

MEASUREMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN AIRBORNE PARTICULATE MATTER AT LOW CONCENTRATIONS

Stephen R. McDow

**National Center for Environmental Assessment
Office of Research and Development
US Environmental Protection Agency**

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE MAR 2012		2. REPORT TYPE		3. DATES COVERED 00-00-2012 to 00-00-2012	
4. TITLE AND SUBTITLE Measurement of Polycyclic Aromatic Hydrocarbons in Airborne Particulate Matter at Low Concentrations				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Environmental Protection Agency, National Center for Environmental Assessment, Two Potomac Yard 2733 South Crystal Dr, Arlington, VA, 22202				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES Presented at the 9th Annual DoD Environmental Monitoring and Data Quality (EDMQ) Workshop Held 26-29 March 2012 in La Jolla, CA.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 37	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

EPA Methods for Species of Greatest Concern

<http://www.epa.gov/osw/hazard/testmethods/sw846/online/>
(Chapter 2 = Choosing the Correct Procedure)

010-100 – air (mostly emissions)

200 Series – inorganics in drinking water

500 Series – organics in drinking water

600 Series – organics in wastewater

1600 Series – “clean methods” (?)

3000 Series – digestion methods for metals

3500 Series – organic extraction methods

3600 Series – organic cleanup methods

5000 Series – VOC preparation for solid waste

7000 Series – atomic absorption methods (+ others?)

8000 Series – organic analysis

TO air toxics (not in sw846)

1,4-Dioxane

- 8260 VOC's by GCMS (often used with purge & trap)
- 8270 Extraction/GCMS
- 8015 Non-halogenated semi-volatiles by GC
- 5030 Purging at Elevated Temperature
- 5031 Azeotropic Distillation
- 624 VOC's by GCMS
- 625 Semi-Volatiles by GCMS
- TO-15 VOC's/canisters

Trichloroethylene

- 8010 Halogenated hydrocarbons by GC
- 8021B Aromatics & Halogens by photoionization
- 8260B VOC's by GCMS (e.g., after purge & trap)
- 524.2 Purgeable Organics by GCMS
- 601,602 Purgeable Aromatics & Halocarbons
- 624 VOC's by GCMS
- TO-15 VOC's/canisters

Dioxins

23	Stationary Source Sampling
1613	GCMS wastewater
8280, 8290	GCMS method specifically for dioxins
TO-9A with high volume PUF sampler:	
Ferrario et al Organohalogen Compounds 50, 35-39	

Hexavalent Chromium

3060	Alkaline digestion
7196A	Soil & Water Colorimetric (diphenylcarbazide)
7199	Hexavalent Chromium by Ion Chromatography
218.6	Low level chelation & extraction
NATTS	Technical Assistance Document for NATTS
	Collection on NaHCO ₃ impregnated cellulose filters
	Analysis by IC (www.epa.gov/ttnamti1/airtox.html)

Polycyclic Aromatic Hydrocarbons

8270C – GCMS

8272 – SPME-GCMS-SIM

8310 – HPLC

550.1 – HPLC (drinking water)

3500 – Organic Extraction

3545 – Pressurized Fluid Extraction

3535 – Solid Phase Extraction

TO-13A

RESEARCH: PM ORGANIC TARGET COMPOUNDS

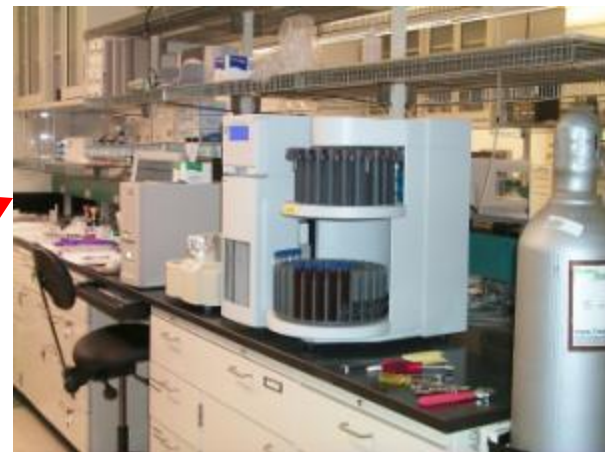
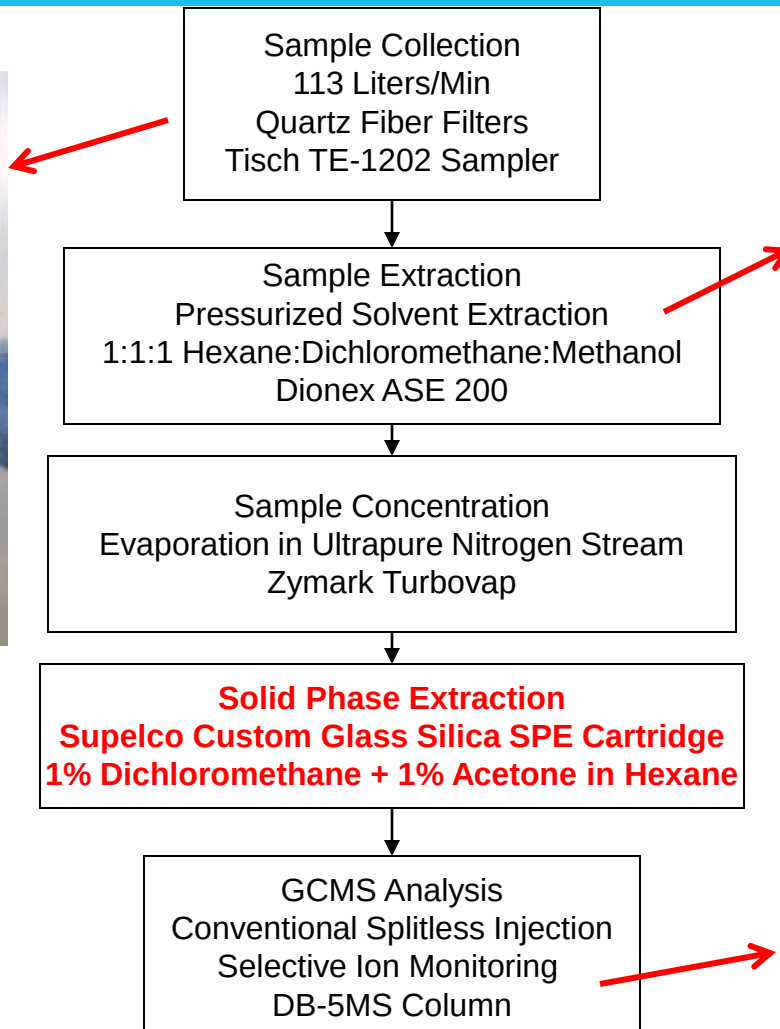
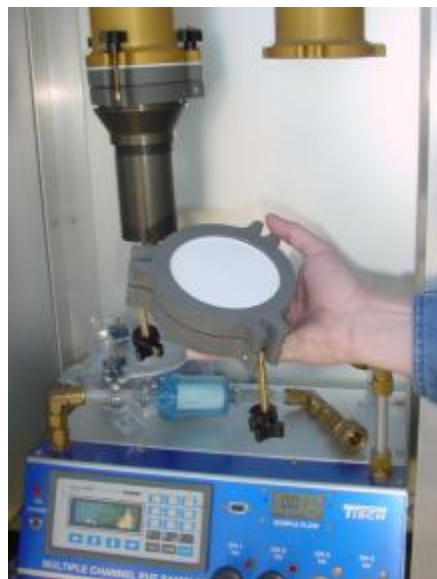
n-Alkanes: C23 to C34

Polycyclic aromatic hydrocarbons: pyrene, chrysene, benzofluoranthenes, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene

Hopanes: norhopane, hopane, homohopane

Aliphatic Acids: C16, C18, C16:1, C18:1

Levoglucosan



A REGIONAL SAMPLING NETWORK FOR SPECIATION OF ORGANICS IN PM-2.5 IN THE NEW YORK CITY AREA

Steve McDow & Min Li - Drexel University

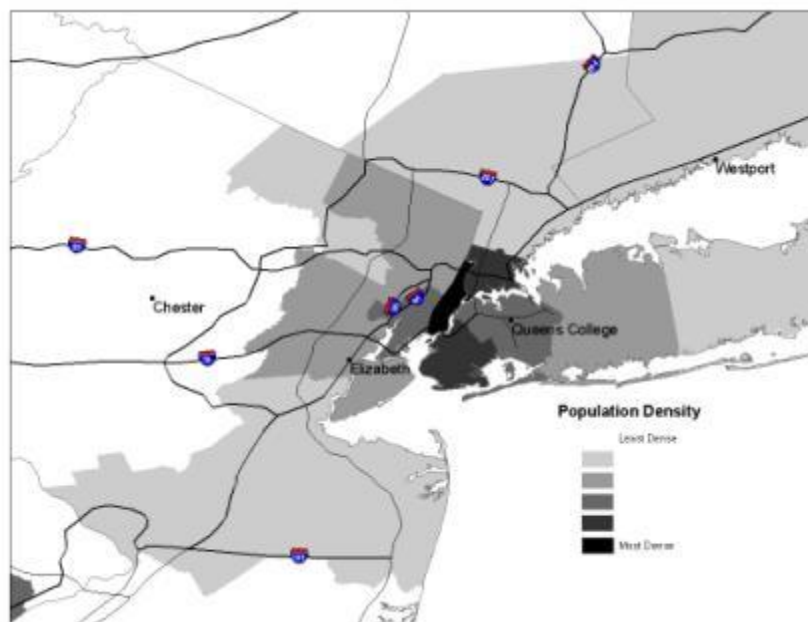
Monica Mazurek - Rutgers University

Lee Alter & John Graham - NESCAUM

Dirk Felton - NY DEC

Tom McKenna & Charlie Pietarinen - NJ DEP

Al Leston - Connecticut DEP



OBJECTIVES

- Collect enough sample to analyze
- Low blank levels

APPROACH

Use extra
Channel from speciation
samplers and analyze
47 mm quartz filter
composites by GCMS



**R&P
Partisol 2300**



Met One SASS

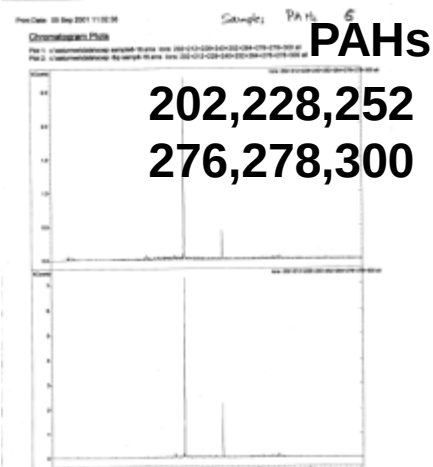
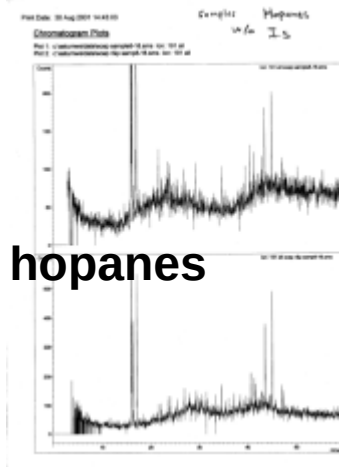
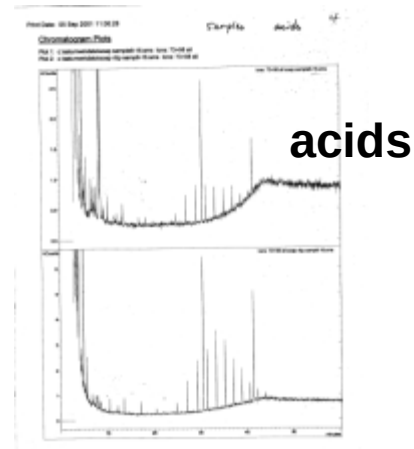
PRELIMINARY FIELD TEST

Insufficient Sample Collection:

- *n*-alkanes C22-C28 concentration ~ 10 to 50 ng/m³
- 2 hopanes barely detectable
- PAH's not detected

High Blanks

- *n*-alkane blank levels ~ 5 to 20% of sample concentrations
- hopanes also detectable in blanks

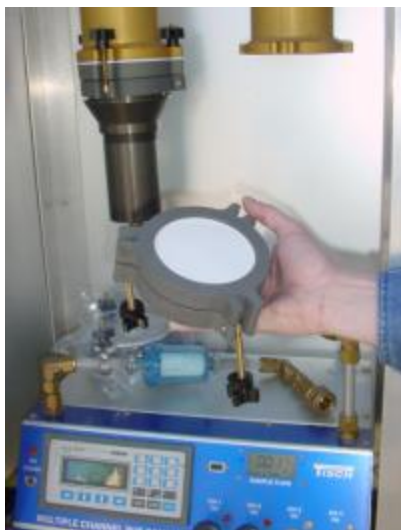


AIR CLIMATE & ENERGY RESEARCH PROGRAM

BUILDING A SCIENTIFIC FOUNDATION FOR SOUND ENVIRONMENTAL DECISIONS

Corrective Action:

- Increase flow rate
- Increase sampling time



Tisch TE-1202 Sampler

(*Large Volume Injection is another option)



DEARS SAMPLING



**Central
Site**



**Residential
Monitor**

Further Method Development and Improvement

Organic Analysis Challenges

**limited standard reference materials
missing calibration standards
non-selective (GCMS not yet developed)
substantial & variable sample loss in workup
time & labor intensive procedures**

Required Method Decisions

**can we analyze without cleanup or fractionation?
internal or external standards?
how many internal standards?**

Desired Analytical Advances

**5-point calibration curves for all analytes
submission of methods paper
recommendation to follow EPA & FDA Methods**

Resources for Development of Quality Assurance Procedures

EPA Forum on Environmental Measurements:
Validation and Peer Review US EPA Chemical Methods of Analysis
www.epa.gov/fem/pdfs/FEM_MV_doc_final_10-14-2005.pdf

Thompson et al. (IUPAC) Harmonized guidelines for single laboratory
Validation of methods of analysis Pure Appl Chem 2002 74, 835-855

Eurachem, The Fitness of Purpose of Analytical Methods 1998

International Organization for Standardization, ISO 5275-1

AOAC Official Methods Program Manual, Appendix D:
Guidelines for Collaborative Study Procedures to Validate Characteristics
Of a Method of Analysis

Resources for Development of Quality Assurance Procedures

Method 8270C (Semi-Volatiles, including PAHs)
Method 8000C (Determinative Chromatographic Separations)
Method 3500 (Organic Extraction)
SW-846 Chapter 1 (Quality Control)
SW-846 Chapter 4 (Organic Analytes)

METHOD PROFICIENCY DEMONSTRATION

- Acceptable average recovery of matrix spike of certified standard solutions (70-130%) (New NIST standards)
- Acceptable reproducibility of matrix spike of certified standard solutions (all 4 replicates 70-130%)

ON-GOING QA

- Method Detection Limit (3σ for 7 injections at 2 to 5 x MDL)
- 1 Calibration check per batch of <20 samples
- 1 Matrix spike of certified standard solutions per batch of <20 samples
- 1 duplicate sample per batch of < 20 samples
- Check surrogate recoveries for each sample

ACCEPTANCE CRITERIA: all analytes or 80% within 20% of target value?

SPIKING LEVEL: 10 to 50 x MDL or typical sample concentration?

