

Associations of PAHs with Size Fractionated Sediment Particles

Jejal Reddy Bathi¹, Robert Pitt² and Shirley E. Clark³

Geosyntec Consultants, Santa Barbara, CA – 93101; PH: (805) 897 – 3800; Email:

jbathi@geosyntec.Com

²Civil, Construction and Environmental Engineering, The University of Alabama, Tuscaloosa, AL 35401; PH: (205) 348 – 0783; Email: rpitt@eng.ua.edu

³Penn State Harrisburg, School of Science, Engineering and Technology, Harrisburg Pike, PA – 17507; PH: (717) 948 – 6580; Email: seclark@psu.edu

ABSTRACT

Sediment samples were collected five times from three different locations and analyzed for selected parameters to study the effects of selected sediment characteristics and contributing source areas on sediment PAHs concentration. For all cases, the particles in the size range of 180 to 355 μm were most dominant in the sediments. Sediment COD, percent of material weight loss on ignition (material composition analysis) and sediment PAH concentrations showed similar trends of smaller and larger particles associations with higher values than with the intermediate sizes. However, most of the mass of the PAHs were associated with the smaller and intermediate sized particles. Sediments affected by commercial area runoff were found to have higher concentration of PAHs than the sediments affected by non-commercial area runoff.

INTRODUCTION

PAHs are ubiquitous environmental contaminants and are an example of persistent organic pollutants of environmental concern (Cheung et al. 2006). Prior to the 1800s, the bulk of PAH discharges to the environment were of natural origin, with limited contributions from anthropogenic sources (Metre et al. 2000). There was a shift in the sources of PAH contamination from uncombusted to combusted fossil fuels. The increase in PAH sediment concentrations was coincident with the increase in automobile use and power production, both major consumers of fossil fuels. The magnitude of PAH pollution in runoff depends on the type of contributing source area. Pitt et al. (1999) found the highest runoff PAH concentrations in sheetflow samples from vehicle servicing and parking areas among samples collected from different source areas, with higher concentrations associated with longer interevent periods between rains. Kuklick et al. (1997) observed extreme variability in PAH concentrations, ranging from 33 $\mu\text{g kg}^{-1}$ dry weight in the Edisto River estuary to 9600 $\mu\text{g kg}^{-1}$ dry weight in some areas of urbanized Charleston Harbor showing large effects of urbanization on sediment PAH contamination. The spatial distribution of

PAHs observed by McCready et al. (2000) indicated increased concentrations of PAHs nearer to areas where stormwater enters the Sydney Harbor, Australia.

PAHs in urban runoff can occur in both particulate and soluble forms, although studies have identified the particulate forms as being the most predominant (Hwang and Foster 2006; Pitt et al. 1999). Due to their extremely low solubility and hydrophobic nature, most PAHs are associated primarily with particulate matter. According to Hwang and Foster (2006), particulate-associated PAHs in urban runoff accounts for 68 to 97% of total PAHs in the runoff. The particulate-bound PAHs tended to settle and accumulate in receiving water sediments. Factors that affect the PAH associations with the particulate matter in the aquatic environment include the physical and chemical properties of the specific PAH contaminant, the physical and chemical properties of the aquatic medium, and the physical and chemical properties of the particulate matter. Zhou et al. (1998) observed no correlation between particulate bound PAH concentrations with salinity of samples, while suspended solids concentrations had negative correlations and particulate organic carbon concentrations had positive correlations with particulate bound PAH concentrations. They also observed higher concentrations of PAHs with finer particles (generally classified as clay materials, which have large surface areas per unit weight) than with the coarser particles (generally classified as sand particles, which have comparatively less of the organic matter needed for greater PAH sorption). A similar pattern was observed by Aryal et al. (2005), who monitored suspended solids and solid-associated PAHs in Swiss highway runoff for four rain events (samples were only collected during the initial 3 mm of runoff). The concentrations of PAHs in fine fractions ($<45\mu\text{m}$) were higher than their concentrations in coarse fractions ($>45\mu\text{m}$). Contributing source areas may also effect the PAHs distribution pattern by solid particle sizes. For example, Guggenberger et al., (1996) noticed homogenous distributions of PAHs by particle sizes in rural soils whereas Muller et al., (2000) observed non-homogeneous distributions of PAHs in urban soils. Recent investigations have also found high PAH concentrations associated with large organic material trapped in stormwater floatable material controls (Rushton 2006), indicating material composition of sediments effects the PAH associations.

