The Ozarks Environmental and Water Resources Institute (OEWRI)
Missouri State University (MSU)

Baseline Study of PAH Sources and Concentrations in Pond and Stream Sediments, Springfield, Missouri

Dr. Robert T. Pavlowsky
Ozarks Environmental and Water Resources Institute,
Missouri State University
bobpavlowsky@missouristate.edu

Completed for: The City of Springfield

FINAL REPORT

October 30, 2012

OEWRI EDR-12-002

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

EXECUTIVE SUMMARY

Polycyclic aromatic hydrocarbons (PAHs) pose an environmental hazard and health concern in urban and industrial areas. While occurring naturally in the environment, the highest levels of PAHs occur in association with particulates from anthropogenic sources released by the ignition of petroleum products and wood, erosion of road asphalt surfaces, and degradation of parking lot sealants (Crane et al., 2010). From these sources they can enter urban streams by atmospheric deposition and storm water runoff, sometimes at levels high enough to contaminate downstream stream and pond sediments (Van Metre et al., 2000; Shi et al. 2005; Wilson et al., 2005; Hwang and Foster, 2006). Elevated levels of PAHs are believed to cause cancer, genetic damage, and newborn development problems in humans, and can negatively affect aquatic life in stream systems (ATSDR, 1995).

Recently published and peer-reviewed studies show the solution and erosion of coal-tar sealant coatings on parking lots may represent the primary contamination source of PAHs to urban streams (Mahler et al., 2005; Van Metre et al., 2009). The weathering or abrasion of coal-tar emulsions have been reported to produce contaminated sediment particles (i.e., "pavement dust") that are enriched in PAHs by 65 to 530 times those from asphalt-based sealcoat, unsealed asphalt, and concrete lots (Mahler et al., 2005 & 2010; Van Metre et al., 2009; Mahler et al., 2012). Given that the reapplication frequency for coal-tar sealants on parking lots is 3 to 5 years, coal-tar sealant sources can provide a steady, long-term source of PAHs to the environment. Although human health is beyond the scope of this study, human exposure to PAHs from coal-tar sources is a concern by government agencies. There is a relatively strong relationship between the presence of coal tar parking lots near a residence and the concentration of coal-tar related PAHs in house dust (Mahler et al., 2010). Non-dietary ingestion of B2 PAH carcinogens, particularly benzo[a]pyrene, in house dust by children is much larger in residences next to coal-tar sealed lots compared to unsealed lots and accidental uptake may exceed published doses via dietary ingestion (Williams et al., 2012).

The purpose of this study is to complete a baseline investigation of PAH sources and concentrations in urban stream and pond sediments in the City of Springfield, Missouri. The main question to be addressed by this study is: Are PAHs found in urban stream and pond sediments at concentrations high enough to raise environmental concerns, and if so, to what degree are coal-tar sealants the source of PAH contamination in the City of Springfield? Four specific objectives will be used to address this question: 1) Assess the degree of land use and sediment source influence on PAH concentrations in sediment samples collected from urban watersheds in Springfield; 2) Determine if coal-tar coated parking lots represent a significant source of PAHs to sediments and local waterways; 3) Determine if other sources of PAHs are responsible for the observed sediment contamination patterns in addition to coal-tar parking lots;

and 4) Evaluate the implications of the findings relative to waters in the Springfield area that have been designated as biologically impaired due to unknown toxicity.

A watershed-based approach is used here to evaluate PAH presence and sources in stream and pond sediments from within and outside the City of Springfield. The methods used involve: (i) sediment sampling at different locations in the channel network including downstream areas as well as points immediately below parking lots; (ii) GIS data analysis to determine watershed characteristics, sampling locations, and street and parking lot source mapping; and (iii) sedimentological and geochemical analysis of sediment samples to evaluate transport mobility and source.

For this study, 72 sediment samples were collected at 58 different sites including 14 duplicate samples. Sediment samples were collected from stream channels, storm water basins, wet ponds, and parking lots in the Springfield area in both urban and rural watersheds to evaluate the spatial variability of PAH contamination, sources, and transport patterns. Overall, 41 sites were located in urban areas within the city limits of Springfield (71% of all sites) and 9 sites were located in urban and suburban areas in Greene County. In addition, 8 rural area control sites were also sampled to determine natural PAH levels with 1 site located in Christian County and 7 sites located in Stone County. Sediment samples for PAH analysis were processed by OEWRI staff and were analyzed for USEPA's 16 Priority PAHs and 35 major and trace metals by certified commercial laboratories.

Urban sediments in Springfield contain PAH concentrations at levels of ecological concern. PAHs were detected in urban sediments at all 49 sites examined within the City of Springfield or in streams draining urban areas. Thirty six percent of the samples were in the threshold effect concentration (TEC) range for toxic effects on sediment dwelling organisms from 1,610 ug/kg to <22,800 ug/kg PAH_{16} and 51% were found to be in the toxic range, exceeding the probable effects concentration (PEC) of 22,800 ug/kg PAH_{16}. Twelve Springfield sites (25% of the total sampled) contain PAH_{16} concentrations exceeding 5x the PEC. All of these high PEC sites drain core urban areas that contain relatively large areas of roads and parking lots with a variety of surface characteristics including coal-tar sealants and mixed sealed and unsealed asphalt lots.

Large commercial and residential parking lots are a major source of PAHs to streams and ponds in Springfield. Sealed parking lots release pavement dusts and other PAH contaminated sediment particles at concentrations almost two orders of magnitude higher compared to unsealed asphalt and concrete parking lots. Sealed parking lots yielded sediment PAH_{16} concentrations that are 148 times higher than those found in sediments from concrete parking lots, 41 times higher than unsealed asphalt parking lots, and 2 times higher compared to mixed sealed and unsealed lots. In other words, unsealed asphalt parking lots yielded on average a 97.6% decrease in sediment PAH_{16} concentrations in comparison to coal-tar sealed lots. The sealed parking lots evaluated in this study are assumed to be coal-tar sealant based on a 2009 industry survey conducted by the

City of Springfield. Information from previous studies suggest that parking lots sediments from coal-tar sealed lots contain PAH concentrations that are six times or more higher than those found on asphalt sealed lots (Maher et al., 2005).

A more detailed watershed-scale analysis showed sediment PAH concentrations in the Galloway Creek watershed are strongly related to the percent of upstream drainage area that is covered in sealed parking lots**.** A total of 382 individual parking lots covering 6.6% of the total land area were mapped within the Galloway Creek watershed . Of all the parking lots mapped, 245 were sealed parking lots representing 71.2 % of the total parking lot area and 4.8% of the watershed area. A relationship between the percentage of sealed lot area (SLA%) and PAH_{16} concentrations was developed to estimate the critical SLA% value that would cause exceedance of the sediment toxicity guidelines. A SLA% value of about 3% is needed to meet the TEC value of 1,610 ug/kg PAH_{16} and a SLA% value of 10% is needed to meet the PEC value of 22,800 ug/kg PAH_{16}.

A regression model approach indicates that a ban on parking lot sealants could decrease total PAH concentrations in stream and pond sediment by 80-90%. The total parking lot area as a percent of the drainage area above a sampling point (TLA%) was added into the regression analysis to evaluate the effects of both sealed and unsealed parking lot areas on sediment PAH concentrations. The expanded model explains almost 86% of the variance in PAH sediment concentration using the predictor variables Log SLA%, Log TLA%, and Log organic carbon content (OC%). In comparing the before and after scenarios for predicted PAH concentration trends over total parking lot area by assuming a SLA value of 1% for all sites, the effect of a reduction of sealed parking lots on sediment and pond sediments was dramatic. In general, total PAH concentrations were predicted to decrease at parking lot sites by typically >96% and stream/pond sites by 80-90%. However, it is not expected that the effect of a ban on reduced PAH levels in streams would be immediate. The time for the sediment quality to recover to predicted lower levels could take 20 years or more depending on the behavior of longer-term sources of PAHs to the watershed including: (i) amount of PAHs presently contained on parking lots within mobile sediments; (ii) type, frequency, and rates of future resealing; and (iii) remobilization rates of PAHs from contaminated channel and floodplain deposits.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) occur at levels of environmental hazard and health concern in storm water and stream sediments in many urban and industrial areas (Beasley and Kneale, 2004; Van Metre & Mahler, 2005; Wilson et al., 2005; Hwang and Foster, 2006; Scoggins et al., 2007; Selbig, 2009). PAHs are composed of two or more fused benzene (aromatic) rings and usually occur as complex mixtures of 100 or more related compounds spanning a range of physical/chemical properties (Neff et al., 2005). Potentially hazardous concentrations of PAHs can accumulate in stream and lake sediments due to pollution by human activities. PAH contamination of stream bed sediment has been shown to degrade macroinvertebrate communities (Beasley and Kneale, 2004; Neff et al., 2005; Scoggins et al., 2007). Further, acute or chronic exposure to PAH contaminated soils, dusts, and aerosols may cause cancer, genetic damage, and newborn development problems in humans (ATSDR, 1995; Crane et al., 2010).

Recent studies have raised questions about new PAH sources and increased environmental exposure risks in urban watersheds (Van Metre and Mahler, 2010; Mahler et al. 2012). While the levels of some point and nonpoint pollutants such as metals and DDT/DDE have been decreasing in US waterways since the 1970s due to regulations on chemical use and improved source controls, sediment PAH concentrations have been increasing in urban watersheds, mostly in the eastern half of the United States (Van Metre et al., 2000 & 2010; Van Metre and Mahler, 2005). While PAHs can be released to the environment from a variety of urban sources, the major contributor to increasing PAH trends in urban streams has been linked to increased coal-tar product use such as sealcoats on parking lots and other urban surfaces and the release of weathered and abraded coating particles to streams (Mahler et al., 2005 & 2012).

The purpose of this study is to complete a baseline assessment of PAH sources and concentrations in urban stream and pond sediments in the City of Springfield, Missouri. The City is concerned about the negative effects that PAHs may have on the environment. In addition, there are questions about how PAH levels in local stream sediments may be related to reported biological impairments and PAH concentrations in stream water in Pearson, Jordan, and Wilson Creeks (URS Corporation 2010a & b). TMDL information sheets describe impairments within Springfield related to “unknown” pollutants from multiple point sources (Wilson Creek), urban nonpoint sources (Jordan and Wilson Creeks), and unknown sources (Pearson Creek) (http://www.dnr.mo.gov/env/wpp/tmdl/info/). Several other cities and states in the USA have already banned the use of coal-tar seal coat products to prevent excessive PAH contamination (Crane et al., 2010; Mahler et al., 2012). However, PAH sediment contamination trends have not yet been investigated in Springfield.

In the City of Springfield, PAHs were previously detected in stream water during base flow and runoff events in Wilson Creek, South Creek, Pearson Creek, and Jones Branch (Richards and Johnson, 2002) and Pearson Creek and Wilson Creek (URS Corporation, 2010a & b). In general, the frequency of PAH detection decreased downstream away from the city core. During baseflow sampling, the most frequently detected PAHs among all the streams were LPAHs, phenanthrene (Phe) and anthracene (Ant), and HPAHs, fluoranthene (Fth) and pyrene (Py). In South and Wilson Creeks during base flow, the detection frequency was relatively high for three additional HPAHs, benzo[a]anthracene (BaA), chrysene (Chr), and benzo[b]fluoranthene (BbF). However, during runoff event sampling, individual PAH detection frequencies and, to varying degrees, concentrations increased compared to base flow conditions. This trend was particularly noticeable for HPAHs and probably reflected the higher concentrations of suspended sediment, organic-rich particles, and sediment-bound PAHs present in storm water runoff. Richards and Johnson (2002) found evidence of genotoxicity in all water samples evaluated and suggested that the presence of PAHs and volatile organic compounds might be the cause. They concluded the report with a statement that water quality and aquatic environments in both Pearson and Wilson Creeks are being degraded by urban derived contaminants (Richards and Johnson, 2002).

One sediment sample collected by the Missouri Department of Natural Resources in August 1999 from the upper pond on Jones Spring Branch, a tributary to Pearson Creek, contained PAH_{16} concentrations over 25,000 ug/kg. This level may be toxic to sediment-dwelling organisms since it is above the probable effects concentration of 22,800 ug/kg PAH_{16} (MacDonald et al., 2000). While these previous studies identified PAH concentrations at levels of potential concern in the urban watersheds draining Springfield, no studies have yet tried to determine the spatial patterns and sources of PAH contaminated sediment and how contamination trends relate to harmful effects on aquatic life.

The main question to be addressed by this study is: Are PAHs found in urban stream and pond sediments at concentrations high enough to raise environmental concerns, and if so, to what degree are coal-tar sealants the source of PAH contamination in the City of Springfield? Four specific objectives will be used to address this question:

1) Assess the degree of land use and sediment source influence on PAH concentrations in sediment samples collected from urban watersheds in Springfield;

2) Determine if coal-tar coated parking lots represent a significant source of PAHs to sediments and local waterways;

3) Determine if other sources of PAHs are responsible for the sediment contamination patterns observed in addition to coal-tar parking lots; and

4) Evaluate a scenario of decreased seal coat use in Springfield and potential effects on the reduction of stream sediment PAH concentrations and associated toxic effects on aquatic sediment dwelling organisms.

Sources of PAHs to the Environment

In general, there are three sources of PAHs to the environment: petrogenic, pyrogenic, and diagenetic. Petrogenic sources are formed by the geochemical alteration of organic matter at moderate temperatures (50 to 150°C) and pressures over geologic time scales including releases of petroleum products like tire particles, deteriorating asphalt or asphalt sealant, coal storage piles and dust, and gasoline and oil spills. Pyrogenic sources are generated when fuels and organic matter are incompletely combusted at high temperatures (>400^{o}C) over very short time periods including gasoline combustion and exhaust, creosote treated lumber, combustion of wood, oil, and coal, and the production of coal-tar, coke, and asphalt. Pyrogenic PAHs in sediments, particularly when they are associated with combustion soot, often are more persistent, less mobile and bioavailable, and less toxic (on a bulk sediment concentration basis) than petrogenic PAHs (Neff et al., 2005). Diagenetic sources are formed naturally in recent sediments by the decomposition or burning of vegetation, wood, coal, or other organic materials, accounting for low levels of "background" PAH concentrations such as naturally-occurring perylene (Crane et al., 2010).

Storm water runoff appears to be the largest source of both petrogenic and pyrogenic PAHs to urban sediments. The most abundant PAHs in urban sediments have relatively high molecular weights and contain 4- to 6-rings (i.e., HPAHs), particularly the fluoranthene and pyrene isomers (Crane et al., 2010). The most common low molecular weight PAHs with 2- to 3-rings (i.e., LPAHs) in urban sediments are the anthracene and phenanthrene isomers. LPAHs degrade more rapidly and are washed downstream at a faster rate compared to HPAHs (Van Metre and Mahler, 2010; USEPA, 2011). HPAHs tend to be less soluble in water, bind more strongly to sediment particles, and last longer in the environment (Neff et al., 2005). Acute toxicity tends to be a greater risk with LPAHs and sediment toxicity criteria tend to be lower or more strict for this group (Canadian Council of Ministers of the Environment (CCME), 1999 and 2002; MacDonald, et al., 2000). However, HPAHs may be associated with more chronic human toxicity effects since six of the ten HPAHs examined in this study are listed as group B2 "probable human carcinogens" by the United States Environmental Protection Agency (USEPA), while none of the LPAHs are presently listed as a carcinogen (Crane et al., 2010) (Table 1).

PAHs are released to urban streams by atmospheric deposition and storm runoff from multiple sources such as roads, parking lots, rooftops, and industrial sites, sometimes at loadings high enough to contaminate downstream stream and pond sediments over long distances below the source (Van Metre et al., 2000; Shi et al. 2005; Wilson et al., 2005; Hwang and Foster, 2006). PAH concentrations in urban sediments can vary greatly since different types of combustion and industrial processes yield different inputs and relative distributions of PAHs. Nonpoint sources of PAHs can be widespread and specific input locations are hard to pinpoint within urbanized areas. Urban runoff typically includes PAHs from automobile exhaust, lubricating oils, gasoline, tire particles, wood and coal smoke, and soot in both dissolved and particulate forms. Point source discharges from industrial sites such as wood-treatment facilities where creosote is used can also produce elevated PAH levels in stream sediments (Walker and Dickhut, 2001; Brenner et al., 2002).

Sediment Contamination and PAH Toxicity to Aquatic Life

Pavement dust particles in storm runoff originating from parking lots in urban areas contain very high total PAH concentrations. Average PAH concentrations in suspended particulates in runoff from parking lots in Austin, Texas were 54,000 ug/kg for unsealed asphalt and concrete lots, 620,000 ug/kg for asphalt sealed lots, and 3,500,000 ug/kg for coal-tar sealed lots (Mahler et al., 2005). The testing of dry pavement dust deposits from the same and additional parking lots in Austin verified this trend (Mahler et al., 2010). In comparison, stream sediments subjected to urban storm water runoff in Austin contained 750 to 32,000 ug/kg total PAHs (n=7) (Scoggins et al., 2007), decreasing in concentration by an order a magnitude or more compared to levels measured in pavement dusts in upstream parking lots (Mahler et al., 2010).

In general, PAH concentrations in stream sediments tend to decrease downstream away from core source areas due to the effects of dilution by low PAH sediment loads from suburban and rural areas, PAH decomposition and volatilization, and sedimentation of PAH contaminated particles (Zhang et al., 2005; Van Metre et al., 2010). In stream sediments affected by urban runoff to varying degrees, the average and maximum total PAH concentrations were: (i) 2,000 and 50,000 ug/kg for relatively small watersheds in Scotland (Wilson et al., 2005), (ii) 11,000 and 1,900,000 ug/kg in small- to medium-sized watersheds in Tianjin, China (Shi et al., 2005); and (iii) 100 and 900 ug/kg in the middle and lower Yellow River in China (Li et al., 2006). Total PAH concentrations were typically 10,000 ug/kg to 50,000 ug/kg in 10 reservoirs and lakes from 6 different metropolitan areas in the United States, with a minimum and maximum of 2,790 ug/kg and 224,000 ug/kg, respectively (Van Metre et al., 2000).

Sediment toxicity criteria are used for screening purposes to identify contaminated sites and to predict the harmful effects of PAHs and other contaminants on bottom-dwelling organisms in freshwater ecosystems (Burton and Landrum, 2003). In the US, PAH sediment toxicity criteria most applied to aquatic systems were developed using the threshold concept based on the results of both previous studies and verification experiments to determine the probability of toxic effects (MacDonald, et al., 2000). The “threshold effect concentration” (TEC) is the value below which harmful effects are unlikely to occur and testing showed that 70-80% of the samples were correctly classified as non-toxic. The “probable effects concentration” (PEC) is the value above which harmful effects are likely to occur and >90% of the samples were correctly classified as toxic. Sediment toxicity criteria are published by MacDonald, et al. (2000) for 11 of the 16 PAHs included in this study and are reported herein in units of microgram per kilogram (ug/kg) or parts per billion (Table 1). TEC and PEC values range from a low of 33 and 140 ug/kg for Dibenz[a,h]anthracene (DahA) to a high of 423 to 2,230 ug/kg for Fluoranthene (Fth), respectively, (MacDonald, et al., 2000). A higher risk of toxic effects is indicated by lower TEC and PEC values. In addition to criteria for individual PAHs, total PAH limits are reported for combined concentrations of 10 to 16 PAHs in a sediment sample with a TEC of 1,610 ug/kg and

PEC of 22,800 ug/kg (MacDonald et al., 2000) (Table 1). Canadian sediment toxicity criteria for individual PAHs are set at similar levels as those found in MacDonald et al. (2000) (CCME, 1999 & 2002).

Sediment Transport of PAHs

PAHs occur in relatively higher concentrations in suspended and bed sediments in urban streams compared to the dissolved forms present. For example, Hwang and Foster (2006) showed that the particulate or suspended phase accounted for 68% to 97% of the total PAH transport during storm runoff events in urban streams in Washington DC. The strong association of PAHs with sediment particles is controlled by both source and chemical factors. From the start, PAHs are typically released to the urban environment in particulate form from the ignition of petroleum products and wood, erosion of road asphalt surfaces, and abrasion of parking lot sealcoats (Neff et al., 2005; Yang et al., 2008; Van Metre and Mahler, 2010). Moreover, PAHs tend to have relatively low chemical solubility in water so that dissolved PAHs will rapidly bind to fine-grained and/or organic-rich sediments in storm water (Evans et al., 1990; Schorer, 1997; Neff et al., 2005; Li et al., 2006; Shi et al., 2007; Gosh and Hawthorne, 2010). Following, sediment PAH concentrations are usually highest in streams and lakes draining dense road systems, heavy vehicular traffic areas, and petroleum/coal processing facilities (Van Metre et al., 2000; Crane et al., 2010). Thus, stream bed and lake bottom sediment sampling is an effective tool for pollution source monitoring since PAH concentrations are (i) readily detectable at levels of concern, (ii) persistent within the sediment for relatively long periods, and (iii) less affected by local factors compared to water and suspended sediment samples (Shi et al., 2005). Moreover, combining information on the geochemical trends of major and trace metals in sediments and soils samples can help to better understand the source locations and transport pathways of PAHs in urban sediments (Schorer, 1997; Wilson et al., 2005; Bentzen and Larsen, 2009).

Sediment composition itself can also influence the transport and deposition patterns of PAHs in streams and ponds. The size distribution of sediment particles can affect PAH concentrations since finer sediments (silt + clay faction) generally have the capacity to bind contaminants at higher rates compared to coarser particles (sand fraction) (Bentzen and Larsen, 2009). However, sometimes the carbon content of the sediment is correlated with PAH concentration regardless of particle size (Schorer, 1997; Shi et al., 2007; Yang et al., 2008; Yang et al., 2010; Ghosh and Hawthorne, 2010). Coal-derived and other organic particles may contain the highest concentrations of PAHs in the sediment, but the most bioavailable and degraded forms may be preferentially bound to the silt/clay fraction, and therefore be of potentially greater concern (Talley et al., 2002). The distribution of organic carbon can be bimodal in sediment samples with peaks in both the finer silt and coarser sand size fractions, thus confusing the particle size-PAH concentration relationship (Evans et al., 1990; Schorer, 1997).

As expected given the strong relationship with organic matter, PAHs tend to accumulate in the lower density fraction of the bulk sediment composed of coal grains, soot particles, wood and plant fragments, and coal tar pitch (Yang et al., 2008; Ghosh and Hawthorne, 2010). From 50% to 80% of the PAHs in contaminated sediments can be found in the low density fraction which accounts for only 3% to 5% of total sediment mass (Rockne et al., 2002; Yang et al., 2008). Erosion and deposition characteristics of lower density organic-rich sediment in urban streams is poorly understood at present. Thus, it may be difficult to manage PAH-contaminated sediment using conventional settling and transport models (Wilson et al., 2005; Bentzen and Larsen, 2009). Further, organic-rich sediment deposits can be disturbed and remobilized more easily by wind, runoff, and bio-turbation compared to mineral-rich sediment, possibly making associated PAHs more available to biota in the process (Eggleton and Thomas, 2004).

Ratios between specific PAHs measured in sediment have been used to identify the different sources of PAHs affecting a waterbody. For example, phenanthrene:anthracene ratio values <10 may indicate pyrogenic sources (wood, auto emission, coal combustion, coal tar) while values >10 may indicate petrogenic sources (crude oil and asphalt) (Neff et al., 2005). Similarly, fluoranthene:pyrene ratios >1 may indicate pyrogenic sources and <1 may indicate petrogenic sources (Neff et al., 2005; Crane et al., 2010). PAH ratios can change over time due to transformations in the environment. Runoff rates of PAHs are highest for the first few runoff events after a new application of coal-tar sealant and then decrease by ten-fold with a shift to a greater percentage of HPAHs (USEPA, 2011). PAHs can degrade by reacting with sunlight and other chemicals in the air over a period of days to weeks (ATSDR, 1995; USEPA, 2011). Microorganisms can break down PAHs in soil or water after a period of weeks to months (ATSDR, 1995), with faster decomposition rates occurring under moist or wet aerobic conditions (Boyd et al., 2005; Quantin et el., 2005). This “weathering” process tends to reduce the concentrations of LPAHs, resulting in the increase in relative proportion of HPAHs in the sediment (Van Metre and Mahler, 2010). PAH ratios can be affected by differential breakdown of individual PAH compounds as well as other factors including sorting during aerial and fluvial transport, evaporation/volatilization processes, and dissolution into water (Zhang et al., 2005; Crane et al., 2010).

Importance of Coal-tar Sealcoat Sources

It is becoming increasingly evident that coal-tar in surface coatings of parking lots may represent the primary contamination source of PAHs to urban streams (Mahler et al., 2005; Van Metre et al., 2009; Yang et al., 2010). Coal-tar road surfacing products typically contain PAH concentrations that are two orders of magnitude greater than asphalt. The Asphalt Institute in Lexington, Kentucky reported total PAH concentrations averaged 24,000 ug/kg (or 2.4%) for 12 different asphalt cements supplied by the Strategic Highway Research Library and Asphalt Roofing Manufacturing Association. However, PAH concentrations were over 2,300 times higher for a low temperature coal tar sample from South Dakota (Blackburn et al., no date). Coal-tar based sealcoat products contain about 1,000 times more PAHs than sealcoat products with an asphalt base (Mahler et al., 2005). In a study of US sealcoat products, the USGS reported that asphalt sealcoat products contained 0.03 to 0.66% of 16 different PAHs (PAH_{16}), while coal-tar sealcoat contained 3.4 to 20% PAH_{16} by dry weight (Mahler et al., 2005). The large differences in PAH content between asphalt and coal-tar sealcoats were also found in the sediment particles produced by parking lots. The weathering of coal-tar sealcoats produced surface sediments (i.e., pavement dust) enriched in PAHs by 65 to 530 times particulate and dust samples from asphalt-based sealcoat, unsealed asphalt, and concrete lots (Mahler et al., 2005, 2010 & 2012; Van Metre et al., 2009).

Given the reapplication frequency for coal-tar sealants on parking lots typically ranges from 3 to 5 years, coal-tar sealant sources can provide a steady, long-term source of PAH-contaminated sediment or pavement dust to nearby streams (Mahler et al., 2012). In a study of storm runoff from experimental parking lots with known composition and sealant history, coal-tar sealed surfaces released 100 to 1,000 times more PAHs to runoff than asphalt-coated, uncoated asphalt, and concrete lot surfaces (USEPA, 2011). The composition of the contaminated sediment also reflects the influence of carbon materials and coal-tar sources for PAHs in urban waterways. Total PAH concentrations were distributed among different particle fractions in a contaminated fresh water harbor sediment in Utica, New York as follows: 13,000,000 ug/kg in coal-tar pitch particles, 4,100,000 ug/kg in coal/coke particles, 1,700,000 ug/kg in wood fragments, and 4,100 ug/kg in sand (Ghosh and Hawthorne, 2010). In Fort Worth, Texas, coal-tar pitch was found to be the dominant source of PAHs to urban streams, contributing 99% of the PAHs in sealed lot dust, 92% in unsealed parking lot dust, and 71% in stream bed sediment (Yang et al., 2010).

The contaminating influence of coal-tar pitch particles and runoff from coal-tar parking lots can be significant even at the watershed-scale. Increasing concentrations of PAHs in lake sediment cores collected from urban and urbanizing watersheds in the eastern USA have been related to expansion of urban road and drainage networks and increased coal-tar sealant use on parking lots beginning in the 1970s (Van Metre et al., 2000; Van Metre and Mahler, 2005 & 2010; Crane et al., 2010). However, trends for other contaminants including chlorinated hydrocarbons (e.g., DDT, DDE, PCBs) and metals (e.g., Pb, Zn, Cu) were found to decrease or not change during the same period (Van Metre and Mahler, 2005; Mahler et al., 2006). The different contamination trends between PAHs and the other nonpoint pollutants underscore the conclusion that coal-tar coated parking lots are a distinct and excessive source of PAH contamination in urban watersheds (Mahler et al., 2005 & 2012; Van Metre and Mahler, 2010; Yang et al., 2010). Indeed, coal-tar sealcoat sources can contribute one-half of the PAH contamination or more to stream and lake sediments in urban areas in central, southern, and eastern US (Van Metre and Mahler, 2010).

There are few field studies of the ecological effects of coal-tar particles and related PAH contaminated sediments. However, it is expected that the probability for toxic effects would increase since sediment contaminated by coal-tar sealant particles typically contains PAH concentrations at levels an order of magnitude or higher than similar inputs from other lot surface types or urban sources (Van Metre et al., 2010). Although the sample size was limited, macroinvertebrate density and taxon richness decreased significantly below storm water outfalls draining coal-tar coated lots in both pool and riffle habitats as compared to upstream controls in Austin, Texas (Scoggins et al., 2007). In a laboratory study where aquatic frogs were exposed to varying mixtures of water and coal-tar sealer flakes, life spans and development rates were reduced at levels equivalent to 3,000 ug/kg total PAH concentrations and just above the TEC published by MacDonald et al. (2000), obvious lethal effects were measured at 30,000 ug/kg (Bryer et al., 2006). While the total PAH concentration is important, the concentrations of specific contaminating PAHs may be more important for evaluating macroinverterbrate effects. In Yorkshire, United Kingdom, the concentrations of benzo(b)fluoranthene, anthracene, and fluoranthene in sediment correlated better with ecological condition than total PAHs (Beasley and Kneale, 2004). Further, PAH contamination and macroinvertebrate effects were spatially distributed in association with “high risk” input source points in the drainage network including (i) commercial vehicle staging areas adjacent to main roads, (ii) on-street residential parking areas, and (iii) street junctions at the bottom of hills where water feeds rapidly to stream channels (Beasley and Kneale, 2004).

Coal-tar sealed parking lots present unique PAH exposure pathways to humans that can potentially result in chronic toxic effects. The pavement dust formed by coal-tar coat weathering and abrasion is easily transported by runoff, wind, and attachment to shoes and cloths. Human contact with coal-tar dust covered surfaces represents a poorly understood threat to human health (Van Metre et al., 2009). There is a relatively strong relationship between the presence of coal tar parking lots near a residence and the concentration of coal-tar related PAHs in house dust (Mahler et al., 2010). Non-dietary ingestion of B2 PAH carcinogens, particularly benzo[a]pyrene, in house dust by children is much larger in residences next to coal-tar sealed lots compared to unsealed lots and accidental uptake might exceed published doses via dietary ingestion (Williams et al., 2012).

METHODS

In this study, a watershed-based approach is used to evaluate PAH presence and sources in stream and pond sediments from within and outside the City of Springfield. The methods used involve: (i) sediment sampling at different locations in the channel network including downstream areas as well as points immediately below parking lots; (ii) GIS data analysis to determine watershed characteristics, sampling locations, and street and parking lot source mapping; and (iii) sedimentological and geochemical analysis of sediment samples to evaluate transport mobility and source. The concentrations of PAHs measured in Springfield sediments are compared to published freshwater aquatic sediment toxicity criteria (MacDonald, et al., 2000). Standard operating procedures (SOPs) for particle-size analysis, X-Ray flourescence spectrometer analysis, and carbon-nitrogen-sulfur analysis used for this study are posted on the OEWRI website (http://oewri.missouristate.edu/80056.htm).

Field Sampling

Sampling Locations

Sediment samples were collected from stream channels, storm water basins, wet ponds, and parking lots in the Springfield area in both urban and rural watersheds to evaluate the spatial variability of PAH contamination, sources, and transport patterns (Figures 1 & 2; Appendix A). Sampling sites were selected by the City of Springfield staff using drainage and land use information provided by existing maps and aerial photography. Stream and pond sediment sampling sites were selected to provide a distribution of sites along an urban-rural gradient within the different watersheds in the study area. Additional considerations for stream and pond site selection included public access, proximity to roads or crossings, and availability of recent sediment deposits. Parking lot sampling sites were selected based on visual interpretation of 2009 aerial photographs and subsequent field inspections to identify seal-coated (shiny dark blue-black colored) and unsealed asphalt (dull gray colored) and concrete (white-yellow brown colored) parking lots in central and southeastern Springfield. A good parking lot for sampling purposes had these characteristics: (i) good public and open access, (ii) drainage areas with a single parking lot type and well-defined source areas, and (iii) probable locations for sedimentation such as in flat areas along lot edges, at breaks in slope below outfalls, or in trickle channels within adjacent storm water basins.

Sample Collection

For this study, 72 sediment samples were collected at 58 different sites including 14 duplicate samples collected within 2 m of the first sample (Figures 1 & 2; Appendix A). The majority of the sites were located in different catchment areas or separated by at least 500 meters along the same stream. However, in some cases, individual sites were separated by <100 m to evaluate local variations in PAH deposition such as within small ponds (sites 2-3, 4-5, 15-16, 17-18, 19-20, and 22-23) or at different locations within the drainage network such as above and below a tributary confluence (sites 8-9, 24-31, and 32-33). Overall, 41 sites were located within the city limits of Springfield (71% of all sites), 9 sites were located in Greene County, 1 site was located in Christian County, and 7 sites were located in Stone County.

Sediment samples for PAH analysis were collected in the field with a shovel and immediately placed into an amber glass jar and capped. A second split of the same grab sample was put in a labeled plastic bag and sealed prior to preparation for major and trace metals, nutrients (N,P,S), carbon (total and organic), and particle-size analysis at the OEWRI water and sediment laboratory located on the MSU campus in Temple Hall. Care was taken to collect the sample from grab material that did not contact the shovel surface. Sample locations were marked by GPS coordinates and mapped to check for watershed location (Figures 1 & 2).

Watershed Coverage

Urban watersheds sampled in this study include Jordan Creek (sites 24-26 & 31), Wilson Creek (sites 27-30), South Creek (sites 8-13), Inman Creek (sites 48-50), Ward Branch (sites 42 & 46-47), Galloway Creek (Sites 14-18, 21-23, & 32-45), Jones Branch of Pearson Creek (sites 2-5) and lower main stem Pearson Creek (sites 6-7) in Greene County (Figure 1). Sediment samples were also collected from sites located outside of urban influence to provide "rural" controls to check for natural or non-urban source effects on PAH concentrations. Rural watersheds sampled in this study include Spring Creek in Christian and Stone Counties (Sites 51-58) and upper main stem Pearson Creek in Greene County (site 1). In addition, two bed samples were collected from impounded flow at the mouth of Sequiota Cave (Sites 19-20) which later was found to contain PAHs levels similar to those from rural areas.

Laboratory Analysis

Sample Preparation

Sediment samples for PAH analysis were processed wet, put into glass jars, packed in a cooler with ice, and mailed to the commercial laboratory by OEWRI staff. Sample splits for textural and geochemical analysis were dried in an oven at 60^{o}C, disaggregated with mortar and pestle, and put through a 2 mm sieve to remove oversize material. Dried samples were stored in plastic bags until subsequent analysis.

PAH Analysis

All sediment samples collected were analyzed for USEPA's 16 Priority PAHs according to USEPA standard method 8270C by a certified commercial laboratory (EMSL Analytical, Inc., Westmont, NJ) (Table 1). PAH concentrations are determined using gas chromatography and mass spectrometry. Analytical error for the method is reported by the laboratory to be <20 percent difference for sample duplicates. The concentrations of selected PAHs measured in sediments were compared to published aquatic sediment toxicity criteria (MacDonald, et al., 2000).

Sample Texture

The grain-size distribution was determined for each sample using laser diffraction analysis in the OEWRI laboratory (see SOP at http://oewri.missouristate.edu/80056.htm). Prior to analysis, samples are pretreated with hydrogen perioxide to remove organic matter and then dispersed by sodium hexa-metaphosphate solution using a sonicator.

Geochemical Analysis

Samples were analyzed for 35 major and trace metals including copper, lead, arsenic, and mercury by hot strong acid extraction and inductively coupled plasma atomic emission spectroscopy analysis (ICP-AES) at a certified commercial laboratory (ALS Minerals, Winnemucca, NV using method ME-ICP41m). Analytical error for the method is reported by the laboratory to be <20 percent difference for sample duplicates. In addition, dry samples were also analyzed for metals and major elements by X-Ray Florescence (XRF) in the OEWRI laboratory (see SOP at http://oewri.missouristate.edu/80056.htm). Analytical error for the method is typically within 10 to 30 percent difference for sample duplicates. The concentrations of selected metals measured in sediments were compared to published toxic criteria (MacDonald, et al., 2000).

Carbon Analysis

Samples were analyzed for total and organic carbon by combustion in a CNS Analyzer in OEWRI laboratory (http://oewri.missouristate.edu/80056.htm). Analytical error for the method is typically within 5 to 20 percent difference for sample duplicates.

Geospatial Databases and Analysis

All Geospatial Information Science (GIS) database operations and analysis was completed by OEWRI. The City of Springfield provided the 2009 aerial photographs and GIS layers describing the storm water infrastructure network of the study area. Other GIS databases were obtained from the OEWRI database or retrieved from the Missouri Spatial Data Information Service (MSDIS).

GPS Data Collection and Site Mapping

Each sampling site was marked by a hand-held geographic positioning system (GPS) receiver. Site locations were verified, and corrected if needed, by displaying the field data over high resolution 2009 aerial photography of the study area.

Watershed Delineation

Upstream drainage areas for the non-parking lot sites were delineated using the Arc Hydro Tools extension within ESRI’s ArcMap 10 GIS software. A 10-meter digital elevation model (DEM) was used for processing. Watershed area for sample sites draining parking lots were estimated using the City of Springfield’s storm water infrastructure layer in GIS, the aerial photo, and field verification.

Land Use Classification

Watershed boundaries were used to calculate upstream land use conditions from a simplified 30-meter 2005 land use classification layer from the Missouri Resources Assessment Partnership

(MORAP). The original 15 classes were simplified to five classes; Urban, Grass/Pasture, Crops, Forest, and Other.

Classification of Parking Lot Surfaces

Parking lots within the Galloway Creek watershed were mapped to evaluate the spatial relationships between sealed parking lot areas and sediment PAH contamination. First, all parking lots within the watershed were visually identified and marked using 6-inch resolution aerial photography from 2009 supplied by the City of Springfield. Parking lots were distinguished from private driveways based on the size of the adjacent buildings, size and shape of the lot, and the presence of painted parking spots. Second, each lot was digitized by hand and classified as either "sealed" or "unsealed." Asphalt parking lots that were sealed could be identified by the dark black color of the surface (Appendix L). Unsealed asphalt parking lots were distinguished from sealed lots by their lighter gray color. Other parking lot types classified as unsealed included concrete, gravel, and dirt lots. Lots that contained large sections of both sealed and unsealed surfaces were divided into two or more polygons. Finally, each parking lot was attributed by size, which was used to calculate percent coverage of the watershed by each lot type.

Quality Control Analysis

This study uses quality control testing to insure that the results are interpreted correctly and according to the scientific principles.

Duplicate testing. The precision of sediment PAH measurements is evaluated by calculating the relative percent difference (RPD%) for duplicate samples collected from within 2 m of one another. This statistic is used to determine the combined sampling and analytical error for PAH concentration measurements. Therefore, the sampling error reported in this study represents the cumulative effects of several variables including site factors, natural sediment heterogeneity, and sample preparation, and as well as analytical limits such as detection limits, standard precision, and spike recovery.

Rural/undisturbed control sites. Sediment samples are collected from outside of urban influence to determine PAH characteristics for rural samples and to compare them to those from urban areas.

Multiple urban source evaluation. PAH concentrations in sediment samples affected by sealed parking lot samples are compared to sediment samples from downstream segments and older industrial areas to provide experimental controls for different land use effects. In addition, comparisons among PAH concentrations and sediment properties from four different lot types provide a control for parking lot effects for this study. If PAH concentrations do not vary among different land use and parking lot types, then sealed lots would not be found to be a distinct and excessive source of PAHs in the City of Springfield.

Statistical data analysis and modeling. Standard statistical practices will be applied during this study. These methods will involve rigorous statistical checks and significance measures upon which to base confidence for conclusions.

Standard methods. Standard methods and certified commercial laboratories will be used to consistently collect, prepare, and analyze sediment samples evaluated for this study.

Geospatial error checks. The accuracy of GIS-based data and mapping is checked by combining GPS field points with high resolution aerial photographs. In addition, site inspections are used to "ground-truth" parking lot classifications in Galloway Creek watershed. Digital camera photographs for each parking lot sampling site were collected at the time of sample collection (Appendix J). Additional photographs were collected during a third round of field checks in January 2012 (Appendix K).

Sediment Sample Characteristics

To evaluate PAH trends and source areas, sediment samples were classified by sedimentation area, location within the drainage network, and deposit type. Three sedimentation areas were sampled in this study: streams, ponds, and parking lots. A "stream" is defined as any drainage channel where sediment has been deposited by flowing water during runoff events including natural streams, constructed drainage channels, and concrete trickle channels in detention basins. A "pond" is defined as any impounded water body that holds water permanently where sediment deposition occurs mainly by settling in relatively slow moving water. A "parking lot" is defined as an area that is used to park vehicles and access relatively large commercial and residential properties. Sediment samples were collected from the edges of the parking lot where sediment deposition occurs after runoff events such as along the curb or grass lines and below lot outfalls near inlet and outlet structures.

The location of the sample site within the drainage network is generally described by the size of the contributing catchment or watershed area above the sample point. Sediment samples collected from smaller urban drainages typically indicate pollution source effects more consistently and at higher concentrations than those collected farther downstream. Downstream sites are influenced by multiple sources of runoff and sediment and therefore sediments will contain a mixture of high and low pollutant concentrations. As sampling site locations move downstream away from core urban developments, drainage area increases and concentrations of urban sediment pollutants tend to become progressively diluted by "cleaner" sediment loads from the increasing proportion of lower source and/or rural areas in the watershed. However, some pollutants may increase or fluctuate in concentration downstream indicating a different source other than the urban core areas targeted for this study. Some other sources could include industrial sites, road drain outfalls, or contaminant inputs from tributaries draining urban areas not sampled in the study.

In this study, recent sediment deposits (<5 years old) were targeted for sampling to improve correlations between contaminant signatures and contemporary pollution sources. Recent deposits are found in depositional areas that shift or erode often so as to “reset the clock” after one or several storm runoff events. In addition, fine-grained sediments (<2 mm in diameter) were collected for analysis since PAHs, metals, and nutrients tend to accumulate in finer sediment particles. Recent, fine-grained deposits were unconsolidated, lacking vegetation growth, and sometimes occurred as distinct layers overlying older soils, artificial surfaces, or seasonal leaf litter. Stream bed and bar sediments are typically remobilized and transported downstream by higher flows or floods that occur at least once or twice a year.

Channel and pond sediments were sampled from bed, bar, and bench deposits. Bed sediments occur on the bottom of the channel or pond. Stream bed samples for this study were collected mainly during dry periods from ephemeral drainage ways or storm water basins. Pond bed or bottom sediments samples were collected from soft, silt and clay deposits within 5 m of the bank edge. Medium and large stream sediment samples were typically collected from bar tail deposits at the fine-grained downstream end of gravel bars that are common to Ozark streams. Bars are formed by the deposition of excess sediment in a discrete sedimentary body on the bed or along inside bends of stream channels. Benches are composed of fine-grained deposits overlying coarser gravel bar surfaces. Sediment accumulates on benches during floods with new sediment being deposited overtop of older layers. In this study, the sampling depth for bench deposits was <2 cm.

Parking lot sediments were sampled from lot edges, inlet structures, and adjacent storm water basin channel beds. Sediment can accumulate along the edges of parking lots where curbs, grass sod banks, and local unevenness of the lot surface impounds runoff and slows flow velocity. Inlet structures that drain runoff from the parking lot surface to a nearby storm water basin can form sediment deposits both within and outside the culvert opening. Sediment can collect just inside the end of the pipe where water is dammed up behind a sod bank or drop structure material and also immediately outside of the pipe where flow spreading and increased bed roughness reduces flow velocity. Sediments originating from parking lot surfaces can also accumulate in the trickle channel of the storm water basin. In this situation, the routing of the sediment from the parking lot into and through the basin was checked to verify that the basin was receiving the entire runoff and sediment load from the intended parking lot.

Coal-Tar Sealant on Parking Lots

Parking lot surface type was relatively easy to determine using high resolution aerial photography and field inspection. Seal-coated lot surfaces were easily distinguished from unsealed asphalt and concrete surfaces. However, information on the type of sealant used by the applicator for a specific parking lot was not available. Therefore, the determination of coal-tar sealant use on the parking lots examined during this study was based on information provided by a previous 2009 survey by the City of Springfield of coal-tar product sales and application within the city limits. The primary wholesaler of coal-tar and asphalt sealers in the Springfield area responded that 85% of their sales is coal-tar sealant and 15% is asphalt-based sealant. While some applicators may get their sealant from another source, we assume that these numbers reflect what was being used in Springfield in 2009, the period which would influence sediment contamination trends being detected in 2011 by this study. Survey responses from applicators also seem to support the assumption that most, if not all, of the seal-coated parking lots for large commercial and residential developments are primarily coal-tar based. One of the largest applicators in town responded that they apply 95% coal-tar sealant. Two other applicators also responded that they apply coal-tar sealant 99% and 100% of the time. However, there were two applicators who responded that they only apply asphalt-based sealant and no coal-tar sealants. Nevertheless, given the above information, the sealed parking lots evaluated in this study are assumed to be primarily, if not entirely, coal-tar based.

Sediment Classification

Given the characteristics of the sediment deposits and sampling locations described above, sediment sampling sites were divided into four parking lot and six stream/pond classes.

Parking lot samples were collected from seal-coated lots (assumed to be coal-tar based as discussed above), mixed seal-coated and unsealed asphalt lots, unsealed asphalt lots, and unsealed concrete lots. The samples collected in each parking lot class are described below (Figure 1; Appendix A):

Coal-tar seal-coated lots (n=4; sites 32, 36, 41-42).

Mixed seal-coated/unsealed asphalt lots (n=4; sites 35, 37, 44-45)

Unsealed asphalt lots (n=6; sites 31, 34, 38, 48-50)

Concrete lots-unsealed (n=4; sites 39, 43, 46-47)

Stream and pond samples were collected from sites with drainage areas ranging from <0.015 km^2 to 152 km^2. Watershed area classes are designated as: (i) “very small” with drainage areas less than 0.5 km^2 (<40 acres); (ii) “small,” 2-4 km^2; (iii) “medium,” 10 to 35 km^2; and (iv) “large,” 50 to 152 km^2 (Figure 3). Percent urban land use decreases slightly as total drainage area increases at sampling sites in Springfield watersheds, ranging from 100% urban area above all parking lot sites to 19% in lower Pearson Creek (Figure 3). Rural control sites not draining Springfield have urban areas <10% with several below 2% (Figure 3). Very small stream sites are mainly located in urban storm water basins draining multiple sources. Only two sites are in the small stream class, both are located on South Creek between National and Campbell Avenues. Small pond sites are located along the Jones Spring Branch of Pearson Creek and upper Galloway Creek in the Southern Hills subdivision. Medium and large stream sampling sites are located at downstream locations on Pearson Creek, Galloway Creek, South Creek, Jordan Creek, and Wilson Creek. Rural watersheds sampled in this study include Spring Creek in Christian and Stone Counties (Sites 51-58) and upper main stem Pearson Creek in Greene County (Site 1). In addition, two bed samples were collected from impounded flow at the mouth of Sequiota Cave (Sites 19-20) which contained PAH levels similar to those from rural areas. The samples collected in each stream and pond class are described below (Figures 1 & 2; Appendix A):

Very small streams (n=5; sites 8-9, 14, 33, & 40)

Small streams (n=2; sites 10-11)

Small ponds (n=8; sites 2-5 & 15-18)

Medium streams (n=8; sites 12-13 & 21-26)

Large streams (n=6; sites 6-7 & 27-30)

Control streams and ponds (n=11; sites 1, 19-20, 51-58)

RESULTS

PAH Detection and Relative Abundance

As reported by the analytical laboratory, the median detection limit for each of the 16 PAH compounds investigated in this study was 33 ug/kg (Table 1). Detectable concentrations of one or more PAHs were measured in sediment samples collected at 51 (88%) out of a total 58 sites evaluated in this study (Appendix A). Considering only the sites within or below Springfield, PAHs were detected at all 49 sites (100%), with 36% in the threshold effect range from 1,610 ug/kg to <22,800 ug/kg PAH_{16} and 51% exceeding the probable effects concentration of 22,800 ug/kg PAH_{16} (Table 1). Twelve Springfield sites (25%) contain PAH_{16} concentrations exceeding five times the PEC. All of these high PEC sites drain core urban areas that contain relatively large areas of roads and parking lots with a variety of surface characteristics including coal-tar sealed and mixed sealed and unsealed asphalt lots (Appendix A).

Sediment PAH concentrations in rural streams and ponds were below detection limits in almost of cases. All PAH analyses for four rural pond sediment samples were below the detection limit. Of the four rural stream samples collected, only four PAHs were detected within three different samples: fluoranthene (Fth), 48 ug/kg; pyrene (Py), 29 ug/kg; benzo[b]fluoranthene (BbF), 240 ug/kg; and benzo[a]pyrene (BaP), 210 ug/kg (Appendix A). The background sediment PAH_{16} concentration for rural areas is uncertain, but probably ranges from 270 ug/kg (½ the detection limit) to 730 ug/kg (sum of the few measured values plus ½ detection limit for the others).

Analytical results of four of the six low molecular weight LPAHs examined in this study including naphthalene (Nap), acenaphthylene (Any), acenaphthene (Ace), fluorene (Flu), and, to lesser degree, anthracene (Ant),were affected by detection limit problems since these PAHs occurred at relatively low concentrations in sediments (i.e., <1% relative abundance) (Tables 1 & 2). Naphthalene is typically found in high concentration in fresh coal-tar standards (Poster et al., 2000; Wise et al., 2010). However, Nap and other LPAHs tend to decrease rapidly in concentration in sediments after release to the environment due to relatively high rates of decomposition, volatilization, and dissolved transport downstream (Van Metre and Mahler, 2010; USEPA, 2011; Van Metre, 2012a & b).

Of the higher molecular weight HPAHs, only dibenz[a,h,]anthracene (DahA) was detected at relatively low levels (1% relative abundance) (Table 2). However, the relative abundance of DahA conspicuously rises to 4% in urban pond sediments (Table 2). It is possible that the relatively high levels of DahA are due to a local pollution source in the relatively small drainage area or that sediments in the pond contain higher amounts of organic matter that preferentially binds this compound. HPAHs as a group tend to strongly bind to fine-grained sediments and organic matter, thus it is expected that HPAHs will be found in higher concentrations in sediments compared to LPAHs (Neff et al., 2005). Given that the relative abundance of individual PAHs are similar across a wide range of sites, the PAH_{16} concentration is sufficient for the evaluation of spatial variations in PAH concentrations in urban sediments in Springfield.

Individual PAH compounds with relatively high relative abundances >10% include Fth, Py, Chr, and BbF (Table 2). Correspondingly, these four PAHs were also found in highest frequency in stream water in Springfield (Richards and Johnson, 2002; URS Corporation, 2010 a & b). Generally, the relative abundance of individual PAHs does not vary by more than 4% among parking lot types and stream/pond sediment classes (Table 2). Two exceptions include Fth and (Indeno[1,2,3-cd]pyrene (InP) which vary in relative abundance by 8.3% and 4.2% among the five sediment classes evaluated, respectively (Table 2).

Downstream variations in the relative abundance of specific PAH compounds in the sediment can indicate source characteristics within the watershed. Total PAH concentration in the sediment will tend to decrease downstream from high source areas due to the influence of dilution and mixing with progressively lower source inputs. However, the relative contributions of different PAHs to the total PAH burden can vary independently of dilution effects due to different source effects and chemical leaching rates in the environment. In this study, downstream trends in the relative abundance of Fth, Py, and Chr appear to identify sealed lot source inputs (Table 2). Sediment Fth abundance decreases downstream from 20-23% in parking lot areas and very small/small streams to 14% at medium to large stream sites (Table 2). The relative abundance of Py in sediment decreases downstream of sealed parking lots and in unsealed lots as follows: sealed parking lots, 22.9 %; mixed and unsealed asphalt lots, 13.5%; concrete lots, 11.8%; very small/small stream, 13.7%; and medium/large streams (11%) (Table 2). Chrysene also shows a similar trend with decreasing abundance in unsealed parking lots compared to sealed lots (Table 2). Conversely, BaP shows an opposite, and slighty weaker trend, increasing in relative abundance downstream from 8.1% abundance in sealed lot sediment to 11% at large stream sites (Table 2).

The first three PAHs described above can potentially be used as tracers of seal-coated lot influence and also possibly the presence of coal-tar particles in urban stream sediments in Springfield. These “pathfinder” PAHs are found in highest abundance at sealed lot sampling sites and decrease by almost half or more downstream. In contrast, BaP does not appear to be a precise indicator of sealed lot influence, since the relative abundance increases downstream by about one-third. Nevertheless, BaP may indicate the influence of urban inputs in general or other localized source inputs downstream on Wilson Creek.

The urban sediment PAH signal within Springfield is: (i) relatively uniform varying more in magnitude than among individual PAH input rates, at least at the scale of analysis used in this study, (ii) associated with mixtures of both petrogenic and pyrogenic PAH sources that are similar across urban land use characteristics, and (iii) influenced similarly by weathering, volatilization, particle geochemistry, and sediment transport within the watersheds investigated. Sedimentological and geochemical processes active within the urban watershed can reduce the influence of source variations on the relative abundance of PAH concentrations in stream sediments over time (Zhang et al., 2005). Nevertheless, Van Metre and Mahler (2010) also found similar relative concentrations of PAHs within cores collected from 40 US lakes, but were able to detect the influence of coal-tar inputs by using a source mixing model and correcting for weathering/volatilization effects on the LPAHs.

Sampling Errors

Relative percent difference values were calculated for each field sample duplicate for which PAHs were detected (Table 3). Errors less than 30% are considered acceptable, particularly since the particle size fraction analyzed was not standardized and generally accepted to be <2 mm. Median error values for particle size measurements range from 6% to 26%, carbon and nutrients from 2% to 26%, major and trace elements from <1% to 13%, LPAHs from 17% to 27%, and HPAHs from 8% to 29% (Table 3). The detection limits for trace metals are relatively low and far below the TEC values (Table 1). However, as described above, this is not the case for all PAH compounds examined in this study. Relatively high detection limits and low TEC values for LPAHs and DahA explain the analytical detection problems observed in this study. The analytical detection limits reported by the commercial laboratory are too high to adequately quantify the distribution and concentrations of LPAHs in rural and, to a lesser degree, urban sediments. However, detection limit problems do not limit the utility of this study to address the proposed objectives, particularly since sampling errors are in acceptable ranges. However, the background PAH signature for rural sediments and related PAH ratios cannot be evaluated due to relatively high detection limits for LPAHs.

Sediment Class Trends

Enrichment Factors

Sealed parking lots and the stream channels that drain them are highly enriched in PAH_{16} relative to rural sediments (Table 2). The eight rural sediments evaluated for this study were usually below detection limits for PAHs. The rural samples are assumed to reflect the lowest PAH concentrations expected in the non-urban areas and were used as both an experimental control for land use influence and analytical control to check for contamination during the sampling process. Following, the mean total PAH concentration for rural sediment is assumed to be 272 ug/kg at one-half the detection limit with an upper limit of 528 ug/kg at the median detection limit (i.e., 33 ug/kg x 16 PAHs). Geometric mean PAH_{16} concentrations varied among urban sediment classes, ranging from 11 times higher than rural levels for large streams to 5,657 higher for sealed parking lot sediments (n=4) (Table 2; Figure 4). Sealed parking lots yielded sediment PAH_{16} concentrations that are 148 times higher than those found in sediments from concrete parking lots, 41 times higher than asphalt parking lots, and 2 times higher compared to mixed sealed and unsealed lots (Table 2). In other words, unsealed asphalt parking lots yielded on average a 97.6% decrease in sediment PAH_{16} concentrations in comparison to coal-tar sealed lots (Table 2; Figure 4). The relative difference in PAH concentration from sealed and unsealed lots in this study compare well with similar sediment PAH studies of parking lot effects in other urban areas (Mahler et al., 2005 & 2010; Van Metre et al., 2009).

The parking lot sediment samples collected for this study contain varying contributions of pavement dust that has been mixed with particles from other sources including: (i) mineral and asphalt particles released from other structures and related construction materials, (ii) organic-rich sediment composed of decomposed vegetation and carbonaceous fragments, and (iii) natural soil materials containing mostly silt and clay. Pavement dust particles are derived specifically from the weathering and abrasion of lot surfaces and sealant coatings, if present. The median PAH_{16} concentrations in pavement dust samples from six central and eastern U.S. cities was 2,700,000 ug/kg for sealed lots and 27,000 ug/kg for unsealed lots (Figure 4). PAH concentrations in sealed lot sediments in Springfield were apparently diluted by sediment contributions from lower PAH sources by almost half those reported for pavement dusts on coated lots in other cities (Van Metre et al., 2009). It is also possible that sealed lots sediment concentrations in this study were lowered by varying sealant weathering conditions or mixtures of coal-tar and asphalt sealants on some parking lots. However, the geometric mean PAH_{16} concentrations reported by this study for unsealed asphalt lots (37,182 ug/kg, n=6) and concrete lots (10,368 ug/kg, n=4) bracket those reported for unsealed pavement dust by Van Metre et al. (2009). This comparison suggests that pavement dust particles generated by unsealed lots in Springfield contain PAH levels similar to or less than other urban PAH sources including road asphalt, petroleum spills, tire wear, and vehicular exhaust. Sealed parking lots in Springfield therefore represent an elevated source of PAHs to the urban environment in contrast to unsealed lots and other urban PAH sources. Given our present understanding of sediment PAH contamination in urban areas (excluding industrial point sources), coal-tar sealants are probably the only source that can explain such high PAH levels (Mahler et al., 2012).

Total PAH concentrations in stream and pond sediments decrease rapidly downstream from urban and commercial core areas in Springfield. Geometric mean sediment PAH_{16} concentrations for stream sediment classes decrease downstream in the order: very small stream, 111,849 ug/kg (n=5); small steam, 107,021 ug/kg (n=2); medium stream, 8,189 ug/kg (n=8); and large stream, 3,080 ug/kg (n=6) (Figure 4). The small stream class contains only two samples from upper South Creek. Stream flow conditions of the small and smaller sediment classes tend to be ephemeral or seasonal in flow and yield poor habitat conditions for aquatic life. Small ponds of course do hold water all year and offer habitat for aquatic life. The small ponds included in this study are located in Southern Hills on upper Galloway Creek and on Jones Branch, a tributary to Pearson Creek (Figure 1). The median PAH_{16} concentration for small pond sediments is 3,965 ug/kg with a highest concentration near 10,000 ug/kg (Table 2). Small pond sediment PAH concentrations are relatively low compared to the downstream trends (i.e., very small and small stream classes, >100,000 ug/kg PAH_{16}). For this study, pond bottom sediment sampling was confined to within 5 meters of the bank edge at water depths <1.5 m and it is possible that the influence of low PAH sediment from local bank or soil erosion sources diluted PAH levels to some degree. Sediment PAH concentration and distribution within the urban ponds in Springfield needs to be studied further to verify the relatively low PAH levels found in the ponds.

Toxicity to Sediment-Dwelling Organisms

To evaluate the significance of high PAH concentrations in urban sediments in Springfield, toxicity criteria are used to determine the probable harmful effects to sediment-dwelling organisms (Table 1; Table 4). Recall, the “threshold effect concentration” (TEC) is the value below which harmful effects are unlikely to occur and the “probable effects concentration” (PEC) is the value above which harmful effects are likely to occur (MacDonald et al. 2000). As expected, sediment classes related to watershed locations closer to urban and commercial core areas and larger parking lot areas tend to be more toxic to aquatic life (Table 5). Three PAH indicators were found at relatively high toxic levels compared to the others. Toxic concentrations of PAH_{16}, Chr, and DahA exceeded 5x the PEC in 100% of the samples tested for both sealed and mixed-surface asphalt parking lots (Table 4). In addition, total PAH concentrations in the toxic range greater than the PEC were frequently measured in sediment samples from concrete lots (50%), asphalt parking lots (100%), and very small/small streams 4>67%) (Table 5). Moreover, with the exception of PAH_{16} concentrations in small pond sediments which were all less than the PEC, all sediment classes contained at least one of the three PAHs above at toxic concentrations above the PEC (Table 4).

PAH concentrations in sediments threaten aquatic life in the streams and ponds of Springfield. For each sediment class, the frequency of sediment samples containing non-toxic levels below the TEC for total PAHs are as follows: sealed lot, 0%; mixed lot, 0%; asphalt lot, 0%; concrete lot, 25%; very small/small stream, 0%; small pond, 12%; medium stream, 12%; and large stream, 50% (Table 4). While reducing the supply rate of PAHs from urban sources such as parking lots and roadways is important, programs aimed at protecting aquatic life need to also focus on improving the habitat conditions present in perennial streams and ponds that are capable of supporting aquatic life in the first place. In this study, sufficient habitat locations have generally been identified by three sediment classes: small ponds, medium streams, and large streams; all have sediment PAH concentration above the TEC and all except the small ponds have concentrations above the PEC (small pond conditions were discussed previously).

In Springfield, sediment PAH concentrations in stream habitats in downstream segments may be harmful to aquatic life and the upstream segments draining core urban areas appear to be contributing to the source of the impairment. PAHs in stream water were previously identified as a potential threat to aquatic life in Springfield (Richards and Johnson, 2002). PAH levels in the main stem of Wilson Creek may also be affected by historical uses of petroleum and coal products for industrial purposes. Macroinvertebrate monitoring programs in Springfield should routinely include sediment PAH sampling as well as other potentially harmful pollutants such as metals, PCBs, and VOCs to evaluate (MacDonald et al. 2000; Scoggins et al, 2007).

Pond Sediment Trends

PAH trends in pond sediments indicate the influence of urban sources on sediment contamination in Pearson Creek and Galloway Creek watersheds (Figure 5). The highest PAH_{16} concentration measured in small pond sediment class for this study was 11,981 ug/kg from the upper pond on Jones Spring Branch in Pearson Creek watershed, about 44 times higher than the PAH concentration in control samples from rural ponds (Table 2; Figure 5; Appendix A). A second sediment sample collected from another site in the upper pond contained 8,051 ug/kg total PAHs. These elevated levels of contamination above the TEC likely indicate that Jones

Spring receives storm-water runoff or seepage from urban or industrial land areas via underground karst conduits since the local area around the spring branch is suburban in character. Recharge contamination of the spring is also indicated since sediment PAH concentrations in Jones Branch decrease downstream by five times to an average of 2,035 ug/kg (n=2) between the upper and lower pond over a distance of a little more than one km downstream (Figures 1 & 5). Moreover, stream sediment PAH concentrations in the main stem of Pearson Creek are relatively low, with concentrations at the site above Jones Branch at FR 199 below detection for all PAH compounds (<528 ug/kg PAH_{16}). Below the Jones Spring Branch confluence, total PAH concentrations in Pearson Creek continue to decrease to 1,280 ug/kg at the USGS gage, 1 km below the confluence, to <742 ug/kg at the railroad bridge which is 0.7 km farther downstream (Appendix A). Again, this pattern indicates a source of PAH contamination from Jones Spring, however, its influence on sediment contamination decreases rapidly downstream to levels below the TEC in the lower segment of Jones Branch and Pearson Creek.

In the Galloway Branch watershed, pond sediments were sampled in the upper and middle ponds in Southern Hills subdivision, Sequiota Cave pond, and where Galloway Branch becomes impounded by Lake Springfield. In Southern Hills, both the upper and middle ponds were sampled at the outlet end of the impoundment. A previous sediment sample collected from the inlet point of the upper Southern Hill pond as a pilot test before the present study contained a PAH_{16} concentration of 3,227 ug/kg. In comparison, on the opposite end of the pond, the mean PAH_{16} concentration in two samples at the outlet of the pond was 4,533 ug/kg. This result indicates that PAH concentrations did not decrease through the pond by sedimentation or dilution by low PAH sediments from other sources. Thus, the lower PAH content of small pond samples collected in Southern Hills, compared to small and medium stream sediment trends (Table 2), probably reflects lower PAH inputs overall from the residential land use in the contributing drainage area.

In contrast to Jones Spring, sediment from Sequiota Spring branch near the cave entrance above Galloway Branch is not contaminated with PAHs, suggesting that its recharge area and karst network is not affected by excessive PAH loads from urban runoff. However, the sediment samples collected from Sequiota pond may have been affected by land disturbances and related sedimentation. Recent construction activities to restore the pond may have removed contaminated sediment or redirected low PAH sediment into the pond. A water line break several years ago caused a cave collapse and soil erosion in the eastern arm of the cave system which flushed significant amounts of uncontaminated residual soil material into the pond.

The two sediment samples collected from the stream-lake transition segment of the Galloway arm of Lake Springfield contain almost 6,000 ug/kg PAH_{16} at a point >5 km below the lower Southern Hills pond outlet (Figures 1 & 5). These elevated PAH levels in Galloway arm may have resulted from widespread urban sources throughout the watershed and/or local sources such as storm-water discharge from the James River Freeway located 1 km upstream or historical inputs from the old industrial sites along lower Galloway Creek.

Sediment Size

Sediment properties including particle size, carbon, or nutrient content can directly indicate PAH concentrations or indirectly relate to the source or transport path of the sediment (Bentzen and Larsen, 2009; Yang et al., 2010; Ghosh and Hawthorne, 2010). Further, the concentrations of major and trace metals and metal contaminants in sediment often are correlated with PAH concentrations and/or specific pollution sources. Thus, data on these parameters are commonly evaluated in pollution source and sediment contamination studies involving PAHs. Springfield sediments typically contain particle sizes in the silt and fine sand range that is easily transported by storm water runoff at the flow velocities and discharges expected for parking lots and streams in the Springfield area. However, particle-size trends fluctuate among sediment classes, with pond sediment being composed of the smallest sediment particles (Table 5; Appendix B & I). This result is expected since wet ponds and impoundments are associated with low energy sedimentary environments and finer-grained sedimentation.

The median particle diameter for all nine sediment classes ranges from 19 um (fine silt) for small ponds to 276 um (fine to medium sand) for large stream samples collected from relatively coarse bar deposits (Table 5). Since the samples were initially prepared by sieving through a 2 mm sieve to remove large grains and coarse organic matter prior to size analysis, the coarsest particles occurring in these samples were limited to the very coarse sand range from 1 to 2 mm in diameter. Sealed parking lot samples were found to contain relatively fine sediment (median size of 24 um with 18% clay) (Table 5). Given that only four sealed lot samples were evaluated, no definitive conclusion is justified. However, it is possible that these finer particles represent the products of the on-going processes of abrasion and weathering of seal-coat applications over time.

Organic Carbon and Nutrients

Organic carbon, nitrogen, and phosphorus concentrations are linked to the abundance of biological material and probably coal-tar sealant and asphalt particles in the sediment. The highest concentrations of each are found in sediments from the coal-tar sealed lot with secondary peaks in small streams and ponds where organic matter tends to accumulate (Table 6; Appendix B & I). Indeed, other studies have found that PAH concentrations in sediments and soils increase with the amount of organic carbon in the sample as related to coal-tar fragments or other combusted particles such as soot or charcoal (Schorer, 1997; Shi et al., 2007; Yang et al., 2010; Ghosh and Hawthorne, 2010). The trend in decreasing organic carbon across the different lot types correlates with similar decreases in PAH_{16} enrichment factors (Tables 2 & 6).

Major and Trace Metals

Metal concentrations in the sediment reflect contributions from both “natural” mineral and anthropogenic contaminant sources. Major metals like Al, Ca, and Fe tend to increase in concentration with the percentage of clay minerals in the sample and are released from the soil during mineral weathering. This relationship is only generally shown in the sediment class trends for this study. The highest concentrations of these three metals are associated with small stream/pond, medium/large stream, and asphalt parking lot sediments (Table 7; Appendix C, D, E, F & I). The highest clay percentages are found in pond sediments and sealed parking lots (Figure 4). The lack of strong correlation between clay content and Al concentration suggests that the main source of clay particles on sealed parking lots may be from the breakdown of the sealant coating and not from alumino-silicate minerals. However, the urban sediments evaluated for this study may contain materials from multiple sources that decrease the effectiveness of statistical trending procedures for identifying source relationships.

The trace metals evaluated in this study can be toxic to aquatic life at relatively low sediment concentrations (Table 1). All eight of the anthropogenic trace metals assessed for this study were detected at levels above the PEC in at least one sample. Both Pb and Zn are frequently found at potentially toxic concentrations in urban sediments in Springfield (Table 7). Maximum sediment class concentrations tended to be above the TEC for Cd. Concentrations of Ni and As tended to be higher downstream of Springfield in medium and large stream sediments (Table 7). While Hg sediment concentrations were typically below the TEC, the highest concentration was found in sediment from a sealed lot. Copper concentrations were sometimes found to be elevated to levels above the TEC in urban sediments. However, the highest Cu concentrations were found at toxic levels in Southern Hills upper pond, probably as a result of copper sulfate treatment to control aquatic weeds (Table 7; Appendix C).

PAH Ratios

PAH ratios are commonly evaluated to determine pollution sources and determine the relative contribution of coal-tar inputs versus other inputs. Three PAH ratios were evaluated for source identification in this study (Figure 6). Phe/Ant ratios tend to be variable, but decrease downstream in small pond and medium/large stream sediments. Ratios <10 are suggested to indicate pyrogenic sources such as coal-tar which was reported to have a Phe/Ant ratio of 3.1 (Crane eta al., 2010). This ratio does not seem to be able to discriminate among source effects in urban sediments in Springfield since the coal-tar lots in the present study have ratios above 10 (Figure 6). Moreover, Fth/Py ratios show no trend along the urban-rural gradient, again suggesting that multiple and mixed PAH sources occur in urban sediments from Springfield (Figure 6). Ratios >1 are reported to indicate pyrogenic sources and a coal-tar sample had a Fth/Py ratio of 1.3 (Crane et al., 2010). While the ratios calculated for the sediment samples in this study suggest a pyrogenic source, there is little change downstream in the ratio even though PAH source inputs would be expected to vary. It may be that pyrogenic sources other than coal-tar are indicated. Nevertheless, the lack of ratio response raises doubt over the resolution of the ratio source identification approach used in this study. Indeed, Bbf/BkF ratios also show no trend downstream. It is possible that sediment source factors associated with particle-size and geochemistry are interfering with ratio trends. Other than source influence, PAH ratios can be affected by differential breakdown of individual PAH compounds as well as other factors including sorting during aerial and fluvial transport, evaporation/volatilization processes, and dissolution into water (Zhang et al., 2005; Crane et al., 2010).

Relationships Among Sediment Composition, Geochemistry, and PAH Concentrations

Correlation matrices are used to determine the direction (+ or -) and statistical strength (significance) of the relationship between two variables. In this case, the relationship to be evaluated is between selected PAHs concentrations and paired sediment variables such as particle-size, organic carbon, and metals. Two different groups of sediment samples were evaluated (Table 8). The first group is composed of parking lot samples and very small stream samples, those sites that are closest to the urban core. The second group consists of stream sediment samples from downstream sites, not including the pond samples.

Sealed parking lot sediment properties indicate a distinct sealant source for particles and organic matter. There is a strong negative relationship between PAH concentrations and particle-size in parking lot sediments indicating that the highest PAH concentrations are associated with smaller particle-sizes or finer sediments (Table 8). This finding supports the previously described observation that coal-tar sealed parking lots tend to have the most clay and organic carbon in comparison to the other sediment classes (Appendix B). Similarly, there is strong positive relationship between organic carbon percentage and PAH concentration in urban sediments (Table 8). The positive relationship between P and PAH concentration is probably related to P being both a chemical component of the organic matter in the sealant and from other nonpoint sources but now bound to sediment surfaces . The positive relationship between Al and PAH concentration is probably related to the composition of the asphalt and possibly clay minerals in the sediment (Table 8).

Correlation analysis of PAHs, OC, P, and metals in parking lot samples generally indicates two different sources for metals: parking lot sealants and more widespread urban sources. There is a strong positive relationship between PAH concentrations and both Hg and P concentrations in parking lot samples suggesting that these elements are also found in relatively high concentrations in the organic component of coal-tar sealants and asphalt to a lesser degree. Since the highest PAH concentrations are found in sediments from sealed parking lots, strong correlations between PAH levels and Hg and Zn and, to a lesser extent, Cu, Cd, and Al concentrations probably indicate a sealant source for these metals in parking lot sediments (Table 8). However, the poor correlation of PAHs with other metals in parking lot sediments including Pb, Cr, As, Mn, Fe, and Ca indicate a poor association with sealant coating sources (Table 8).

These metals are probably released to the environment from more widespread and variable urban sources such as tire and brake wear, exhaust emissions, and building materials that are not specifically related to the presence or weathering of lot sealants. Indeed, correlations increase between PAHs and urban source metals (Pb, Cr, As, Mn, and Fe) in stream and pond sediments downstream of parking lots. Moreover, correlations between PAHs and sealant source metals (Al, Cd, Hg, and Zn) decrease downstream as sediment mixing and variable source inputs dilute parking lot-sediment geochemistry relationships. The identification of the specific geochemical processes involved during pollution transport is beyond the scope of this study. However, it is clear that pollution sources and sediment particle-size, organic carbon, and geochemistry affect PAH and metal concentrations differently in parking lot areas in the urban core compared to downstream stream sediments.

Parking Lot and PAH Assessment in Galloway Creek Watershed

Parking Lot Areas and Distribution

The total drainage area of Galloway Creek is 18.2 km^2 (Figure 7). The total area of mapped parking lots is 1.2 km^2 and includes 382 individually mapped parking lots. The total area of sealed parking lots is 0.90 km^2 or 71.2 % of the total lot area and includes 245 parking lots. Unsealed parking lots cover 0.35 km^2 or 28.8% of the total mapped lot area and includes 137 lots. Sealed parking lots cover 4.8% of the total land area of the watershed, while unsealed lots cover 1.9% of the area. The spatial distribution of parking lots within the Galloway Creek watershed shows significant clustering along main road corridors (Figure 7). Most parking lots within the watershed are located within commercial areas along Glenstone Avenue, Sunshine Street, Battlefield Road, and U.S. Highway 65.

PAH Relationship with Seal-Coated Lot Area

There is a strong relationship between the percent sealed parking lot area (SLA%), defined as the percentage of the total sealed lot area within the drainage area above a sampling site, and the sediment PAH$_{16}$ concentration measured at the site (Table 9; Figure 8). Twenty two sampling sites were located in Gallaway Creek watershed including 12 parking lot, 6 pond, and 4 stream samples. Three of the parking lot sites only drained unsealed lots. A single parameter regression equation using data from the sites draining sealed parking lot areas (n=19) using Log$_{10}$ SLA% to predict Log PAH$_{16}$ concentration explains 79% of the variance (Table 9). Adding Log$_{10}$ percent OC as a second parameter to the equation further reduces the error by 4% and adding a third parameter, Log$_{10}$ median particle size, only reduces the error an additional 2%. Thus, this three-parameter regression model explains 85% of the variance in PAH$_{16}$ concentrations in parking lot and stream sediments.

The overall trend of the equation is produced by a sediment transport process of progressive sediment mixing and PAH dilution downstream away from the sealed parking lot source areas. The diluting sediment is supplied from soil erosion, bank erosion, and other low PAH sources.

The equation can be used to estimate the critical SLA% value required to meet downstream sediment toxicity guidelines (Table 1). A minimum SLA% value of about 3% is needed to meet the TEC value of 1,610 ug/kg PAH_{16} and a SLA% value of 10% is predicted to result in the PEC value of 22,800 ug/kg PAH_{16} (Figure 8).

There is a strong relationship between sealed lot area (SLA%) in the watershed above a sediment sampling point and the PAH sediment concentration measured ($p > 0.01$) (Figure 9). However, this same trend is not shown for metals such as Cd, Pb, Cu, and Zn that are also associated with variable urban sources (Figure 10). For the most part, metals are poorly to weakly correlated with sealed lot area ($p << 0.1$). This pattern suggests that sealed lot area is uniquely linked spatially, probably as a major source, of PAHs in the Galloway Creek watershed. However, metals are supplied from a variety of urban sources, including roadways and urban runoff not uniquely affected by sealed lots.

To improve the regression model to include analysis of all sediment samples collected from Galloway watershed (n=22), the total parking lot area as a percent of the drainage area above a sampling point (TLA%) was added into the regression analysis (Table 9). This allowed the inclusion of the three sites that did not drain sealed lot areas so that the equation could be applied to both of sealed and unsealed parking lot areas. Regression results indicate that a 3-parameter model explains almost 86% of the variance and predicts Log PAH_{16} concentration using Log SLA%, Log TLA%, and Log OC% (Table 9). To include the extra sites into the model, a 1% SLA% value was assumed for the three sites not draining sealed lots as determined in this study. This substitution was needed since the log of zero cannot be determined. Other values of SLA% were tested including 0.01, 0.1, 2, 3, and 5 percent with values ranging from 1 to 3 yielding the best results. The “all site” model (n=22) had a similar r^2 value compared to the “sealed lot site” model (n=19). However, the all site model had some additional advantages including a lower standard error, the more significant effect by OC%, and not including median particle size (Table 9). It is clear from the analysis of the relationship of parking lot area to total PAH concentration that sealed lot area is significantly related to high PAH levels in sediments and that organic carbon is also positively related and significantly related to PAH concentrations.

PAH Ratios and Seal-Coated Lot Area

The influence of SLA% on PAH ratio trends is mixed. There is a lot of scatter with little source differentiation in the downstream direction (decreasing SLA%) for the Phe/Ant ratio (Figure 11). However, both Fth/Pyr and BbF/BkF ratios indicate pyrogenic source inputs at sites close to coal-tar lot areas. Sediment samples collected from sites located near coal-tar lot areas (>70 SLA%) produce similar Fth/Pyr values as pure coal-tar samples at 1.3 (Crane et al., 2010), but there are some samples further downstream (near 30% SLA) that also produce low ratio pyrogenic values. Moreover, even though BbF/BkF values increase with SLA%, a high value is also found near 10% SLA (Figure 11). More research is needed to develop ratios that can identify PAH sources with adequate precision in Springfield.

Potential Effect of a Ban on Coal-tar Sealant Use

In general, urban stream sediments in the City of Springfield are contaminated with Total PAHs to levels that have been found to be toxic to aquatic life (Tables 1 & 2). However, streams that drain greater percentages of rural, suburban, and residential land uses, tend to have lower PAH concentrations such as found in: (i) upper and middle ponds in Southern Hills, (ii) main stem Pearson Creek, and (iii) downstream segments that are further away from urban core areas as in "large streams" such as Wilson Creek (Appendix A). It has been shown that large commercial parking lots are a major source of PAHs to the environment and that sealed parking lots release pavement dusts and other sediment particles that are contaminated with PAHs to concentrations almost two orders of magnitude higher compared to unsealed asphalt and concrete parking lots (Table 2). But a critical question still remains: Would stream sediment contamination decrease to levels less harmful to aquatic life if parking lot sealants were banned in the City?

To address this question, the 3-parameter all-sites regression model developed for Galloway Creek (Table 9) was used to evaluate changes in parking lot source effects (Figure 12). PAH_{16} sediment concentrations were calculated using the equation under two scenarios. In the "before" coal-tar sealant ban scenario, the OC concentration for all the sediment samples was set to a constant 7.12 %, which was the median for all the Galloway Branch samples, and then PAH concentrations were calculated using the same sealed and total lot area values. In the second "after" ban scenario, OC concentration was again set to a constant of 7.12% and the sealed lot area % was set to 1% for all the sites in an attempt to remove the effect of sealed lot contamination on sediment PAH concentrations from the equation. In general, total lot area is positively correlated with sealed lot area, except where the sealed lot area is zero (n=3). Also, total parking lot area is inversely related to drainage area or distance downstream. Therefore, higher values of total lot area % indicate a relatively small stream or pond close to urban core areas.

In comparing the before and after scenarios for predicted PAH concentration trends over total parking lot area, the effect of a reduction of sealed parking lots on sediment and pond sediments was dramatic (Figure 12). In general, total PAH concentrations in parking lot sites with >50% TLA% decreased by two-orders of magnitude and stream/pond sites with <20% TLA decreased by one-order of magnitude (Figure 12). Correspondingly, the percent decrease for parking lot sites was typically >96% and for stream/pond sites the decrease ranged from 80-90% (Figure

12). Recall, there is a 98% difference between the geometric mean of sealed lots and unsealed asphalt lots (Table 2). Further, it would be expected that PAH levels at more distant sites would be lower and closer to rural background levels thus reducing the relative range of decrease possible. The effects of asphalt sealants in contrast to coal-tar sealants were not evaluated in this study. However, if it is assumed that sediment PAH concentrations for asphalt sealed parking lots are six times less than those for coal-tar based sealants (Mahler et al., 2005), then the "after" trend in Figure 12A would increase by only15% or less. If so, then the predicted effects on improved sediment quality described above would be the same with regards to effect on reduced toxicity to sediment dwelling organisms.

These modeling results suggest that elimination of the use of coal-tar sealants in Springfield would decrease the PAH concentrations in stream sediment by >80%. Further, the concentrations at all sites decreased to levels below the PEC and those sites with <20% TLA decreased to levels below the TEC. Importantly, sediment PAH concentrations at all perennial stream and pond sites with sufficient aquatic habitat in Galloway Creek watershed were reduced to below the TEC. However, a ban would only eliminate the new addition of coal tar sealants to the environment. The time for existing coal tar sealants on lots to wear off and contaminated material to work it way though the system to allow sediments recovery to predicted lower levels could take 20 years or more depending on past and future sealant use, supply of residual contaminated sediment, and behavior of other PAH sources.

CONCLUSIONS

The main question to be addressed by this study is: Are PAHs found in urban stream and pond sediments at concentrations high enough to raise environmental concerns, and if so, to what degree are coal-tar sealants the source of PAH contamination in the City of Springfield? Six major conclusions were produced by this study.

1) Urban sediments in Springfield contain PAH concentrations at levels of ecological concern. PAHs were detected in urban sediments at all 49 sites examined within the City of Springfield or in streams draining urban areas. Thirty six percent of the samples were in the threshold effect range from 1,610 ug/kg to 22,800 ug/kg PAH_{16} and 51% exceeded the probable effects concentration of 22,800 ug/kg PAH_{16}. Twelve Springfield sites (25% of the total sampled) contain PAH_{16} concentrations exceeding 5 times the PEC. All of these high PEC sites drain core urban areas that contain relatively large areas of roads and parking lots with a variety of surface characteristics including coal-tar sealants and mixed sealed and unsealed asphalt lots.

2) Similar to findings in other cities in the USA, sediments from sealed parking lots and the streams that drain them are highly enriched in PAHs relative to unsealed asphalt and concrete lots. Sealed parking lots yielded sediment PAH_{16} concentrations that are 148 times higher than those found in sediments from concrete parking lots, 41 times higher than asphalt parking lots, and 2 times higher compared to mixed sealed and unsealed lots. In other words, unsealed asphalt parking lots yielded on average a 97.6% decrease in sediment PAH_{16} concentrations in comparison to coal-tar sealed lots.

3) Metal concentrations are elevated in urban sediments and occur at levels of toxic concern at several locations within Springfield. All eight of the anthropogenic trace metals assessed for this study were detected at levels above the PEC in at least one sample. Both Pb and Zn are frequently found at potentially toxic concentrations in urban sediments. Sediment Ni and As concentrations were higher at downstream locations compared to urban areas. The highest Cu concentrations were found at toxic levels in the upper pond in Southern Hills, probably as a result of copper sulfate treatment to control aquatic weeds.

4) Sealed parking lots cover 4.8% of the Galloway Creek watershed. Large commercial and residential parking lots were mapped and classified according to presence of sealcoat, the majority of which is assumed to be coal-tar sealant based on a 2009 industry survey conducted by the City of Springfield. The total drainage area of Galloway Creek is 18.2 km^2. The total area of mapped parking lots was 1.2 km^2 and includes 382 individual parking lots. The total area of sealed parking lots is 0.90 km^2 or 71.2 % of the total lot area and includes 245 parking lots. Unsealed parking lots cover 0.35 km^2 or 28.8% of the total mapped lot area and includes 137 lots. The spatial distribution of parking lots within the Galloway Creek watershed is not random and shows significant clustering along road corridors.

5) Sediment PAH concentrations in the Galloway Creek watershed are strongly related to the percentage of sealed lot area within the total drainage area upstream of the sampling site (i.e., SLA%). A regression equation using Log_{10} SLA% to predict Log sediment PAH_{16} concentration has an R^2 value of 0.79. Adding organic carbon content and median particle size as predictor variables to the regression equation only increases the R^2 value to 0.85. The overall trend of the equation is described by progressive sediment mixing and PAH dilution downstream away from sealed parking lot source areas. The PEC value of 22,800 ug/kg PAH_{16} is typically exceeded at sites where the SLA is >10%. Sites with SLA% values <3% are predicted to contain sediments with total PAH_{16} concentrations below the TEC value of 1,610 ug/kg. However, only 3 of 22 sampling sites in the watershed had SLA values less than 3% and two of these exceeded the TEC so perhaps this percentage should be lower. Generally, urban metal concentrations in stream and pond sediments are poorly correlated with sealed lot area in contrast to PAHs. This observation suggests that sealed lots are a specific source of PAHs to the environment that is distinct within the urban core areas of Springfield.

6) A regression model approach indicates that a ban on parking lot sealants has the potential to eventually lower the total PAH concentrations in stream and pond sediments

by 80-90%. To evaluate the effects of both sealed and unsealed parking lot areas on sediment PAH concentrations, the total parking lot area as a percent of the drainage area above a sampling point (TLA%) was added into the regression analysis. The expanded model explains almost 86% of the variance in PAH sediment concentration using the predictor variables Log SLA%, Log TLA%, and Log OC%. In comparing the before and after scenarios for predicted PAH concentration trends over total parking lot area by assuming a SLA value of 1% for all sites, the effect of a reduction of sealed parking lots on sediment and pond sediments was dramatic. In general, total PAH concentrations were predicted to decrease at parking lot sites by typically >96% and stream/pond sites by 80-90%. However, the time for sediment PAH concentrations to reach predicted lower levels could take 20 years or more depending on the amounts of PAHs stored in mobile sediments and channel and floodplain deposits that could act as long-term sources of PAHs to the environment due to erosion.

In summary, urban stream sediments in the City of Springfield are contaminated to levels above the TEC and sometimes the PEC. However, streams that drain greater percentages of rural, suburban, and residential land uses, tend to have lower PAH concentrations. It has been shown that large commercial parking lots are a major source of PAHs to the environment and that sealed parking lots release pavement dusts and other sediment particles that are contaminated with PAHs to concentrations almost two orders of magnitude higher compared to unsealed asphalt and concrete parking lots. Results of an industry survey by the City strongly suggest that most if not all of the sealed lots sampled in the study are coated with coal-tar sealants. Banning the use of coal-tar sealants has the potential to eventually reduce sediment PAH levels by 80-99% and improve sediment quality to the levels needed to support healthy ecological communities.

Future work to determine the fate of PAHs in urban streams in Springfield should concentrate on two areas. First, a long-term sampling program should be implemented to monitor PAH concentrations in sediment at key locations over time to understand the temporal dynamics of transport and to set up a baseline to evaluate management decisions and potential harm to aquatic organisms. Possibly implement this within a broader environmental programs and biological testing. Second, an effort should be made to determine the effectiveness of natural or artificial buffers or sedimentation areas to reduce PAH transport to downstream areas.

In conclusion, parking lot sediments collected from unsealed lots in Springfield contain PAH levels similar to or less than other urban PAH sources including road asphalt, petroleum spills, tire wear, and vehicular exhaust. Sealed parking lots in Springfield therefore represent an elevated source of PAHs to the urban environment in contrast to unsealed lots and other urban PAH sources. Given our present understanding of sediment PAH contamination in urban areas (excluding industrial point sources), coal-tar sealants are probably the only source that can explain such high PAH levels (Mahler et al., 2012).

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TABLES

Table 1. Toxicity and Detection Limits for USEPA's 16 Priority PAHs and Selected Metals

PAH Compound		CAS #	Rings	Sediment Toxcity Guidelines[#] ug/kg		Laboratory Detection Limits (ug/kg)			
						Rural (n=8)[&]		Max PAH_{16} (n=6)[+]	
				TEC[$]	PEC[%]	median	max	median	max
1) Naphthalene	Nap	91-20-3	2	176	561	33	48	280	670
2) Acenaphthylene	Any	208-96-8	3			33	48	280	670
3) Acenaphthene	Ace	83-32-9	3			33	48	280	670
4) Fluorene	Flu	86-73-7	3	77	536	33	48	280	670
5) Phenanthrene	Phe	85-01-8	3	204	1,170	33	48	885	5,900
6) Anthracene	Ant	120-12-7	3	57	845	33	48	280	670
7) Fluoranthene	Fth	206-44-0	4	423	2,230	33	48	1,900	5,900
8) Pyrene	Py	129-00-0	4	195	1,520	33	48	1,900	5,900
9) Benzo[a]anthracene*	BaA	56-55-3	4	108	1,050	33	48	885	5,900
10) Chrysene*	Chr	218-01-9	4	166	1,290	33	48	1,900	5,900
11) Benzo[b]fluoranthene*	BbF	205-99-2	5			33	48	1,900	5,900
12) Benzo[k]fluoranthene*	BkF	207-08-9	5			33	48	620	5,900
13) Benzo[a]pyrene*	BaP	50-32-8	5	150	1,450	33	48	1,150	5,900
14) