Distribution of PAHs among Sediment Size Fractions Determined by Thermal Desorption Gas Chromatography Mass Spectrometry

Jejal Reddy Bathi[1], Robert Pitt[1], Robert Findlay[2], Shirley E. Clark[3]

[1]Department of Civil, Construction and Environmental Engineering
University of Alabama, Tuscaloosa, AL 35487
[2]Department of Biological Sciences, University of Alabama
Tuscaloosa, AL 35487
[3]Penn State - Harrisburg, School of Science, Engineering and Technology, Middleton, PA - 17507

1

Overview of Presentation

- Introduction
- Thermal Desorption (TD) Method Development
- Sample Collection and Analyses
- Conclusions
- Question and Answers

2

Introduction

- Steps for PAH analyses
  - Sample preparation
  - Extraction and Concentration
  - Detection and Quantification
- Liquid-liquid extraction by separatory funnel and Solid Phase Extraction (SPE) are the most common PAH extraction methods for liquid samples.
- SPE method is ineffective for liquid samples with high concentrations of solids.

3

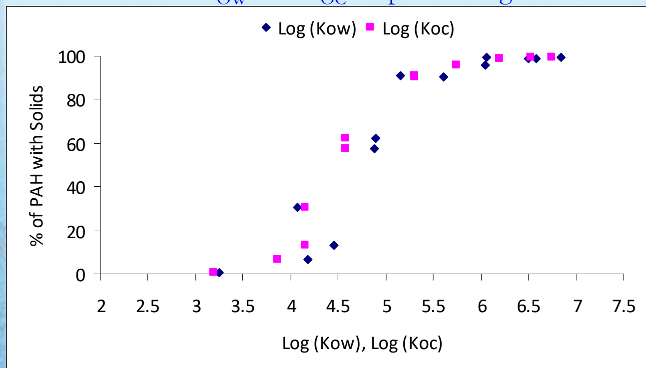
Introduction

- For solid samples, Soxhlet, automated Soxhlet, and ultrasonic extraction are the most common PAH extraction methods.
- Disadvantages of traditional methods include,
  - Time consuming
  - Labor intensive
  - Use of large amounts of toxic solvents
  - Exposure of toxic organic solvents to the operators

4

Introduction - Fugacity Modeling

- Contaminant partition constants (K_{OW}, K_{OC}, Henry's constant) are key factors in their fate.
- Fugacity Level I equilibrium model (Mackay et al. 1992) was used for predicting the phase partitioning of PAHs. The following graph illustrates the effect of K_{OW} and K_{OC} on partitioning onto solids.



5

After Hurricane Katrina, and other devastating hurricanes of the 2005 season, EPA reviewed several monitoring and cleanup programs in the days following the events. The selection of the right analytical and sampling methods for water and sediment were all found to be very critical in reducing the risk to the cleanup crews, emergency workers, and residents.

6

Analytical Method Development

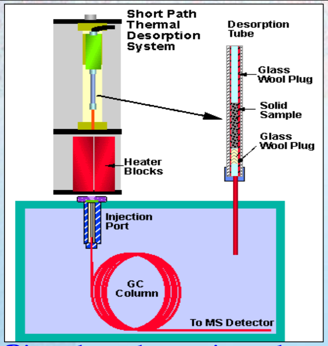
- The main transport mechanisms and fate of PAHs in the aquatic environment are closely related to their major associations with particles. Therefore, it is essential that rapid and sensitive analytical tools be used that can measure PAHs in samples having large amounts of suspended sediment.
- During the aftermath of natural disasters, homeland security incidents, and accidental releases of hazardous and toxic materials, the rapid analyses of samples is needed to identify areas for priority cleanup and in preventing dangerous exposures to cleanup personnel and residents.
- Analytical tools need to be developed and tested on a variety of samples to ensure their applicability to a wide range of emergency situations.
- With these objectives in mind, a TD-based GC/MSD method was developed and tested using urban stream sediments for PAH contamination.

