



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

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Overview of Presentation

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

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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.

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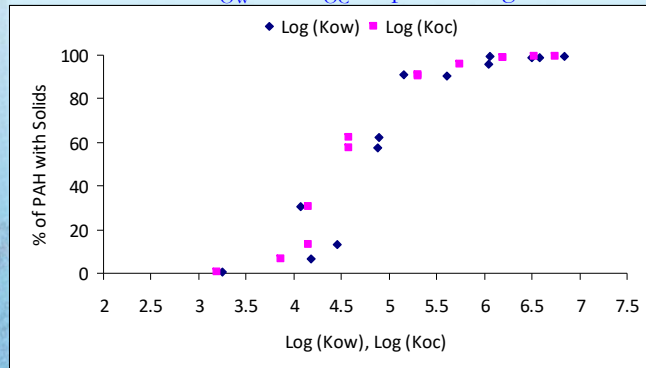
Introduction

- 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

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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.



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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.

Raft and other material leakage from damaged boats. Hurricane Katrina (NSAA photo)

Katrina oil refinery damage (EPA photo)

Waste sorting area with field labs (EPA photo)



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Analytical Method Development

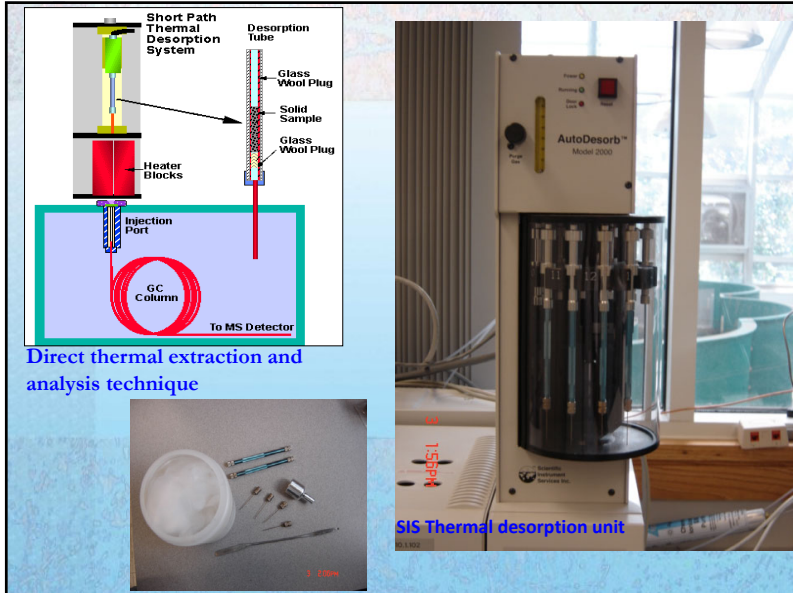
- The main transport mechanisms and fate of PAHs in the aquatic environment are closely related to their major associations with particles. Therefore, it is essential that rapid and sensitive analytical tools be used that can measure PAHs in samples having large amounts of suspended sediment.
- During 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.

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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.

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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.

Pyrene

Time (min)	Area Counts
2	1.12E+08
3	1.20E+08
5	1.28E+08
10	1.25E+08
15	1.30E+08
20	1.28E+08

Benz(ghi)perylene

Time (min)	Area Counts
2	0.05E+08
3	0.08E+08
5	0.12E+08
10	0.35E+08
15	0.95E+08
20	0.92E+08

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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.

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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

Naphthalene

$y = 1.2481x + 6.1919$
 $R^2 = 0.9854$

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

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TD Method Recovery Calculations

PAH	% Recovery from Solid Samples	Acceptable Range of % Recovery from EPA Methods (Aqueous Samples)	Acceptable Range of % Recovery from <i>Standard Methods</i> (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

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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

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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

