organic Analysis:

- Largest dataset planned for organic source apportionment
- Low collection volumes (10 liters/minute)
- Daily samples

Challenges:

1) Can we detect source markers with sufficient sensitivity in 24 hour, 10 liter/minute samples?

2) Can we adequately estimate source contributions with a limited set of organic markers?

3) Can we achieve low enough uncertainties to adequately resolve sources?

1) Can we detect source markers with sufficient sensitivity in 24 hour, 10 liter/minute samples?

Methods Considered:

- Thermal Desorption
- Large Volume Injection
- Splitless/Selective Ion Monitoring

Large Volume Injection Problems

- Contamination (solved)
- High Blanks (solved)
- Rapid column deterioration (probably solvent related)*

*Recalibration usually required after column maintenance

Sampling & Analysis Methods

ORGANIC AEROSOL LAB
SAMPLING AND ANALYSIS SCHEME

Tisch TE-1202
Quartz Filters
113 liters/minute

↓

Dionex Accelerated Solvent Extractor 200
Hexane/Dichloromethane/Methanol

↓

Zymark Turbovap
Concentration to 0.30 ml

↓

Gas Chromatogaphy/Mass Spectrometry
Selective Ion Monitoring

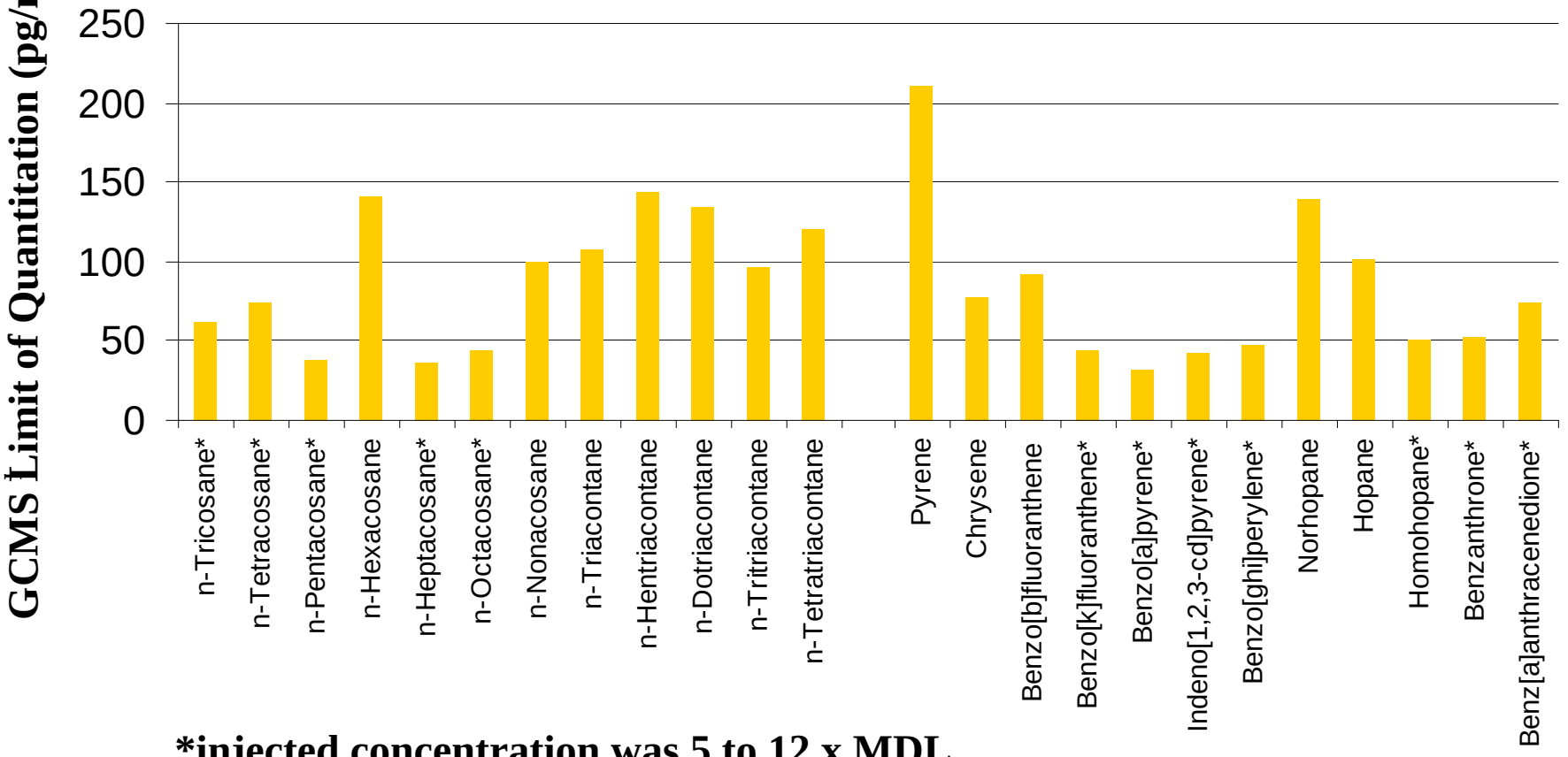
Determining Method Detection Limits

1) Prepare standard 1-5 x MDL
2) Analyze at least 7 aliquots
3) Calculate variance (s^2)
4) Calculate MDL for t = n-1, α=0.99 (=3.143s)
5) Verify average is 1 to 5 x MDL
6) Adjust standard concentration and repeat if necessary

Source: 40CFR136, Appendix B

GCMS Limits of Quantitation

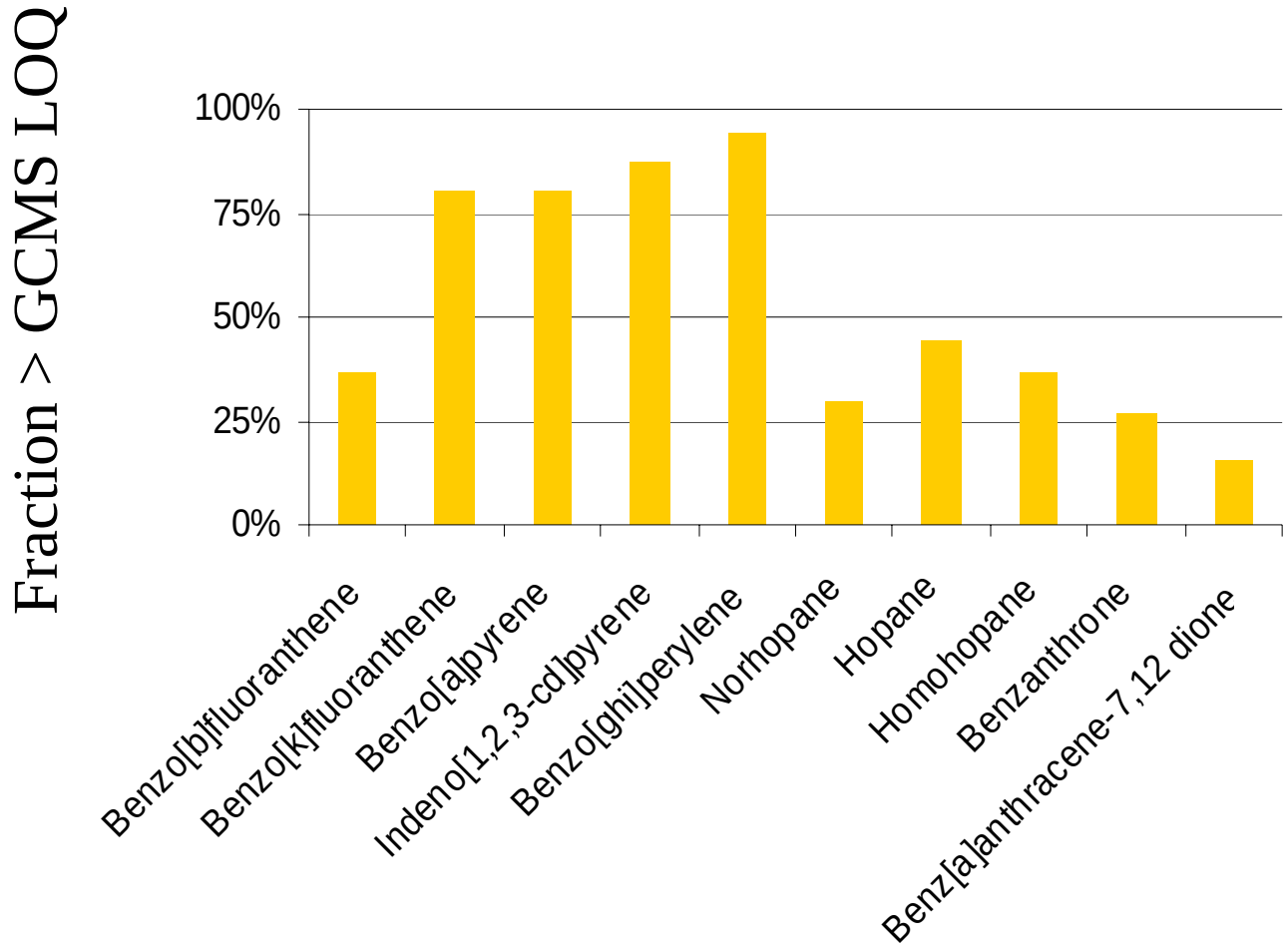
LOQ = 10s (from 40CFR136B)