7

TD Method Development

- The TD analytical method is rapid, uses no solvent, and is less labor intensive than other PAH analytical methods, especially for samples having high sediment concentrations.
- TD uses elevated temperatures as a means to directly transfer the analytes from solid sample matrices to the gaseous analytical system of the GC/MSD.
- The desorbed analytes are concentrated in a cyrotrap at the head of the GC column and are then re-vaporized into the column for separation and final detection.
- Final desorption temperature and temperature holding times are two important factors to be optimized for better recovery of PAHs from solid matrices.

8

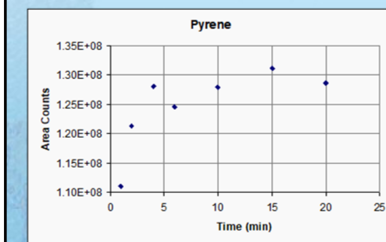


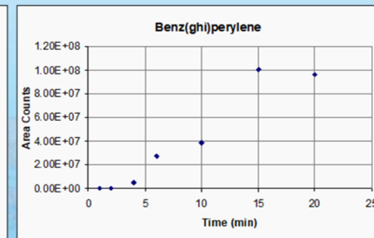
Direct thermal extraction and analysis technique

SIS Thermal desorption unit

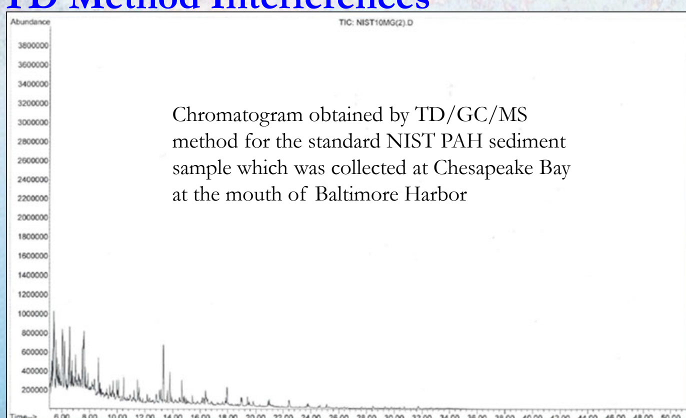
TD Method Development

- A desorption temperature of 350°C produced the largest peak areas for the individual PAHs, for the tested range of temperatures 250°C to 375°C with 25°C step changes.
- A final temperature holding time of 15 min produced maximum peak areas for the individual PAHs in the resulting chromatograms.





TD Method Interferences



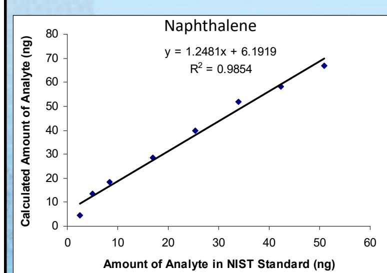
Chromatogram obtained by TD/GC/MS method for the standard NIST PAH sediment sample which was collected at Chesapeake Bay at the mouth of Baltimore Harbor

- Other major findings included the addition of small amounts of copper to avoid interfering sulfur compounds and freeze drying the samples to reduce the moisture content in the samples to prevent ice blockages in the GC column. Local urban stream sediments were sufficiently dried using a conventional drying oven.

TD Method Detection Limits

- $DL = Y_0 + S_y Z_\alpha$ (McCormick and Roach 1987)
- NIST sediment was tested in the weight range 3 – 60mg

PAH	R^2	Detection Limit (ng)
Naphthalene	98.5	9.63
Fluorene	96.4	2.62
Phenanthrene	97.1	6.37
Anthracene	94.1	3.83
Fluranthrene	98.8	2.67
Pyrene	93.2	9.81
Benzo(a)anthracene	96.8	2.25
Chrysene	96.5	2.63
Benzo(b)flouranthrene	97.6	4.15
Benzo(a)pyrene	97.5	4.2
Indeno(1,2,3-cd)pyrene	93.1	1.34
Dibenz(a,h)anthracene	52.2	1.05
Benzo(ghi)perylene	97.1	0.97