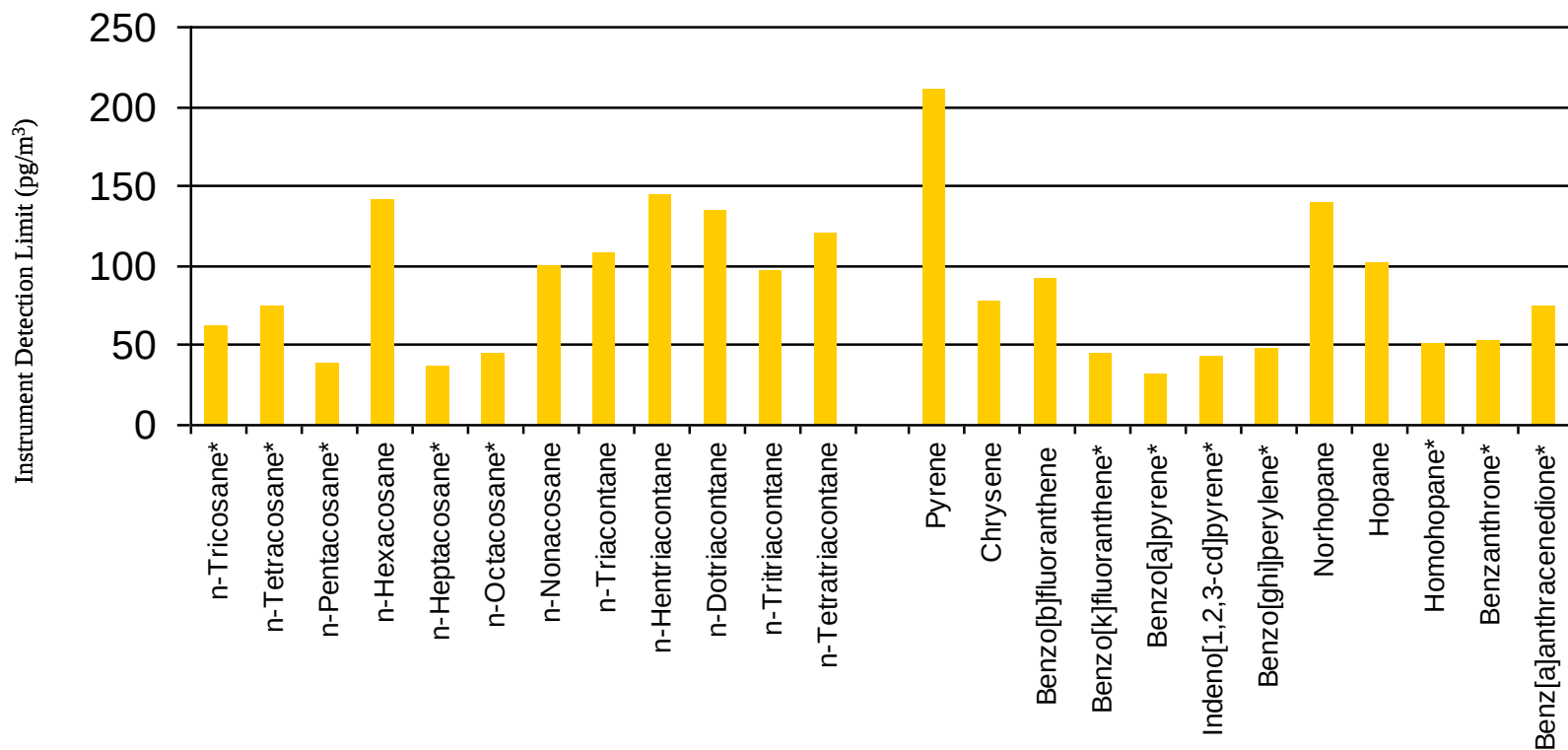
Determining Method Detection Limits

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

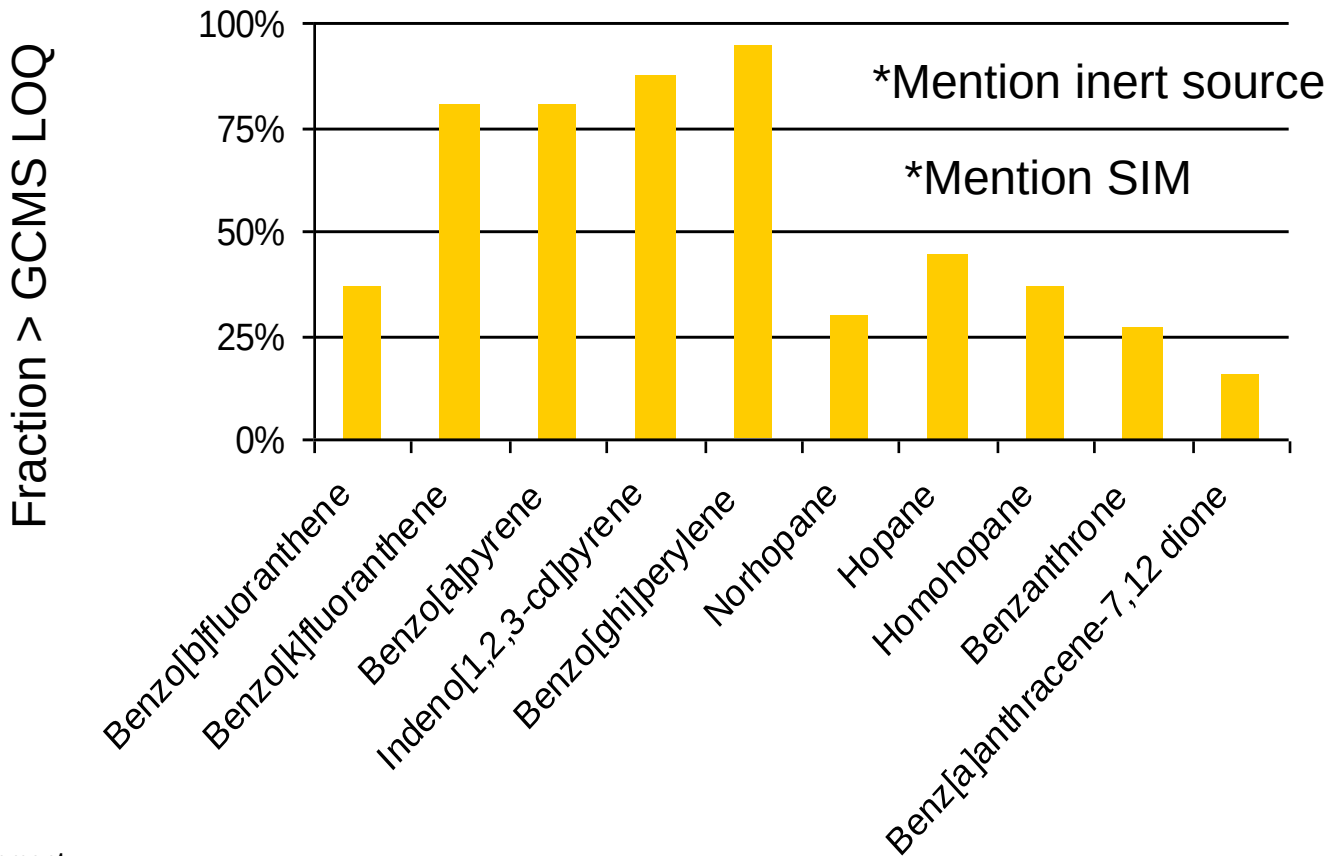
Source: 40CFR136, Appendix B

GCMS Limit of Quantitation (pg/m³ equivalent)

GCMS Limits of Quantitation
LOQ = 10s (from 40CFR136B)



Fraction of TACS Samples > GCMS LOQ
n =84



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

High volume PM samples (DEARS)

- Hexane, methanol, dichloromethane extraction
- Leads to column degradation
- Frequent recalibrations

Low volume PM samples (TACS)