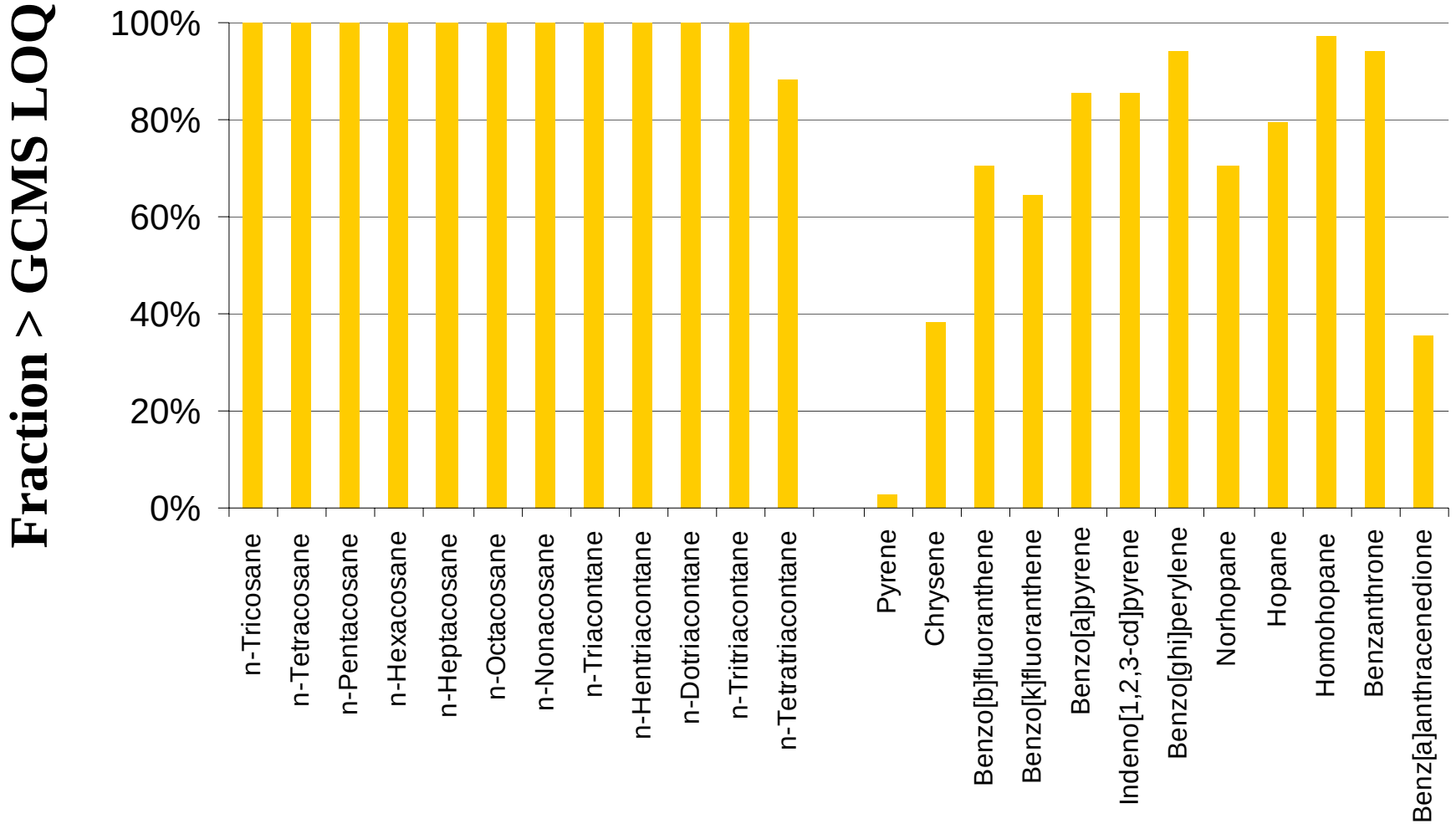
***injected concentration was 5 to 12 x MDL**

Fraction of TACS Samples > GCMS LOQ

n =84



Fraction of 113 lpm Samples from DEARS that *would be* > LOQ at 10 lpm (n=34)



2) Can we adequately estimate source contributions with a limited set of organic markers?

DEARS Organic Source Markers

(limited for higher throughput + SIM)

Tricosane
Tetracosane
Pentacosane
Hexacosane
Heptacosane
Octacosane
Nonacosane
Triacontane
Hentriacontane
Dotriacontane
Tritriacontane
Tetratriacontane

Pyrene
Chrysene/Triphenylene
Benzo[b]fluoranthene
Benzo[k]fluoranthene
Benzo[a]pyrene
Indeno[1,2,3-cd]pyrene
Benzo[ghi]perylene
Benzanthrone
Benzanthracenedione

Norhopane
Hopane
Homohopane

Hexadecanoic acid
Cis-Hexadecenoic acid
Octadecanoic acid
Cis-Octadecenoic acid

Fundamental Questions:

How many fitting species are needed?

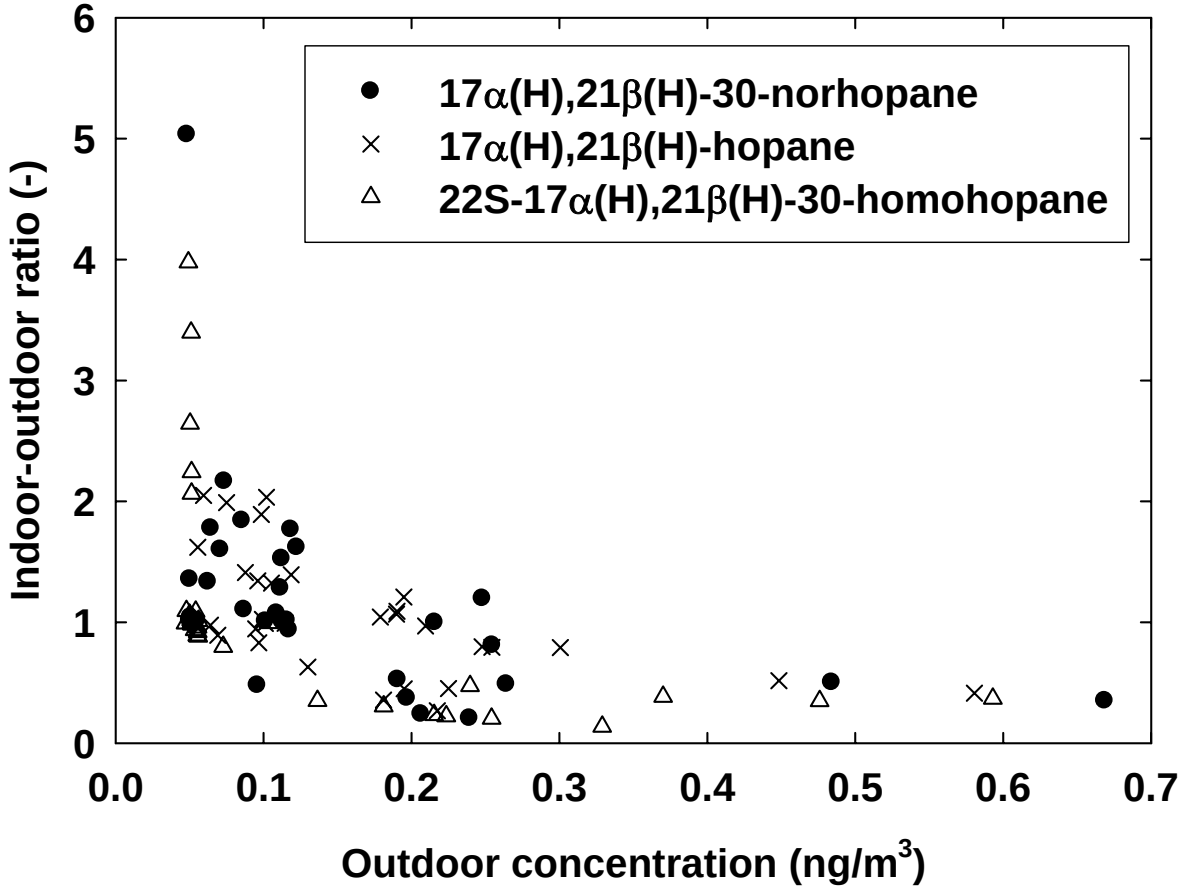
Friedlander 1973 – Fitting Species: Al, Na, K, Mg, Ca, V, Pb
Sources: auto, diesel, aircraft, oil, industrial

How much are CMB fits improved by reducing measurement uncertainties?