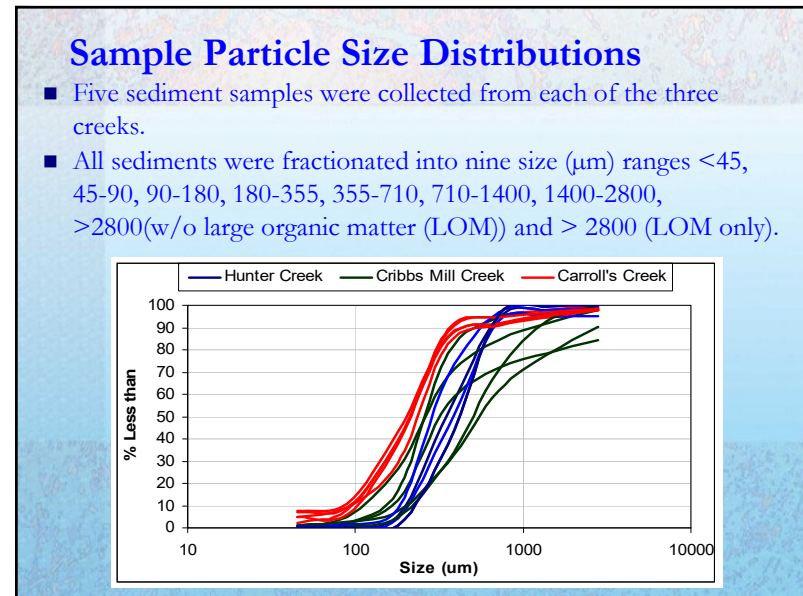
- Source areas: automobile service commercial areas, heavy traffic along McFarland Blvd., and runoff from trailer park residential areas

Site 3: Carroll Creek

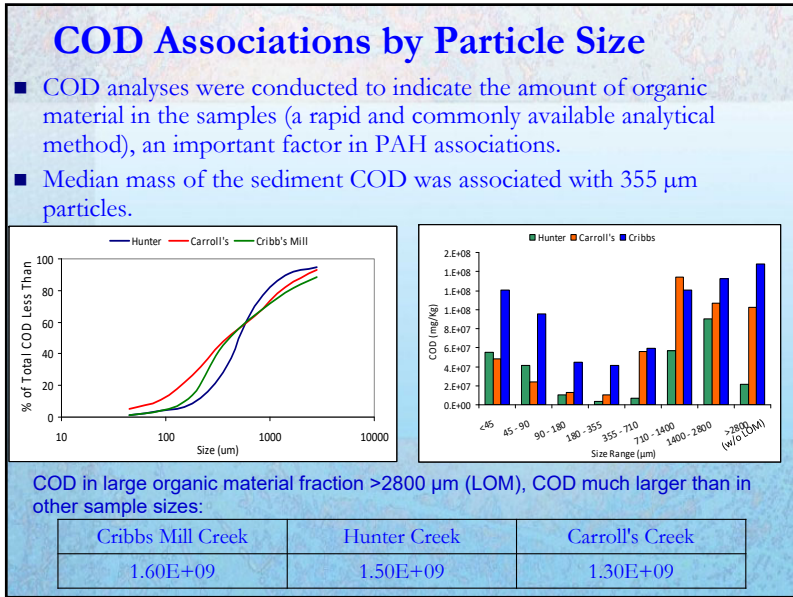
- Source areas: A residential area on one side and forested lands on the other side of the creek
- Has a recent history (in 2006) of sanitary sewer overflows (SSOs) into the creek (ADEM Consent Order No. 07-139-CWP to City of Northport)