This paper describes the measured PAH concentrations on size fractionated sediment particles analyzed using Thermal Desorption analytical methods, PAH trends with respect to selected sediment parameters, and possible major source area effects on sediment PAH pollution. Selected parameters examined for analyzing the trends of PAHs on size fractionated particulate matter included material composition (such as paper debris, organic matter, rubber, or asphalt) and Chemical Oxygen Demand (COD). The sediments affected by residential runoff, commercial area runoff and runoff from residential area with a known history of separate sewer overflows (SSOs) were studied during this research.

MATERIALS AND METHODS

Study Area and Sampling Sediment samples were collected from three different creeks in and around Tuscaloosa and Northport, AL. One sampling area along each of the three creeks was chosen in such a way that the sediment analysis scheme for PAHs represented the sediments affected by different known urban conditions.

One of the sampling areas was along Cribbs Mill Creek, which is an urban creek in Tuscaloosa, AL. The sampling area along the creek was chosen at the downstream end of a few hundred foot long concrete-lined channel in a residential neighborhood. The sediment (bed load) on the concrete channel was therefore mainly affected by the runoff from the surrounding residential areas, with minimal bank erosion material. Another sampling area was along Hunter Creek, which is an urban creek originating in Tuscaloosa County and passes through Northport before joining the Black Warrior River. The sediment at the sampling location was mostly affected by runoff from heavy traffic along McFarland Blvd., commercial areas, and runoff from a trailer park residential area. Physical observations at the site indicated that an outfall from an automobile maintenance shop on the side of the creek directly affected the sediment at the sampling location. The third sampling area was along Carroll's Creek, which starts in Fayette County and joins Lake Tuscaloosa in Tuscaloosa County. The sediment at the sampling location was directly affected by runoff from a high-density residential area on one side of the creek and forested lands on the other side of the creek. The sediment at the sampling point has a history of contamination from sanitary sewage overflows from a separate sewer system (SSOs) in the adjacent residential area (Consent Order NO. 07-139-CWP from the Alabama Department of Environmental Management (ADEM) to the City of Northport, issued in July 2007, there were three SSO incidents during 2006).

All 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 in aluminum trays at 104°C to remove moisture and then were sieved using a set of stainless-steel sieves with openings of 45, 90, 180, 355, 710, 1400, and 2,800 µm and a mechanical shaker. In addition, large organic material (leaves and other debris) were manually separated from the largest particle fraction and analyzed separately.

Analyses for Material Composition and COD: The material composition of sediments was determined using "Thermal Chromatography" (an expansion of the volatile solids analyses) techniques (Ray 1997). A known amount of sediment sample was placed in a crucible that was heated to higher temperatures, progressively, at set intervals, from 104 to 550°C. After each heating interval, the crucible (with sample) was cooled and weighed in order to determine the percent mass burned off since the last temperature. A heating time of 1 hour at each temperature was maintained to ensure stable weights. Table 1 shows the corresponding temperatures where different material would be combusted. COD analysis of size fractionated sediments was conducted by reactor digestion HACH method 8000.

Analyses for PAHs Concentration: The thermal desorption (TD) sample preparation method uses elevated temperatures as a means to transfer the analytes from solid sample matrices to the gaseous analytical system. This unit was directly attached to the inlet of a gas chromatograph / mass spectrometry (GC/MS) for quantification of PAHs on the size fractionated sediment samples. This TD/GC/MS method was developed and tested for urban creek sediments for PAHs as part of the research activities. The instruments used during this procedure were an

AutoDesorb™ unit (Scientific Instrument Services, Inc. Ringoes, NJ, USA) coupled to a gas chromatograph (Agilent 6890) and a mass spectrograph (Agilent 5973N).

Table 1. 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 are non-combustible

RESULTS AND DISCUSSION

Sediment Particle Size Distribution: Five samples from each of three creeks were collected and analyzed for particle size distributions (psd). Figure 1 shows the observed psd and box-whisker plots of the particle size ranges observed in the samples. For all cases, the particles in the size range of 180 to 355 μm were dominant. Overall, most of the particles were distributed in the size range of 90 to 710 μm .

