



Spatial Analysis and Potential Source of Polycyclic Aromatic Hydrocarbons (PAH) in Austin's Streams

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Abstract

The presence of polycyclic aromatic hydrocarbons (PAH) in sediment in Austin's urban streams is examined in this report. A preliminary spatial analysis identifying areas of elevated concentrations of PAH in stream sediment was conducted based on samples collected in the six month period beginning November 2015. Confidence intervals of the mean PAH concentration were calculated to find the central tendency of the data collected with the aim to compare these intervals with the probable effect concentration and the threshold effect concentration, two metrics involved in determining the potential for impacts to aquatic life from these PAH. Results show that PAH have been detected in Barton Creek immediately upstream of Barton Springs and upstream to Spyglass Road in quantities that might impact aquatic life. High levels of PAH have been detected in Harper's Branch that require further investigation. Sites in upper Shoal Creek (Crestmont Park and Crosscreek Drive) also indicate the presence of PAH and some legacy pesticide, such as DDD, DDE, and/or DDT. Waller Creek also contains intermediate levels of PAH at the Hemphill Tributary at 26th Street and at 19th St. Other sites on Waller and Shoal creeks and Harper's Branch may also contain substantial levels of PAH in the sediment; however, additional sampling is required to verify this. Future sampling can be reinforced with a geographic analysis to find potential point sources of PAH.

Additional analysis showed that the PAH sampled at these sites can mostly be characterized as pyrogenic. This determination was based on applying empirical research performed by others on the ratios of the PAH individual constituents to the data collected. The soil texture of the sediment was also examined for factors that may indicate a correlation to high levels of PAH. This examination found that particle size provides conditions which may allow retention of more PAH in the sediment.

Introduction

Polycyclic aromatic hydrocarbons (PAH) are a group of chemical compounds consisting of three or more fused benzene rings. The number of rings and the shape of the ring structure both play a role in the chemical properties of PAH. These compounds are currently listed on both the Toxic Pollutant List (Code of Federal Regulations at 40 CFR 401.15) and the Priority Pollutant List (40 CFR 423 Appendix A). PAH are considered Toxic Pollutants because they persist in the environment; several are carcinogenic, mutagenic, and/or teratogenic to aquatic life and seven are probable human carcinogens (U.S. Environmental Protection Agency 2015).

DDT (1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane) is an insecticide previously used in the United States to control insects on agricultural crops and to kill insects that carried diseases such as malaria and typhus. DDD (1,1-dichloro-2,2-bis(p-chlorophenyl)ethane) and DDE (1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene) are breakdown products (metabolites) of DDT. Both DDD and DDE are present in the environment as a result of the breakdown of DDT. DDD was also used as a pesticide, but to a far less extent than DDT. Human and animal exposure to DDT/DDD/DDE affects the nervous system (can cause tremors or convulsions), causes cancer (primarily liver) in animals, have been assigned as probable human carcinogens by the U.S. Environmental Protection Agency (EPA), and alters the development of reproductive organs in animals (ATSDR 2002, US EPA 2015). The EPA banned the use of DDT in 1972, except for use in public health emergencies. Today, DDT cannot be legally sold or distributed inside the United States; however, it is still used in other countries to control insect populations that might spread disease. DDT has a long half-life and is not readily degraded through hydrolysis, oxidation, or direct photolysis which leads to the pollutant being very persistent in the environment (US EPA 1979). In fact, the half-life of DDT in soil has been estimated at 15 years or longer. While the use of DDT in the United States has been banned since the 1972, DDT continues to be detected in sediment and aquatic biota across the United States (Nowell et al. 1999).

DDT (and its metabolites) and PAH are hydrophobic and tend to sorb to particulates in the water column, eventually settling to the substrate of water bodies as sediment. Thus, concentrations in the sediment tend to be much higher than concentrations in the water column (Moore and Ramamoorthy 1984). Accumulation in the sediment can lead to toxic effects to the surrounding biological communities. State of Texas regulations in 30 Texas Administrative Code 307.6 and associated guidance protect aquatic life from toxic conditions in both the water column and the sediment (TCEQ 2012). MacDonald *et al.* (2000) developed consensus-based sediment quality guideline concentrations for 28 chemicals of concern which included metals, PAH, polychlorinated biphenyls, and pesticides. The threshold effect concentration (TEC) was developed as the concentration below which adverse effects are not expected to occur and the probable effect concentration (PEC) was developed as the concentration above which adverse impacts are expected to occur (McDonald et al. 2000). Currently the Texas Commission on Environmental Quality (TCEQ) identifies a concern for aquatic life if more than 20% of sediment samples collected contain contaminants exceeding the PEC using the binomial method for ten PAH (TCEQ 2012).

Several reports by the City of Austin Watershed Protection Department have documented either total PAH or individual PAH concentrations above or near the probable effect concentration (PEC)

in sediment samples collected within the Barton Creek, East Bouldin Creek, Harper's Branch, Shoal Creek, and Waller Creek watersheds (Richter 2012, 2015). Sampling within these watersheds has historically been limited to sites located at the mouth of each creek, however samples collected in East Bouldin Creek have documented PAH concentrations above the PEC threshold in multiple sites spanning from the mouth of the creek up through the headwaters. Additionally, high PAH concentrations have been documented near the University of Texas campus in Waller Creek. As a result of this spatial limitation, sampling at additional sites along the main channels of Barton Creek, Waller Creek, Shoal Creek, and Harper's Branch was warranted. This study aimed to gain resolution on the distribution and spatial trends in concentration across these watersheds in order to identify specific reaches that should be sampled more intensely in a future phase. The purposes of this study are:

- 1) Corroborate historic high concentrations in total or individual PAH at these streams;
- 2) Identify spatial distribution of PAH concentrations;
- 3) Classify potential sources of PAH; and
- 4) Examine sediment gradation as a factor in explaining high PAH concentrations in the streams.

Methods

The methods and analyses used to characterize the PAH concentrations of the streams are based on a set of basic assumptions. The main assumption is that the sampled population is similar to the target population. In this assumption, the "sampled population" is composed of the sediment samples collected over a six month period at different locations from within the four urban creeks. The "target population" is the total sediment of each of the stream reaches. Thus, it is assumed that sediment sampled over this six month period at set locations is representative of overall sediment PAH concentrations for each watershed. Locations for sample sites were influenced by convenience of access. To overcome this spatial bias it was assumed that adequate mixing of the sediment occurs so that each sample of sediment is just as likely to be selected as any other. Given the appropriateness of these assumptions, statistical intervals and/or inferences can be computed.

All sites were sampled three times under baseflow conditions over a six month period (November 2015 to March 2016). At least one discrete sample was collected at each site during a visit. Additionally, two field replicates were consistently collected at two sites within each watershed surveyed in order to determine variability of a sample. Accordingly, sites with field replicates consisted of a total of nine samples collected on three different dates during the sampling period, while other sites consisted of a total of three samples collected on three different dates. The dates for sample events were selected using a random number generator in order to ensure a random sample in time.

Confidence Intervals

Confidence intervals of the mean PAH concentrations were developed to corroborate the total and individual PAH concentrations at the sites. These intervals convey not only an approximation of the central tendency of the data, but also express the uncertainty of this central tendency. This is

useful in postulating prior distributions for future studies to compare between sites or over time. For this study, however, confidence intervals are employed to simply characterize the concentration of PAH at each site. The equation for the upper and lower confidence intervals is:

$$[LCI, UCI] = \bar{x} \pm t_{(1-\frac{\alpha}{2}, n-1)} s / \sqrt{n} \quad (1)$$

This equation is based on the assumptions of the Central Limit Theorem and random sampling, as discussed above. In Equation 1, \bar{x} is the sample average, s is the sample standard deviation, n is the number of samples, α is the error rate, and $t_{(a,b)}$ is the value of the Student's t-distribution with a probability a and degree of freedom b . These intervals are used to address the first two purposes of this study.

Source Characterization

In addition to characterizing the PAH concentrations at the different urban streams, this report also aims to classify the sources of the PAH. Petrogenic sources, generally associated with motor oils, often consist of PAH with lighter molecular weights due to the low temperatures present during its production. Conversely, pyrogenic sources consist of PAH with higher molecular weights because the high temperatures during combustion of fossil fuels eliminate the lower molecular weight PAH. Work performed by Yunker *et al.* (2002) examined the identification of PAH sources based on ratios of a set of PAH with similar molecular weights but different thermodynamic stabilities. The ratios provide information on the relative abundance of this set of PAH, which can signify a potential source. For example, pyrogenic sources would have a different relative abundance of PAH with the same molecular weight than petrogenic sources of PAH with the same molecular weight due to differences in temperature involved in their production and their different thermodynamic stabilities. However, the use of these ratios is not without problems. Primarily, there is a high level of uncertainty regarding the thresholds that determine the source of the PAH in the Yunker *et al.* (2002) paper. Yunker *et al.* (2002) revealed that the thresholds are most appropriate for individual PAH with large differences in their thermodynamic stabilities.