Kowalczyk et al. 1978 – Improved measurements gave better fits

What is the practical optimum balance between adding fitting species and increasing measurement uncertainty?

TACS Concentration Effect on Indoor/Outdoor Ratios



Which species influence source contribution?

The MPIN matrix identifies which fitting species have the largest influence on the source contribution estimates from each profile.

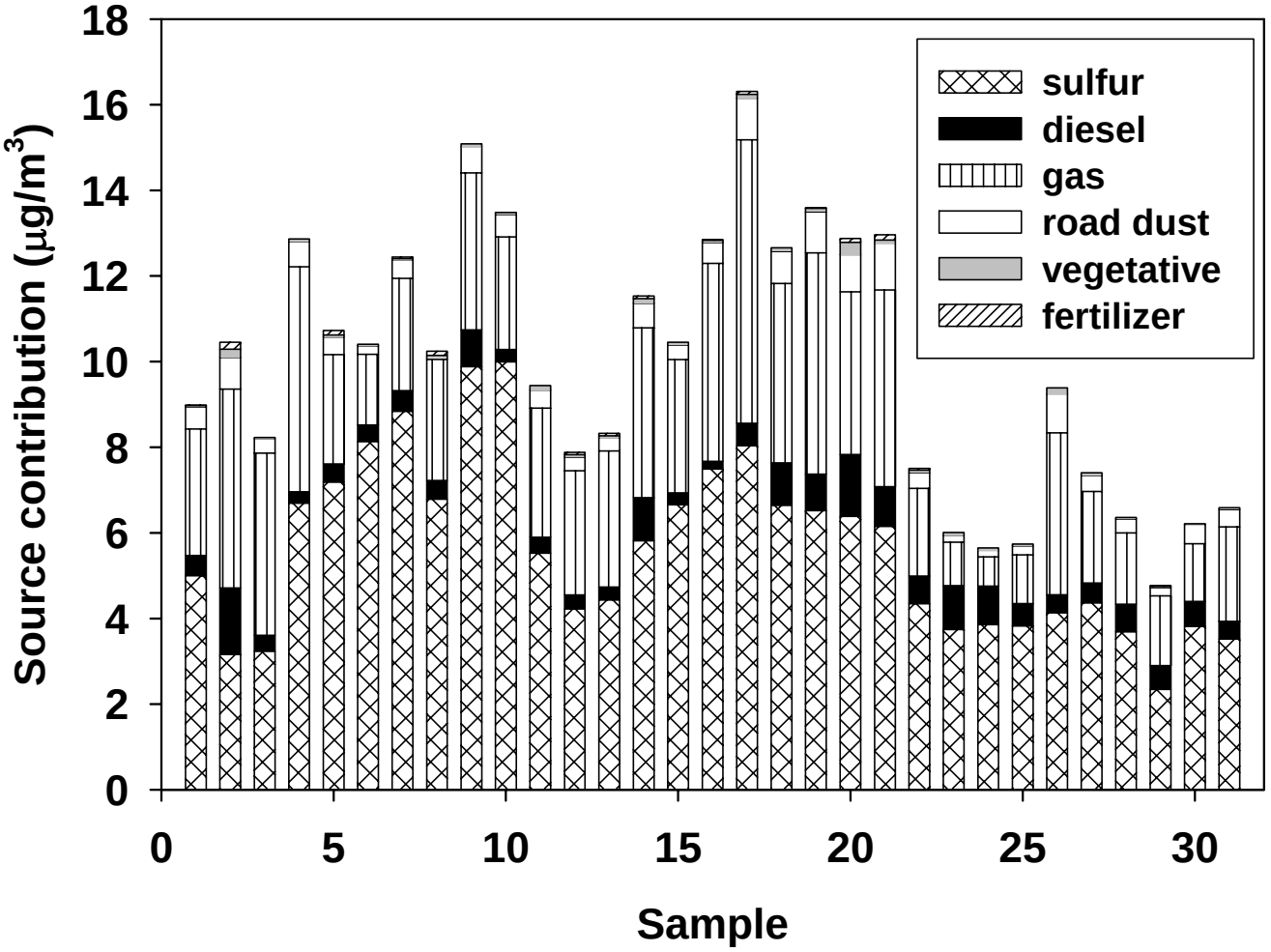
Species with MPIN absolute values of 0.5 to 1.0 are considered influential species.

WARNING: binoculars required for next slide…

MPIN Matrix:

SPECIES	CLRTON	NFRDSL	PTLEAF	EWHTPS	EHMLKS	GASLIN	FRY90
ECC	0.01	1.00	-0.06	0.02	-0.01	-0.66	-0.42
NAL03C	0.01	0.03	0.01	0.00	0.01	0.03	0.00
NAL04C	0.05	0.15	0.01	-0.01	0.01	-0.06	0.13
NAL05C	0.00	-0.05	0.03	0.00	0.00	0.21	0.15
NAL06C	0.09	0.39	-0.01	-0.02	0.01	-0.18	-0.08
NAL07C	0.03	0.11	0.30	-0.01	-0.01	-0.05	0.00
NAL08C	0.09	0.34	0.03	-0.01	-0.01	-0.32	0.00
NAL09C	0.00	-0.02	0.79	0.02	-0.08	0.00	0.03
NAL11C	-0.01	-0.05	1.00	0.02	-0.10	0.03	-0.03
NAL12C	0.00	0.00	0.08	0.00	-0.01	0.00	0.00
NAL13C	-0.01	-0.02	0.40	0.01	-0.04	0.01	-0.01
NACD6C	-0.01	-0.22	-0.02	0.01	0.02	0.14	0.81
NACD8C	-0.03	0.11	-0.05	0.00	0.00	-0.09	1.00
SNDPMC	-0.03	-0.03	0.00	0.59	-0.13	0.02	0.01
OXDROC	0.00	0.00	0.00	0.07	0.01	0.00	0.00
SYALDC	-0.04	0.00	0.11	-0.19	0.98	0.01	-0.04
ACSYNC	-0.03	0.00	-0.07	-0.22	1.00	0.00	-0.02
SYNCDC	0.00	0.00	0.00	0.00	0.00	0.00	0.00
LEVOGC	-0.03	0.00	-0.05	-0.16	0.73	0.00	-0.02
CHLTLC	-0.01	-0.15	-0.02	0.01	-0.02	0.09	0.53
HOP2C	-0.14	-0.14	0.00	0.00	0.00	0.90	0.00
HOP3C	-0.15	-0.17	0.00	0.00	0.00	1.00	0.01
STRN1C	0.00	0.05	0.00	0.00	0.00	-0.04	-0.02
STR1BC	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BNZBF	0.53	0.00	0.00	0.00	0.00	-0.06	0.00
BNZKF	0.82	0.00	-0.01	0.00	0.00	-0.08	0.00
BNZEP	0.69	0.00	-0.01	-0.01	0.00	-0.04	-0.01
INDCDP	0.62	-0.01	0.00	-0.01	0.00	-0.04	0.00
BNZGHI	0.67	-0.05	0.00	-0.01	-0.01	0.09	0.01
CORON	1.00	-0.10	-0.01	0.02	0.01	0.16	0.02
RSNSMC	-0.05	-0.05	0.00	1.00	-0.33	0.03	0.02
SRHHPN	-0.10	-0.06	0.00	0.00	0.00	0.62	-0.02
SRBHPN	-0.09	-0.01	-0.01	0.00	0.00	0.51	-0.03

TACS CMB Results with limited "DEARS" source markers



3) Can we achieve low enough uncertainties to adequately resolve sources?*

*How well are we estimating uncertainty?

