

## Analyses of PAHs in Urban Stormwater Particulates

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### Abstract:

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants of concern in many receiving waters. The transport and fate of PAHs in the environment depends primarily on their physical and chemical properties and the reactivity of the compound. A fugacity calculation method presented by Mackay, et al (1992) was used to predict the partitioning of selected PAHs into different environmental media using a full 2<sup>4</sup> factorial experimental design. Another aspect of the research developed an efficient laboratory extraction and analysis method for PAHs in stream sediments, a major fate for many of the PAHs examined. A thermal desorption based analytical method is presented in the paper which is rapid, requires no solvents, and is easy to use. Unfortunately, increased maintenance of the GC/MSD may be required when using this method. Sediments from three different urban creeks in central Alabama were analyzed for PAHs concentrations for different particle sizes. Sediments were also analyzed for COD, material composition, and particle sizes to correlate with the associated PAH concentrations.

**Keywords:** PAHs, Fugacity modeling, Thermal desorption, Sediment

### Introduction:

Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants of concern. Some of the PAHs have been determined to be carcinogenic by the US Environmental Protection Agency, US Department of Health and Human Services, and the International Agency for Research on Cancer. Examining the factors influencing the partitioning of the organic contaminants is very important in understanding the treatability of the organics and when conducting risk assessments associated with contaminated receiving waters. Efficient and flexible analytical techniques are needed for determining the fate of pollutants in the environment, as several different media may need to be analyzed. The behavior of contaminants in the environment depends primarily on their physical and chemical properties, along with their reactivity. The important properties of compounds that affect their treatability and fate include their partition coefficients, Henry's law constant, and water solubility, amongst others. Urban runoff contains both dissolved and particle-bound PAHs, with the majority of these pollutants present in the particulate phase (Pitt *et al.* 1999, Barbara, *et al.* 2003, Hwang *et al.* 2006). For example, Hwang and Foster (2006) found particle-bound PAHs accounted for 68-97% of total PAHs in urban stormwater runoff in Washington DC. However, little is known about the distribution of PAHs for different size particles present in urban runoff; this information is needed for effective control of PAH transport from urban surfaces to receiving waters.

### Modeling Partitioning of PAHs in the Aquatic Environment

The following is a summary of the partitioning calculations of the PAHs most commonly detected in stormwater that were conducted as part of this research. The partitioning phases examined were water, suspended solids, and sediment using the fugacity calculation method presented by Mackay, *et al* (1992). Typical stormwater and urban receiving water conditions were used in these calculations, as described later. This discussion also presents our findings on the effects of selected variables on the partitioning using a full 2<sup>4</sup> factorial experimental design as presented in Box, *et al.* (1978).

Mackay's level I fugacity model describes the partitioning of the chemical contaminant into solid, liquid and gaseous phases once they are released into the environment, and assume equilibrium conditions. The equations involved in the model calculations are:

$$C = Z * f \quad (\text{or}) \quad f = \frac{M}{\sum (V_i * Z_i)}$$

Where, C = Concentration of contaminant, mol/m<sup>3</sup>; Z = fugacity capacity constant, mol/m<sup>3</sup>; f = fugacity, Pa; M = Moles of compound; V<sub>i</sub> = Volume of the corresponding phases; and Z<sub>i</sub> = fugacity capacities of phases for air, water, sediment and suspended sediment for i = 1, 2, 3, 4 respectively and are defined as follows.

$$Z_1 = \frac{1}{RT}; \quad Z_2 = \frac{1}{H}; \quad Z_3 = Z_2 * P_3 * \phi_3 * \frac{K_{OC}}{1000}; \quad Z_4 = Z_2 * P_4 * \phi_4 * \frac{K_{OC}}{1000}$$

Where, R = gas constant (8.314 J/mol K); T = absolute temperature (K); H = Henry's law constant (Pa.m<sup>3</sup>/mol); K<sub>OC</sub> = Organic-water partition coefficient; P<sub>3</sub> = density of sediment (kg/m<sup>3</sup>); P<sub>4</sub> = density of suspended sediment (kg/m<sup>3</sup>);  $\phi_3$  = organic fraction of sediment; and  $\phi_4$  = organic fraction of suspended sediment