Yunker *et al.* (2002) looked at the relative abundance of four pairs of PAH, and from existing data estimated the thresholds of the relative abundance that would indicate a pyrogenic or a petrogenic source. These thresholds are:

1. For PAH with a molecular weight of 178, ratios of anthracene to phenanthracene plus anthracene greater than 0.10 indicate pyrogenic sources;
2. For PAH with a molecular weight of 202, ratios of fluoranthene to fluoranthene plus pyrene greater than 0.50 indicate pyrogenic sources;
3. For PAH with a molecular weight of 228, ratios of benzo(a)anthracene to benzo(a)anthracene plus chrysene greater than 0.35 indicate pyrogenic sources; and
4. For PAH with a molecular weight of 276, ratios of indeno[1,2,3-cd]pyrene to indeno[1,2,3-cd]pyrene plus benzo[g,h,i]perylene greater than 0.50 indicate pyrogenic sources;

Confidence intervals of these ratios were developed for each of the sites to examine the degree to which a source can be attributed and its variability.

Sediment Characterization

Information on the sediment texture of the sediment samples was obtained from the laboratory. The sediment was partitioned into four categories based on grain size: clay (particles less than 0.002 mm), silt (particles between 0.002 and 0.05 mm), sand (particles between 0.05 and 2.0 mm), and gravel (particles greater than 2.0 mm). From this, a grain size distribution curve was developed, which plotted the grain size on the x-axis with the percent of sediment passing the corresponding grain size on the y-axis. The importance of the grain size distribution curve is that it distills information on the four dependent variables (i.e. clay, silt, sand, gravel) into independent parameters of the distribution curve. These independent curve parameters can then be used to investigate various characteristics of the sediment at a site.

One problem in this approach lies in deciding on an appropriate curve to fit the data. The solution could be inferred based on the presumed characteristics of the curve. In the case of a grain size distribution curve, at some small grain size, no sediment is presumed to pass through. At the other end of the curve, for large grain sizes, all of the sediment in the sample will pass. Thus, one can infer that the grain size distribution curve would start at 0% passing for small grain sizes and monotonically increase to 100% passing. A potential curve that may fit these characteristics is a logistic curve.

The logistic curve is non-linear, and as such, a modification to the traditional statistical method of fitting data to a curve is needed. To begin developing this method to fit the logistic curve to the grain size distribution data, a function of minimizing the error between the curve and the data is needed:

$$Q = \sum_{i=1}^n [y_i - f(x_i)]^2 \quad (2)$$

In this equation, y_i is the percent of sediment passing given its grain size, x_i . This is compared to the functional value, $f(x_i)$, of the logistic curve given grain size, x_i . The squared difference in the two is denoted the error, Q . The logistic curve is given by the equation:

$$f(x_i) = (1 + e^{-k(x_i - x_{mid})})^{-1} \quad (3)$$

For Equation (3), the curve parameter, k , is the slope of the curve, and x_{mid} denotes the midpoint of the curve along the x-axis. The curve fitting, then, amounts to finding suitable curve parameters, k and x_{mid} , in Equation (3) that will generate a minimum square of errors in Equation (2).

Since the logistic curve is non-linear, finding the curve parameters is not a trivial matter. One method, the *brute force method*, includes finding the error, Q , for a large number of (k , x_{mid}) pairs at small intervals within a finite interval. However, this can be time-consuming. A more common (and elegant) method involves calculus. To find the minimum of any function, the derivative of that function with respect to the parameter of interest is set to zero. The value of the parameter at which the derivative is zero is the minimum of the function. In the case of Equation (2), the derivatives with respect to the parameters k and x_{mid} are:

$$\frac{\partial Q}{\partial x_{mid}} = -2 \cdot \sum_{i=1}^n \left[\left(y_i - \frac{1}{1 + e^{-k(x_i - x_{mid})}} \right) (1 + e^{-k(x_i - x_{mid})})^{-2} (k \cdot e^{-k(x_i - x_{mid})}) \right]$$

$$\frac{\partial Q}{\partial k} = -2 \cdot \sum_{i=1}^n \left[\left(y_i - \frac{1}{1 + e^{-k(x_i - x_{mid})}} \right) (1 + e^{-k(x_i - x_{mid})})^{-2} \left((x_i - x_{mid}) \cdot e^{-k(x_i - x_{mid})} \right) \right]$$

Setting these two equations to zero and solving for k and x_{mid} will provide the parameter values which produces the minimum error, Q . Unfortunately, solving for this set of equations algebraically appears to be intractable. To solve this, vector calculus is needed.

Begin with an initial point (k, x_{mid}) and then advance in the direction of the negative steepest gradient ($-\partial Q/\partial k, -\partial Q/\partial x_{mid}$) by a small increment Δ so that the next point is the initial point plus the negative gradient times the increment. Iterate several times to converge on a local minimum. However, nonlinear functions will often produce a *rugged landscape*, and using calculus may result in finding a local minimum, but not the global minimum. The approach used in this report to find the global minimum involves a hybrid of the *brute force* method and calculus. Using this hybrid approach, the brute force method is used first to scan the landscape coarsely for minimums. The region with the smallest minimum is then explored further using vector calculus.

A sediment gradation curve was developed for every site using the techniques described above. Parameters from this curve were then used as factors in developing a linear model to explain the amount of total PAH.

Results

Characterization/Confidence Intervals of the Mean

Confidence intervals of the mean were developed for each of the nineteen individual PAH constituents and three forms of pesticides at various locations in four creeks: Barton, Harper's Branch, Waller, and Shoal. Confidence intervals were not developed for individual PAH or pesticides that were not detected in at least 2 of the 3, or 7 of the 9 sediment samples. If a site had at least one non-detected value at a site visit, later visits to that site also were likely non-detects.

Barton Creek

The sampling locations along Barton Creek (Figure 1) are listed in Table 1 in ascending order from downstream (Sample Site #35, Barton Creek at Barton Springs) to upstream (Sampling Site #48, Barton Creek at HWY 71 downstream of Little Barton Creek).

Table 1: Barton Creek Sampling Site List

SAMPLE SITE #	SITE NAME
35	BARTON SPRINGS
53	BARTON UPSTREAM BARTON SPRINGS
1233	BARTON CREEK @ SPYGLASS SPRING
1240	EG TRIBUTARY @ BARTON CREEK DOWNSTREAM OF LOOP 360
13447	BARTON CREEK DOWNSTREAM OF GAINES CREEK
51	BARTON CREEK DOWNSTREAM OF LOST CREEK BLVD
1270	BARTON CREEK DOWNSTREAM OF BCT
48	BARTON CREEK @ HWY 71 DOWNSTREAM OF LITTLE BARTON

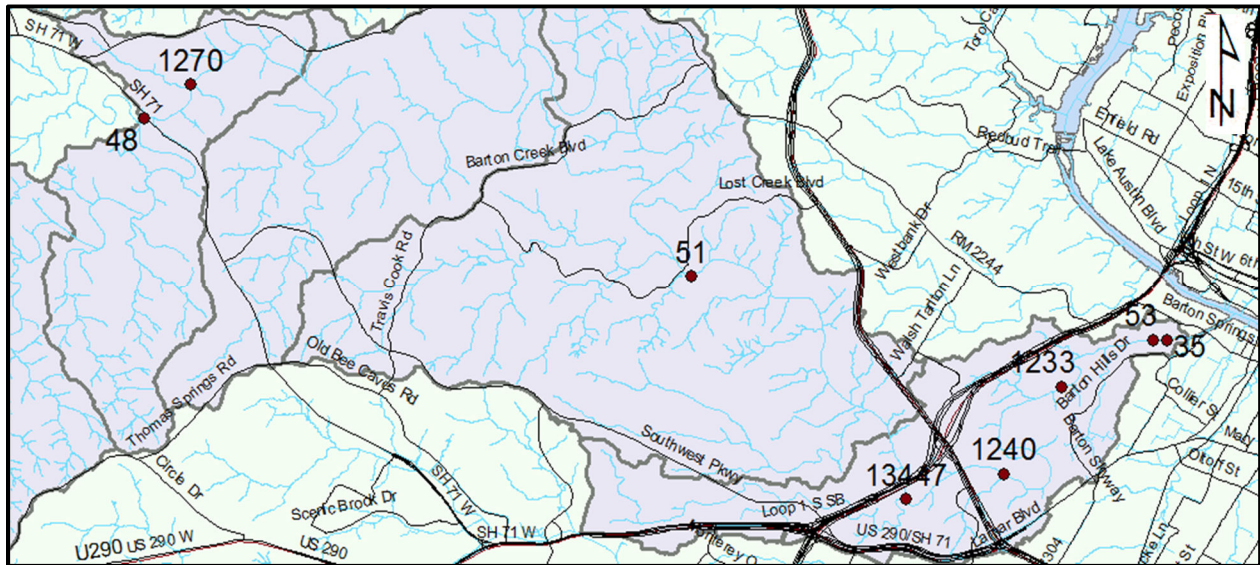


Figure 1: Map of Barton Creek Sampling Sites (Scale: 1 in = 2 miles)

The confidence intervals for the PAH constituents detected at Barton Creek are shown in Table 2. Note that some confidence intervals drop below zero because of the high variability resulting from small sample size. In these cases, the lower confidence intervals of the means were replaced in the table with a “<DL” designation. In these instances, it is possible that one or more means were below the detection limit. Additional sampling would reduce that uncertainty in the confidence intervals. This is illustrated by the small spread of the confidence intervals of site #51 which consisted of nine samples rather than the three samples collected at sites #53 and #1233. Also note that confidence intervals for sites not shown in the table are a result of non-detects of PAH in the sampled sediment.