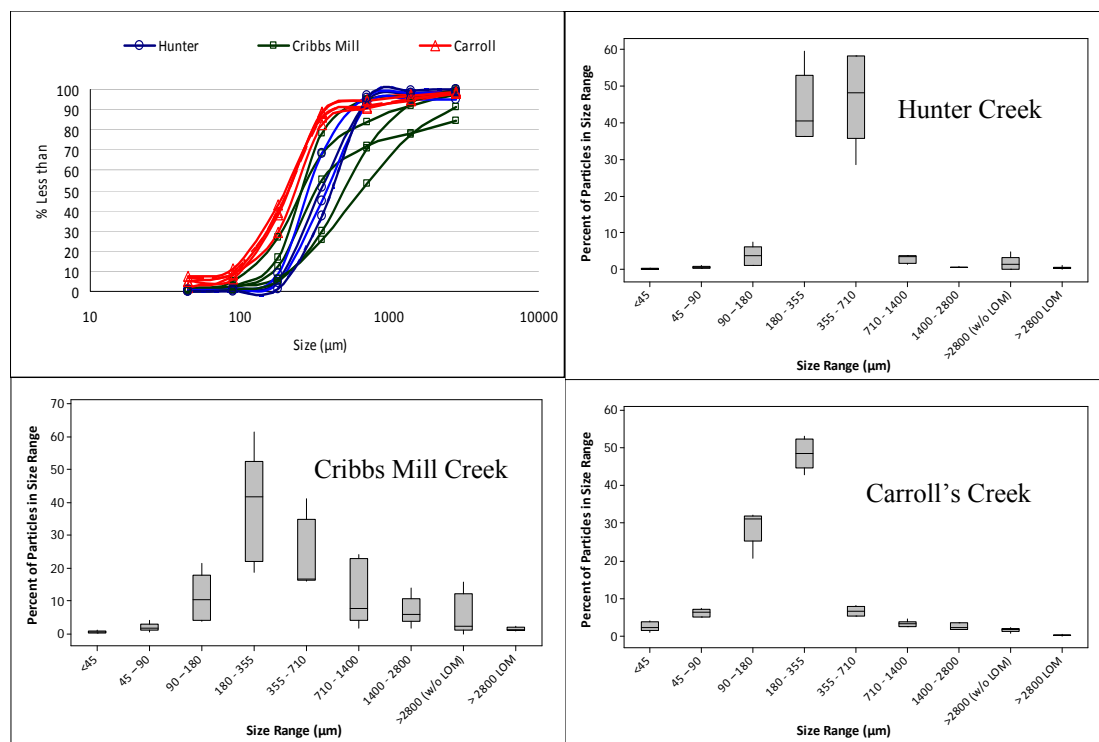


Figure 1. Observed particle size distribution of sediments

Sediment Material Composition and CODs: A composite sediment sample created from the five samples collected at each sampling location was prepared and analyzed for major material composition using thermal chromatography. Table 2 shows the

percentage weight losses observed. Material lost between 240 and 365°C indicates the amount of leaves and grass associated with each particle size that may preferentially sorb PAHs, while material lost between 365 and 550°C indicates rubber and asphalt material that likely have substantial PAH concentrations as part of the component material. Other than for the case of the largest size fraction (> 2800 µm) large organic material (LOM), all other fractions were mostly non-combustible (or non volatile). For the > 2800 µm LOM fraction, most of the material was found to be volatile, and mostly consisted of leaves, grass clippings, etc. The thermal chromatography analyses of sediments indicated that the smaller and larger sediment fractions were associated with a larger volatile content compared to intermediate-sized fractions (Figure 2). The high volatile contents of the large size sediments are caused by presence of relatively large portions of leaf and grass clippings in these sample components.

All sediment fractions of the individual samples were analyzed for COD, as shown in Figure 3. For the >2800µm (LOM only) fraction, the observed CODs for Hunter Creek, Cribbs Mill Creek and Carroll's Creek are 1.6×10^9 , 1.5×10^9 and 1.3×10^9 mg/kg respectively. Similar to the total volatile content of sediments, smaller (< 90µm) and larger (> 710µm) size fractions had higher COD concentrations when compared to the intermediate-sized particles. The median COD was found to be associated with particles of about 355µm in size. Log-transformed volatile solids concentrations and associated COD concentrations were strongly linearly related. The regression ANOVA p value was below 0.05 and the response factor (slope term) of the regression was also significant ($p < 0.05$) at 95% C.I.