The calculated results for three phases (water, suspended sediment and sediment) are shown in Table 1. Air was not considered in the calculation as the fraction of air (or dissolved gases) in the closed system is very small. Most of the PAHs examined are partitioned preferentially onto the sediment than into the water, as expected, due to the hydrophobic nature of PAHs and as observed during prior field measurements (Pitt, *et al.* 1999). If air was considered in the system, the low molecular weight PAHs (generally having high Henry's law constant) would have a small percentage of their total amount partitioned into the air phase; whereas for high molecular weight PAHs, very little, if any of the PAHs would partition into the dissolved gases. Figure 1 shows the relationships between the logK<sub>oc</sub> (organic partition coefficient) values and the partitioning into the sediment phase for the different PAHs. PAHs having logK<sub>oc</sub> values greater than about 4.5 are mostly partitioned onto sediment. Of the PAHs examined, only naphthalene, anthracene, and fluorene are expected to be predominantly associated with the water phase.

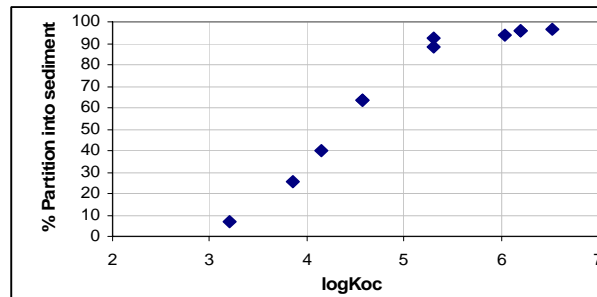


Figure 1. LogK<sub>oc</sub> versus % partition of PAHs into sediment phase

The full 2<sup>4</sup> factorial (Box, *et al.* 1978) calculations were helpful in identifying the effects of individual variables and their interactions on the partitioning of the PAHs. The factors studied, and their low and high values used in the calculations, are shown in Table 2. The design matrix used in this factorial study is shown in Table 3. The low and high values of the factors were chosen based on typical low and high Table 1. Predicted Partitioning of PAHs into Water, Suspended Solids, and Sediment Phases

PAH	% Partition into		
	Water	Suspended Solids	Sediment
Naphthalene	93	0	7
Anthracene	59	1	40
Fluorene	74	1	26
Fluoranthene	35	2	63
Pyrene	35	2	63
Chrysene	9	3	88
Benzo(a)anthracene	5	3	92
Benzo(b)fluoranthene	4	3	94
Dibenzo(a,h)anthracene	1	3	96
Indeno(1,2,3-cd)pyrene	1	3	96
Benzo(ghi)perylene	1	3	96

Table 2. Values used in factorial analysis

Variable	Low value	High value
Temperature (A), °C	5	25
Concentration of PAH compound (B), µg/L	10	300
Concentration of Suspended Solids(C), mg/L	10	500
Organic Fraction of Suspended Solids (D)	0.05	0.2

Table 3. 2<sup>4</sup> Factorial Design Showing Experimental Conditions for 16 Runs (Box, *et al.* 1978)

Run	A	B	C	D	AB	AC	AD	BC	BD	CD	ABC	ABD	ACD	BCD	ABCD
1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
2	+	+	+	-	+	+	-	+	-	-	+	-	-	-	-
3	+	+	-	+	+	-	+	-	+	-	-	+	-	-	-
4	+	+	-	-	+	-	-	-	-	+	-	-	+	+	+
5	+	-	+	+	-	+	+	-	-	+	-	-	+	-	-
6	+	-	+	-	-	+	-	-	+	-	-	+	-	+	+
7	+	-	-	+	-	-	+	+	-	-	+	-	-	+	+
8	+	-	-	-	-	-	-	+	+	+	+	+	+	-	-
9	-	+	+	+	-	-	-	+	+	+	-	-	-	+	-
10	-	+	+	-	-	-	+	+	-	-	-	+	+	-	+
11	-	+	-	+	-	+	-	-	+	-	+	-	+	-	+
12	-	+	-	-	-	+	+	-	-	+	+	+	-	+	-
13	-	-	+	+	+	-	-	-	-	+	+	+	-	-	+
14	-	-	+	-	+	-	+	-	+	-	+	-	+	+	-
15	-	-	-	+	+	+	-	+	-	-	-	+	+	+	-
16	-	-	-	-	+	+	+	+	+	+	-	-	-	-	+

(+ indicates the factor at its high value and – indicates factor at its low value)