Table 2: Barton Creek PAH Upper and Lower Confidence Intervals of the Mean Concentrations (mg/kg) and their Respective Exposure Limits (mg/kg)

Parameter	Sampling Site Numbers			Exposure Limits	
	53 (n=3)	1233 (n=3)	51 (n=9)	TEC	PEC
ANTHRACENE	<DL <DL	0.24 <DL	<DL <DL	0.0572	0.845
BENZO(A)ANTHRACENE	1.65 <DL	4.22 <DL	0.40 0.23		
BENZO(K)FLUORANTHENE	1.04 <DL	2.32 <DL	0.27 0.15		
BENZO(GHI)PERYLENE	1.71 <DL	3.80 <DL	0.39 0.22		
BENZO(A)PYRENE	1.94 <DL	4.52 <DL	0.48 0.27	0.15	1.45
CHRYSENE	2.37 <DL	5.53 <DL	0.59 0.35		
DIBENZ(AH)ANTHRACENE	0.42 <DL	0.88 <DL	0.10 0.05		
FLUORANTHENE	3.35 <DL	7.49 <DL	1.05 0.58		
INDENO(1,2,3- CD)PYRENE	1.49 <DL	3.27 <DL	0.34 0.20		
PHENANTHRENE	1.04 <DL	1.62 <DL	0.37 0.14		
PYRENE	2.77 <DL	6.37 <DL	0.81 0.46	0.20	1.52
BENZO(B)FLUORANTHENE	2.27 <DL	5.28 <DL	0.58 0.32		
BENZO(E)PYRENE	1.50 <DL	3.49 <DL	0.40 0.24		
Total PAH	20.18 <DL	45.50 <DL	5.33 3.08		

Most of the individual PAH concentrations at Barton Creek followed the same spatial pattern. This pattern consists of detections upstream of Barton Springs at site #53 and #1233 (upstream of Barton Springs and at Spyglass Springs, respectively) and then further upstream at site #51 (in Barton Creek downstream of Lost Creek Boulevard). Furthermore, the pattern of high variability at sites #53 and #1233 (n=3 each) and low variability at site #51 (n=9) extended to most of the other individual PAH concentrations. Thirteen of the nineteen PAH constituents sampled were detected for at least three of these sites.

Table 2 also displays the exposure limits, PEC and TEC. All of the individual PAH concentrations that were present at site #51 had the upper confidence interval of the mean above the TEC, but

below the PEC. The upper confidence intervals of the mean at sites #53 and #1233 exceeded the PEC threshold; however, the lower confidence intervals for those sites were below detection limits. As described earlier, wider confidence intervals are expected with low sample size and high variability in the samples collected. The presence of PAH points to sources at, or around Lost Creek and Spyglass. Note that DDD, DDE, and DDT were not detected at any of the Barton Creek sites.

Harper's Branch

Harper's Branch included three sampling sites, which are listed in Table 3 below. Sites are listed in ascending order from downstream (site #484, Riverside Drive) to upstream (site #5810, Parker Park).

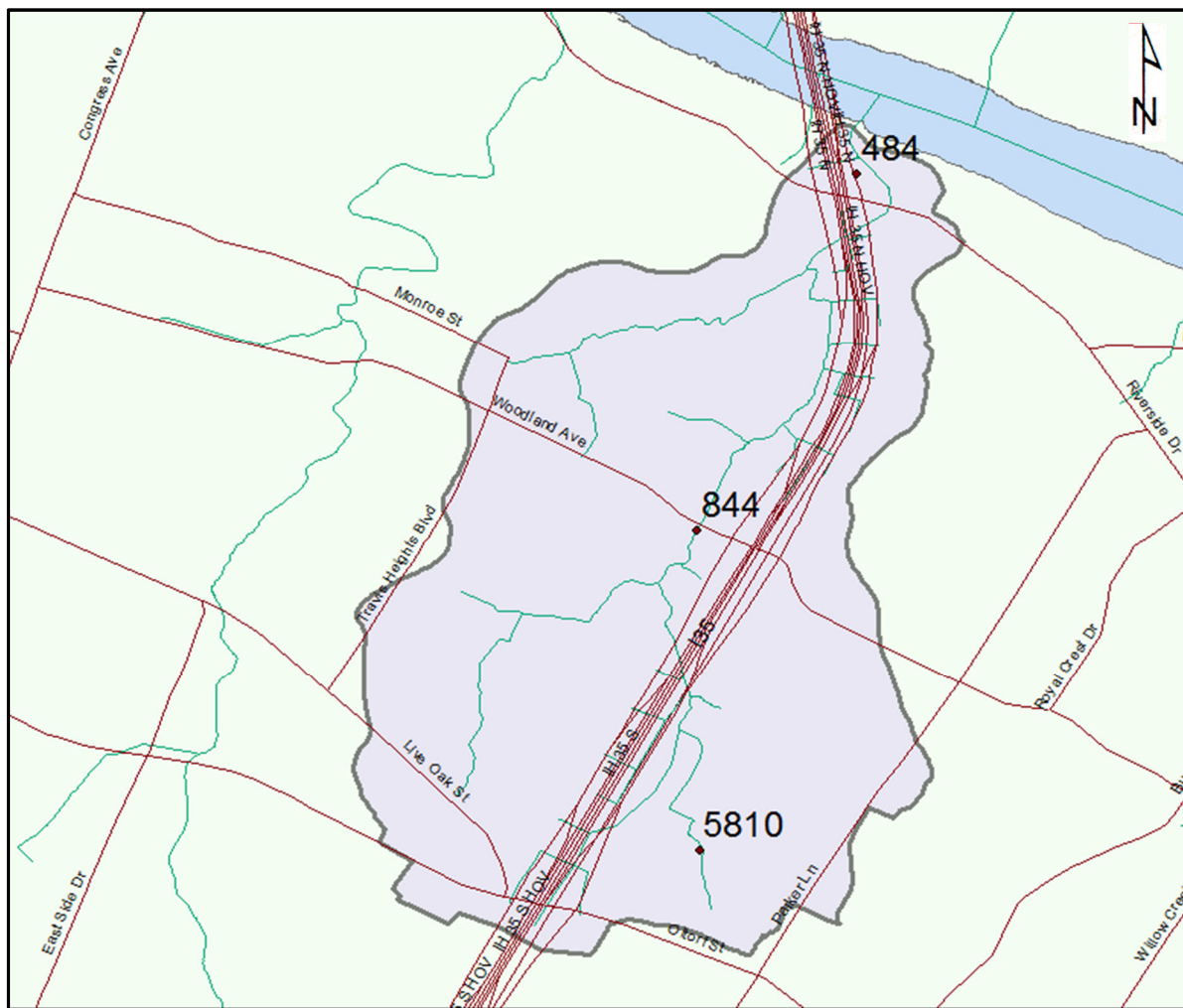


Figure 2: Map of Sampling Sites at Harper's Branch (Scale: 1 in = 1500 ft)

Table 3: Harper's Branch Sampling Site List

SAMPLE SITE #	SITE NAME
484	HARPERS BRANCH CREEK @ RIVERSIDE DR
844	HARPERS BRANCH CREEK @ WOODLAND AVE
5810	HARPERS BRANCH TRIB @ PARKER PARK

Results from the sampling are displayed in Table 4. Seventeen of the nineteen PAH constituents were detected in at least one of these three sites.