PAH Content of Size Fractionated Sediment Fractions: Thirteen PAH compounds which were considered to be of most interest due to their potential harmful effects, and which were most abundantly found in earlier stormwater research (Pitt, et. al., 1999), were quantified, with the concentration results shown in Table 4. As shown during the ANOVA analyses, the variations in the PAH concentrations within each size fraction group were smaller than the variations in the concentrations between the size fraction groups. The analytical results showed that, generally, smaller sized and larger sized particles (especially LOMs) were associated with higher concentrations of selected PAHs compared to the medium sized particles (Table 4). This trend is similar to previously reported PAH data (Rushton, 2006). The bimodal distribution of the PAH concentrations was similar to the bimodal distributions observed for volatile content. Prior fugacity modeling by Bathi, et al (2007) showed that PAHs are strongly associated with the organic content of the particulates in aquatic systems. The leaf fractions are therefore found to have the highest concentrations of some of the PAHs because of their higher organic content. Higher concentration of PAHs in the smaller size fractions was also likely associated with their higher organic content

Table 2. Sediment Thermal Chromatography analytical results for material composition (Table 1 shows the likely materials lost for the different temperature ranges)

Size range (µm)	Percentage of weight loss over temperatures range (°C)											
	Cribbs Mill Creek				Hunter Creek				Carroll's Creek			
	105 – 240	240 – 365	365 – 470	470 – 550	105 – 240	240 – 365	365 – 470	470 – 550	105 – 240	240 – 365	365 – 470	470 – 550
<45	3.70	1.85	0.00	1.85	2.23	0.48	0.00	0.34	1.12	0.96	0.94	0.84
45 – 90	0.96	2.88	0.96	0.00	1.24	0.61	0.00	0.44	0.55	0.85	0.48	0.66
90 – 180	0.21	0.85	0.64	0.00	0.37	0.29	0.00	0.15	0.36	0.34	0.41	0.26
180 - 355	0.24	0.85	0.48	0.00	0.40	0.02	0.18	1.56	0.35	0.48	0.32	0.35
355 - 710	0.48	1.69	1.21	0.00	0.24	0.13	0.00	0.26	0.52	0.59	0.51	0.23
710 - 1400	2.57	5.15	3.31	0.00	1.80	2.01	0.71	0.96	1.36	3.47	2.72	1.13
1400 – 2800	3.76	8.65	0.00	6.02	2.65	5.98	2.29	0.71	1.03	4.55	2.50	1.24
>2800 (w/o LOM)	0.84	15.73	0.00	2.81	1.54	2.76	0.65	1.10	0.82	1.04	7.00	0.65
>2800 LOM only	NA*	NA	NA	NA	8.63	42.49	28.33	1.33	20.42	33.46	3.88	0.89

* Not available

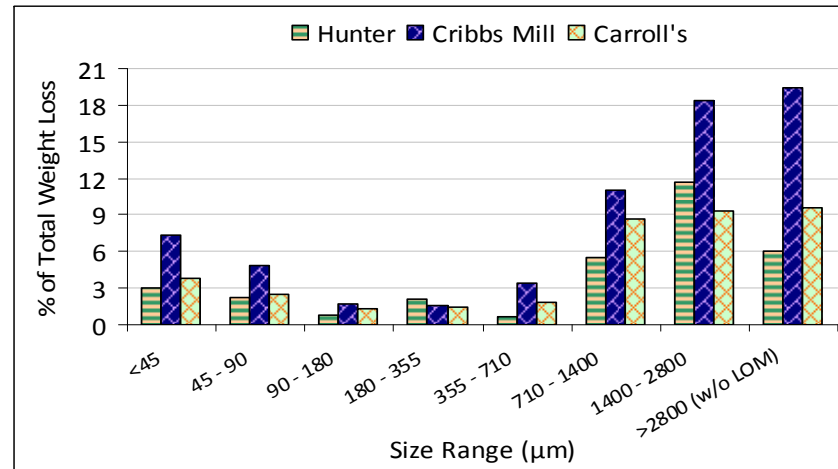


Figure 2. Cumulative weight loss of sediments in Thermal Chromatography over temperature range of 104 – 550 °C