QA Based on EPA Method 8000 Series with modifications

-Initial Demonstration of Proficiency includes:

- Initial calibration
- Multi-level replicate recoveries

- Each batch of 12 samples includes:

- 2 replicate injections
- 1 method blank
- 1 matrix control
- 1 calibration verification standard
  - level?
  - acceptance criteria? (next slide)

- Each sample includes:

> internal standards by class, volatility (return to later)

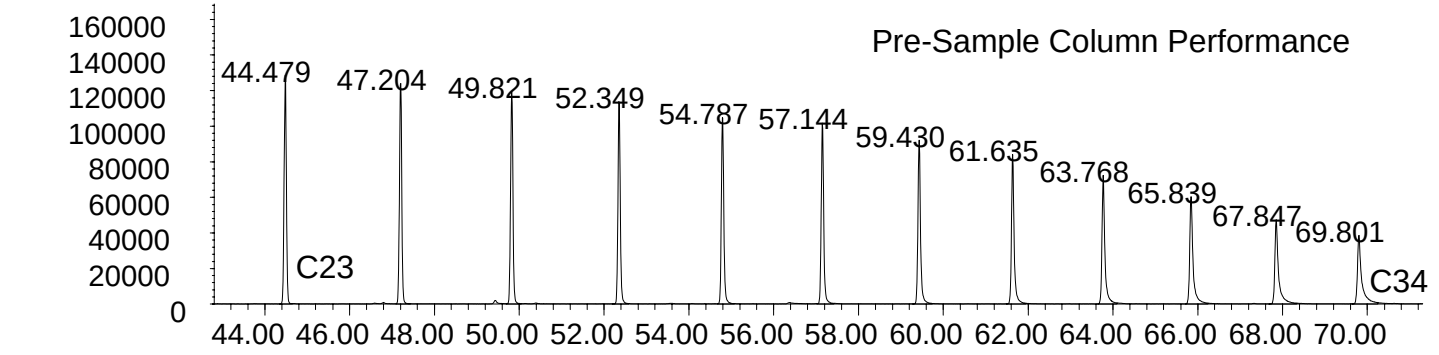
> Surrogate standards by class, volatility

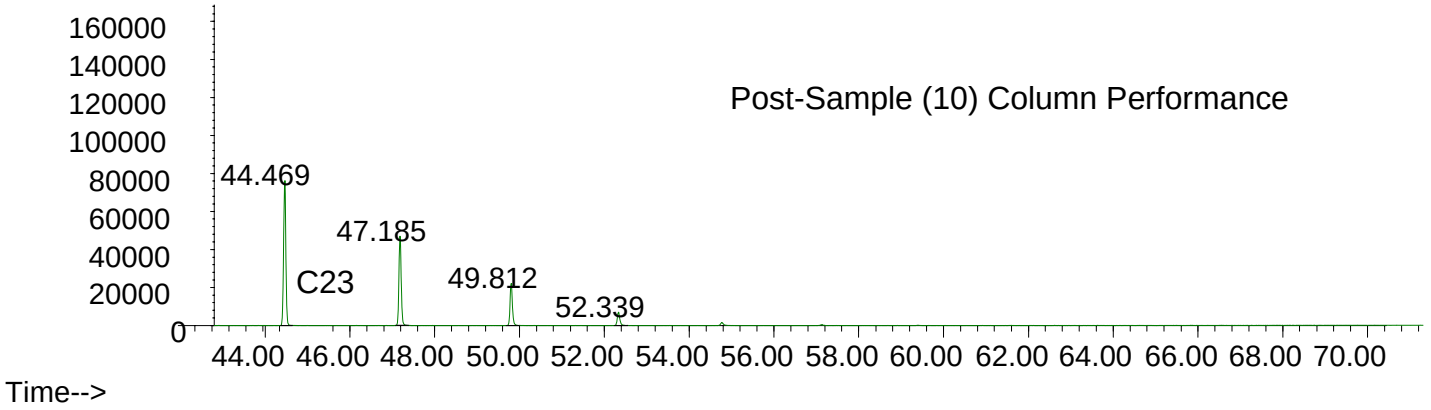
What if we accept calibration if 80% of species are within 20%?

- Important Source Markers:

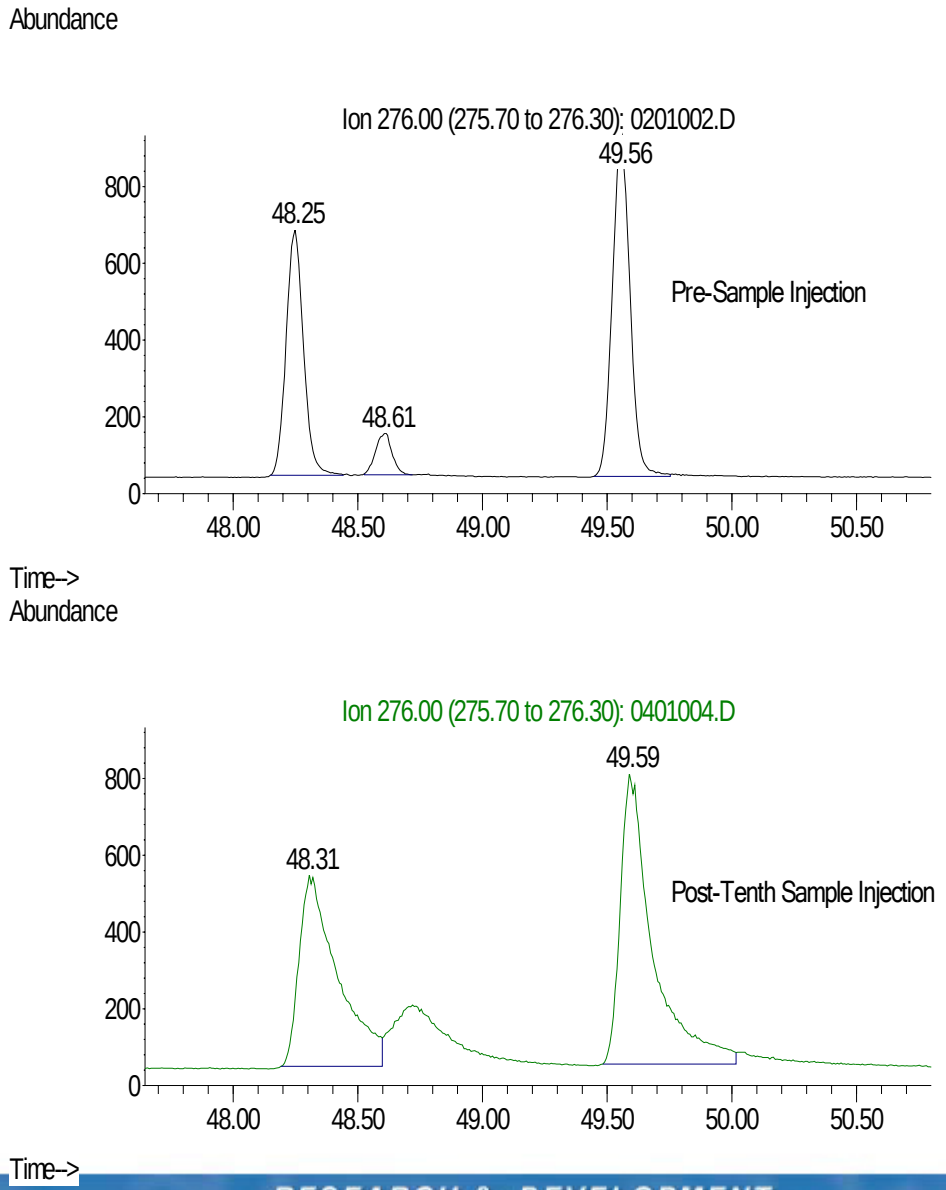
  > C29 and C31 alkanes
  > Indenopyrene + Benzoperylene
  > Hopane + Norhopane

Pre-Sample vs. Post-Sample Column Performance (TACS)