Table 4: Harper's Branch PAH Upper and Lower Confidence Intervals of the Mean Concentrations (mg/kg) and their Respective Exposure Limits (mg/kg)

Parameter	Sampling Site Numbers			Exposure Limits	
	484 (n=9)	844 (n=3)	5810 (n=9)	TEC	PEC
ACENAPHTHENE	<DL	<DL	0.23		
	<DL	<DL	0.02		
ACENAPHTHYLENE	<DL	0.09	0.31		
	<DL	0.04	0.13		
ANTHRACENE	0.16	0.22	0.86	0.0572	0.845
	0.04	0.02	0.18		
BENZO(A)ANTHRACENE	1.76	2.61	4.71	0.11	1.05
	0.47	0.65	2.00		
BENZO(B)FLUORANTHENE	2.43	3.40	6.49		
	0.85	1.59	4.93		
BENZO(K)FLUORANTHENE	1.18	1.84	2.96		
	0.36	0.44	2.02		
BENZO(GHI)PERYLENE	1.57	3.86	6.28		
	0.70	0.04	3.87		
BENZO(A)PYRENE	1.97	2.43	5.53	0.15	1.45
	0.67	1.44	3.30		
BENZO(E)PYRENE	1.78	2.51	5.03		
	0.59	1.06	3.48		
CHRYSENE	2.83	3.87	6.55	0.17	1.29
	0.87	1.89	4.62		
DIBENZ(AH)ANTHRACENE	0.38	0.79	1.24		
	0.16	0.12	0.79		
FLUORANTHENE	5.03	6.27	11.82	0.42	2.23
	0.86	1.57	3.68		
FLUORENE (9H-FLUORENE)	<DL	<DL	0.27		
	<DL	<DL	0.02		
INDENO(1,2,3-CD)PYRENE	1.36	3.16	5.04		
	0.60	0.18	3.13		
PHENANTHRENE	1.49	2.20	4.18	0.20	1.17
	0.27	0.35	0.63		

Parameter	Sampling Site Numbers			Exposure Limits	
	484 (n=9)	844 (n=3)	5810 (n=9)	TEC	PEC
PYRENE	3.30	4.37	9.66	0.20	1.52
	0.96	1.67	3.31		
ALPHA-CHLORDANE	<DL	<DL	0.01		
	<DL	<DL	0.01		
4,4'-DDE	0.013	<DL	<DL		
	0.006	<DL	<DL		
4,4'-DDT	0.009	<DL	<DL		
	0.004	<DL	<DL		
TOTAL PAH	23.5	26.4	63.8	1.61	22.8
	6.97	18.8	34.9		

For Harper's Branch, most of the locations sampled contained at least one detection of a PAH constituent. DDE and DDT were also detected at the downstream site on Riverside Drive. Perhaps more important, the lower confidence intervals of the mean concentrations of benzo(a)anthracene, benzo(a)pyrene, chrysene, fluoranthene, and pyrene all exceeded their respective PEC. This indicates a near certainty that the mean of the PAH concentration at this location is above the PEC. This exceedance occurs at the most upstream location sampled at Parker Park (n=9), but may also be true for chrysene and pyrene at the next downstream station, Woodland Avenue (n=3). The PEC for total PAH is also exceeded at the most upstream station. These statistics signal a concern for high levels of PAH at Parker Park and require further investigation. All three sites in this watershed indicate an elevated level of PAH concentration.

Shoal Creek

Sampling at Shoal Creek consisted of six sampling sites, which are listed in Table 5 below, and again are listed in ascending order from downstream (site #122, upstream of 1st St.) to upstream (site #118, at Crosscreek Drive).

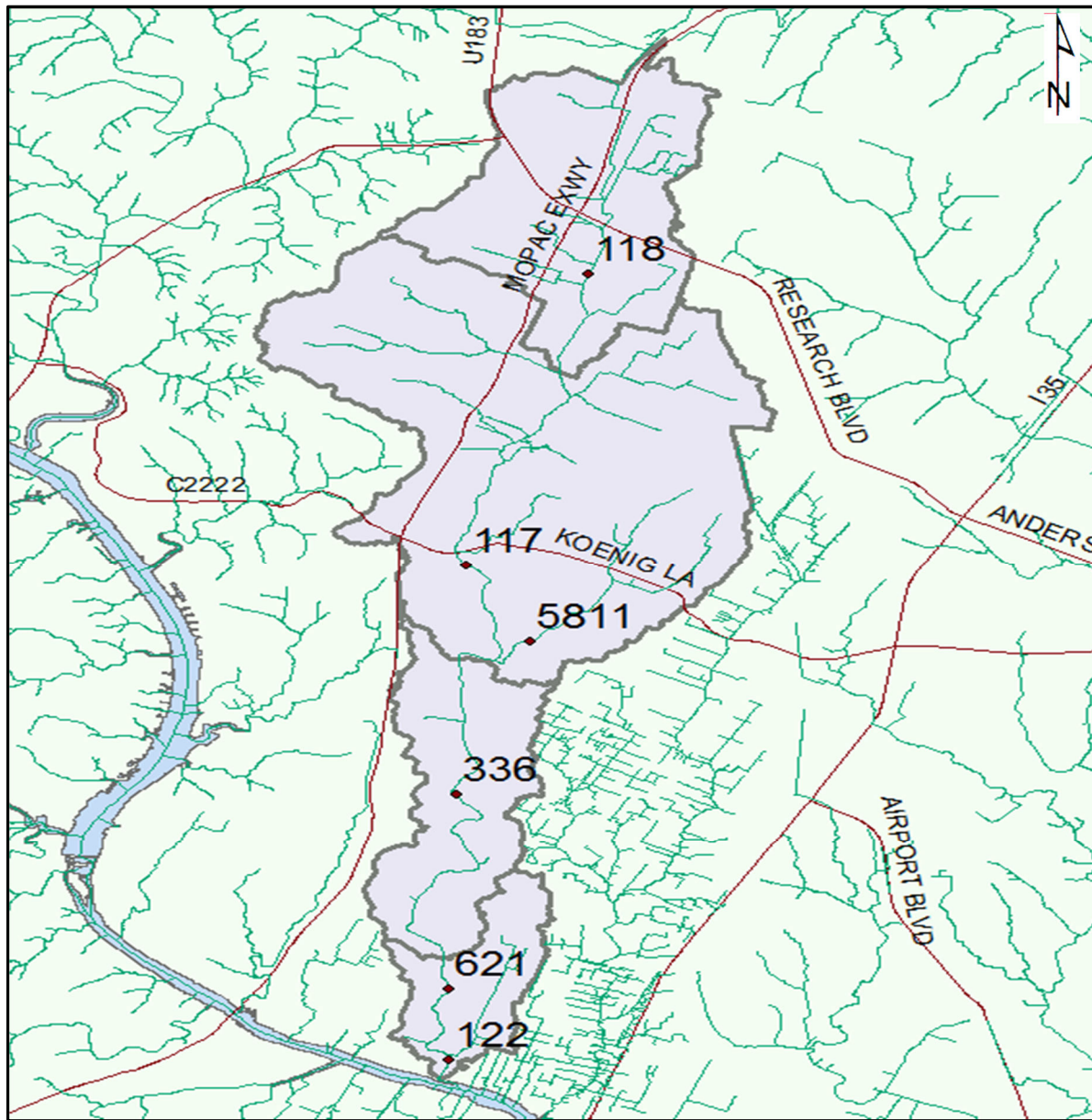


Figure 3: Map of Shoal Creek Sampling Sites (Scale 1 in = 1 mile)

Table 5: Shoal Creek Sampling Site List

SAMPLE SITE #	SITE NAME
122	SHOAL CREEK UPSTREAM OF 1ST ST.
621	SHOAL CREEK @ 12TH STREET (USGS)
336	SHOAL CREEK @ WEST 31ST STREET
5811	SHOAL TRIB @ CRESTMONT PARK
117	SHOAL CREEK @ SHOAL EDGE COURT (EII)
118	SHOAL CREEK DOWNSTREAM OF CROSSCREEK DRIVE

Results from the sampling are displayed in Table 6. Seventeen of the nineteen PAH constituents were detected in at least one of these three sites.

Table 6: Shoal Creek PAH Upper and Lower Confidence Intervals of the Mean Concentrations (mg/kg) and their Respective Exposure Limits (mg/kg)

Parameter	Sampling Site Numbers						TEC	PEC
	122 (n=3)	621 (n=3)	336 (n=3)	5811 (n=9)	117 (n=3)	118 (n=9)		
ACENAPHTHENE	0.13 <DL	<DL <DL	<DL <DL	<DL <DL	0.29 <DL	<DL <DL	0.00671	0.0889
ACENAPHTHYLENE	0.16 <DL	<DL <DL	<DL <DL	<DL <DL	<DL <DL	<DL <DL	0.00587	0.128
ANTHRACENE	0.28 <DL	<DL <DL	<DL <DL	0.15 0.05	0.48 <DL	0.16 0.05	0.057	0.85
BENZO(A)ANTHRACENE	2.18 <DL	0.73 <DL	0.83 <DL	1.25 0.45	2.82 <DL	1.45 0.44	0.11	1.05
BENZO(B)FLUORANTHENE	3.26 <DL	1.03 <DL	1.19 <DL	1.77 0.69	3.59 <DL	2.04 0.75		
BENZO(K)FLUORANTHENE	1.42 <DL	0.52 <DL	0.57 <DL	0.81 0.33	1.71 <DL	0.93 0.35		
BENZO(GHI)PERYLENE	2.27 <DL	0.36 <DL	0.94 <DL	1.28 0.51	3.00 <DL	1.33 0.44		
BENZO(A)PYRENE	2.45 <DL	0.85 <DL	0.98 <DL	1.49 0.54	3.08 <DL	1.63 0.59	0.15	1.45
BENZO(E)PYRENE	2.22 <DL	0.75 <DL	0.81 <DL	1.25 0.51	2.44 <DL	1.38 0.55		
CHRYSENE	3.52 <DL	1.07 <DL	1.26 <DL	1.97 0.82	4.10 <DL	2.14 0.73	0.166	1.29
DIBENZ(AH)ANTHRACENE	0.52 <DL	<DL <DL	0.23 <DL	0.30 0.11	0.69 <DL	0.32 0.09		
FLUORANTHENE	6.78 <DL	1.79 <DL	1.72 <DL	3.48 1.14	7.82 <DL	3.44 0.73	0.423	2.23
FLUORENE (9H-FLUORENE)	0.19 <DL	<DL <DL	<DL <DL	<DL <DL	0.22 <DL	<DL <DL		
INDENO(1,2,3-CD)PYRENE	1.97 <DL	0.33 <DL	0.82 <DL	1.11 0.41	2.58 <DL	1.18 0.36		
NAPHTHALENE	0.34 <DL	<DL <DL	<DL <DL	<DL <DL	<DL <DL	<DL <DL	0.176	0.561
PHENANTHRENE	3.35 <DL	0.94 <DL	0.68 <DL	1.67 0.48	5.21 <DL	1.17 0.08	0.204	1.17
PYRENE	5.25 <DL	1.38 <DL	1.27 <DL	2.67 0.84	5.77 <DL	2.75 0.60	0.195	1.52
4,4'-DDE	0.013 <DL	<DL <DL	<DL <DL	0.027 0.016	<DL <DL	<DL <DL	0.00316	0.0176
4,4'-DDT	0.021 <DL	<DL <DL	<DL <DL	0.018 0.005	<DL <DL	<DL <DL	0.00416	0.0629