TD Method Recovery Calculations

PAH	% Recovery from Solid Samples	Acceptable Range of % Recovery from EPA Methods (Aqueous Samples)	Acceptable Range of % Recovery from *Standard Methods* (Aqueous Samples)
Naphthalene	125	D – 122	21 – 133
Fluorene	142	D – 142	59 – 121
Phenanthrene	110	D – 155	54 -120
Anthracene	104	NG	NG
Fluranthrene	62	14 – 123	26 – 137
Pyrene	33	D – 140	52 – 115
Benzo(a)anthracene	109	33 – 143	33 – 143
Chrysene	140	17 – 168	17 – 168
Benzo(b)flouranthrene	35	24 – 159	24 – 159
Benzo(a)pyrene	41	17 – 163	17 – 163
Indeno(1,2,3-cd)pyrene	34	NG	NG
Dibenz(a,h)anthracene	46	NG	NG
Benzo(ghi)perylene	43	NG	NG

13

Effect of Recovery by Particle Size

- Concentrations of PAHs in three replicates of two coarse samples were compared with PAH concentrations in the same samples that were ground to <180 µm to test the effect of particle sizes on PAH recovery. Only one PAH of one sample was significantly affected by grinding.

PAH	ANOVA P Value (95% C.I) of Comparing Concentrations	
	Comparing the Coarser 710 - 1400µm with Its Ground Sample	Comparing the Coarser 1400 - 2800µm with Its Ground Sample
Naphthalene	0.122	0.128
Fluorene	0.064	0.118
Phenanthrene	0.618	0.052
Anthracene	0.776	0.204
Fluranthrene	0.786	0.135
Pyrene	0.516	0.076
Benzo(a)anthracene	0.052	0.368
Chrysene	0.36	0.249
Benzo(b)flouranthrene	0.342	0.409
Benzo(a)pyrene	0.048	0.45
Indeno(1,2,3-cd)pyrene	0.175	0.67
Dibenz(a,h)anthracene	0.376	0.294
Benzo(ghi)perylene	0.100	0.660

14

Sampling Sites

- Sediment samples were collected from three urban creeks in the Tuscaloosa and Northport, Alabama, areas

Site 1: Cribbs Mill Creek

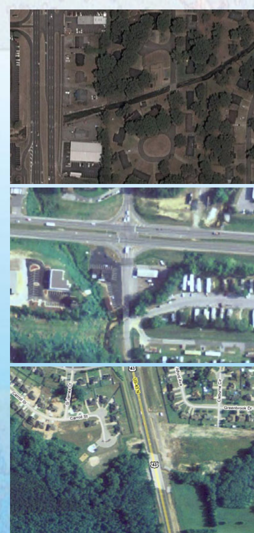
- Source areas: medium density two story family home residential area
- No history of sanitary sewage contamination (Pitt, *et al* 2005)

Site 2: Hunter Creek

- Source areas: automobile service commercial areas, heavy traffic along McFarland Blvd., and runoff from trailer park residential areas

Site 3: Carroll Creek

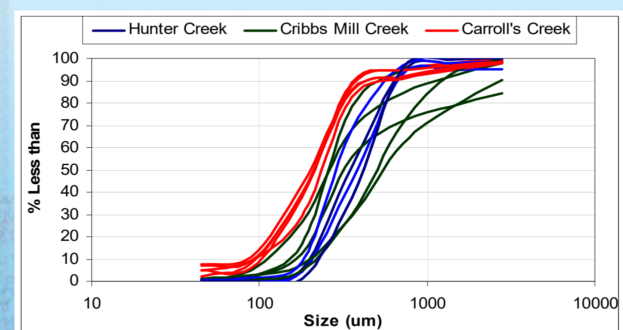
- Source areas: A residential area on one side and forested lands on the other side of the creek
- Has a recent history (in 2006) of sanitary sewer overflows (SSOs) into the creek (ADEM Consent Order No. 07-139-CWP to City of Northport)



15

Sample Particle Size Distributions

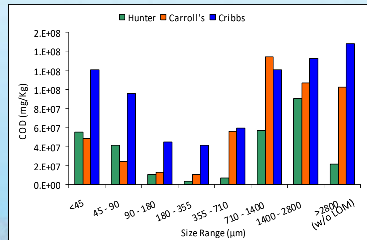
- Five sediment samples were collected from each of the three creeks.
- All sediments were fractionated into nine size (µm) ranges <45, 45-90, 90-180, 180-355, 355-710, 710-1400, 1400-2800, >2800(w/o large organic matter (LOM)) and > 2800 (LOM only).



16

COD Associations by Particle Size

- COD analyses were conducted to indicate the amount of organic material in the samples (a rapid and commonly available analytical method), an important factor in PAH associations.
- Median mass of the sediment COD was associated with 355 µm particles.



COD in large organic material fraction >2800 µm (LOM), COD much larger than in other sample sizes:

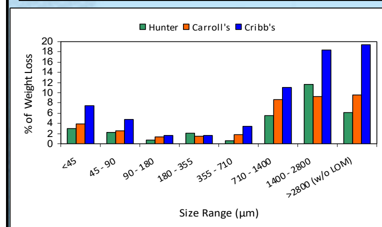
Cribbs Mill Creek	Hunter Creek	Carroll's Creek
1.60E+09	1.50E+09	1.30E+09

17

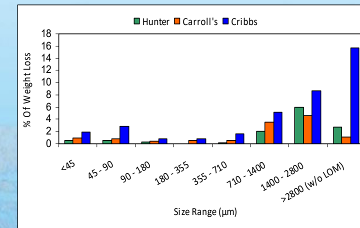
Thermal Chromatography used to Identify Major Sample Components

Temperature (°C)	Material Lost at These Temperatures
up to 104	Moisture
104 - 240	Paper debris
240 - 365	Leaves and grass
365 - 470	Rubber
470 - 550	Asphalt
Above 550	Remaining material is inert

Temperature Range (°C)	LOM % Weight Loss	
	Hunter	Carroll's
104 - 240	8.6	20.4
240 - 365	42.5	33.5
365 - 470	28.3	3.9
470 - 550	1.3	0.9
% Inert Material	19.2	41.4



Temperature range of 104 – 550 °C (total volatile fraction)

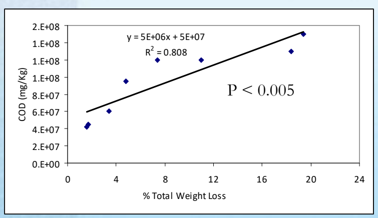


Temperature range of 240°C – 365 °C (mostly leaves and grass fraction)

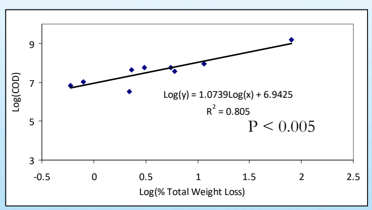
18

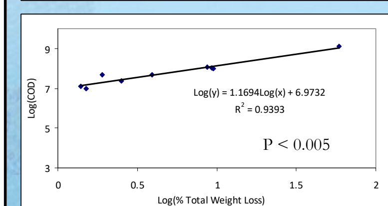
COD vs. Expected Leaves and Grass Fraction

Cribbs Mill Creek



Hunter Creek





Carroll's Creek

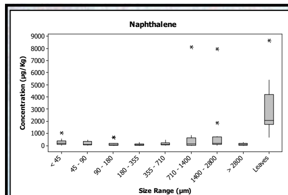
Creek	ANOVA P Value of Regression	
	Slope	Constant
Cribbs Mill Creek	< 0.005	< 0.005
Hunter Creek	< 0.005	< 0.005
Carroll's Creek	< 0.005	< 0.005

