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## **Polycyclic Aromatic Hydrocarbon Monitoring through 2016: Ten Years after the Coal Tar Sealant Ban**

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### **Abstract**

*Polycyclic Aromatic Hydrocarbons (PAH) are a group of chemicals consisting of three or more fused benzene rings. Many of this group of compounds are considered toxic and listed as Priority Pollutants by the EPA. In 2006, the City of Austin enacted a ban on coal-tar sealant to remove a source of PAH contamination to Austin creeks and reservoirs. Sediment samples collected from 13 site locations where the concentration of PAH have historically been above the Probable Effect Concentration (above which adverse effects on aquatic organisms are expected to occur) were analyzed for this report. The total PAH concentration of these samples was calculated as the sum of the 16 compounds found within the first EPA Priority Pollutant list. LOESS regression analysis was used to determine any temporal trends at the locations. The concentration of Total PAH has decreased at 6 sites to a level that is below the Probable Effect Concentration, decreased at 3 sites that still remain a concern due to lack of confidence, and remain high at 4 site locations. The 7 sites where the concentration of PAH remains a concern require additional investigation to isolate and remediate sources of PAH.*

### **Introduction**

Polycyclic Aromatic Hydrocarbons (PAHs) 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 the different PAH. These compounds are currently on the Toxic Pollutants and Priority Pollutants lists of the Code of Federal Regulations in 40 CFR 401.15 and 40 CFR 423 Appendix A, respectively. PAH are considered Toxic Pollutants because they persist in the environment; several are toxic, carcinogenic, mutagenic, and/or teratogenic (causing birth defects) to aquatic life; and seven are probable human carcinogens (US EPA 2015).

PAH are able to persist in the environment because they generally have a high affinity to sediment, low volatility, and a high resistance to biodegradation (McElroy et al. 1989). These compounds are hydrophobic and tend to sorb to particulates in the water column, eventually settling to the substrate of water bodies as sediment. Concentrations in the sediment tend to be much higher than concentrations in the water column due to the low solubility of PAH (Moore and Ramamoorthy 1984). The solubility

decreases as molecular weight increases, so PAH with 4 or more rings (heavier) are likely to sorb to sediments more than the PAH with 2 or 3 rings. PAH with 2 or 3 rings can readily volatilize while PAH with 4 or more rings show limited volatilization under many environmental conditions (Moore and Ramamoorthy 1984). The main source of decomposition of PAH in sediments is microbial degradation (Cerniglia 1992). Lower molecular weight PAH can be degraded readily under aerobic and anaerobic conditions while higher molecular weight PAH are more resistant (Mrozik et al. 2003, Leduc et al. 1992, Cerniglia 1992). However, bacteria do exist that are known to degrade higher molecular weight PAH at slower rates (Krivobok et al. 2003). It has also been shown that PAH introduced into a pristine system may not be degraded at first; however, microorganism communities can develop over time in a polluted site that can degrade both high and low molecular weight PAH (Coates et al. 1997). Thus, if sources of PAH contamination can be eliminated the concentration of PAH can return to a background level given enough time.

PAH are formed whenever carbon-based compounds experience incomplete combustion. This can occur naturally from combustion of organic matter. However, natural sources are not thought to make significant contributions to the concentration of PAH in modern urban environments (Sims and Overcash 1983, Wild and Jones 1995). Problems tend to occur in urban environments where the concentration of PAH is higher due to an increased number of anthropogenic sources (Stout et al. 2004). Major anthropogenic sources include the combustion of fossil fuels in heat and power generation, gasoline-based vehicle emissions, and waste incineration (Ramdahl et al. 1983, Wild and Jones 1995).

Due to the abundance of compounds classified as PAH and the fact that these compounds are typically found in groups, there exist over 100 known combinations of PAH. The most common grouping that is evaluated for regulatory purposes is the EPA Priority Pollutant list of 15 PAH (acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, ideno(1,2,3-cd)pyrene, phenanthrene, and pyrene) with one bicyclic aromatic hydrocarbon (naphthalene). The sum of the 16 EPA Priority Pollutant PAH concentrations is denoted the total PAH (TPAH) concentration. Sediments with a TPAH concentration above 20 mg/kg are considered to occur at a level above urban background (Stout et al. 2004). In addition, harmful effects are expected to occur on bottom-dwelling biota when sediments contain 22.8 mg/kg TPAH, the Probable Effect Concentration (PEC), although toxic effects for individual components of PAH are as low as 1.6 mg/kg (MacDonald et al. 2000).

Research conducted by the US Geological Survey (USGS) has identified coal tar-based pavement sealant as a significant anthropogenic source of PAH (Mahler et al. 2005, Mahler and Van Metre 2011). Pavement sealant is a coal tar- or asphalt-based black liquid sprayed on asphalt pavements, primarily parking lots. Once dry, the sealant binds to the surface layer and may slow the wear and degradation of the asphalt to prolong its useful life. Coal tar-based sealants contain about 20 to 35 percent coal tar pitch which is 50% or more PAH by weight and a known human carcinogen (Mahler and Van Metre 2011, US Department of Human Health Services 2011). During a 2007-08 study by USGS, dust collected from parking lots sealed with a coal tar-based sealant had a median PAH concentration of 2,200 mg/kg while dust collected from parking lots that used an asphalt-based sealant had a median PAH concentration of 2.1 mg/kg (Mahler and Van Metre 2011). In a related study, the USGS collected sediment cores in 40 US lakes in order to determine sources of PAH in the sediment. Using the chemical “fingerprint” of PAH the USGS was able to show that coal tar-based sealant accounted for half of all PAH in the lakes (Van Metre and Mahler 2010). Concentrations in lakes contaminated by PAH from coal tar sealant were higher than the PEC while concentrations of PAH from other sources were not above this level.

The City of Austin (COA), in cooperation with the USGS, conducted several studies from 2000 to 2005 that examined concentrations and sources of PAH in creeks and lakes in Austin, Texas (Great Lakes

Environmental Center 2005, Mahler et al. 2005, Geismar 2000). The COA found that not only was coal tar sealant from parking lot run-off a source of contamination to the Austin waterways, but the PAH levels in some of the creeks were detrimental to aquatic life (Bryer et al. 2006, Bryer et al. 2010, Great Lakes Environmental Center 2005, Scoggins et al. 2007). Based on the information in these studies the COA enacted a ban on coal tar-based pavement sealant in 2006. The COA examined the level of PAH throughout Austin using data collected through 2010 in a previous report (Richter 2012). The majority of locations examined in this previous report were determined to contain non-toxic sediment (TPAH below the urban background concentration). Sediment from 13 locations consistently contained concentrations of PAH that were of concern (above the PEC) and it was recommended that these 13 locations continue to be monitored to determine if the concentration of PAH would decrease given more time. This report examines the concentration of PAH at these 13 locations through 2016.