Effect of Column Deterioriation on indenopyrene + benzoperylene

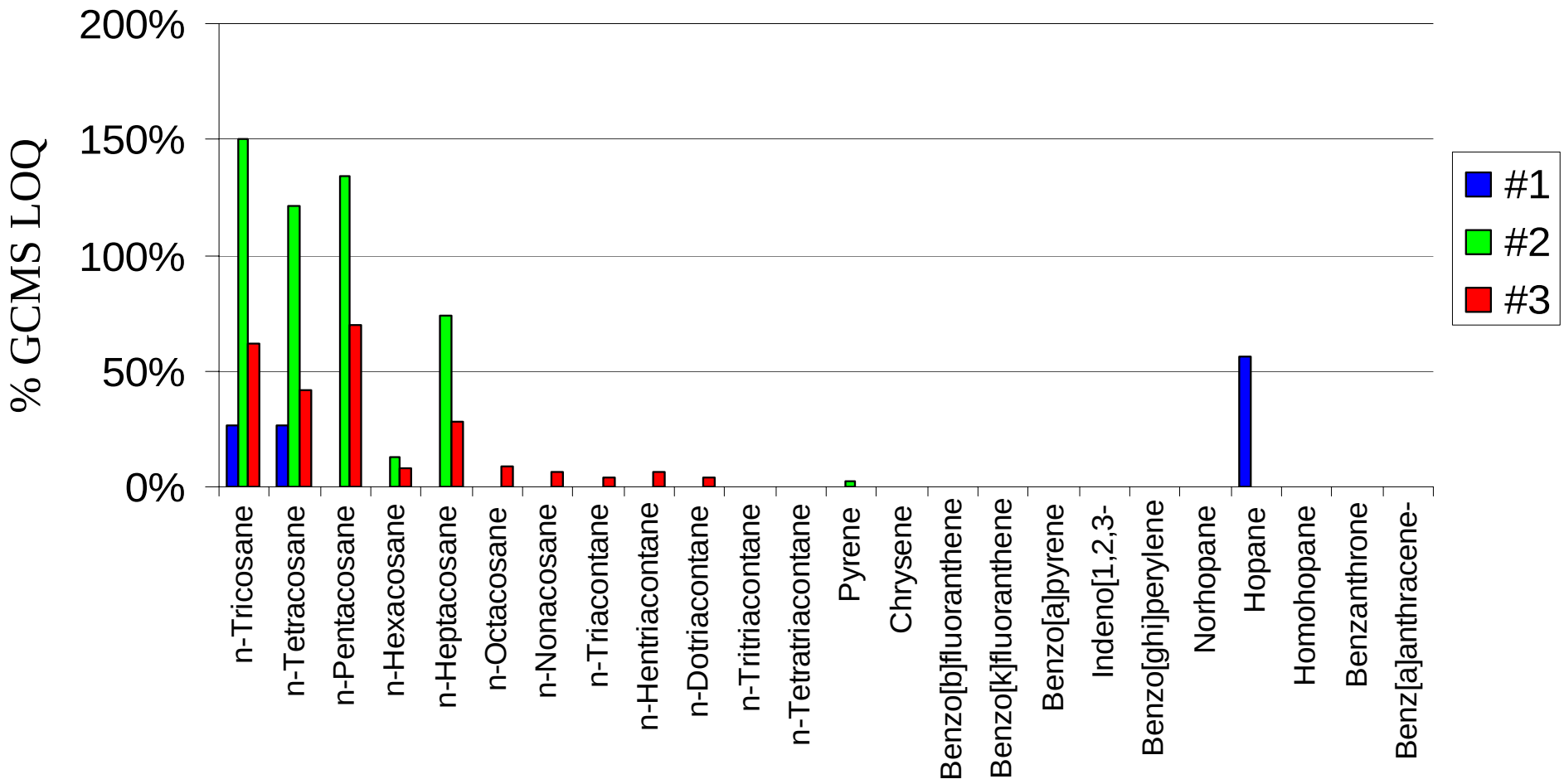


Each week of sampling includes:

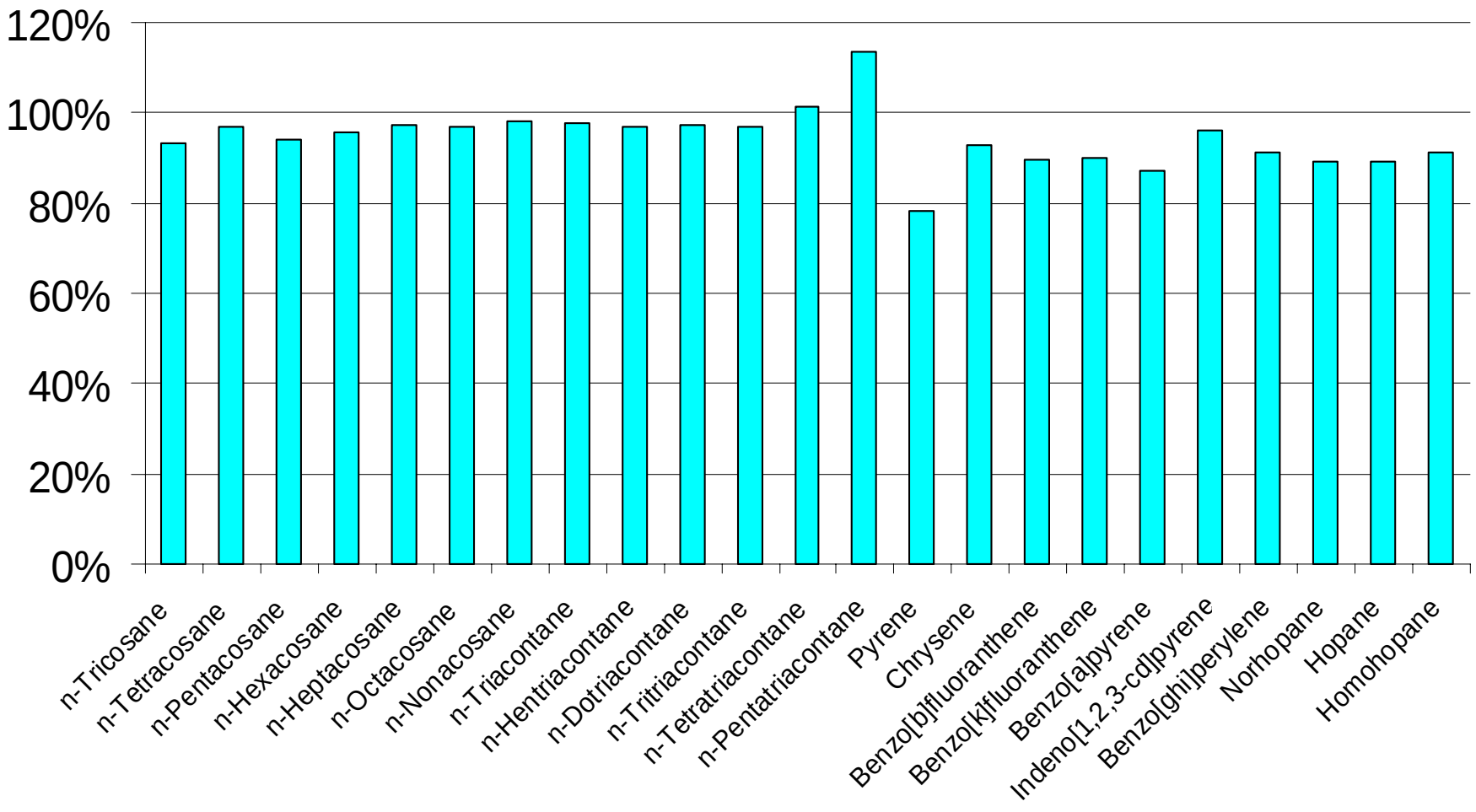
- Samples for Tuesday through Sunday
- Duplicate sample each Wednesday (2 seasons)
- Field Blank (placed in sampler for 1 day with no flow)*
- Travel Blank (not removed from shipping container)*