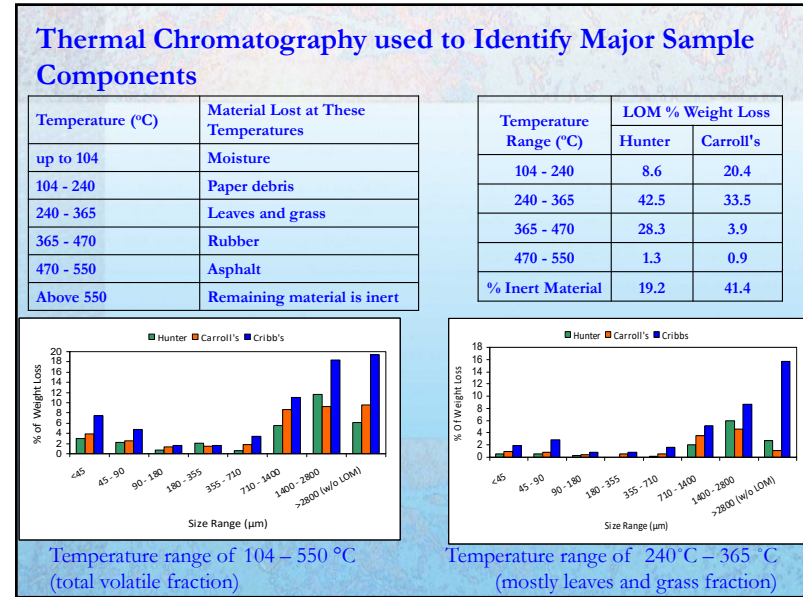
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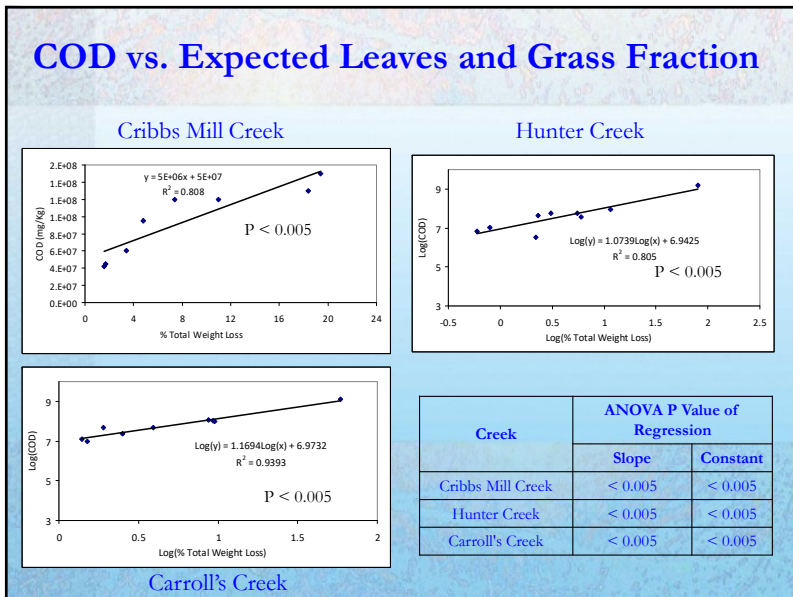
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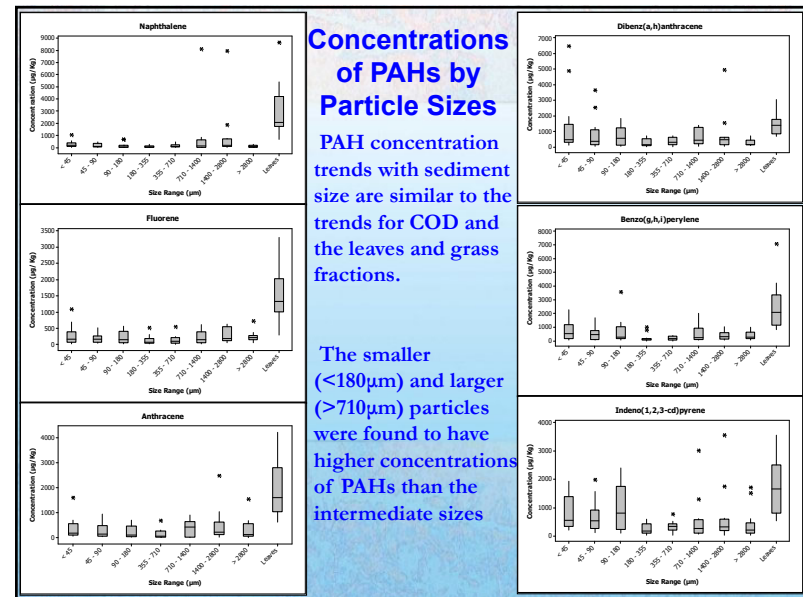
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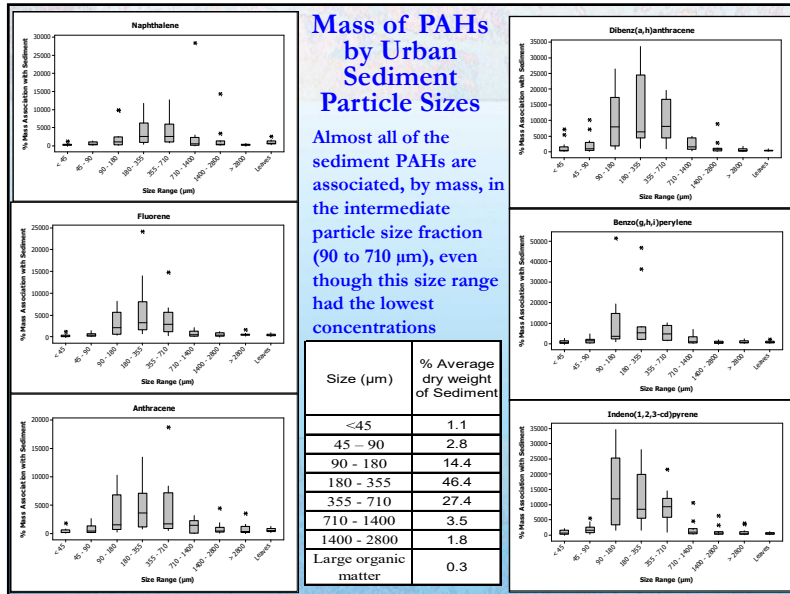
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Conclusions

- 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.

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Thank you

Questions?

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