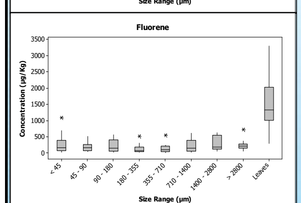
19

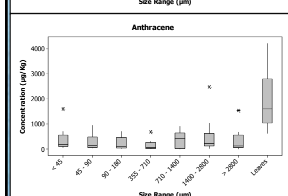
Concentrations of PAHs by Particle Sizes

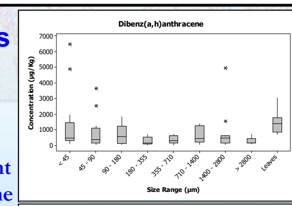
PAH concentration trends with sediment size are similar to the trends for COD and the leaves and grass fractions.

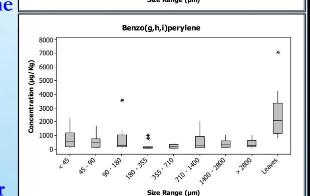
The smaller (<180µm) and larger (>710µm) particles were found to have higher concentrations of PAHs than the intermediate sizes

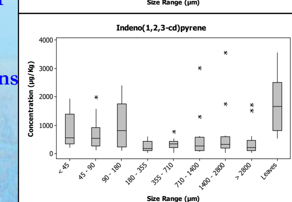




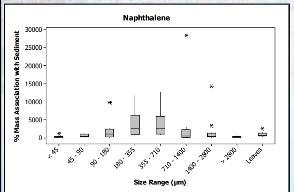


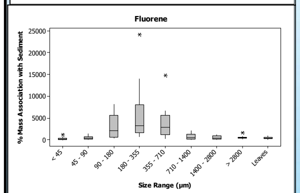


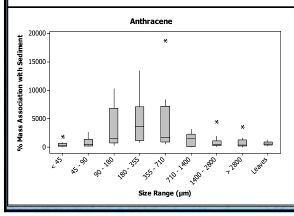




20



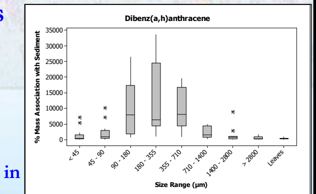


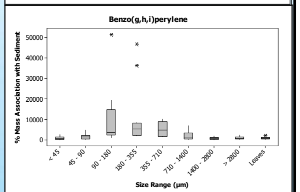


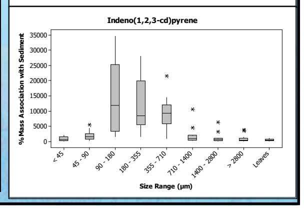
Mass of PAHs by Urban Sediment Particle Sizes

Almost all of the sediment PAHs are associated, by mass, in the intermediate particle size fraction (90 to 710 µm), even though this size range had the lowest concentrations

Size (µm)	% Average dry weight of Sediment
<45	1.1
45 – 90	2.8
90 - 180	14.4
180 - 355	46.4
355 - 710	27.4
710 - 1400	3.5
1400 - 2800	1.8
Large organic matter	0.3







Conclusions

- When discharged into the aquatic environment, PAHs are mostly associated with particulate matter, rather than in the dissolved form.
- Thermal desorption (TD) is rapid, minimizes the likelihood for human errors and contamination, and uses no solvents.
- The leaf and grass content, COD and PAH concentrations in the urban creek sediments showed similar trends: smaller and larger sized particles were associated with higher concentrations compared to the intermediate sized particles.
- However, most of the mass of the PAHs were associated with the intermediate particle sizes (90 – 710 µm) in the stream sediments which were in the greatest abundance, even though their PAH concentrations were the lowest.

Acknowledgments

- NSF EPSCoR, COSS research center for funding this research work
- Fellow graduate students in the department of civil engineering at The University of Alabama

- **Disclaimer:**
  This material is based upon work supported by the National Science Foundation under Grant No. EPS-0447675. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

Thank you

Questions?