*Shipping & storage described in detail AS&T, in revision

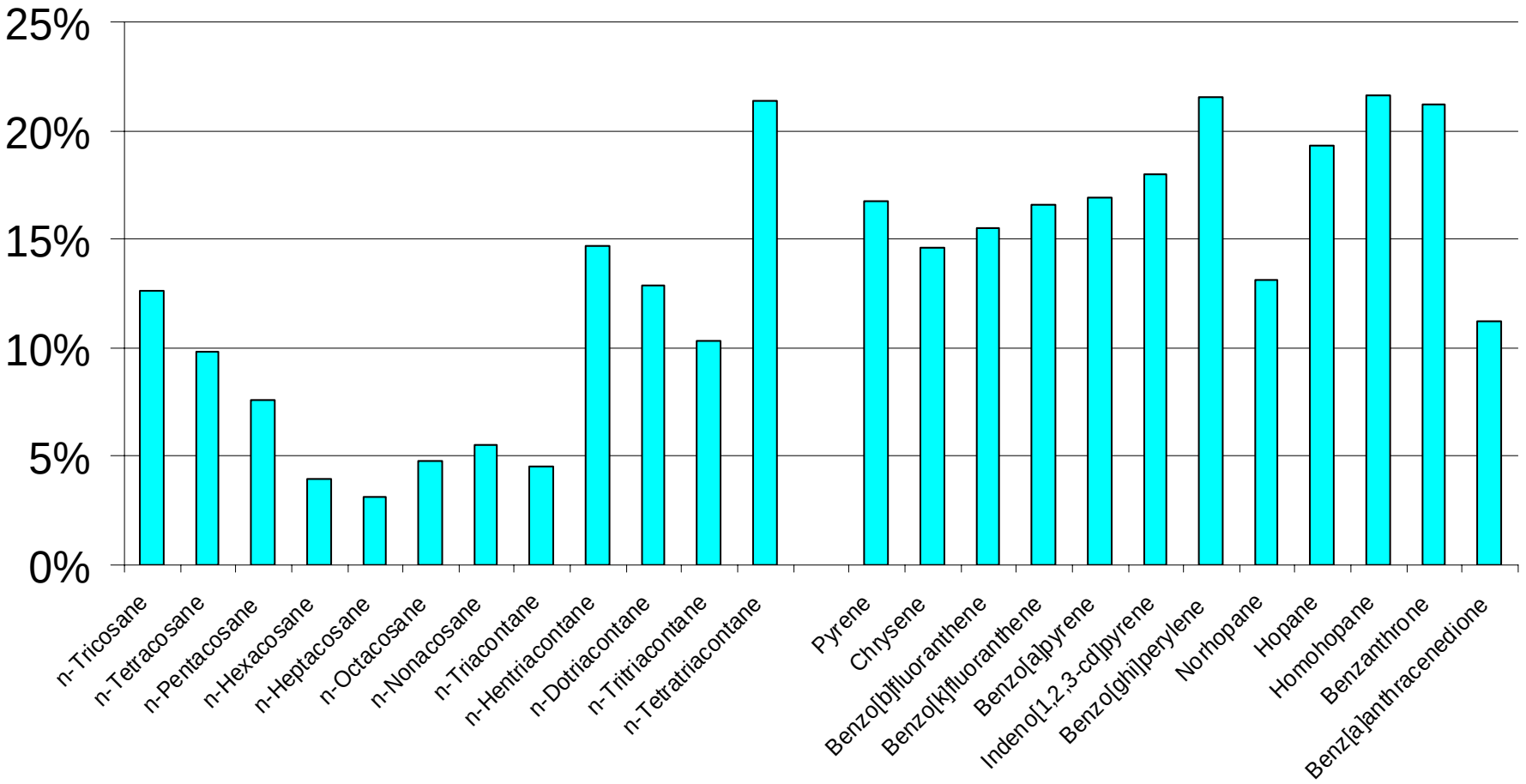
DEARS Matrix Blanks

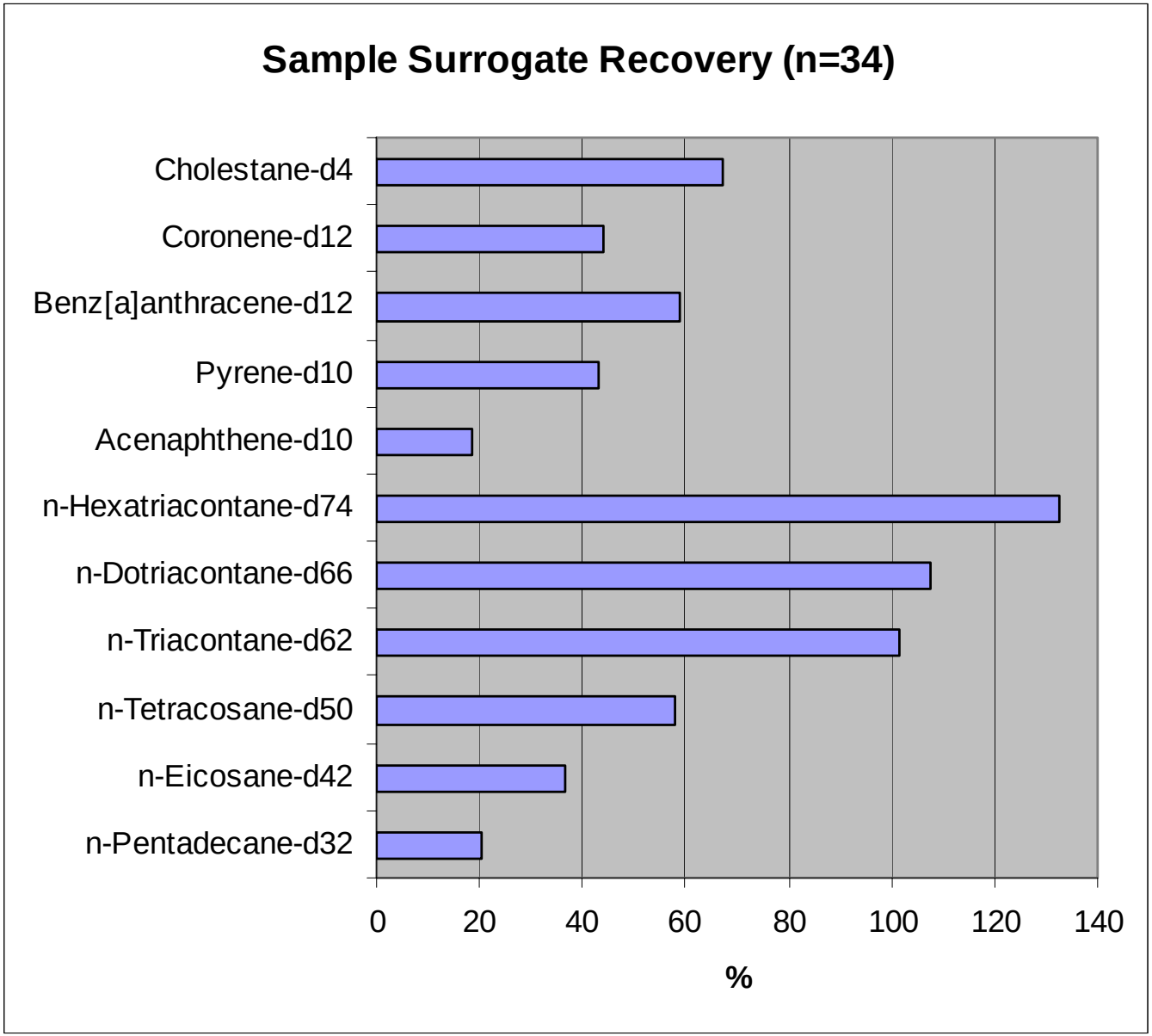


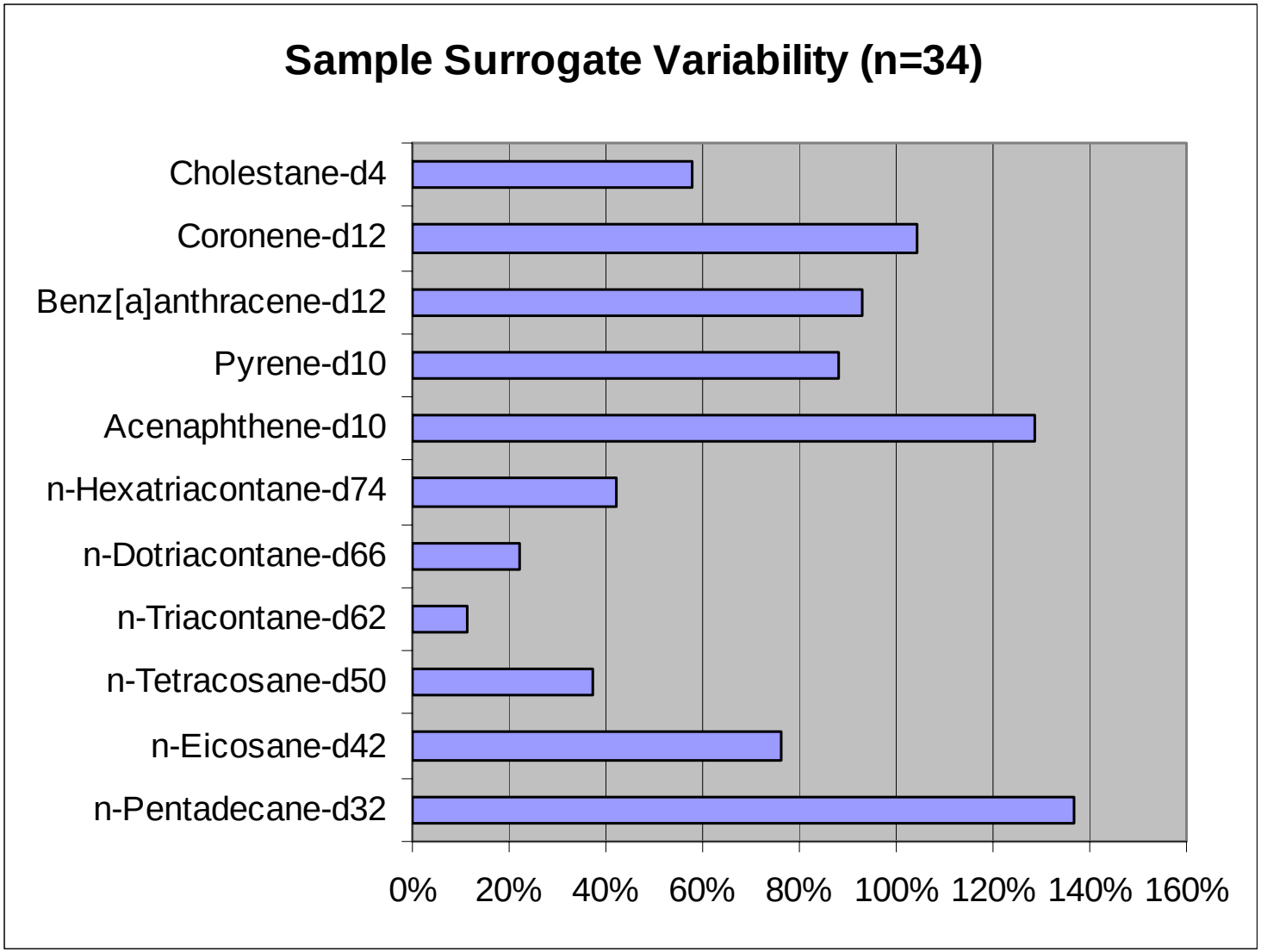
Preliminary Recovery



Duplicate Analysis







Summary of Season 1 High Volume Samples

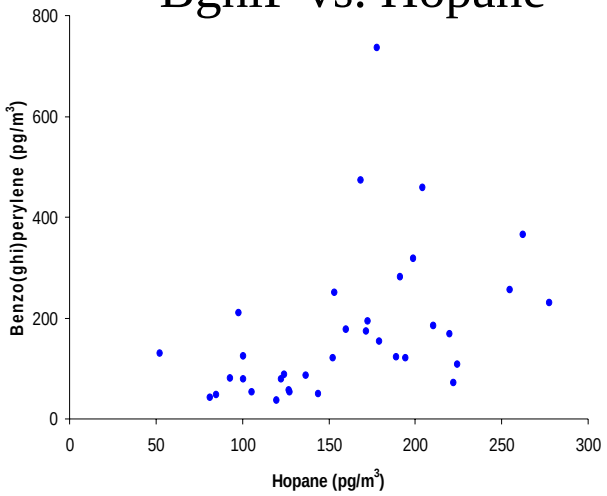
Analytical blanks – acceptable
Analytical precision – acceptable
Sampling blanks & precision – not evaluated

Calibration frequency – **not acceptable**
> solid phase extract step required
> (extremely low concentrations!)

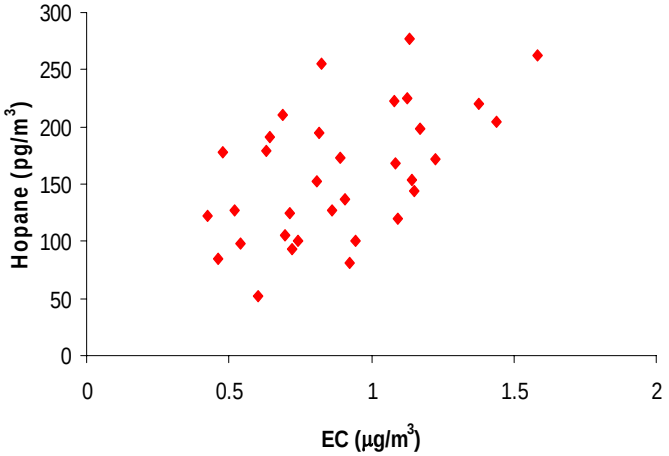
Surrogate recoveries – **not acceptable**
> collected PM strongly influences surrogate recovery
> internal standards for a range of volatility are necessary
> surrogate standards need to better align with targets

Associations Between Key Species

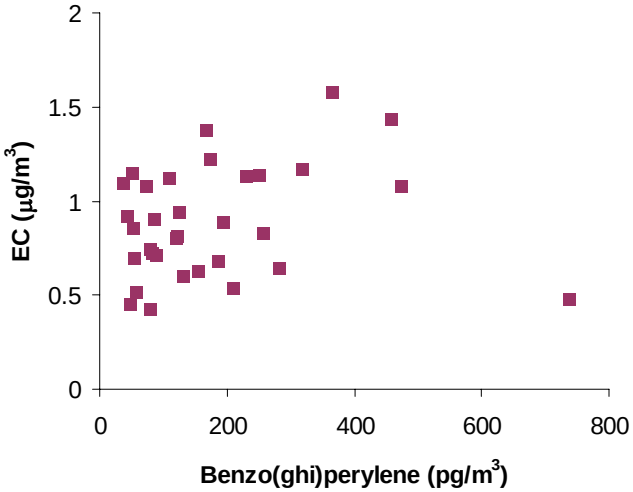
BghiP vs. Hopane



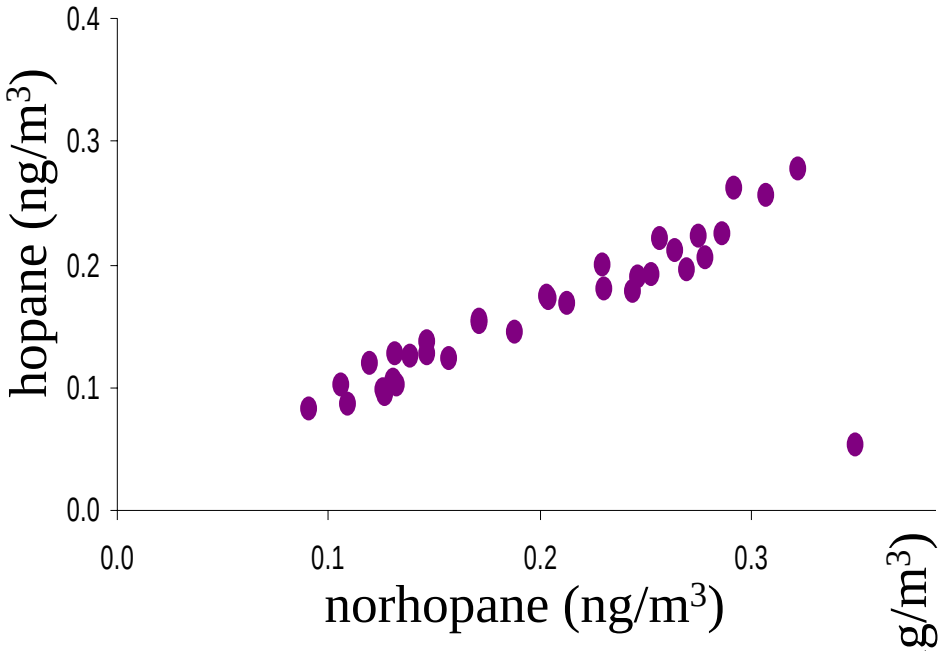
Hopane vs. EC

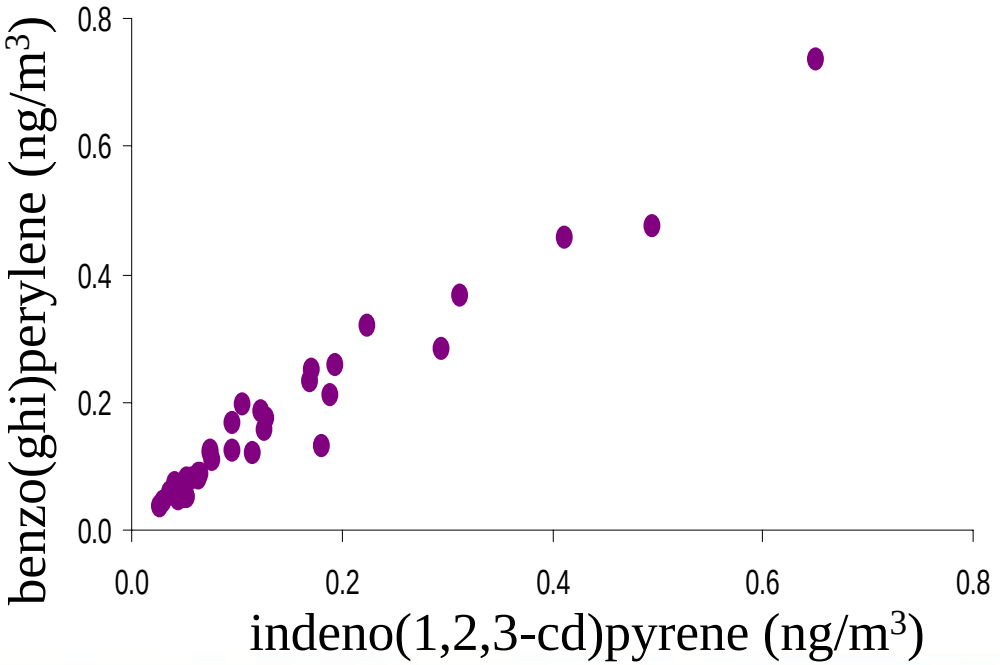


BghiP vs. EC

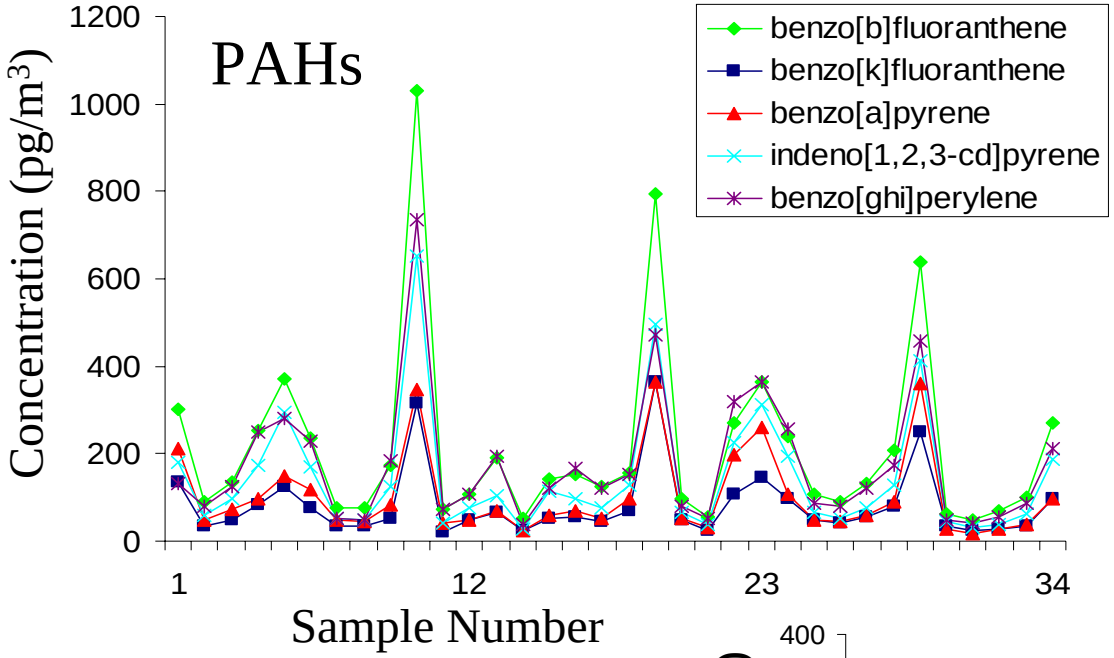


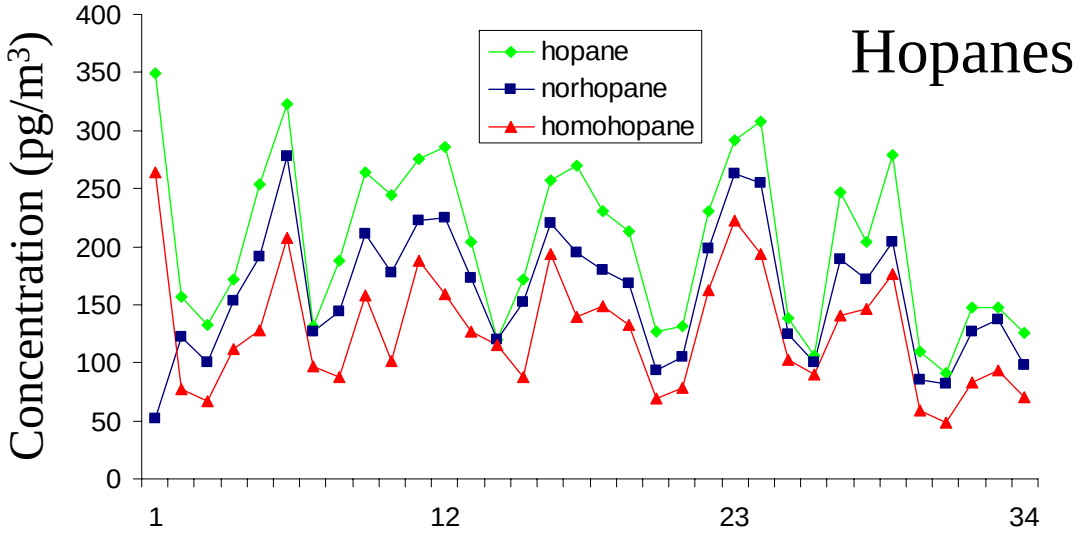
Associations Between Key Species



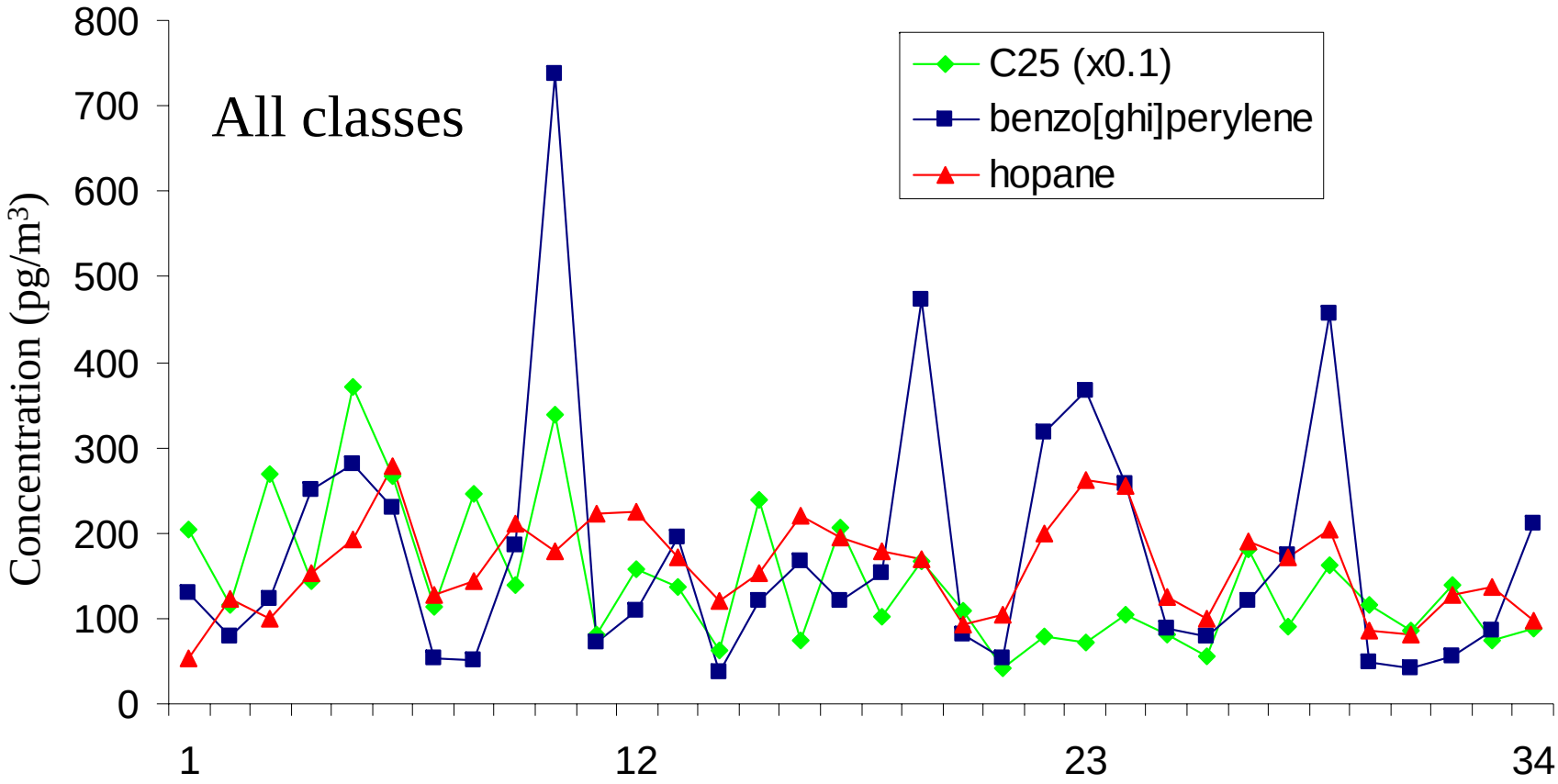


Variation in Daily Concentration





Variation in Daily Concentration



Conclusions

- Average concentrations fairly low (~100 to 200 pg/m^3)
- Strong associations observed *between* different PAHs and between different hopanes
- Associations of PAHs *with* hopanes (e.g. hopane vs. benzo[ghi]perylene) generally not as strong
- PAH concentrations exhibited considerably more day to day variability (CV ~ 100%) than hopane concentrations (CV<50%)

Next Steps

- *Add Solid Phase Extraction Step*
- *Determine Method Detection Limits*
- *Demonstrate Method Proficiency (recoveries)*
- *Proceed with Seasons 2-6 and low volume samples*