When examining the results from the factorial analysis, the concentrations of the PAH compounds and the concentrations of the suspended solids were found to have the greatest positive effects on the partitioning of the PAHs onto the suspended sediment. The organic content of the suspended solids also affects the partitioning of the PAHs into the suspended solids, but to a lesser extent. The concentrations of the PAHs was found to have the greatest positive effect when examining the partitioning of the PAHs into the water phase, while the

concentration of the suspended solids had a significant negative effect on the partitioning into the water (the higher the SS concentrations, more of the PAHs were associated with the sediment). As an example, Figures 2 and 3 are probability plots indicating the significant factors affecting anthracene partitioning into the water phase and suspended sediment phase, respectively. The significant factors indicated are B, C, and D. Where B is the concentration of contaminant, C is the concentration of suspended solids, and D is the organic fraction of the suspended solids. The term BC indicates the interaction of factors B and C (the joint effect of concentration of the contaminant and the concentration of the suspended solids).

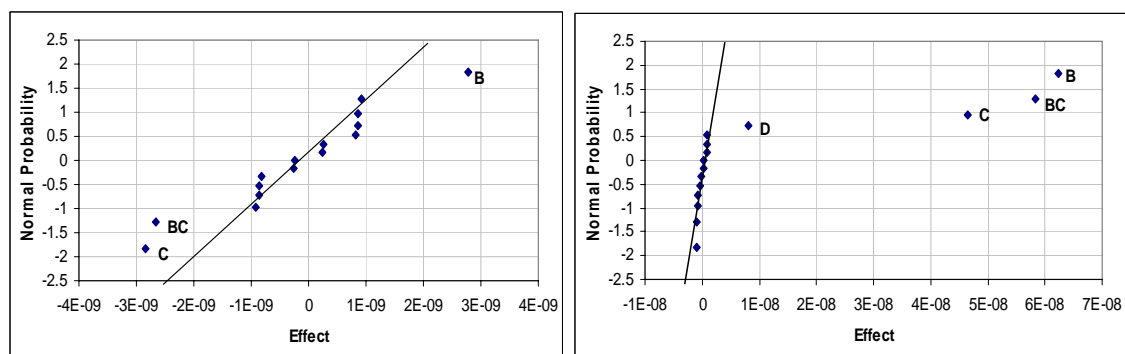


Figure 2 and 3. Probability plot to identify important factors affecting anthracene partition into water and suspended sediment phases respectively

#### Development of New Analytical Techniques

Model prediction calculations and available literature (Pitt *et al.* 1999, Hwang *et al.* 2006) have shown that particulate associations are the main fate of many of the PAHs in the aquatic environment. It is therefore essential that the analytical methods used for PAH analyses be sensitive to particulate forms of the contaminants, and that separate analyses of the particulate and filtered portions also be conducted, if possible. Traditional Solid Phase Extraction (SPE) methods for PAHs may not be suitable in dealing with samples having high concentrations of suspended solids due to extremely low recoveries during the extraction (Pitt, *et al.* 1999). Separating the solids from the liquid and analyzing the individual sample portions (filtered and particulate fractions) separately is one method for complete PAH analyses. Soxhlet (EPA method SW-848), automated Soxhlet (EPA method 3540), and ultrasonic extraction (EPA method 3550) methods are the common solvent extraction methods for PAHs from solid samples. However, these methods have some inherent disadvantages, such as requiring large amounts of samples and organic solvents, they are time consuming and complex, and involve multi-step processes that are subject to errors (Zhang *et al.*, 1994).

Another aspect of this research modified and tested an alternative PAH extraction procedure that used a SIS AutoDesorb<sup>TM</sup> thermal desorption method. Thermal extraction, or thermal desorption, techniques use elevated temperatures as a means to transfer the analytes from solid sample matrices to the gaseous analytical system. The analytes desorbed from the solid sample matrices are concentrated in a cryotrap at the head of a GC column. The concentrated analytes are then separated and detected using a standard GC column and MS detector which is similar to the analysis of liquid samples when concentrated into a solvent. The equipment used during this method development included the AutoDesorb<sup>TM</sup> unit, Glass wool, Tenax®, PAH liquid standards obtained from SUPELCO® (47930-U QTM PAH Mix), NIST1941b sediment standard, and desorption tubes and tube conditioning oven.

**Operating procedure:** The AutoDesorb<sup>TM</sup> unit uses desorption tubes containing the samples. Prior to their use, the thermal desorption tubes are conditioned at elevated temperatures to eliminate all foreign volatile materials which may contaminate the analysis. The tubes are conditioned by holding them at room temperature for several minutes, followed by heating to 350°C at a rate of 4°C/min, while purging with nitrogen gas. The tubes are maintained at an elevated temperature of 350°C for four hours with the nitrogen flow set at 60 mL/min. At the end of the conditioning period, the tubes are cooled to room temperature and capped on both ends with pre-conditioned steel caps to keep them clean before they are loaded with samples. The same procedure is used to condition the needles. Conditioned tubes are packed with a known amount (about 10 mg of sample, depending on the expected PAH concentration) of the solid sample to be analyzed. Both ends of the tubes are plugged with glass wool to hold the sample in place and to reduce the loss of fine particulates into the analytical stream that would plug the needle and accelerate contamination of the MS.

The packed tubes, which are ready for analysis, are then loaded onto the system carousel and the analysis process is initiated using the AutoDesorb<sup>TM</sup> software. The desorption tubes are then purged to remove oxygen, excess water and volatile materials that are present in the tube. The needle is then lowered into the GC inlet and the injection period starts. The injection time period is set to allow the injection port pressures to equilibrate and the proper split flow to be reached before the injection time expires. At the end of the injection time, the heater blocks close around the desorption tube and the tube is heated at a rate specified in the method. Carrier gas transports the desorbed analytes into the inlet of the GC. The cryotrap then traps the analytes entering the GC inlet by condensing the organic gases and focus the analytes for their concentration. The cryotrap is then rapidly heated to release the focused analytes instantaneously into the GC column, where the analytes are separated based on their volatility and mobility through the GC column, and are then detected by the MS, based on their charge to mass ratios.

**Thermal Desorption method optimization:** The selected conditions for the thermal desorption extraction were determined based on a series of experiments conducted to obtain optimal recovery of analytes from the solid samples and to have good separation of the analytical peaks. For this purpose, standard solid samples were prepared by spiking 10µL of the 20 mg/L PAH mixed standard onto pre-treated glass wool. The thermal desorption unit was subjected to different desorption times and desorption temperatures. The final desorption temperatures that were tested ranged from 250°C to 375°C. Final desorption temperatures of 350°C produced higher peaks of individual PAHs. Similarly, different desorption times were tested to obtain maximum peak areas. A series of runs was made with different holding times at the final desorption temperature. The range of final temperature holding times tested ranged from 1 min to 20 min. It was found that the peak areas obtained for individual PAHs increased as the holding time increased from 1 min to 15 min, but then decreased as the holding time further increased to 20 min. Therefore, the optimum desorption time for the highest recovery of PAHs was found to be 15 min. For three replicate runs, the coefficients of variation (COV) showed that low molecular weight and high molecular weight PAHs have high variations in the peak areas (naphthalene 49%, fluorene 24%, dibenzo(a,h)anthracene 15%, benzo(ghi)perylene 16%), while the intermediate PAHs had much lower variations (COVs ranging from 0.5% - 4.0%).

The developed method was tested for linear responses for selected PAHs. For these tests, challenge solid matrices were prepared by spiking Tenax® with 10, 50, 100, 200 and 400 ng

of the PAH liquid standard mixture. The obtained regression index of determination ( $R^2$ ) values for selected PAHs are reasonable for this method, and are shown in Table 5.

Table 4. Final Optimal Conditions of Thermal Desorption System

Purge duration:	1.00 min	Cryotrap:	enabled
Injection duration:	1.00 min	Cryo cool temperature:	-40°C
Initial temperature:	50°C	Cryo heat temperature:	300°C
Temperature ramp rate:	100°C	Cryo heat duration:	10.00 min
Final temperature:	350°C	GC start time:	26.50 min
Final temperature holding time:	15 min		

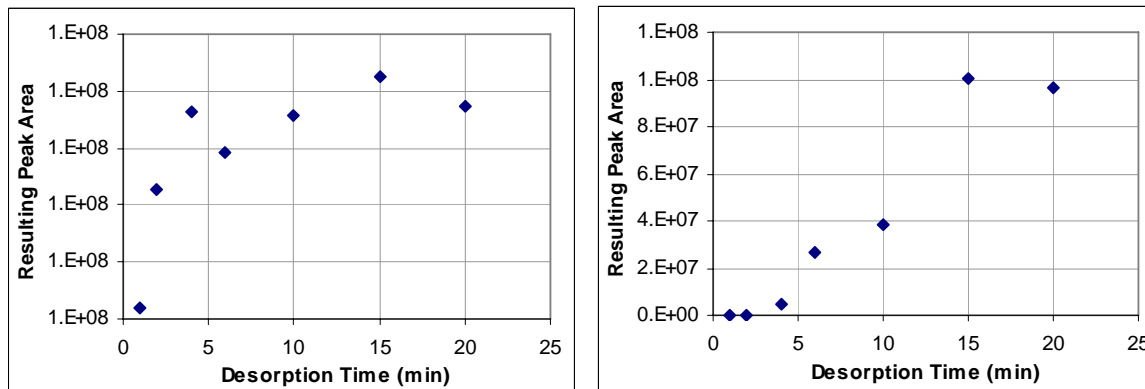


Figure 4 and 5: Desorption time versus peak areas for pyrene and benzo(ghi)perylene respectively

Table 5. Regression Index of Determination Values for Linearity Tests

PAH	$R^2$	PAH	$R^2$
Naphthalene	0.9958	Chrysene	0.9961
Fluorene	0.9848	Benzo(b)fluoranthrene	0.9925
Phenanthrene	0.9969	Benzo(a)pyrene	0.9881
Anthracene	0.9944	Indeno(1,2,3-cd)pyrene	0.9819
Fluoranthene	0.9978	Dibenzo(a,h)anthracene	0.9593
Pyrene	0.9975	Benzo(ghi)perylene	0.9657
Benzo(a)anthracene	0.9934		

**Analysis of standard sample using the developed TD extraction method:** A marine sediment standard, NIST1941b obtained from the National Institute of Standards and Technology (NIST), was tested using the developed TD extraction method. This standard sample was collected from Chesapeake Bay at the mouth of Baltimore (MD) Harbor near the Francis Scott Key Bridge using a Kynar-coated grab sampler. The standard is certified for 119 different constituents including PAHs, PCBs, and chlorinated pesticides. The sample was ground and sieved so the sediment particles were finer than 150  $\mu\text{m}$ .

A 10 mg portion of NIST1941 was used to test the method described above. Most of the analytes present in the standard sample were detected and clear individual peaks were shown. However, there were two major problems identified during the analysis of the standard material using thermal desorption GS/MS analysis, as discussed below.

**Presence of sulfur:** Due to the presence of sulfur in the sediment sample, there were many unwanted sulfur-containing analytical peaks in the gas chromatogram. There is also a chance that the sulfur products of PAHs bond to particulate solids, making them difficult to extract.

As copper forms copper sulfide when reacted with sulfur, the addition of small amounts of copper wire cuttings (about 4 – 5 mg of copper wire cuttings for 10 – 15 mg of sample) into the thermal desorption tube, along with the sediment sample, helped in avoiding the sulfur products of PAHs.

**Moisture in the sample:** Even after standard oven drying, the moisture content of the standard sample caused ice plugging in the GC column during the cryofocusing step and obstructed the flow of analytes through the column. This problem resulted in tremendous reductions in the peak areas obtained for the individual analytes, and in some cases there were no peaks observed. To further reduce the water content in the samples, they were also freeze-dried overnight before analysis.

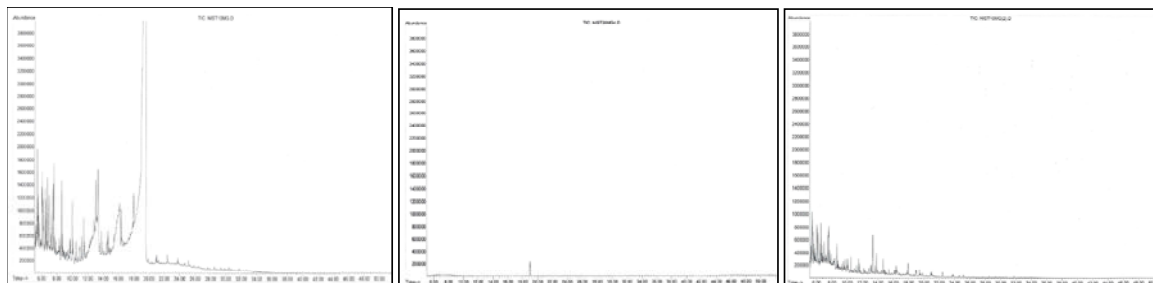


Figure 6,7 and 8. Chromatogram of NIST standard with dominant peaks of sulfur compounds, ice plugging problem and after added copper and further sample drying, respectively

**Measuring PAH concentrations in different sized creek sediment subsamples:**

PAH contaminants associated with particulate matter may be reduced by commonly available sedimentation and filtration stormwater control practices. However, these unit processes are less effective for the removal of soluble forms of PAHs. Understanding the association of contaminants with different particle sizes is important for determining the most effective treatment of the runoff, as the design of particulate removal controls is highly dependent on particle size information. The main objective of this research is therefore to quantify the concentrations of selected PAHs associated with different particle sizes. These analyses used the above described thermal desorption technique. Sediment samples were collected from three different creeks (Cribbs Mill Creek, Hunter Creek, and Carroll Creek) in the central Alabama cities of Tuscaloosa and Northport. These are all urban creeks, but with different characteristics. The samples from Cribbs Mill Creek are mainly affected by runoff from the surrounding medium density single-family residential areas. For Hunter Creek, the sediment at the sampling location is mostly affected by runoff from the heavily traveled McFarland Blvd. road, commercial areas, and runoff from trailer park residential areas. The sediment at the sampling location at Carroll Creek is directly affected by runoff from a high density residential area on one side and forested lands on the other side of the creek and has a recent history of contamination from sanitary sewer overflows (SSOs) in the surrounding residential areas. Besides examining the PAH concentrations for the different particle sizes, supporting information that likely affects the PAH partitioning is also being examined, namely material composition of the sediment (such as paper debris, organic matter, rubber, or asphalt) and Chemical Oxygen Demand (COD).

**Procedure:** All the samples were collected in pre-cleaned and autoclaved glass sample bottles using a manual dipper sampler made from polypropylene. The collected sediment samples were dried overnight at 104°C and then sieved using a set of stainless steel sieves having

openings of 45, 90, 180, 355, 710, 1400 and 2,800  $\mu\text{m}$ . In addition, large organic material (leaves and other debris) were manually separated from the largest particle fraction for separate analyses. All size separated fractions are subjected to Thermal Desorption (TD) extractions followed by GC (HP6890N)/MS (HP5975) analyses for PAH measurements.

A “thermal chromatography” method developed by Ray (1997) was used to identify the major components of the sediment samples. A known amount of sediment was heated in a crucible at progressively higher temperatures, at set intervals, from 104 to 550°C and corresponding weight losses were noted after cooling after each step. Table 1 shows the temperatures and corresponding weight losses associated with each material component. The HACH COD method was used to measure the COD of the size fractionated sediment particles.

Table 6. Ray (1997) Thermal Chromatography Method Parameters

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 (mostly soil)

**Results and Discussion:** A total of 15 sediment samples, five from each of the three creeks, were collected and processed for particle size distributions (psd) (Figure 9). In all cases, the particles in the size range of 180 to 355  $\mu\text{m}$  were most dominant in the sediments. Overall, most of the particles are distributed in the size range of 90 to 710  $\mu\text{m}$ . The COD analysis results of sediments from the three creeks showed similar trends. Smaller (< 90  $\mu\text{m}$ ) and larger (> 355  $\mu\text{m}$ ) particles were found to have higher concentrations of COD (mg/Kg) compared to intermediate sized particles. This trend is similar to observations made previously for size fractionated street dirt particles from urban areas (Pitt, *et al.* 2005). The accumulative COD mass with respect to the observed psd of the sediment particles showed that particles of 355  $\mu\text{m}$  in size are associated with the median mass of the creek sediment COD (Figure 10) (half of the mass is associated with smaller particles and half is associated with larger particles). Table 7 shows the thermal chromatography results used to identifying the major material composition of the creek sediment particles; almost all is inert material except for the leaf fraction.

The preliminary results of the PAH concentrations associated with size fractionated Cribbs Mill Creek sediments showed that smaller sized particles, and especially large sized particles, are associated with higher concentrations of selected PAHs, compared to medium sized particles (Table 8). This trend is similar to the observed trend of particle COD and thermal chromatography results. However, most of the mass of the PAHs are associated with the smaller and intermediate sized creek sediment particles, as very little of the sediment is associated with the large organic matter.

As there has been a delay associated with the laboratory PAH analyses, all of the sample results are not presented in this paper. By the time of the conference, we expect to have all the analytical results available, along with the associated statistical analyses. Multivariate statistical analyses along with a 2<sup>3</sup> full factorial analyses will be conducted on the observed results. These analyses will examine the effects of particle size, COD, and material composition on associated PAH concentrations.



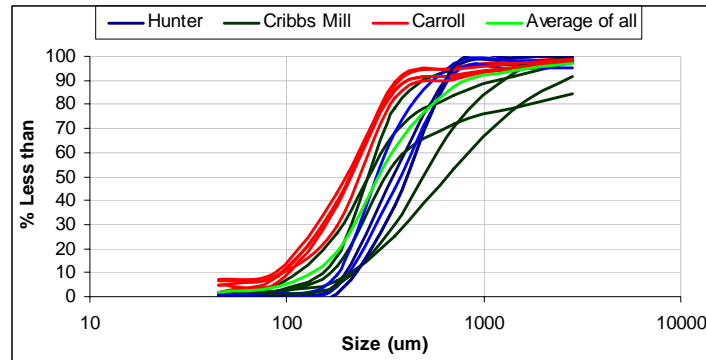


Figure 9. Observed creek sediment particle size distributions



Figure 10. Observed cumulative COD of creek sediments

Table 7. Sediment Thermal Chromatography Analytical Results for Material Composition

Size range ( $\mu\text{m}$ )	Average percentage of weight loss over temperatures range ( $^{\circ}\text{C}$ )				Remaining inert material
	105 – 240 (paper debris)	240 – 365 (leaves and grass)	365 – 470 (rubber)	470 – 550 (asphalt)	
<45	2.35	1.10	0.31	1.01	95.2
45 - 90	0.92	1.45	0.48	0.37	96.8
90 - 180	0.31	0.49	0.35	0.14	98.7
180 - 355	0.33	0.45	0.33	0.64	98.3
355 - 710	0.41	0.80	0.57	0.16	98.1
710 - 1400	1.91	3.54	2.25	0.70	91.6
1400 - 2800	2.48	6.39	1.60	2.66	86.9
>2800	1.07	6.51	2.55	1.52	88.4
Leaves	14.53	37.98	16.11	1.11	30.3

### Conclusions

Model predicted partitioning results and prior analyses have clearly show that adsorption onto solids is the dominant fate of most of the PAHs detected in urban stormwater. This is expected based on their high hydrophobic nature and high partitioning coefficients. These results indicate that most of the PAHs found in stormwater can be controlled when their associated particulates are also controlled. The results from this research will identify the varying concentrations of the PAHs for different particle sizes of urban sediment. This information can then be used to optimize the designs of stormwater controls for PAH reductions.

Thermal desorption analytical techniques for PAHs analyses are rapid, solvent free, easy to use, and satisfactory for detecting PAHs in sediments. However, increased GC/MS

maintenance may be needed using this method unless fine particulate contamination of the instrument can be controlled. Preliminary results of the partitioning of PAHs on different sized particulates show that large organic material, such as leaves, has the highest concentrations of the PAHs. This can be expected based on the fate modeling which showed that PAHs preferentially sorb to particulates having high organic matter. Although the concentrations of the PAHs are highest on the large organic matter found in the sediments, the associated weight fraction of this material was much less than 1% for these samples. These results also indicated that for most PAHs, the smaller-sized particles (<100 µm) have higher concentrations of PAHs compared to larger sized particles (except for the leaf fraction).

Table 8. Preliminary Results of Selected PAHs in Cribbs Mill Creek Sediment Samples

PAH	Concentration (µg/kg) for size range (µm)							
	<45	45 – 90	90 - 180	180 - 355	355 - 710	710 - 1400	1400 - 2800	Large organic matter
Fluoranthene	331	441	245	141	138	398	366	2240
Pyrene	313	405	178	117	98	272	261	2230
Benzo(a)anthracene	270	321	179	93	97	185	170	4350
Chrysene	418	507	307	161	158	350	313	3010
Benzo(b)fluoranthrene	1010	105	593	259	320	741	735	4390
Benzo(a)pyrene	665	882	512	196	159	269	345	4650
Indeno(1,2,3-cd)pyrene	732	281	374	131	219	269	261	1520
Benzo(ghi)perylene	548	153	235	84	135	190	313	988
Average % dry weight of sediment (all creeks combined)	1.1	2.8	14.4	46.4	27.4	3.5	1.8	0.3

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