## **Methods**

The COA has collected sediment samples near the mouths of creeks since 1996 as a component of the Environmental Integrity Index project (EII). Sampling of different watersheds was rotated every three years from 1996 to 2008 so that one sediment sample was collected for each Austin watershed every three years. In 2009, EII sampling frequency increased so that watersheds were sampled on a two year cycle.

In 2005, the COA began a project called PAH Specific Monitoring to monitor additional sites for PAH in sediment. This project was designed to annually monitor the sediment concentration of PAH at locations downstream of likely sources of PAH. Some of these site locations coincided with locations that were already being monitored through EII, thus data from both projects was used in analysis (Table 1, Figure 1).

Data from two additional COA projects was determined to be useful in analyzing trends for these site locations. Sediment samples were collected from Waller Creek at a pipe Upstream of 24<sup>th</sup> Street in 2003-2004 as a part of the Waller Creek Study, while sediment samples were collected from Harpers Branch at Woodland Avenue in late 2015 and early 2016 as a part of the Spatial Distribution of PAH/DDT in Sediment project.

For all sampling, composite samples were collected following the procedures outlined in the Water Resource Evaluation Standard Operating Procedures Manual (WRE SOP 2010). Samples were collected in glass jars, preserved on ice, and sent to DHL Analytical, a NELAP approved laboratory in Austin, Texas, for analysis. The TPAH was calculated for each sediment sample.

Table 1: Site location and project for sediment samples collected.

SITE LOCATION	PROJECT
Bull Creek at Loop 360 First Crossing	EII/PAH Monitoring
Buttermilk Creek at Little Walnut Creek	EII/PAH Monitoring
Carson Creek at US 183	PAH Monitoring
Dry Creek (North) at Highland Pass	PAH Monitoring
Eanes Creek at Camp Craft Road	EII/PAH Monitoring
East Bouldin Creek Downstream of W. Alpine Rd.	PAH Monitoring
East Bouldin Creek at Elizabeth St.	PAH Monitoring
East Bouldin Creek at Post Oak	EII/PAH Monitoring
Harpers Branch Creek at Woodland Ave	EII/PAH Monitoring & Distribution
Little Walnut Creek at Golden Meadow Rd	PAH Monitoring
Taylor Slough North at Pecos St (TSN)	EII/ PAH Monitoring
Waller Creek at Pipe Upstream of 24 <sup>th</sup> Street	PAH Monitoring/Waller Creek Study
Walnut Creek Downstream of Metric Blvd	PAH Monitoring

In order to assess and possibly mitigate the concentrations of PAH at locations it is necessary to determine the source of the PAH. Source classification was evaluated using PAH ratio thresholds introduced by Yunker et al. (2002). These thresholds are:

1. Ratios of anthracene to anthracene plus phenanthrene (An/An+Ph) less than 0.1 likely indicate petroleum sources while ratios above 0.1 likely indicate combustion sources.
2. Ratios of fluoranthene to fluoranthene plus pyrene (Fl/Fl+P) less than 0.4 likely indicate petroleum sources while ratios between 0.4 and 0.5 likely indicate liquid fossil fuel combustion and ratios greater than 0.5 are characteristic of grass, wood, or coal combustion.
3. Ratios of indeno(1,2,3-cd)pyrene to indeno(1,2,3-cd)pyrene plus benzo(ghi)perylene (IP/IP+BPe) less than 0.2 likely indicate petroleum sources while ratios between 0.2 and 0.5 likely indicate liquid fossil fuel combustion and ratios greater than 0.5 are characteristic of grass, wood, and coal combustion.
4. Ratios of benzo(a)anthracene to benzo(a)anthracene plus chrysene (BaA/BaA+Chr) less than 0.2 likely indicate petroleum sources while ratios between 0.2 and 0.35 likely indicate a mix of petroleum and combustion sources and ratios greater than 0.35 are characteristic of combustion.

Additionally, the ratio of benzo(a)pyrene to benzo(a)pyrene plus benzo(e)pyrene was used in this project analysis (Ahrens and Depree 2010). These ratios have become important tools for identification of PAH sources. Tobiszewski and Namieśnik (2012) discussed many cases where diagnostic ratios were used to correctly identify pollution sources of PAH but also advocate for caution when making inferences about sources because of the non-conservative fate of PAH in the environment along with the intrasource variability and intersource similarity of the ratios. Ratios were coupled with percent composition to assess likely sources of pollution in an attempt to limit poor inferences.

Tracking sites where the sediments were polluted with coal tar is of special interest to the COA to determine how long sediments might continue to contain high levels of PAH after the citywide ban of coal tar sealant. In 2014, the USGS released a paper where they examined sediment from Lady Bird Lake, a major receiving water body for urban runoff in Austin. The USGS found that since the ban, concentrations of PAH in the lake have decreased but that coal tar is still a large portion of the pollution in Austin sediments (Van Metre and Mahler 2014). In regards to the above ratios, it is important to note that coal tar ratios are typically high and fall into the ranges of combustion sources.

Following source classification, Locally Weighted Regression (LOESS) was used to statistically analyze temporal trends in the concentration of TPAH at each location. LOESS is a non-parametric technique that produces a weighted least squares fit to neighborhoods of data which was introduced by Cleveland (1979). Data points are considered to be in a neighborhood if they are close together for some variable. In our analysis data points are neighbors if they are collected close together temporally. The size of the neighborhoods of data, or the fraction of the data points present in each neighborhood, must be determined by the analyst. The size of the neighborhoods is determined by the smoothing parameter and in this analysis the improved Akaike Information Criterion ( $AIC_C$ ) was used to determine the appropriate smoothing parameter for each location. There are many tools to determine the smoothing parameter for LOESS regression but the  $AIC_C$  was chosen because it has been shown to be a competitive predictor when other methods work well in choosing appropriate smoothing parameters and also performs well when other methods fail to choose an appropriate smoothing parameter (Hurvich and Simonoff 1998). Models were run using smoothing parameters ranging from 0 to 1 changing by 0.1 each run. A smoothing parameter of 0.9 produced the best fit model for each location according to the  $AIC_C$ . Confidence limits (95%) of the predicted trend line were also computed at each location. Additional analyses not shown in this report included a temporal trend evaluation of total organic carbon (TOC) concentrations and grain size distribution of sediment at each location. No trends were noted in either grain size distribution or TOC with the exception of a decreasing trend over time for TOC concentrations in Little Walnut Creek at Golden Meadow Rd.

## Results

### PAH Source

An/An+Ph, Fl/Fl+P, IP/IP+BPe, and BaA/BaA+Chr ratios for every location were combined into a single graph for evaluation (Figure 2). Ratios of PAH do not vary greatly between locations; however, ratios of An/An+Ph for samples collected at Taylor Slough North at Pecos and Waller Creek at Pipe Upstream of 24<sup>th</sup> Street ranged from under 0.1, indicating petroleum sources, to well over 0.1, indicating combustion sources, while the other locations contained samples with An/An+Ph ratios that were near 0.1 or above, indicative of combustion sources. The ratio of Fl/Fl+P and BaA/BaA+Chr at all sites were almost always above 0.5 and 0.35, respectively, indicating combustion sources. IP/IP+BPe ratios at all sites were mostly near but below 0.5, indicating petroleum combustion.

Reported ratios of coal tar or coal tar pavement samples range from 0.18-0.29, 0.48-0.58, 0.50-0.60, and 0.51-0.69 for An/An+Ph, Fl/Fl+P, IP/IP+BPe, and BaA/BaA+Chr, respectively (Yunker et al. 2002, Wise et al. 1988, Ahrens and Depree 2010). Sediment samples collected at project locations have typically contained Fl/Fl+P ratios within the coal tar ranges but have contained ratios of An/An+Ph, IP/IP+BPe, and BaA/BaA+Chr that are typically lower than the coal tar ranges. In fact, a large number of samples contained An/An+Ph, IP/IP+BPe, and BaA/BaA+Chr ratios within a range that was more indicative of asphalt pavement sources (0.05-0.28, 0.12-0.47, and 0.16-0.39, respectively) (Ahrens and Depree 2010).

Ahrens and Depree (2010) found that samples of road pavement containing coal tar had a higher percent composition of phenanthrene, fluoranthene, and pyrene with relatively high concentrations of benzo(a)anthracene, benzo(a)pyrene, and indeno(1,2,3-cd)pyrene, while samples of pavement containing asphalt had a higher percent composition of methyl-phenanthrenes, chrysene, benzo(e)pyrene, and benzo(g,h,i)perylene. Findings of Yunker et al. (2002) were consistent with the above. Petrogenic sources (i.e. asphalt) were dominated by alkylated phenanthrenes (such as methyl-phenanthrene) and more stable PAH isomers, such as chrysene, benzo(e)pyrene, or benzo(g,h,i)perylene. Pyrogenic sources (i.e. coal tar) were dominated by phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, benzo(a)pyrene, and indeno(1,2,3-cd)pyrene. The composition of PAH collected at these locations indicated that fluoranthene and pyrene made up the largest percentage of TPAH but samples also contained a large percentage of chrysene (Figure 3).

PAH in sediment are often from a mixture of sources, especially in urban environments. If sediment pollution is occurring from multiple sources then it would follow that the composition of PAH in sediment samples would not match a single pollution source but be more consistent with a composition of PAH from a mixture of those sources. Ahrens and Depree (2010) realized this phenomena and created a simple mixing model using “pure” coal tar and asphalt as the two end points of the mixture model. Ratios of BaA/BaA+Chr, IP/IP+BPe, and benzo(a)pyrene/benzo(a)pyrene plus benzo(e)pyrene (BaP/BaP+BeP) were modeled because the authors noted that these three diagnostic ratios showed the greatest differentiation between asphalt and coal tar samples. End points from this mixing model were plotted against data collected from this project (Figure 4A-C). IP/IP+BPe plotted against BaA/BaA+Chr in the mixing model showed an almost linear relationship between two end points while samples collected in this project were not consistent with this linear relationship (Figure 4A). Larger proportions of chrysene in project samples most likely drive the ratios of BaA/BaA+Chr down. BaP/BaP+BeP plotted against BaA/BaA+Chr and BaP/BaP+BeP plotted against IP/IP+BPe in the mixing model showed relationships that were close to linear but incorporated a slight curvature. Samples collected in this project were more consistent with the mixing model relationships of BaP/BaP+BeP against BaA/BaA+Chr and BaP/BaP+BeP against IP/IP+BPe (Figure 4B-C). In all three plots, samples collected for this project were much closer to the coal tar end point of the mixing model.

Based on these results, it is likely that coal tar is still a major source for sediment pollution for the locations in this project. This would be consistent with the most up-to-date analysis for sediment collected in Lady Bird Lake, a receiving water for much of the urban runoff of Austin, TX, by the USGS which concluded that coal tar was still a major source of contamination in the lake sediments (Van Metre and Mahler 2014).

#### Temporal Trends

Concentrations of TPAH in Bull Creek at Loop 360 First Crossing, Carson Creek at US 183, Taylor Slough North at Pecos St. (TSN), and Walnut Creek Downstream of Metric Blvd. have decreased to well under the urban background level in samples collected since 2011 (Figure 5). Concentrations of PAH in Eanes Creek at Camp Craft Road and Waller Creek at Pipe Upstream of 24<sup>th</sup> Street indicate some decrease over time; however, the concentrations remained at a level of concern (Figure 6). The predicted trend line for TPAH in 2016 was close to the urban background in Eanes Creek and just below the PEC threshold in Waller Creek. The variability over time at these two locations was large which led to large confidence limits with upper values well over the PEC in 2016. This indicates that concentrations of PAH in samples collected at these two locations are not consistently below the PEC.

Concentrations of TPAH collected in East Bouldin Creek showed different trends over time dependent on location. Concentrations were consistently above the PEC and showed no trend over time downstream of W. Alpine (Figure 7A), while concentrations decreased to levels below the urban background threshold at Elizabeth Street and Post Oak (Figure 7B-C).

Concentrations of TPAH in Buttermilk Creek, Dry Creek (North), Harper’s Branch, and Little Walnut Creek are more complex than the above locations (Figure 8). Concentrations of TPAH in Buttermilk Creek at Little Walnut Creek showed no trend over time with large temporal variability (Figure 8A). Three sediment samples collected from the Buttermilk Creek location contained PAH at a level above the urban background threshold and the upper confidence limit was above the PEC in 2016. This indicates that concentrations of TPAH at this location could possibly be above the PEC but are not consistently above the PEC. Concentrations of TPAH in Dry Creek (North) at Highland Pass have decreased in the most recent years of sampling but a high concentration from a sample collected in 2013 raises some concern about availability of pollutants in the surrounding landscape (Figure 8B). Concentrations in Harper’s Branch at Woodland Ave. have decreased substantially in recent samples but still remain at a

level close to the urban background and PEC thresholds (Figure 8C). It is unclear if this downward trend will continue. Finally, concentrations of TPAH in Little Walnut Creek at Golden Meadow Rd. have not shown a trend over time in the last five years of sampling and the upper confidence limit in 2016 is above the PEC (Figure 8D). In addition, the TOC concentrations in sediment samples collected in Little Walnut at Golden Meadow Rd. have shown decreasing trends over time (not shown). As PAH strongly bind to organic carbon in sediment, it is unclear if the pollutant load at this location is lower than it was prior to 2012 or if the concentrations are lower due to a decrease in TOC.