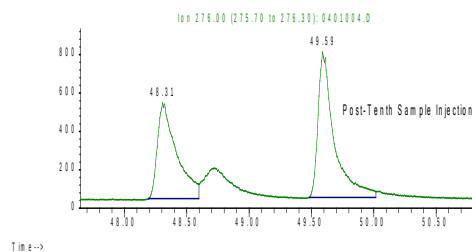
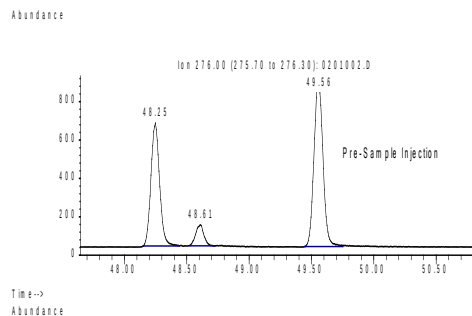
- Pentane, methanol, dichloromethane extraction
- Large volume leads to very severe column degradation (major peak loss)
- Splitless leads to slower column degradation but frequent recalibrations

Non-samples (wet or dry blank quartz filters), Splitless injection

- Hexane, methanol, dichloromethane extraction
- No apparent chromatography issues
- Problems only arise from extraction of real PM samples

Dichloromethane extractions

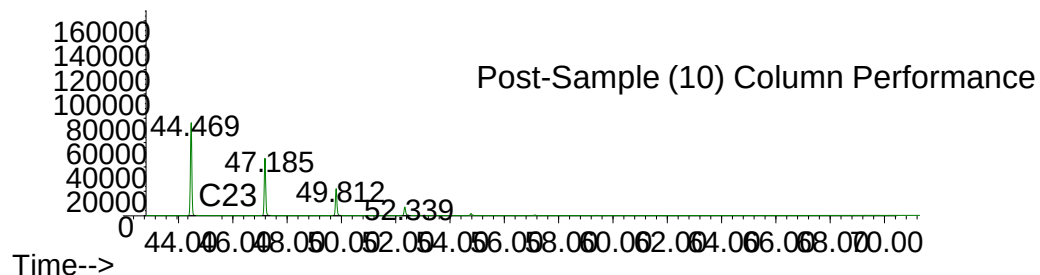
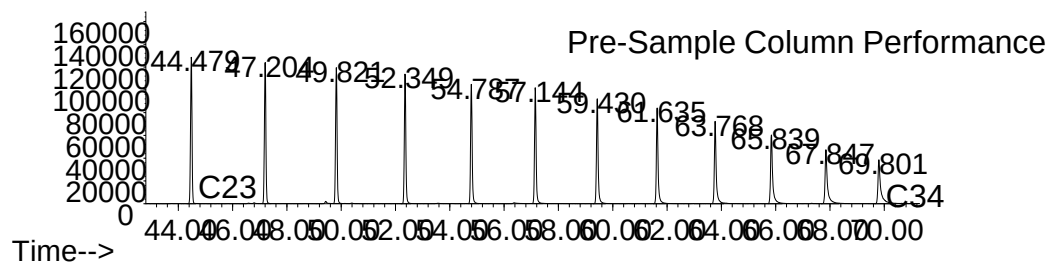
- Degradation slowed but not eliminated