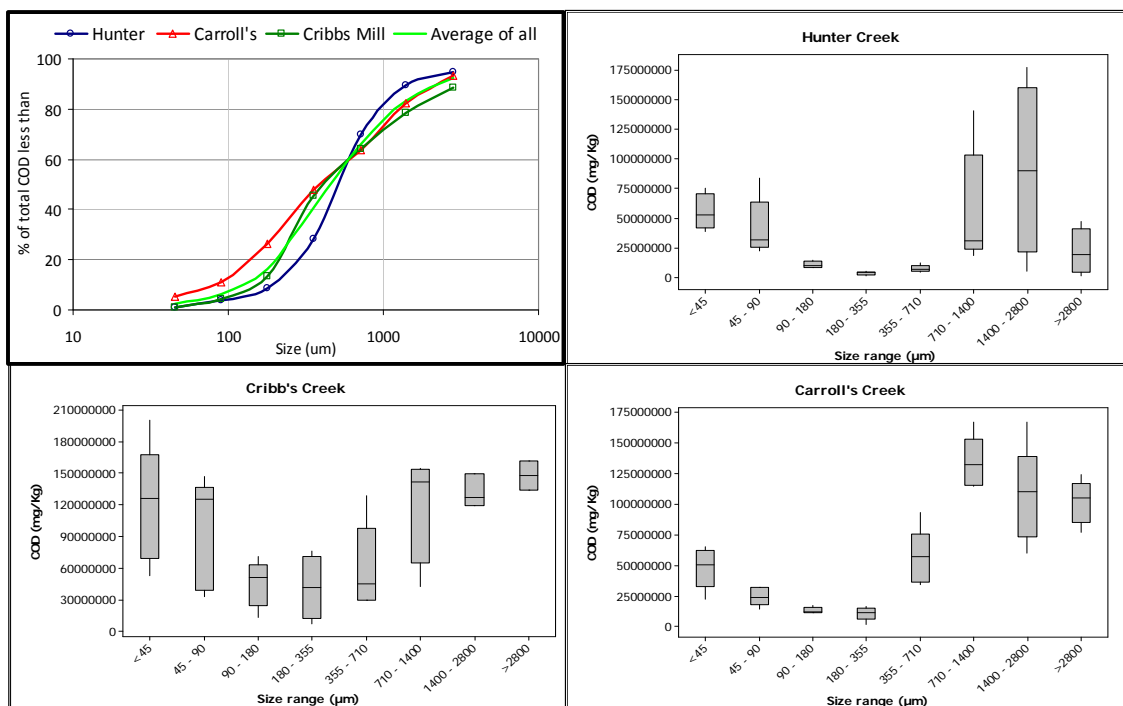


Figure 3. Observed COD of urban creek sediments

and large surface areas of these small particles. Earlier studies by Boehm and Farrington (1984) also found a direct positive relationship between PAH content and the silt/clay fraction of sediments. One-way ANOVA analysis showed significant difference in the analyte concentrations for the different particle sizes ($p < 0.05$). Cluster analyses of the PAH data by particle sizes indicated that for most of the analytes, the $>2800\mu\text{m}$ LOM fraction was a separate group compared to all the other sizes combined (Analyses results are not shown in this paper). Although the smaller ($< 90 \mu\text{m}$) and larger ($> 710 \mu\text{m}$) size fractions of the creek sediments were found to contain the highest levels of PAHs, these fractions only represented $<1\%$ of the total sediment mass. Therefore, the greatest mass load of the the PAHs was associated with the intermediate sized sediment fractions.

Linear regressions of COD to PAH concentrations on each particle size for each creek showed a significant response factor (slope term) for slightly more than half of the cases tested. When the large-sized LOM samples alone were considered, about 90% of the conditions had significant slope terms, indicating strong linear relations between COD and PAH concentrations. Two-way ANOVA analyses of the PAH concentrations were conducted to investigate the particle size and location as variables. These tests indicated that, except for naphthalene, fluorene, phenanthrene, and indeno(1,2,3-cd)pyrene, all the other PAH analytes were affected by the sediment locations. One-way ANOVA analyses of the concentrations for different particle size ranges comparing the locations showed that for most of the analytes, there were a larger number of significant differences between the creek locations for the smaller particle sizes (<45 and $45 - 90 \mu\text{m}$) than for the other sizes (Analyses results are not showed in this paper). Using probability plots and other graphical analyses, Hunter Creek was found to have significantly higher concentrations than the other creeks, especially for the small particle sizes. Hunter Creek sediment had a history of

contamination of hydrocarbons from creek-side businesses that caused the increased PAH concentrations. Cribbs Mill Creek generally had higher PAH concentrations than the sewage-contaminated Carroll's Creek sediments. This might be due to the long lapse in time since the Carroll's Creek sediments were affected by the SSOs (more than a year). The contaminated sediment at Carroll's Creek was either flushed from the contamination site or buried below the surface sampling depth. The Cribbs Mill Creek sampling location was in a long concrete channel with no bank erosion material affecting the sediment concentrations. The concrete lining also had obvious algae growths that may have preferentially sorbed PAHs.

Table 2. Two-Way ANOVA P Values for Analyte Concentrations

PAH	P Value		
	Size	Location	Size*Location
Naphthalene	0.000	0.088	0.116
Fluorene	0.000	0.721	0.481
Phenanthrene	0.000	0.389	0.043
Anthracene	0.000	0.032	0.821
Fluranthene	0.000	0.000	0.000
Pyrene	0.000	0.000	0.000
Benzo(a)anthracene	0.000	0.005	0.002
Chrysene	0.000	0.004	0.000
Benzo(b)flouranthrene	0.000	0.002	0.254
Benzo(a)pyrene	0.004	0.032	0.022
Indeno(1,2,3-cd)pyrene	0.000	0.284	0.250
Dibenz(a,h)anthracene	0.000	0.019	0.002
Benzo(ghi)perylene	0.000	0.041	0.493

Conclusions

Selected characteristics were analyzed for fifteen sediment samples from urban creeks. Sediments were found to be mostly composed of particles in the size range of 90 – 710 μm . The volatile content, COD and PAH content of the sediment particle size fractions had a bimodal distribution, with smaller and larger particles containing relatively higher values than the intermediate particles. The highest concentrations were associated with the LOM fractions. The volatile content and COD of the size fractionated sediments showed strong first order polynomial relationships. The presence of fragmentary plant material in the larger size fractions and the high clay/silt content in the smaller size fractions caused higher PAH concentrations. Positive linear relationships was also seen between PAH and COD content, but was most obvious in the sediment fractions with higher volatile (or COD) content. Sediment samples affected by commercial area runoff were found to have higher PAHs concentration than the samples affected by runoff from non-commercial areas.

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.*

Table 4. Observed PAH content in size fractionated urban stream sediments

PAH	Mean concentration ($\mu\text{g}/\text{kg}$) (standard deviation) for all 15 samples combined								
	< 45 μm	45 – 90 μm	90 – 180 μm	180 – 355 μm	355 – 710 μm	710 - 1400 μm	1400 - 2800 μm	> 2800 μm (w/o LOM)	> 2800 μm LOM
Naphthalene	255 (275)	177(156)	163 (224)	94 (87)	124 (131)	790 (2046)	891(2014)	124 (74)	2637 (2107)
Fluorene	257 (295)	189 (134)	225 (187)	125 (135)	139 (140)	196 (144)	293 (173)	216 (161)	1771 (945)
Phenanthrene	264 (278)	205 (211)	140 (158)	92 (92)	110 (85)	130 (136)	197 (230)	188 (164)	2007 (1422)
Anthracene	354 (397)	288 (273)	261 (253)	152 (150)	182 (182)	366 (314)	491(614)	218 (152)	2255 (1089)
Fluoranthene	650 (868)	624 (753)	345 (372)	202 (242)	247 (336)	259 (237)	237 (197)	191(173)	1520 (902)
Pyrene	653 (738)	519 (548)	412 (577)	175 (174)	240 (405)	207 (153)	192 (122)	172 (129)	2054 (954)
Benzo(a)anthracene	501 (595)	408 (537)	258 (286)	169 (171)	224 (229)	167 (134)	271 (252)	278 (371)	2164 (1045)
Chrysene	591 (618)	602 (689)	363 (363)	202 (199)	273 (268)	190 (125)	296 (242)	171 (130)	1810 (852)
Benzo(b)fluoranthrene	597 (522)	517 (598)	358 (389)	402 (671)	227 (150)	316 (262)	375 (369)	329 (375)	2179 (1425)
Benzo(a)pyrene	1474 (2210)	1524 (3079)	662 (459)	434 (513)	351 (210)	502 (533)	1119 (2086)	392 (255)	2330 (1866)
Indeno(1,2,3-cd)pyrene	787 (544)	657 (538)	942 (794)	258 (187)	332 (189)	576 (774)	706 (917)	357 (424)	1774 (933)
Dibenz(a,h)anthracene	1267 (1864)	787 (1022)	675 (545)	276 (234)	355 (226)	687 (511)	835 (1254)	286 (191)	1492 (775)
Benzo(g,h,i)perylene	706 (686)	465 (451)	591 (691)	199 (226)	174 (116)	551 (567)	396 (299)	348 (229)	2236 (1728)

References:

- Aryal, R. K., Furumai, H., Nakajima, F., and Boller, F. (2005). Dynamic behavior of fractional suspended solids and particle bound polycyclic hydrocarbons in highway runoff. *Water Research* 39: 5126-5134.
- Bathi, J. R., Pitt, R. (2007) "Fates of Polycyclic Aromatic Hydrocarbons (PAHs) Affect Treatability." World Environmental & Water Resources Congress 2007. ASCE - EWRI. Tampa, FL.
- Boehm, P. D., and Farrington, J. W. (1984). Aspects of the polycyclic aromatic hydrocarbon geochemistry of the recent sediments in the Georges Bank region. *Environmental Science and Technology* 18: 840-845.
- Cheung, K. C., Leung, H. M., K. Y. Kong, H. M., and Wong, M. H. (2006). Residual levels of DDTs and PAHs in freshwater and marine fish from Hong Kong markets and their health risk assessment. *Chemosphere* 66: 460-468.
- Guggenberger, G., Pichler, M., Hartmann, R., and Zech, W. (1996). Polycyclic aromatic hydrocarbons in different forest soils: Mineral horizons. *Z. Pflanzenernähr. Bodenk.* 159:565-573.
- Hwang, H. M., and Foster, G. D. (2006). Characterization of polycyclic aromatic hydrocarbons in urban stormwater runoff flowing into the tidal Anacostia River. *Environmental Pollution* 140: 416-426.
- Kuklick, J. R., Siverten, S. K., Sander, M., and Scott, M.I. (1997). Factors influencing polycyclic aromatic hydrocarbon distribution in South Carolina estuarine sediments. *Journal of Experimental Marine Biology and Ecology* 213: 13-29.
- McCready, S., Slee, D. J., Birch, G. F., and Taylor, S. E. (2000). The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia. *Marine Pollution Bulletin* 40(11): 999-1006.
- Metre, V. P. C., Mahler, B. J., and E. T. Furlong. 2000. Urban sprawl leaves its PAH signature. *Environmental Science & Technology* 34(1): 4064-4070.
- Müller, S., W. Wilcke, N. Kanchanakool, and W. Zech. (2000). Polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in particle-size separate of urban soils in Bangkok, Thailand. *Soil Sci.* 165:412-419.
- Pitt, R., R. Field, M. Lalor, and M. Brown. "Urban Stormwater Toxic Pollutants: Assessment, Sources and Treatability." *Water Environment Research*. Vol. 67, No. 3, pp. 260-275. May/June 1995.
- Ray, H. (1997). Street Dirt as a Phosphorus Source in Urban Stormwater. Department of Civil and Environmental Engineering, MSCE, University of Alabama at Birmingham, USA.
- Rushton, B. (2006). Broadway outfall stormwater retrofit project, monitoring CDS unit and constructed pond. South Florida Water Management District and City of Temple Terrace, W241. Brooksville, FL.
- Zhou, J. L., Fileman, T. W, Evans, S., Donkin, P., Llewellyn, C., W. Readman, J., Mantoura, R.F., and Rowland, S. J. (1998). Fluoranthene and pyrene in the suspended particulate matter and surface sediments of the Humber Estuary, UK. *Marine Pollution Bulletin* 36(8): 587-597.