## Conclusions

Sediment pollution at all 13 locations seems to be related to combustion sources with one likely candidate being coal tar. Thus, 10 years after a ban on coal tar-based pavement sealant, sediments in Austin, TX, are still impacted by coal tar-based products. However, at six locations the concentration of TPAH has decreased to a level below the PEC. Specifically, concentrations of TPAH in Bull Creek at Loop 360 First Crossing, Carson Creek at US 183, East Bouldin Creek at Elizabeth St., East Bouldin Creek at Post Oak, Taylor Slough North at Pecos St., and Walnut Creek Downstream of Metric Blvd. have decreased to levels which are typical of background in urban areas and are not expected to negatively impact sediment biota. It may be that sediments at these locations are still being impacted by old infrastructure where coal tar products were employed, but as time has passed since the ban, less coal tar product is contributed to sediment pollution and the overall concentrations of PAH in sediment has decreased as a result.

It is likely that the TPAH in Buttermilk Creek at Little Walnut Creek and Dry Creek (North) at Highland Pass are also below the level of concern, however inferences are not as strong in these two creeks. Variability and lack of a trend for TPAH in Buttermilk Creek at Little Walnut Creek does not inspire confidence that the TPAH will consistently be below the PEC in subsequent sampling at this location. TPAH in Dry Creek (North) at Highland Pass have been low in recent years with one exception in which the concentration of TPAH was above 50 mg/kg. This sample introduces some uncertainty to what a typical concentration is for TPAH at this site. More frequent sampling of these two site locations would improve inferences about the typical concentration of PAH present.

While increased sampling may be all that is necessary to increase confidence about TPAH present at the Buttermilk Dry Creek (North) locations, an altered sampling plan may be needed in Little Walnut Creek at Golden Meadow Rd. to fully understand the trend of PAH. Concentrations of TPAH show a decrease from early sampling but are still fairly likely to be above the urban background level and the PEC. The fact that the trend of TPAH is coupled to the negative trend of TOC at this location is also problematic. It is unclear if sources of PAH have decreased or if the concentration of TPAH has just decreased because TOC has decreased, which could happen simply due to a decreased sediment load.

Concentrations of TPAH within this project have typically been the highest in Waller Creek at Pipe Upstream of 24<sup>th</sup> St., East Bouldin Creek Downstream of W. Alpine Rd., Harpers Branch at Woodland Ave., and Eanes Creek at Camp Craft Rd. More recent samples taken from Harpers Branch at Woodland Ave. have shown a decrease in TPAH but concentrations remain at a level of concern. Ponds have been noticed upstream of the locations in Harpers Branch and East Bouldin Creek through visual inspection of aerials in ArcGIS along with personal confirmation from staff conducting monitoring events. Sediments collected from the pond upstream of the Harpers Branch location have indicated that total PAH in the pond is well above the PEC. It may be that each pond is holding toxic sediments which are being flushed out in small increments during storm events. Sediment samples should be collected in the pond above East Bouldin Creek at W. Alpine Rd. to determine if high concentrations of TPAH are present. Stormwater runoff contributing to each pond should be sampled to determine if current runoff is contributing to the concentration of PAH or if the source is primarily historic sediments. If concentrations of PAH are elevated in stormwater runoff, then sources and resolutions should be

investigated. If concentrations of PAH in current stormwater runoff is determined to be low, then remediation of the sediments present in each pond should be implemented.

It is unclear why samples collected in Eanes Creek at Camp Craft Rd. and Waller Creek at Pipe Upstream of 24<sup>th</sup> St. continue to have TPAH at such high concentrations. A large amount of the land contributing to Eanes Creek above Camp Craft Rd. is within the jurisdiction of the City of Westlake Hills, which is outside of the area impacted by the official COA ban on coal tar sealants. Waller Creek at Pipe Upstream of 24<sup>th</sup> St. is located within the University of Texas campus (UT) which is regulated by the State of Texas and the land immediately contributing to this site would not be subject to the COA ban either. In addition, there are a number of pipes coming from UT contributing to the drainage above this site location. Any inference to the source of pollution at these two site locations would be speculative and more intensive follow up is required to determine why the concentrations of TPAH remain high.

## **Recommendations**

- Discontinue sampling in Bull Creek at Loop 360 First Crossing, Carson Creek at US 183, East Bouldin Creek at Elizabeth St., East Bouldin Creek at Post Oak, Taylor Slough North at Pecos St., and Walnut Creek Downstream of Metric Blvd.
- Implement a more intensive sampling plan for Buttermilk Creek at Little Walnut Creek, Dry Creek (North) at Highland Pass, Little Walnut Creek at Golden Meadow Rd. in order to raise confidence that the concentration of TPAH is below a level of concern.
- Sample the ponds above Harpers Branch at Woodland Ave. and East Bouldin Creek at W. Alpine Rd. to determine concentrations of PAH within sediments. If high concentrations of PAH are present, stormwater samples of runoff to both ponds should be collected to determine if current runoff is contributing to the concentration of PAH or if historic sediments continue to release PAH. Stormwater controls and/or sediment remediation should be implemented where appropriate.
- Determine if COA has the capability to remediate pollution of PAH in Eanes Creek at Camp Craft Rd. or Waller Creek at Pipe Upstream of 24<sup>th</sup> St. through communication with UT and the City of Westlake Hills. Implement a more intensive plan to determine exact sources of contamination at these two locations.

## Figures

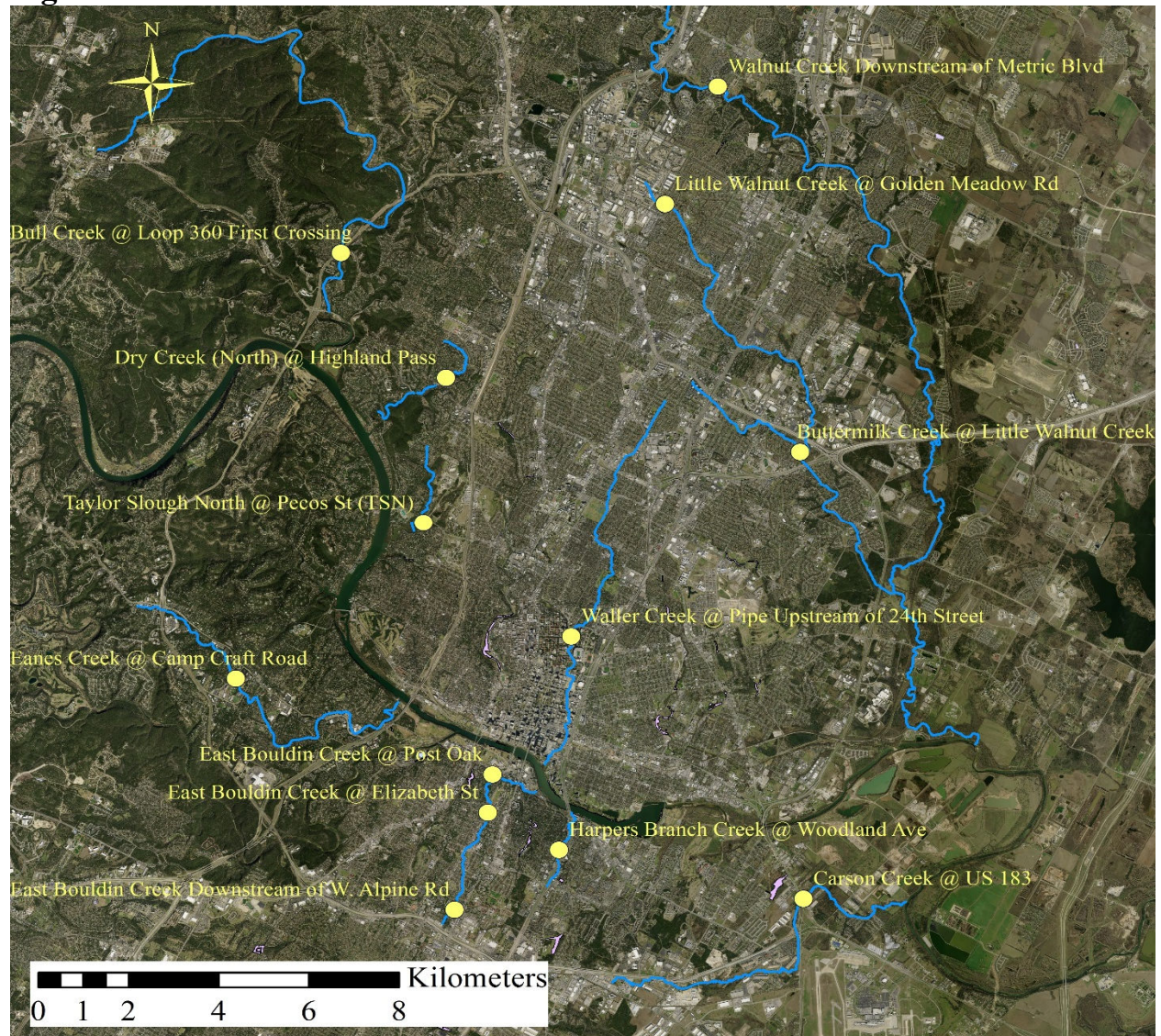


Figure 1: Monitoring locations of PAH.

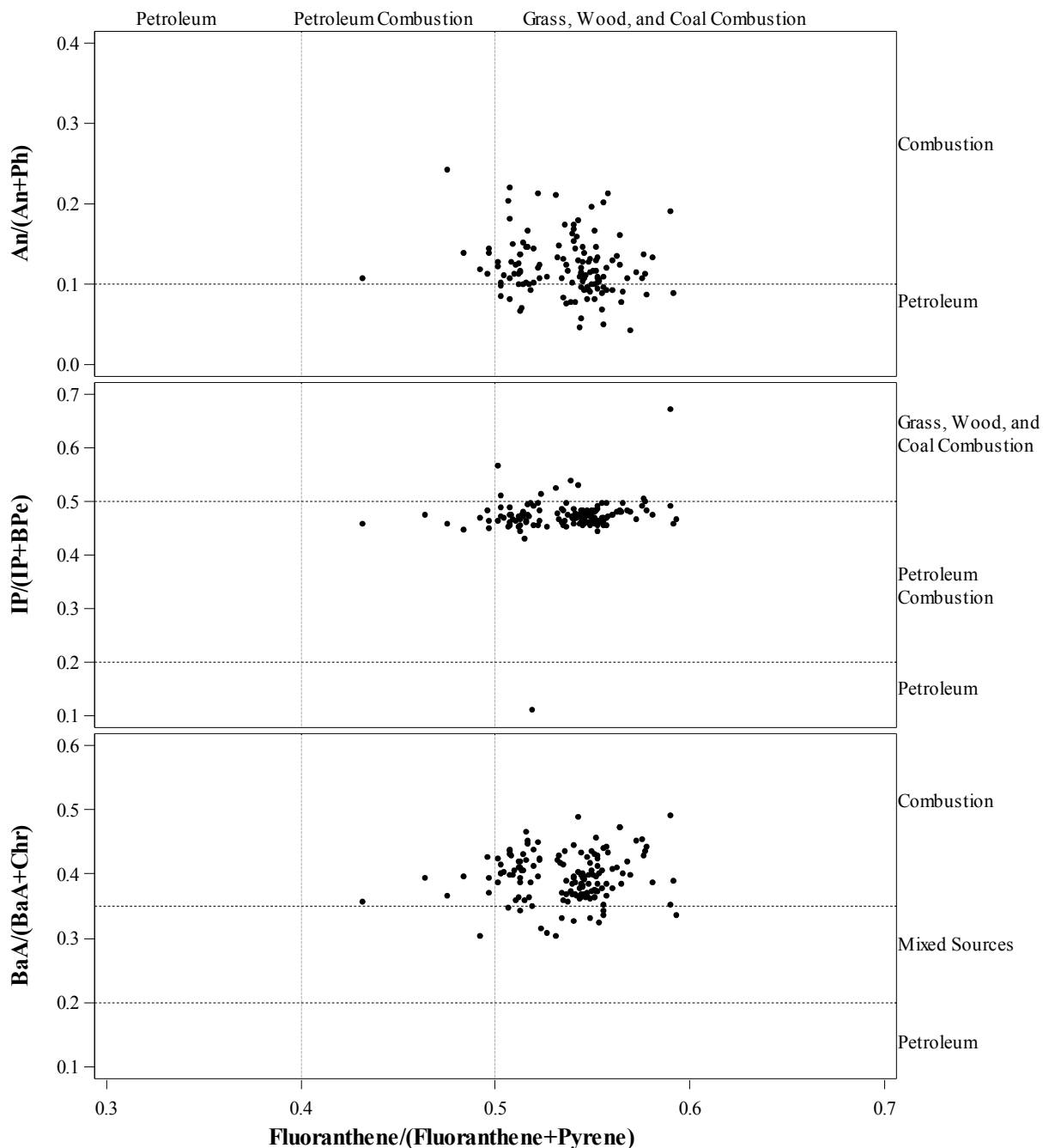


Figure 2: Ratios of PAH from sediment samples collected at all site locations compared to thresholds proposed by Yunkers et al. (2002) for categorizing the source of pollution. Ratios support ranges that indicate combustion sources. This does not exclude coal tar as a possible source. Abbreviations: An – anthracene, Ph – phenanthrene, IP – indeno(1,2,3-cd)pyrene, BPe – benzo(ghi)perylene, BaA – benzo(a)anthracene, Chr – chrysene.

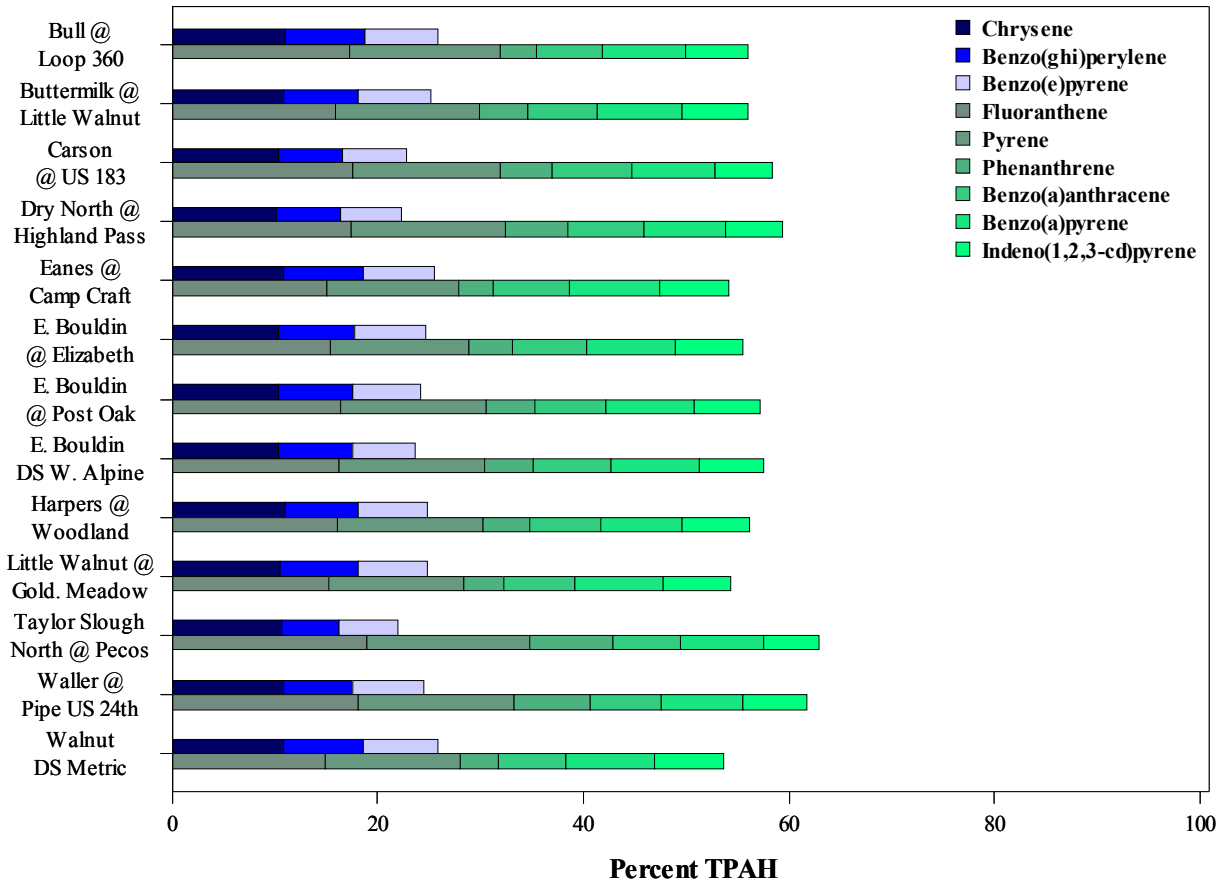


Figure 3: Average percent composition of chrysene, benzo(g,h,i)perylene, benzo(e)pyrene, fluoranthene, pyrene, phenanthrene, benzo(a)anthracene, benzo(a)pyrene, and indeno(1,2,3-cd)pyrene at each site. Note that total PAH was re-calculated when benzo(e)pyrene was present as this is not one of the standard 16 PAH used to compute total PAH. Petrogenic sources tend to have higher proportions of chrysene, benzo(g,h,i)perylene, and benzo(e)pyrene while pyrogenic sources tend to have higher proportions of the remaining PAH (Yunker et al. 2002, Ahrens and Depree 2010). Sediments at these locations tend to be dominated by fluoranthene, pyrene, and chrysene.

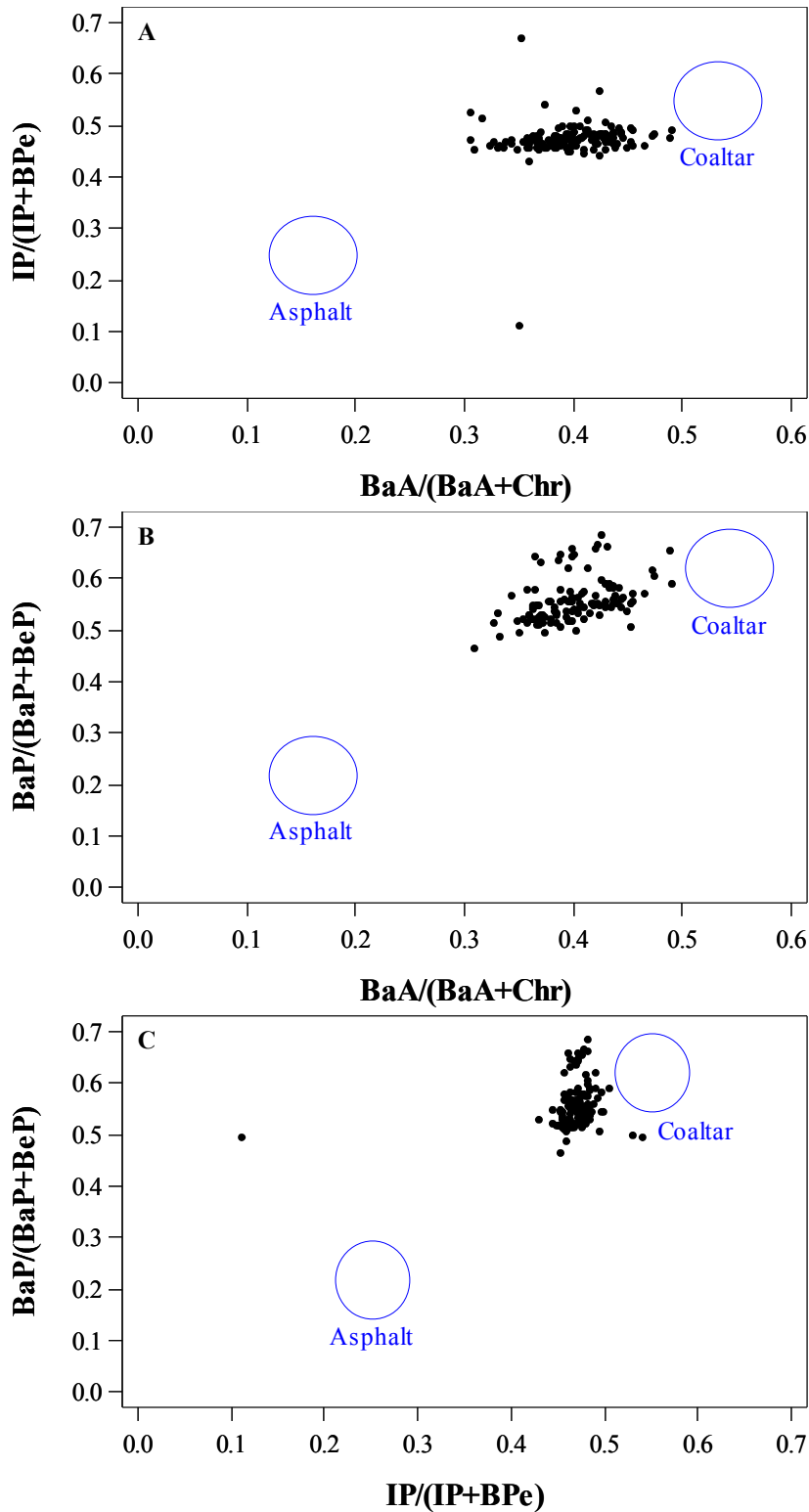


Figure 4: Ratios of PAH in sediment collected by COA compared to end points of a mixing model developed by Ahrens and Depree (2010). Ratios of sediment collected in this study are close to the end point of the mixing model which represents coal tar, thus it is likely that the sediments are slightly impacted by runoff from asphalt pavement but heavily influenced by runoff from coal tar pavements.

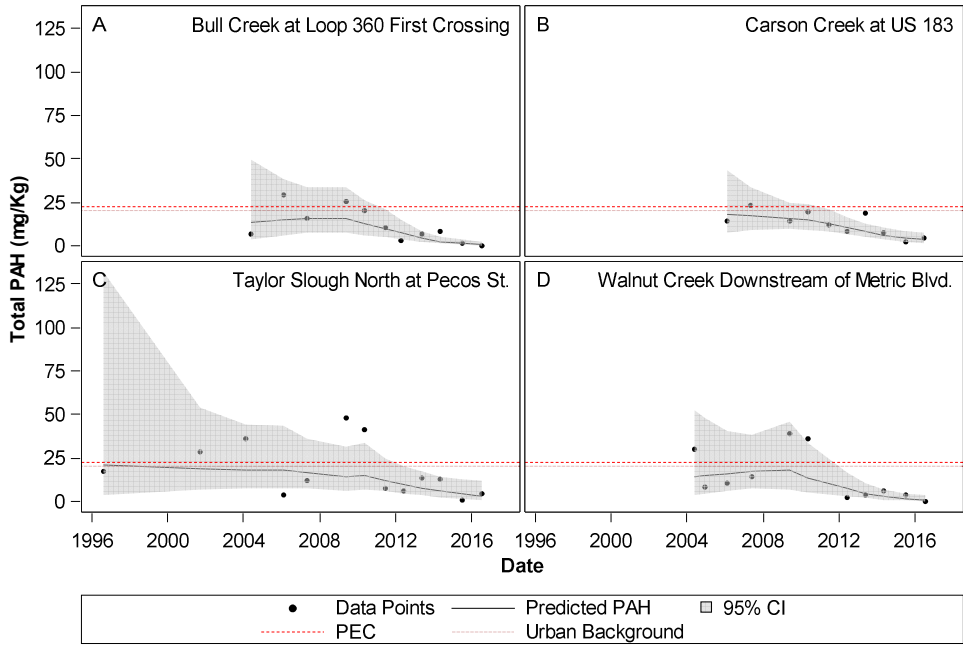


Figure 5: Total PAH (mg/kg) from sediment samples collected in A) Bull Creek at Loop 360 First Crossing, B) Carson Creek at US 183, C) Taylor Slough North at Pecos St., and D) Walnut Creek Downstream of Metric Blvd. Concentrations of Total PAH have decreased to a level below the urban background threshold (Stout et al. 2004).

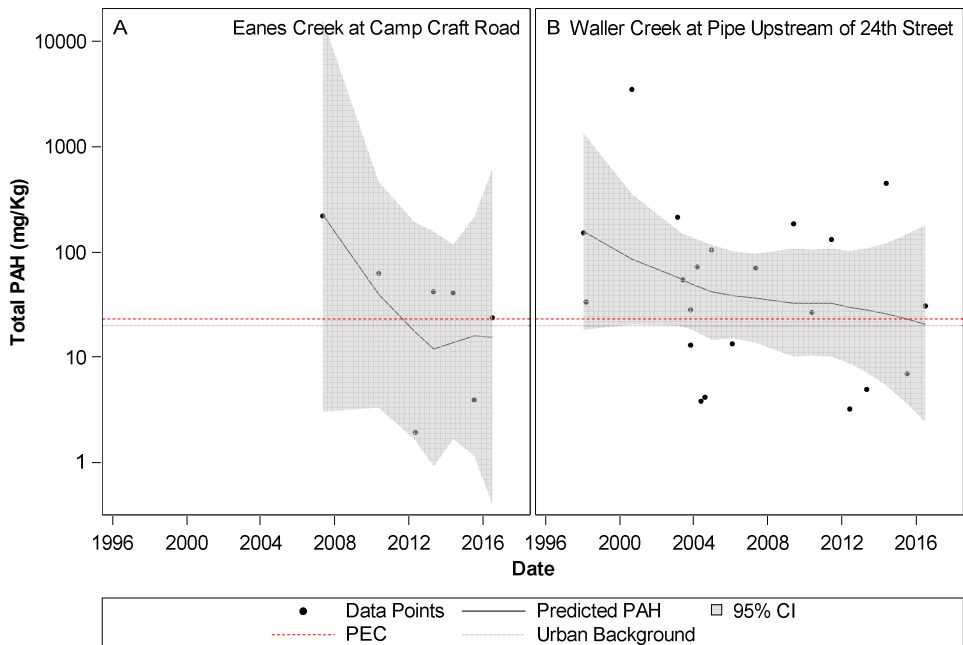


Figure 6: Total PAH (mg/kg) from sediment samples collected in A) Eanes Creek at Camp Craft Road and B) Waller Creek at Pipe Upstream of 24<sup>th</sup> Street. PAH at each location have been above the PEC (MacDonald et al. 2000) in the majority of samples collected. Concentrations remain at a level of concern even though there seems to a decreasing trend in the concentration of PAH at each location.

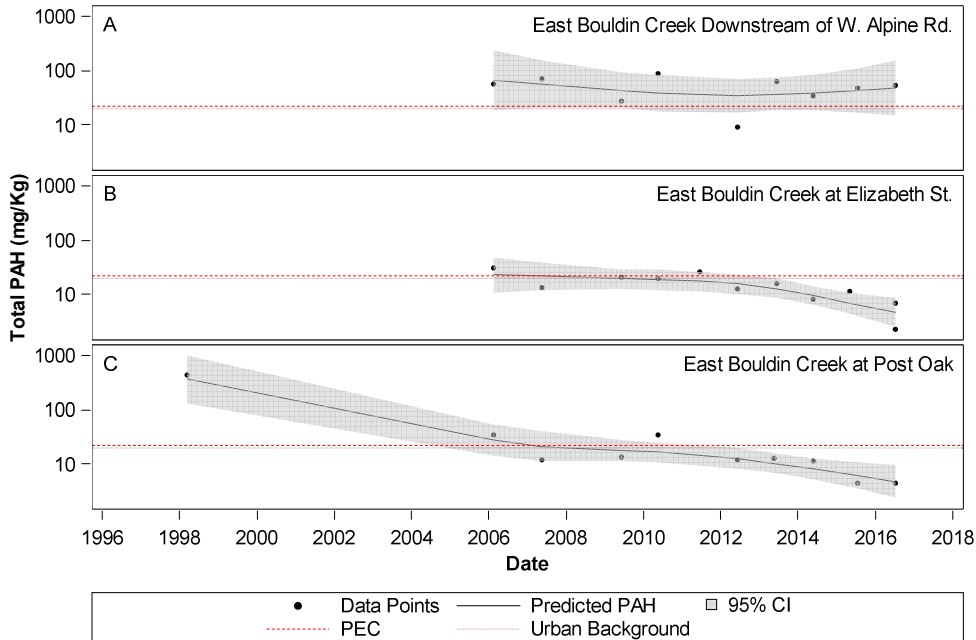


Figure 7: Total PAH (mg/kg) from sediment samples collected in A) East Bouldin Creek Downstream of W. Alpine Rd. (most upstream location), B) East Bouldin Creek at Elizabeth St., and C) East Bouldin Creek at Post Oak (most downstream location). Samples collected downstream of W. Alpine Rd. continue to contain concentrations of PAH above the PEC (MacDonald et al. 2000) while samples collected at Elizabeth St. and Post Oak have decreased to below the urban background threshold (Stout et al. 2004).

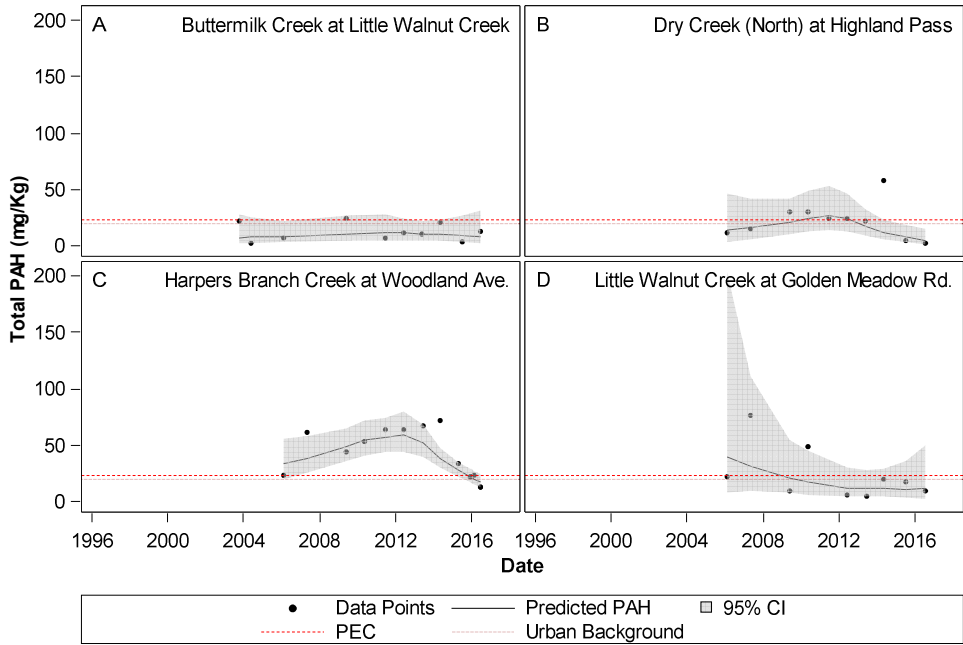


Figure 8: Total PAH (mg/kg) from sediment samples collected in A) Buttermilk Creek at Little Walnut Creek, B) Dry Creek (North) at Highland Pass, C) Harpers Branch Creek at Woodland Ave., and D) Little Walnut Creek at Golden Meadow Rd. Most recent samples collected from each location are below the urban background threshold (Stout et al. 2004) but this seems to be a more recent phenomena and confidence limits in 3 of the 4 sites are still above the PEC (MacDonald et al. 2000).

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