Parameter	Sampling Site Numbers						TEC	PEC
	122 (n=3)	621 (n=3)	336 (n=3)	5811 (n=9)	117 (n=3)	118 (n=9)		
TOTAL PAH	34.2	9.2	10.4	18.0	40.9	18.6	1.61	22.8
	<DL	<DL	<DL	6.5	<DL	5.3		

Results from analyses at Shoal Creek point to the higher concentrations at the mouth of the stream and then unevenly distributed throughout the upper half of the watershed. The upper confidence interval of the mean exceeded the PEC at site #122 (1st St, n=3), #5811 (Crestmont Park, n=9), #117 (Shoal Edge Court, n=3), and/or #118 (Crosscreek Dr., n=9) for benzo(a)anthracene, benzo(a)pyrene, chrysene, fluoranthene, phenanthrene, and pyrene. The lower confidence interval of the mean was computed to be in between the PEC and TEC, indicating the possibility of a lower exposure. In addition, the presence of DDE and DDT was detected at sites #122 (1st St) and #5811 (Crestmont Park) with the confidence intervals of DDE at Crestmont Park exceeding the PEC. Note that even with nine samples taken at sites #5811 (Crestmont Park) and #118 (Crosscreek Dr.), there still exists moderate variability at these sites. The sampling site at Crestmont Park is situated in a tributary of Shoal Creek.

Waller Creek

Sampling at Waller Creek consisted of five sites, which are listed in Table 7 below in ascending order from downstream (site #38, downstream of Cesar Chavez St.) to upstream (site #780, at 51st St.).

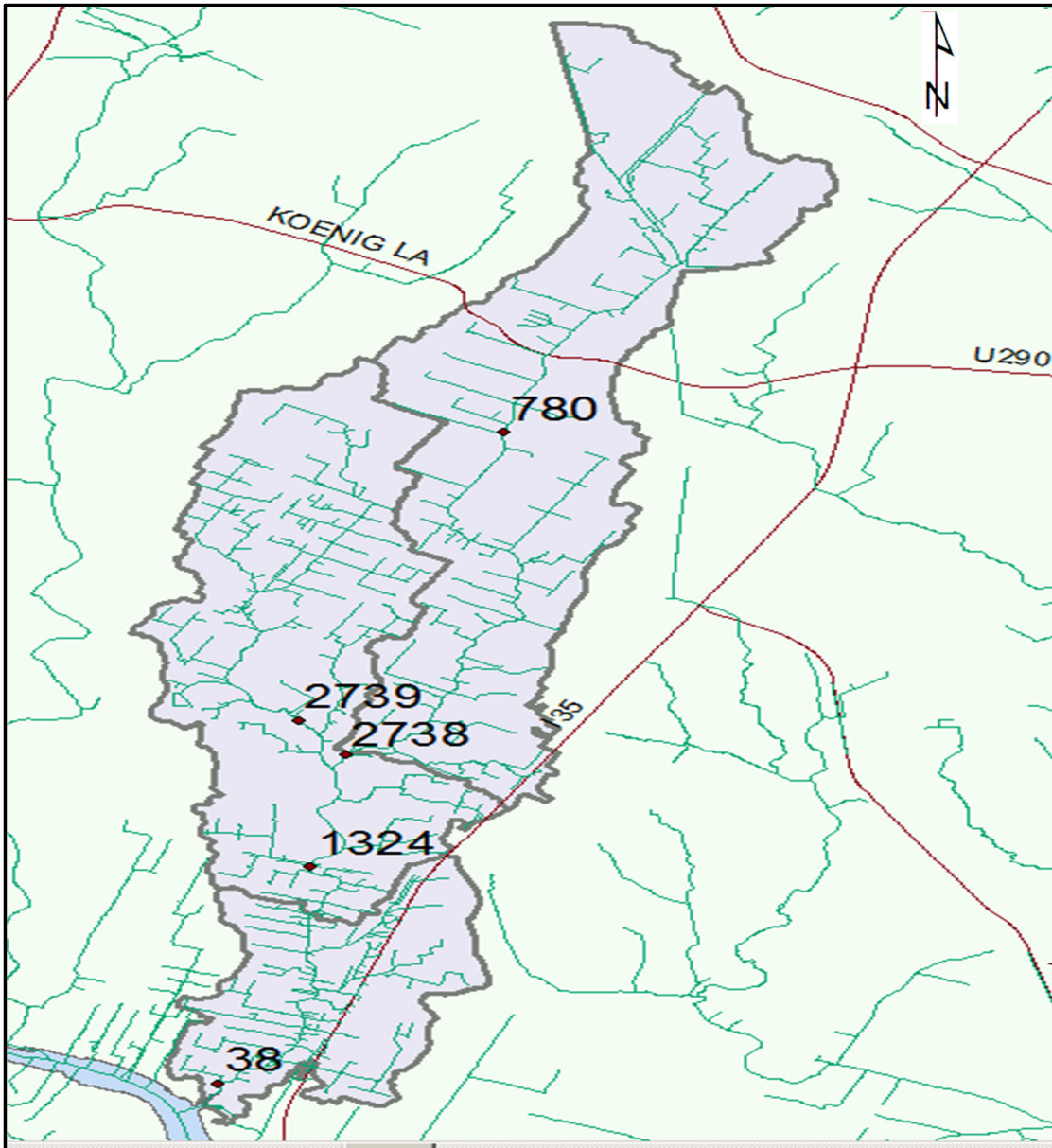


Figure 4: Map of Waller Creek Sampling Sites (Scale: 1 in = 2000 ft)

Table 7: Waller Creek Sampling Site List

SAMPLE SITE #	SITE NAME
38	WALLER CREEK DOWNSTREAM OF CESAR
1324	WALLER CREEK DOWNSTREAM OF 19TH @
2738	WALLER CREEK DOWNSTREAM OF 26TH
2739	HEMPHILL TRIBUTARY DOWNSTREAM OF
780	WALLER CREEK @ 51ST STREET

Results from the sampling are displayed in Table 8. Fifteen of the nineteen PAH constituents were detected in at least one of these three sites.

Table 8: Waller Creek PAH Upper and Lower Confidence Intervals of the Mean Concentrations (mg/kg) and their Respective Exposure Limits (mg/kg)

Parameter	Sampling Site Numbers					Exposure Limit	
	38 (n=3)	1324 (n=9)	2738 (n=3)	2739 (n=9)	780 (n=3)	TEC	PEC
ACENAPHTHENE	<DL <DL	<DL <DL	0.36 <DL	<DL <DL	<DL <DL	0.00671	0.0889
ANTHRACENE	<DL <DL	<DL <DL	0.64 <DL	<DL <DL	1.10 <DL	0.0572	0.845
BENZO(A)ANTHRACENE	0.76 <DL	0.38 0.14	3.00 <DL	0.42 0.04	5.17 <DL	0.108	1.050
BENZO(B)FLUORANTHENE	1.10 <DL	0.56 0.22	3.24 <DL	0.57 0.08	7.23 <DL		
BENZO(K)FLUORANTHENE	0.50 <DL	0.25 0.11	1.54 <DL	0.25 0.03	2.99 <DL		
BENZO(GHI)PERYLENE	0.77 <DL	0.40 0.16	2.17 <DL	0.43 0.08	6.25 <DL		
BENZO(A)PYRENE	0.87 <DL	0.45 0.18	2.83 <DL	0.45 0.05	6.34 <DL	0.150	1.450
BENZO(E)PYRENE	0.77 <DL	0.40 0.17	2.17 <DL	0.40 0.07	5.04 <DL		
CHRYSENE	1.17 <DL	0.58 0.23	3.81 <DL	0.61 0.07	7.53 <DL	0.166	1.290
DIBENZ(AH)ANTHRACENE	0.17 <DL	0.09 0.04	0.58 <DL	0.09 0.02	1.28 <DL		
FLUORANTHENE	1.96 <DL	0.96 0.35	6.05 <DL	0.72 0.13	12.95 <DL	0.423	2.23
FLUORENE (9H- FLUORENE)	<DL <DL	<DL <DL	0.31 <DL	<DL <DL	<DL <DL		
INDENO(1,2,3- CD)PYRENE	0.66 <DL	0.33 0.13	2.00 <DL	0.36 0.06	5.10 <DL		
PHENANTHRENE	0.49 <DL	0.27 0.09	3.51 <DL	0.15 0.04	5.96 <DL	0.204	1.17

Parameter	Sampling Site Numbers					Exposure Limit	
	38 (n=3)	1324 (n=9)	2738 (n=3)	2739 (n=9)	780 (n=3)	TEC	PEC
PYRENE	1.62	0.77	4.59	0.62	10.48	0.195	1.52
	<DL	0.29	<DL	0.10	<DL		
4,4'-DDD	0.015	<DL	<DL	0.011	0.021	0.0048	0.028
	<DL	<DL	<DL	0.006	<DL		
4,4'-DDE	0.011	<DL	0.021	0.010	0.092	0.00316	0.0313
	0.006	<DL	<DL	0.005	<DL		
4,4'-DDT	0.022	<DL	<DL	<DL	0.054	0.00416	0.0629
	<DL	<DL	<DL	<DL	<DL		
TOTAL PAH	2.70	3.52	7.67	2.70	21.15	1.610	22.800
	1.86	1.60	6.72	2.04	12.85		

Results from sampling of Waller Creek show much higher concentrations at the uppermost sampling site relative to the rest of the sites. Upper confidence intervals of the mean PAH concentrations at Waller Creek exceeded the PEC at site #780 (Waller Creek at 51st St., n=3). This holds for anthracene, benzo(a)anthracene, benzo(a)pyrene, chrysene, fluoranthene, phenanthrene, pyrene, as well as DDE. However, due to the high variability, the lower confidence intervals of the mean PAH concentration was computed to be less than the detection limit. Upper confidence intervals of the mean also exceeded the PEC at site #2738 (Waller Creek downstream of 26th St., n=3) for the same individual PAH and DDE. However, the uncertainty in the mean concentrations at these locations is still large and would require additional sampling to reduce this uncertainty. Sites #1324 (Waller Creek at 19th St.) and #2739 (Hemphill Tributary at 26th St), each with n = 9, had an upper confidence interval of the mean concentration above the TEC, but below the PEC for benzo(a)anthracene, benzo(a)pyrene, chrysene, fluoranthene, phenanthrene, and pyrene. The upper confidence interval of the mean concentration of DDD was higher than the TEC, but less than the PEC at site #2739 (n=9). Site #1324 was the only site in Waller Creek which consisted of non-detects for the pesticides. To reiterate, sediment sampling detected the presence of DDD, DDE, and/or DDT at sites #38, #2738, #2739, and #780. Site #780 contained the highest levels of the pesticides with its upper confidence interval for the concentration of DDE being above the PEC.

Source Classification

Figures 5 through 8 show confidence intervals of mean ratios at each site for each watershed to facilitate identification of possible sources of PAH contamination. Each figure contains all of the locations sampled where PAH was detected. Accordingly, the figures show sites #51, #1233, and #53 for Barton Creek (BAR), and all of the stations for Harper's Branch (HRP), Shoal Creek (SHL), and Waller Creek (WLR).

The ratio of anthracene to anthracene plus phenanthrene is shown in Figure 5. A value of 0.10 was determined by Yunkers et al (2002) as the threshold for classification. Ratios higher than 0.10 indicate a combustion source. Ratios less than 0.10 imply a petroleum source. Using this ratio,

most of the sampled sites (with PAH detections) bordered this threshold, making a source classification ambiguous.

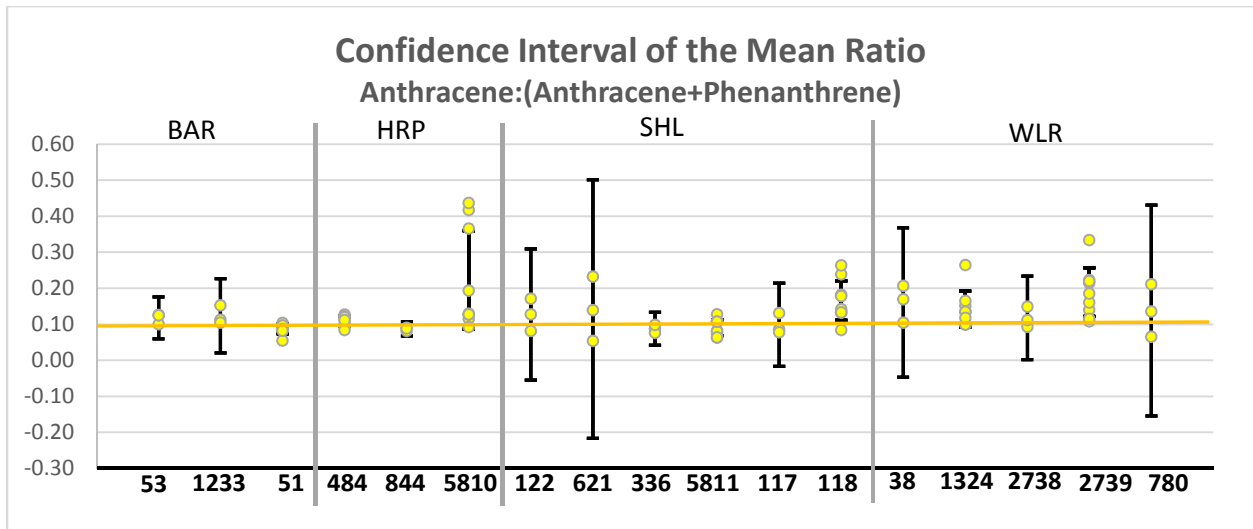


Figure 5: Confidence Interval of the Mean Ratio for PAH with Molecular Weights of 178

Figure 6 shows less ambiguous results. The threshold for the fluoranthene to fluoranthene + pyrene ratio is 0.50. Most of the confidence intervals of the mean ratio are above this threshold, indicating a combustion source, and only three of the sites had a confidence interval of the mean below this threshold.

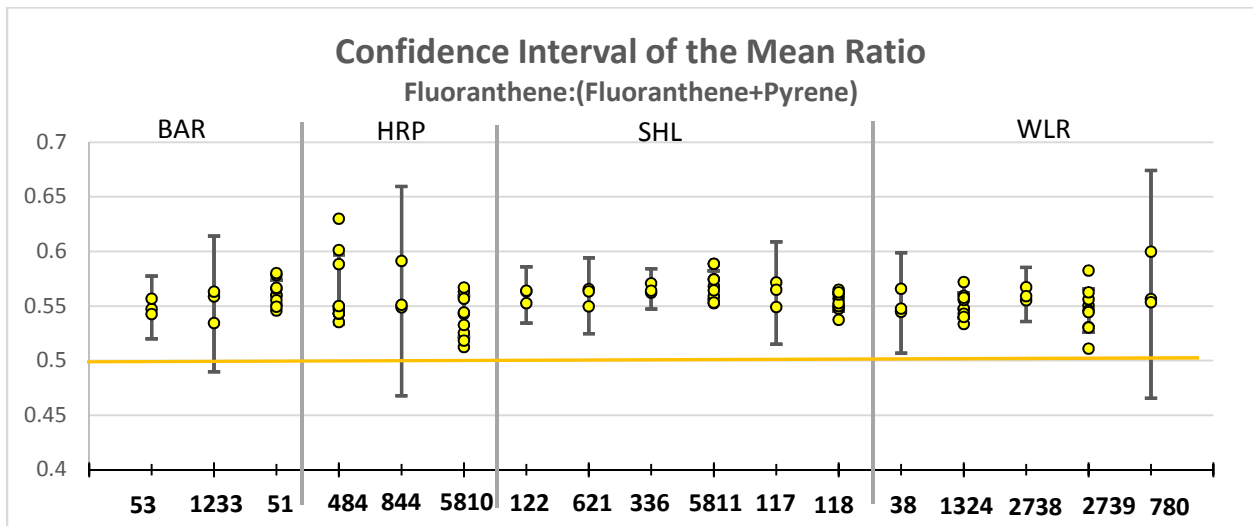


Figure 6: Confidence Interval of the Mean Ratio for PAH with Molecular Weights of 202

Results from the third ratio, benzo[a]anthracene to benzo[a]anthracene + chrysene, were also mixed (Figure 7). Yunker *et al.* (2002) include two thresholds. Ratios above the higher threshold, 0.35 suggest combustion sources, while ratios below the lower threshold of 0.20 denote unspent petroleum sources. Ratios in between these two thresholds indicate a combination of the two sources. Most of the sample sites had confidence intervals of the mean ratio extending in between

the two thresholds, which may indicate an uncertain source, but still point to a mostly combustion source.

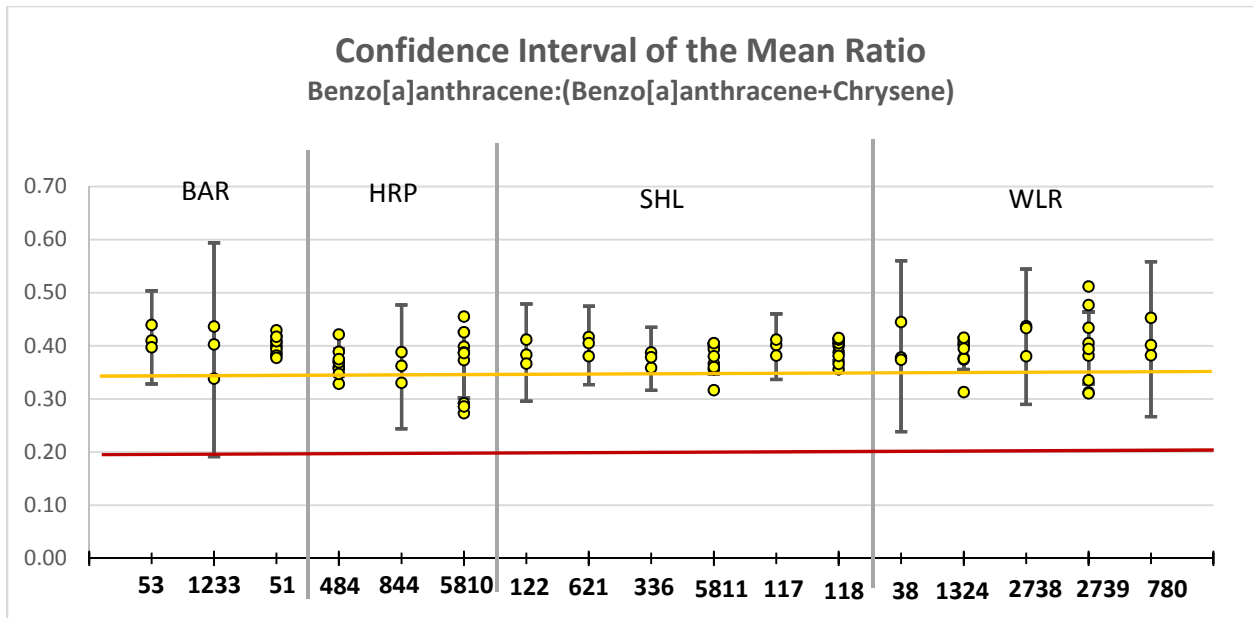


Figure 7: Confidence Interval of the Mean Ratio for PAH with Molecular Weights of 228

Finally, results from the fourth ratio, indeno[1,2,3-cd]pyrene to indeno[1,2,3-cd]pyrene +benzo[g,h,i]perylene, consisted of samples above the threshold of 0.50 (Figure 8). This points to types of combustion other than petroleum.

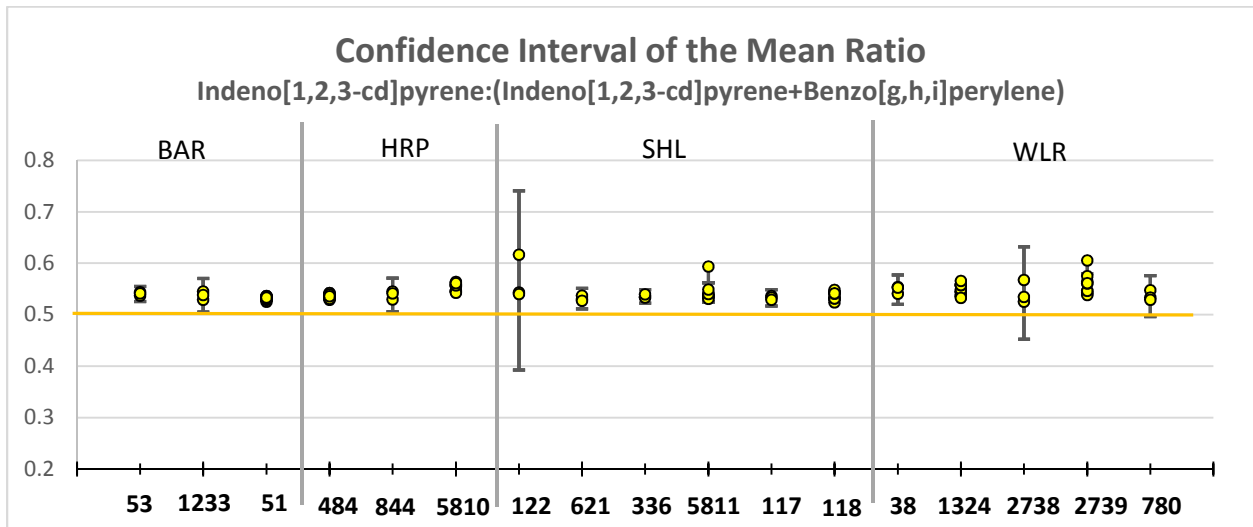


Figure 8: Confidence Interval of the Mean Ratio for PAH with Molecular Weights of 276

Ratios for PAH with molecular weights of 276 and 202 showed the least indeterminate results for source determination. This substantiates work by Yunker *et al.* (2002) predicting that these PAH would give clear results due to their thermodynamic stability.

Sediment Gradation

The relationship between grain size distribution and PAH concentrations is shown in Figure 9, as an example. This grain size distribution curve was developed from the nine samples for Barton Creek downstream of Lost Creek Boulevard.

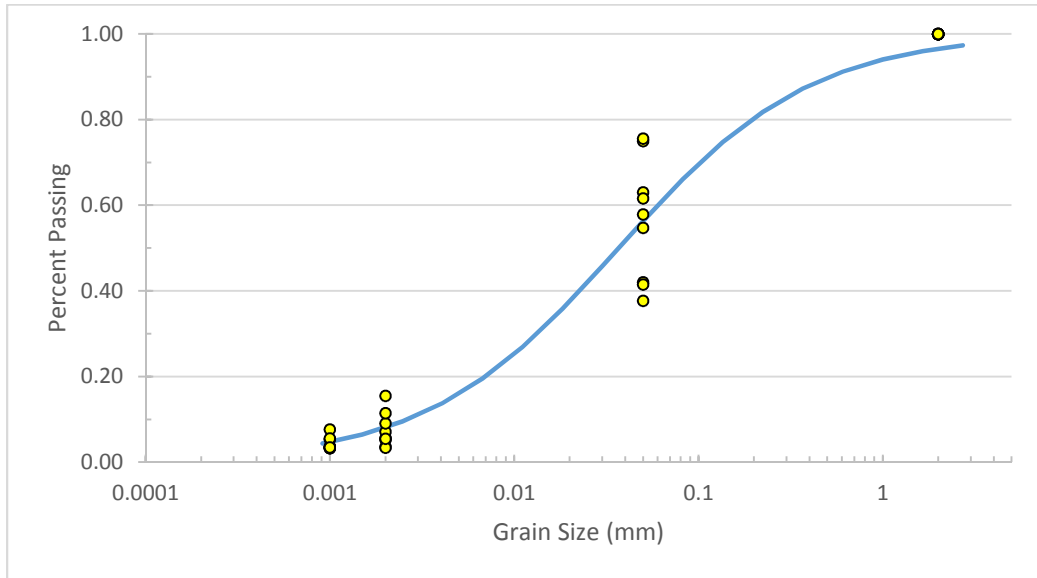


Figure 9: Soil Gradation Curve for Samples Obtained at Barton Springs at Lost Creek Boulevard

The yellow dots represent the laboratory estimate of the percent of sediment that can pass through each of the four particle sizes. Thus, for these Barton Creek samples, the fitted distribution curve estimates that approximately 95% of the sediment can pass through a sieve of 2.0 mm. On the other end of the distribution curve, about 5% of the sediment can pass through a sieve of 0.001 mm. The midpoint of the curve on the x-axis lies at about 0.0037 mm indicating that about 50% of the sediment can pass through a sieve of this size. The shape of the curve is determined by the curve parameter, k . For this site, the distribution curve of the sediment had a k of 0.83. Smaller k values indicate flatter curves, and subsequently, a more well graded sediment.

The logistic curves were developed for each site by adjusting values of k (the shape factor) and x_{mid} (the midpoint of the logistic curve) based on the data (Grain size and percent passing) collected at each site and utilizing the hybrid approach discussed in the Methods Section. Table 9 lists the logistic curve parameters for all of the sites.

Table 9: Estimates of the Parameter Values for the Sediment Gradation Curve at each Site

Creek and Site Sample #	Midpoint, x_{mid} (mm)	Shape factor, k
BAR 48	0.052	0.69
BAR 51	0.037	0.83
BAR 53	0.019	0.60
BAR 1233	0.015	0.66
BAR 1240	0.043	0.82
BAR 1270	0.064	1.25
BAR 13447	0.096	0.79
HRP 484	0.052	0.68
HRP 844	0.037	0.66
HRP 5810	0.015	0.59
SHL 117	0.049	0.74
SHL 118	0.063	0.68
SHL 122	0.067	1.51
SHL 336	0.061	1.21
SHL 621	0.088	2.01
SHL 5811	0.065	0.57
WLR 38	0.079	1.95
WLR 780	0.024	0.56
WLR 1324	0.091	2.07
WLR 2738	0.074	1.40
WLR 2739	0.087	2.21

The parameter values across all of the sites are fairly consistent with the midpoint for the logistic curve ranging between 0.015 mm (BAR #1233 and HRP #5810) and 0.096 mm (BAR #13447). The shape factor, k , consisted of a greater range with the most well graded sediment at WLR 780 ($k = 0.56$) and the most poorly graded soil at WLR #2739 ($k = 2.21$). Figure 10 illustrates the impact of the range of the shape factors on the curve using sites WLR #2739 and HRP #5810. WLR #2739 had large x_{mid} and k values, while HRP #5810 had small x_{mid} and k values. It should be noted that the data and the resulting curve are rough representations of the grain size and its distribution. Better curve fitting can be accomplished with additional soil size categories.

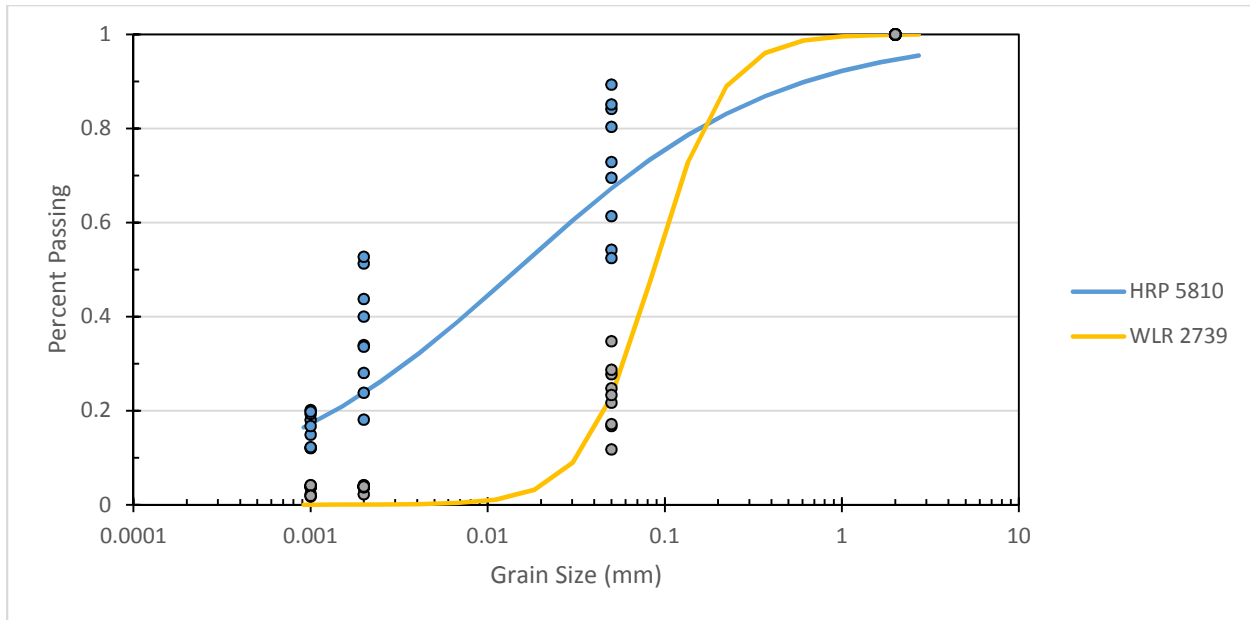


Figure 10: Soil Gradation Curves for Harper's Branch at Parker Park and Waller Creek at Hemphill Tributary

This information on grain size distribution provides an independent set of parameters on which to characterize the grain sizes. Rather than examine grain size as a set of dependent parameters¹, data on total PAH concentration was investigated to determine if it was a function of these two independent set of parameters. A linear model was developed to determine whether k , the shape factor, and x_{mid} , the midpoint of the curve, was a factor in the total PAH concentration. Based on a these preliminary results, it appears as if x_{mid} , was the only significant factor. Figure 11 shows the results of this model with the factor k removed from the plot.

¹ Using the four soil groups (clay, silt, sand, and gravel) as covariates in explaining PAH concentrations will result in at least one covariate dependent on another. As an example, as percent clay goes up, percent sand will go down.

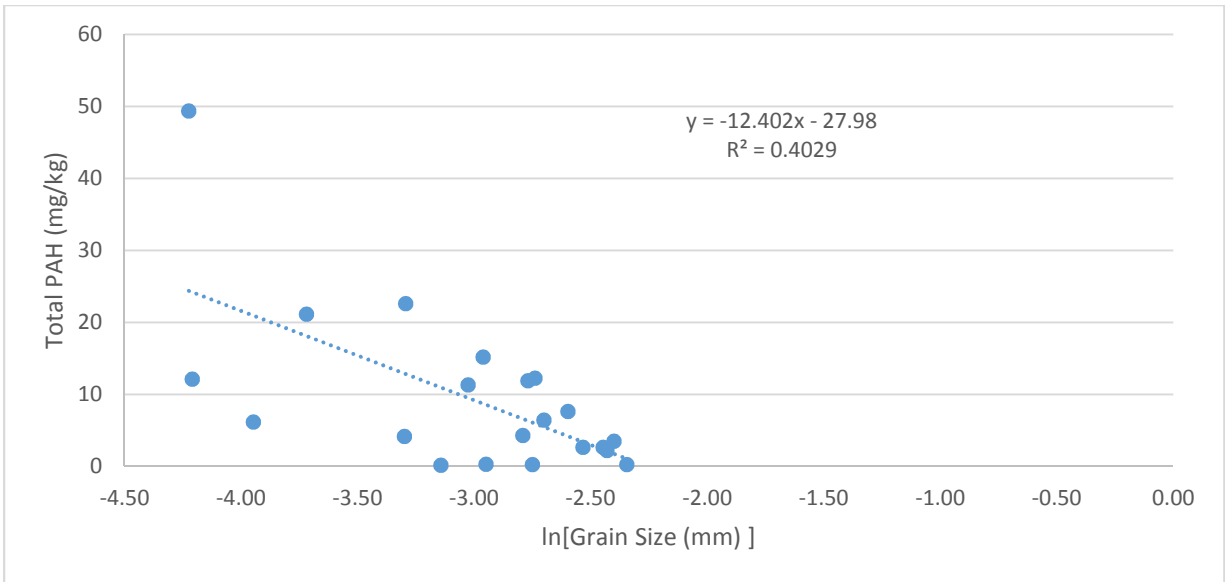


Figure 11: Plot and linear regression model of x_{mid} parameter values versus the total PAH for each site

The model indicates that as the grain size of the midpoint gets smaller, the total PAH gets larger. Thus, having more silt and clay in a sample (or stream bed) may be an environmental condition that would allow retention of more PAH. This model indicates that the midpoint of the curve distribution explains about 40% of the variability, and this can be considered a fair to good fit of the data.

Recommendations

Additional sampling is recommended at sites which had detections of PAH, but were limited to three samples. A minimum of six additional samples at each of these sites (over the course of several months) is proposed to reduce the uncertainty (i.e. the confidence intervals) of the mean concentration at the site.

Longitudinal sampling at more closely-spaced intervals at sites of interest within the watershed is recommended in order to determine the extent of, and possible sources of, PAH contamination at those sites with significantly higher levels of PAH. Specifically, additional samples need to be collected over the area from just upstream of Barton Springs Pool, to Barton Creek at Spyglass Road; just upstream of the pond at Parker Park in Harper's Branch; the upper half of the Shoal watershed including just upstream of the convergence with the tributary at Crestmont Park; and the upper half of the Waller watershed including just upstream of the convergence with the Hemphill Tributary.

Finally, it is recommended that once the first two recommendations are implemented, a regular monitoring program is initiated over the course of a year to determine the dynamics of the pollutant transport. The monitoring program can be developed to see if PAH concentrations at these select locations are aggrading, degrading, or remaining constant over time. Sites that are recommended for this additional sampling include:

- BAR 53 (Barton Creek upstream Barton Springs)
- BAR 1223 (Barton Creek at Spyglass)
- HRP 5810 (Harper's Branch Trib at Parker Park)
- SHL 122 (Shoal Creek upstream of 1st St)
- SHL 5811 (Shoal Trib at Crestmont Park)
- SHL 117 (Shoal Creek Downstream of Cross Creek)
- WLR 2738 (Waller Creek downstream of 26th Street)
- WLR 780 (Waller Creek at 51st Street)

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