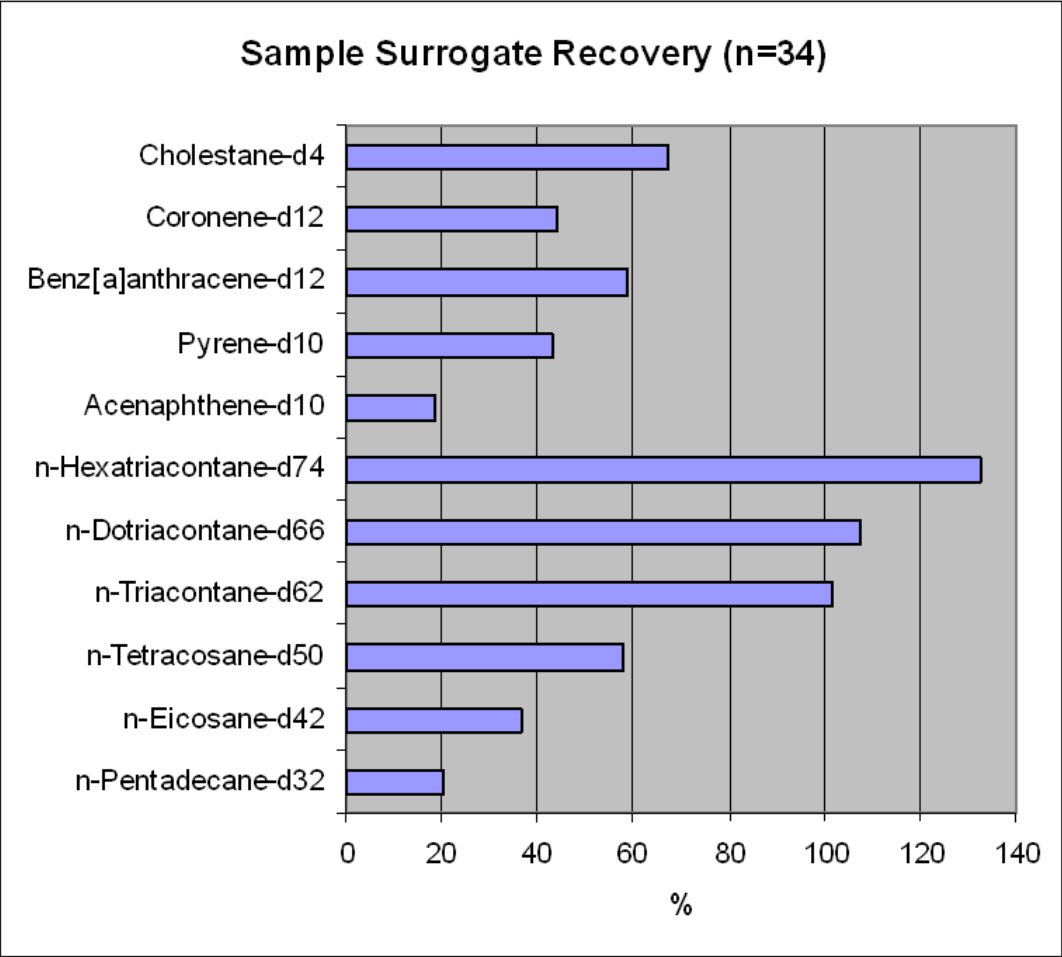


Pre and Post-Sample Column Performance

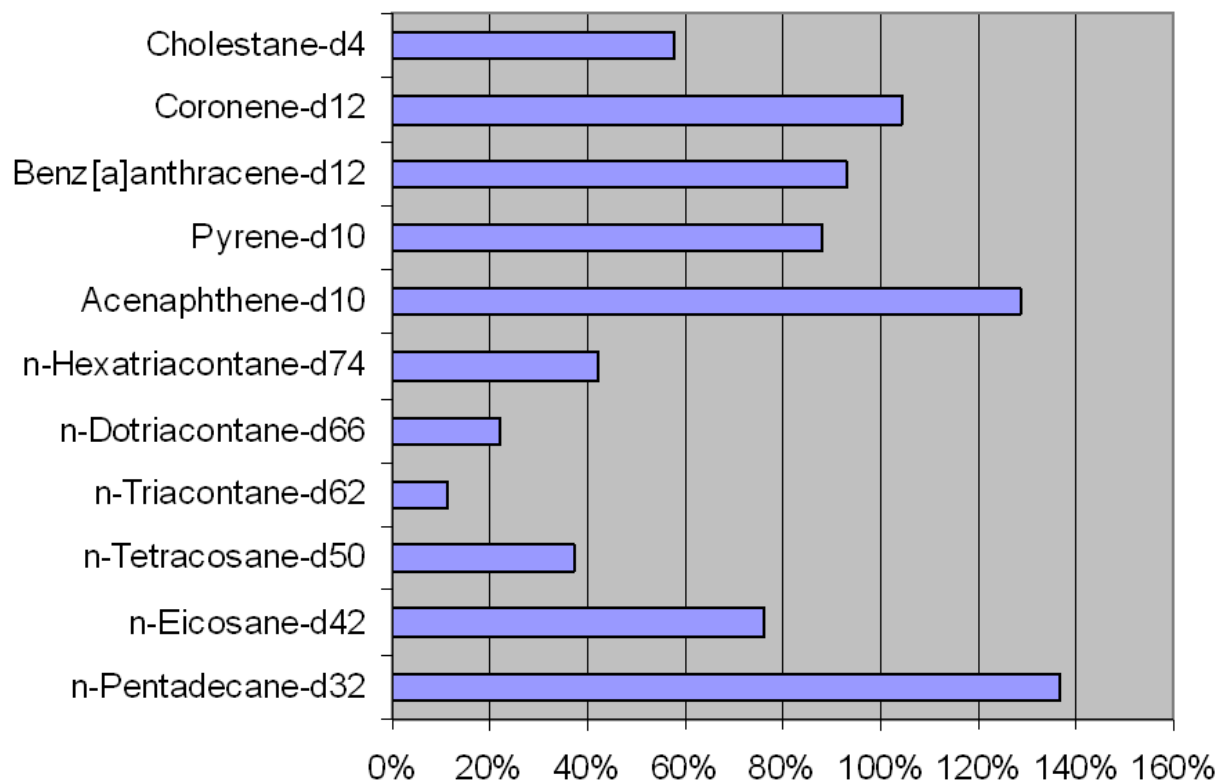
85 TACS samples analyzed

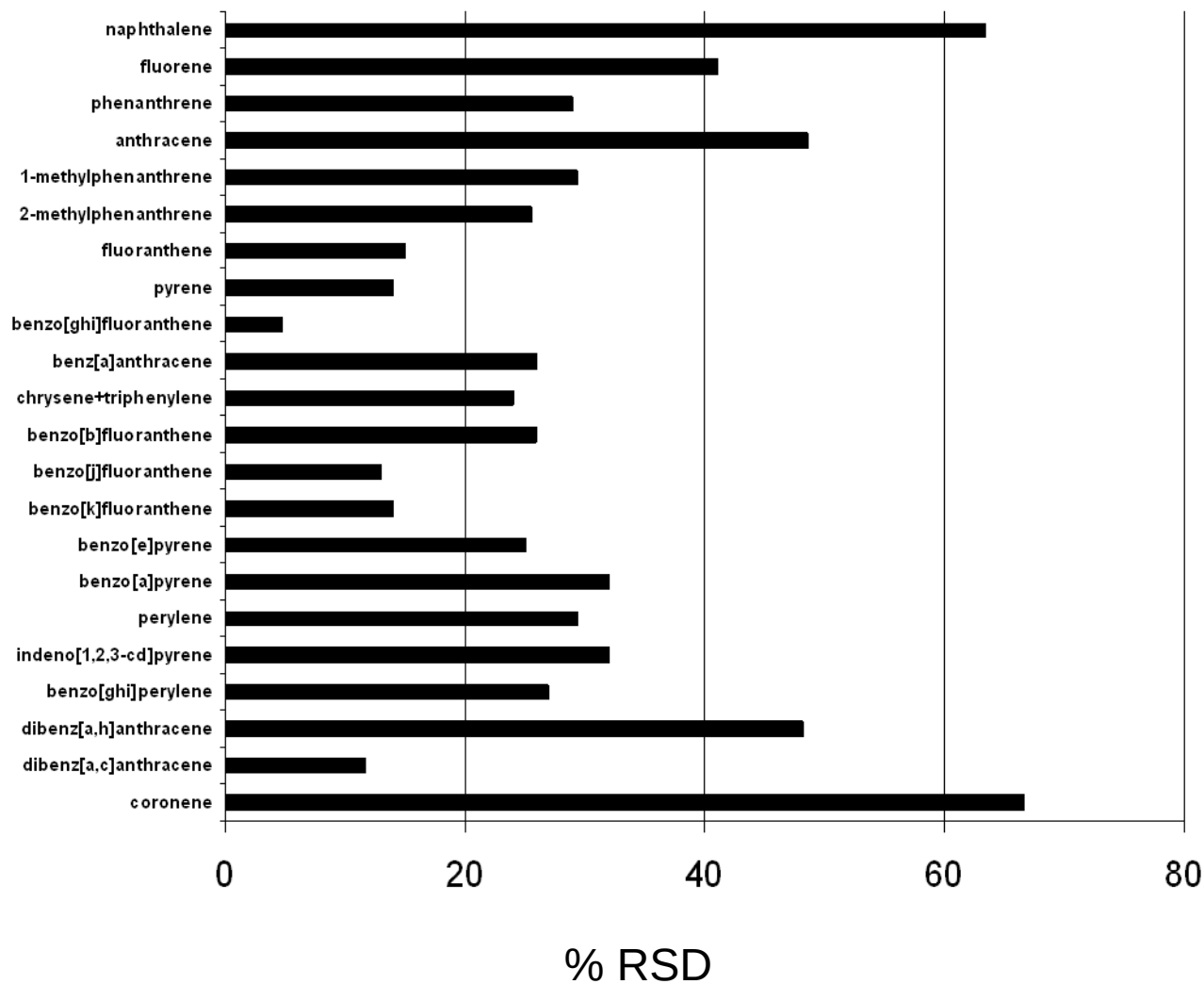
**Persistent Column degradation
Frequent recalibration required**





Sample Surrogate Variability (n=34)





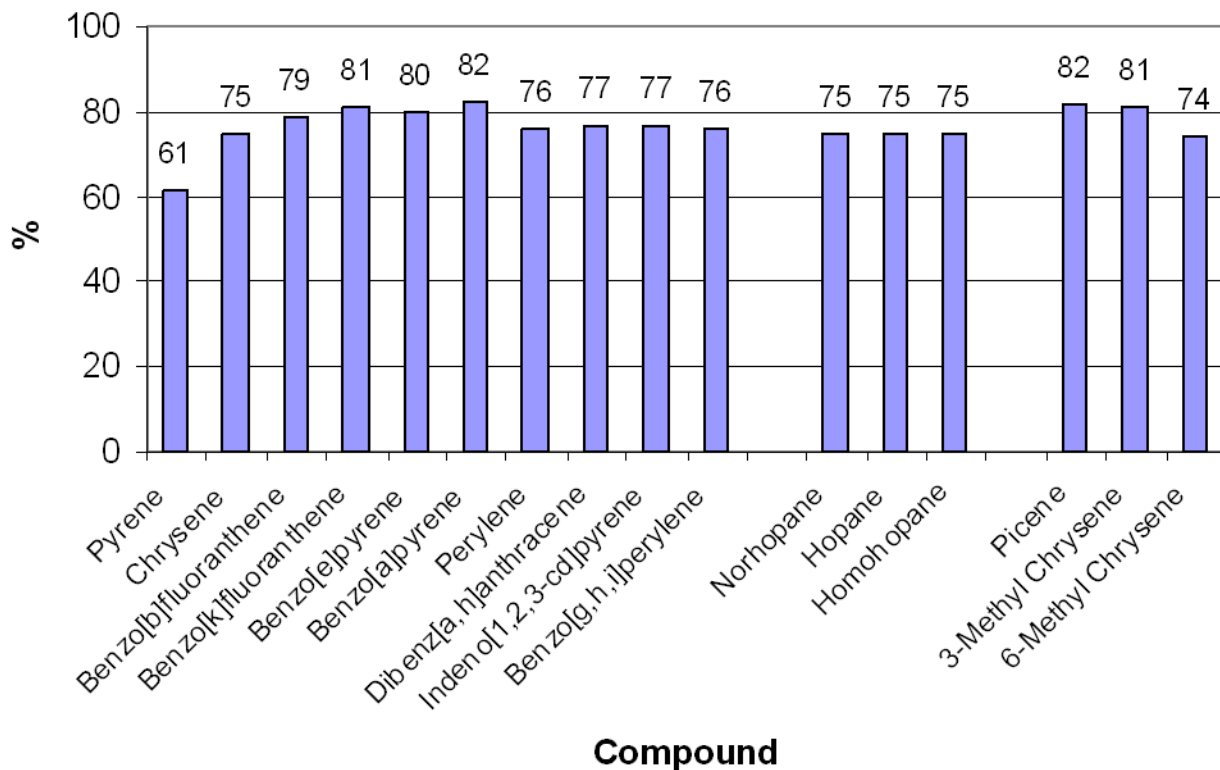
Without Solid Phase Extraction

- 2 - 3 samples: Peak shape, calibration suffer
- 30 - 40% deviation from calibration target
- Frequent maintenance, recalibration

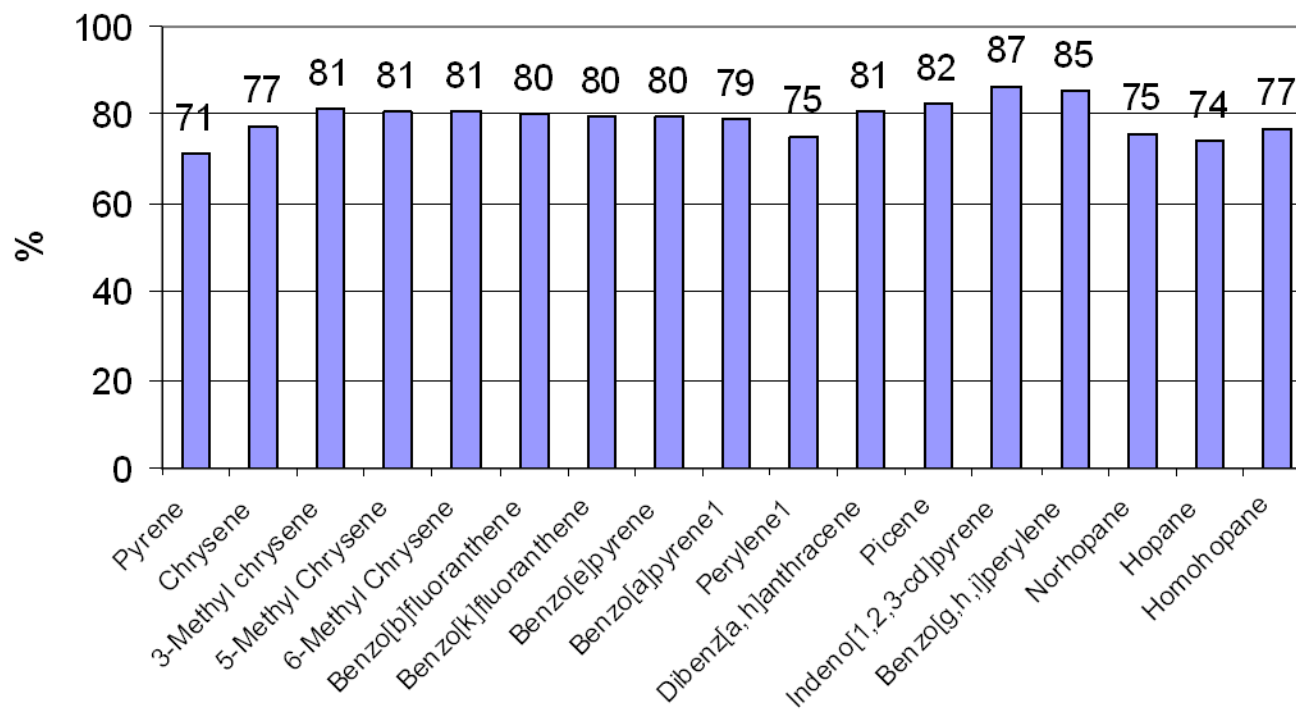
With Solid Phase Extraction

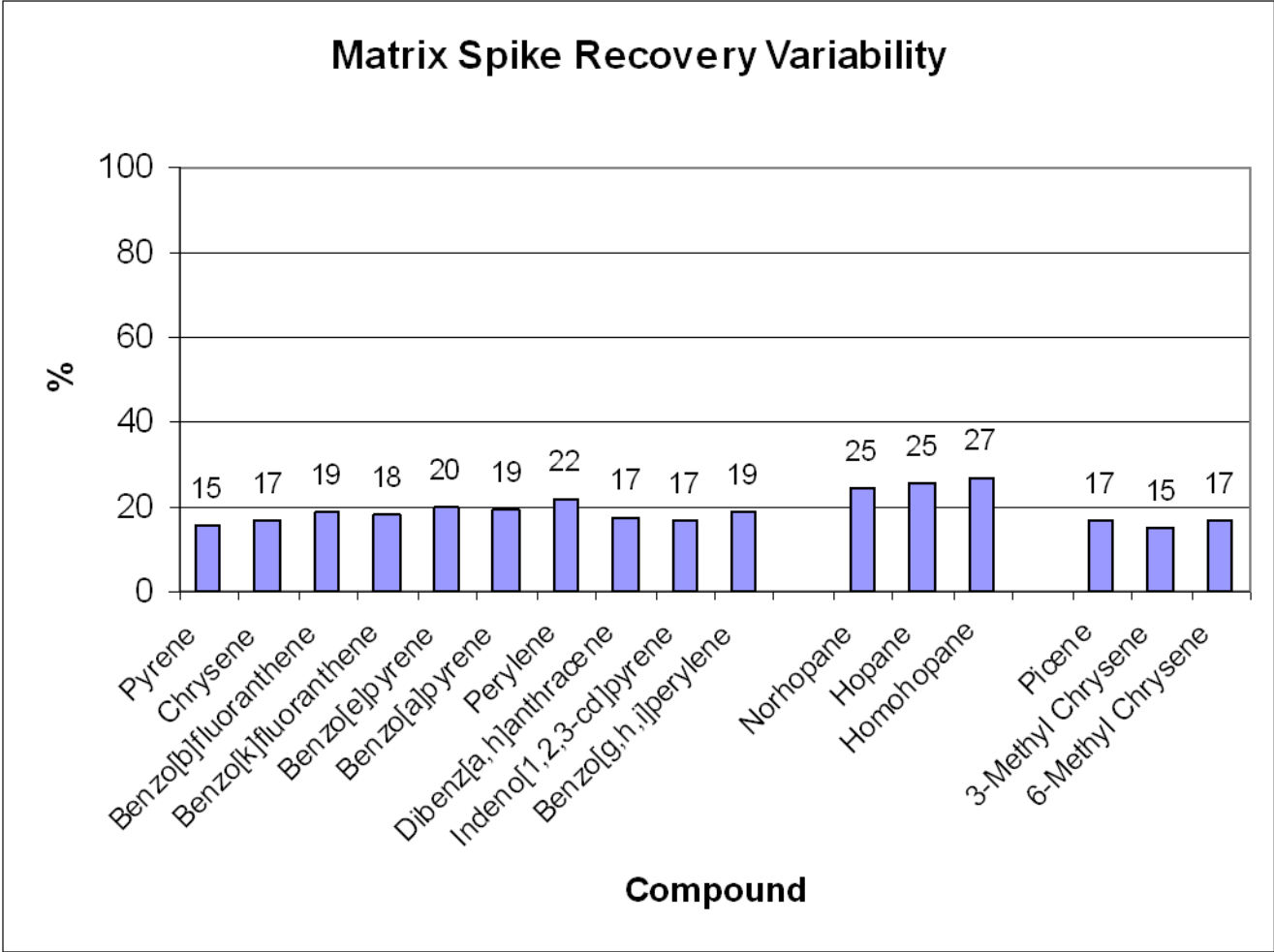
- Noted chromatography/calibration improvement
- Generally < 20% deviation from calibration target

Matrix Spike Recoveries

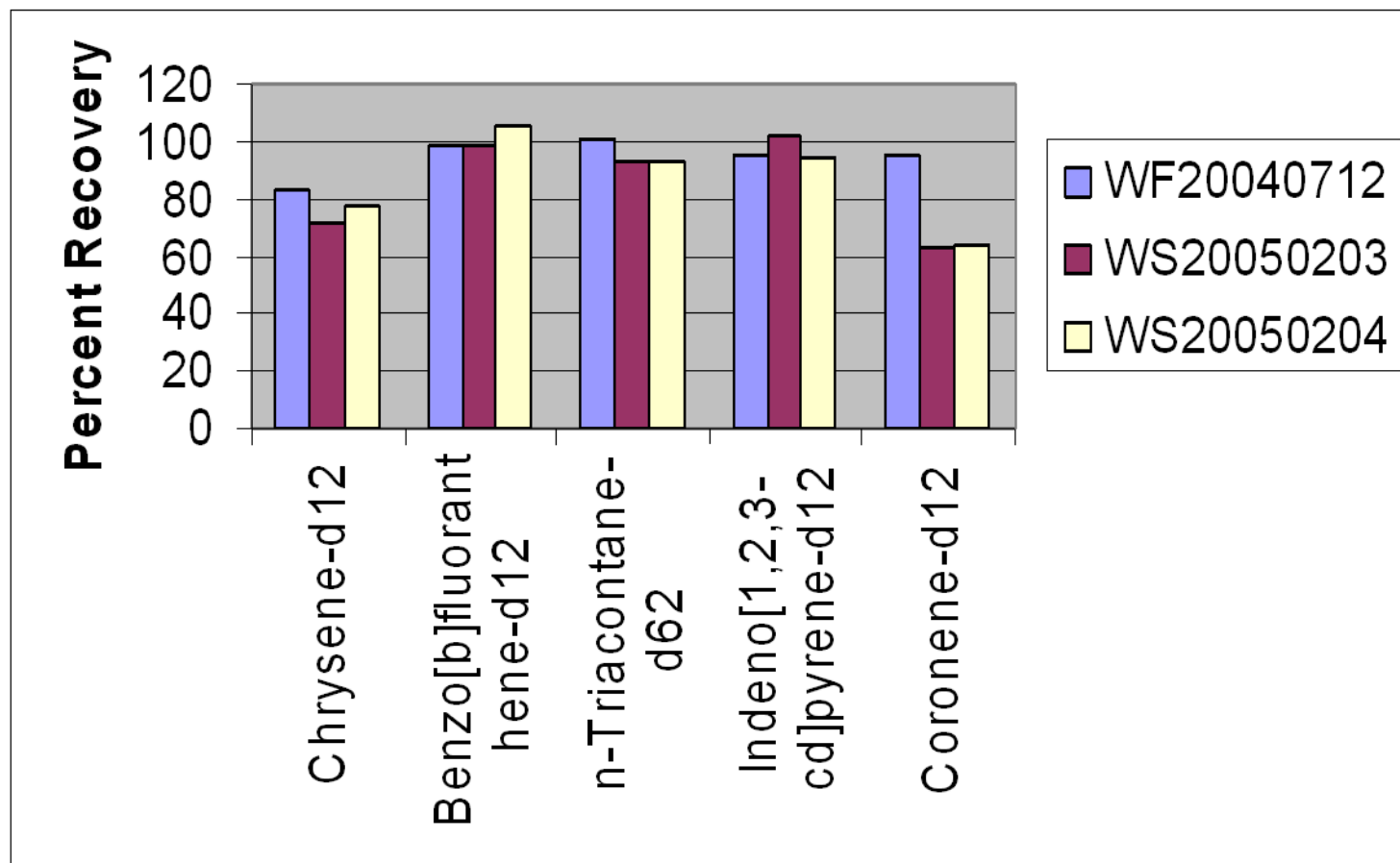


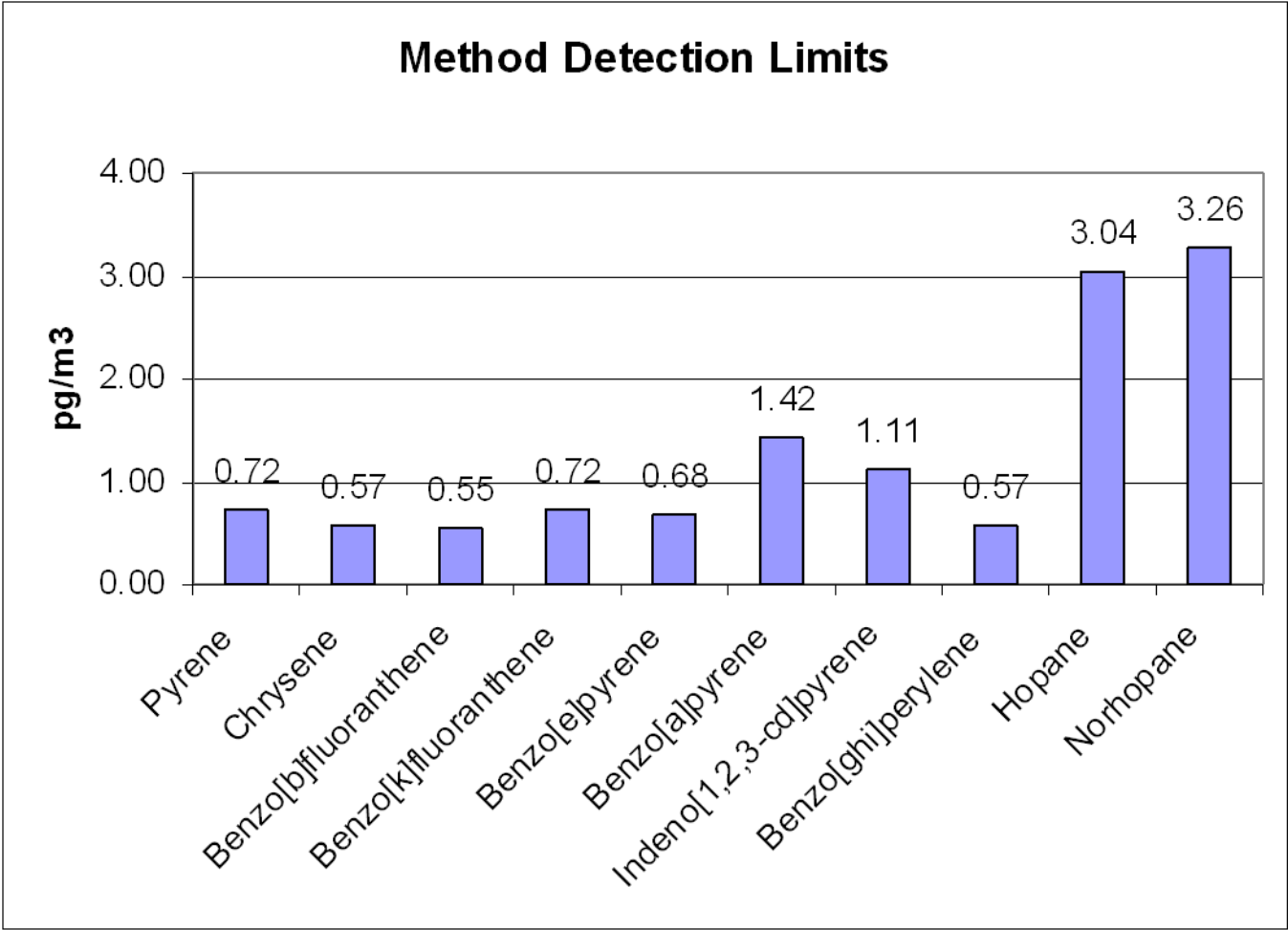
Method Proficiency Recoveries

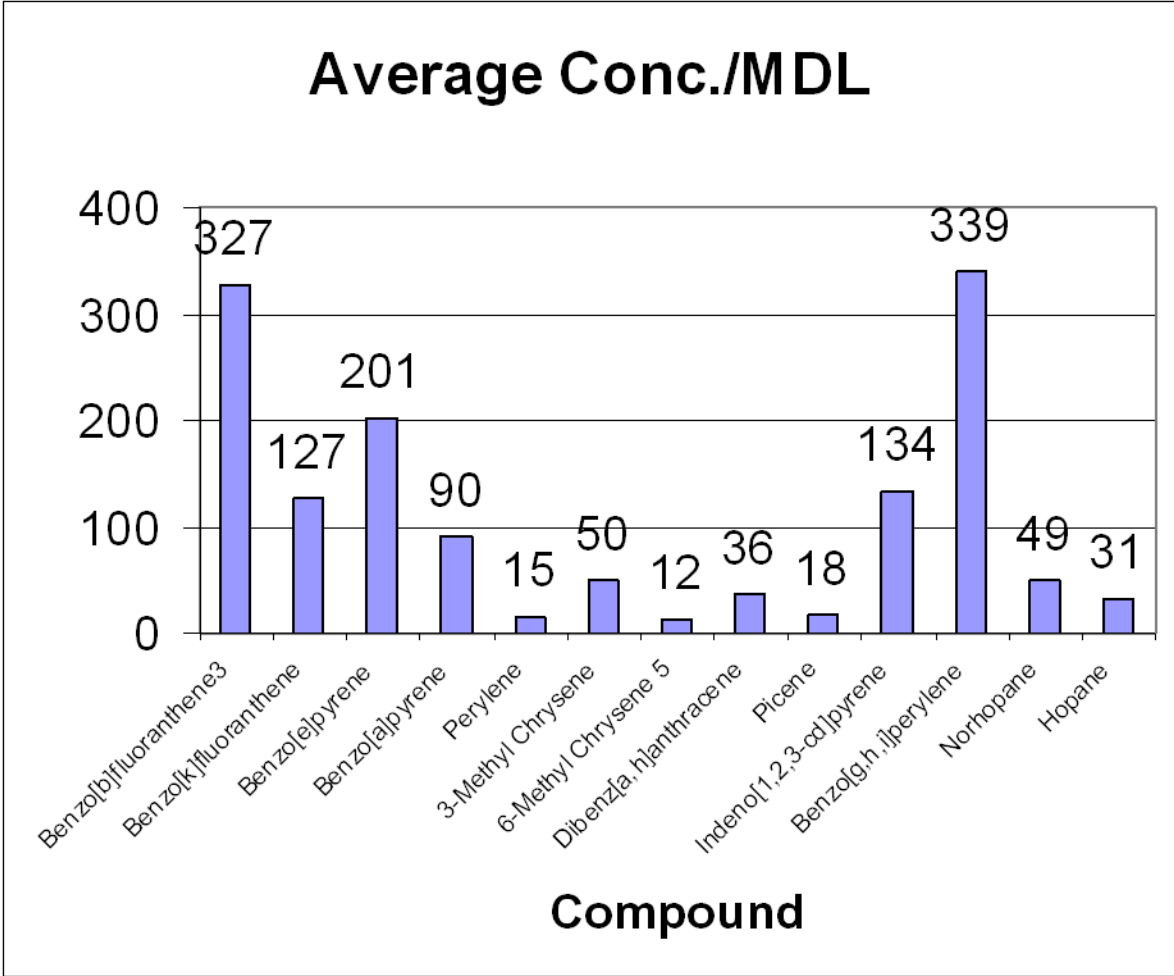




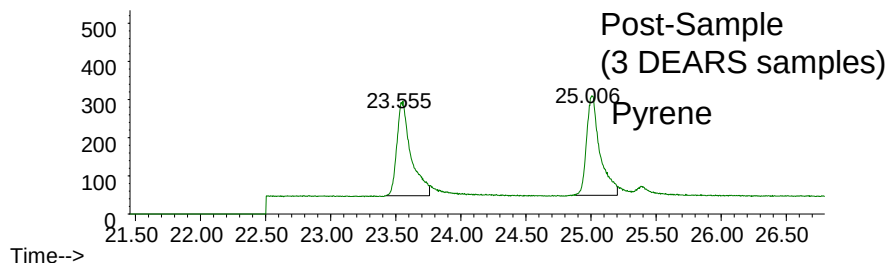
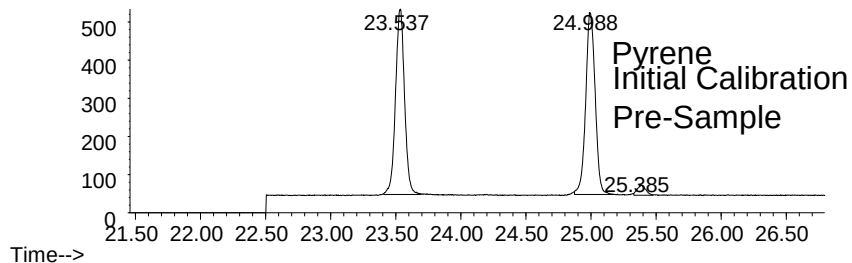
Surrogate Recoveries



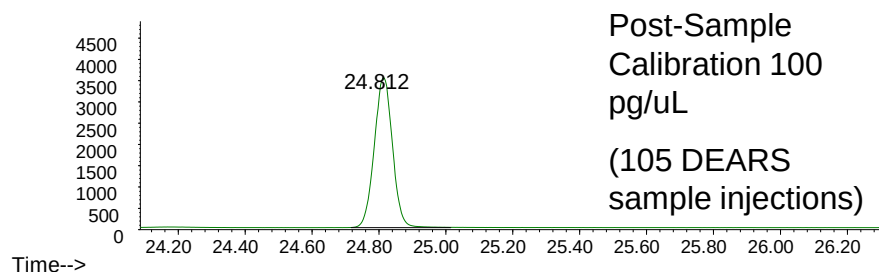
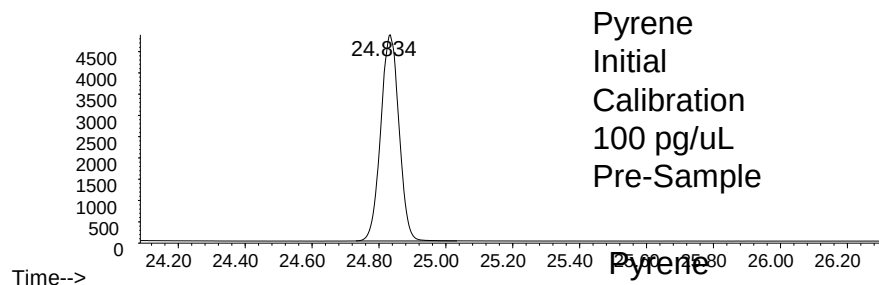




Initial Calibration vs. Post-Sample Comparison (SPE Cleanup)



(No SPE Cleanup)



LESSONS LEARNED

GCMS analysis without a cleanup or fractionation step is impractical for meeting typical Method 8270 QA requirement for PM sample analysis, especially at low concentrations

Sub-100 pg/m³ concentrations are possible to measure for PAHs, but more difficult for other organic compounds with less prominent base peaks

Large Volume Injection could be further evaluated as an alternative to high volume sampling.

Disclaimer

The views expressed in this presentation are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

Details:

S.R. McDow, M.A. Mazurek, M. Li, L. Alter, J. Graham, H.D. Felton, T. McKenna, C. Pietarinen, A. Leston, S. Bailey, S. Tong Argao, Speciation and atmospheric abundance of organic compounds in PM_{2.5} from the New York City area. I. Sampling network, sampler evaluation, molecular blank evaluation. *Aerosol Science & Technology* 42, 50-63, 2008.

J.M. Turlington, S.R. McDow, Solid phase extraction cleanup for non-polar molecular markers of PM_{2.5} sources. *Atmospheric Environment*, 44 2161-2165, 2010.

J.M. Turlington, S.R. McDow, Trueness, precision and detectability for sampling and analysis of organic species in airborne particulate matter. *Analytical and Bioanalytical Chemistry* 397, 2451-2463, 2010.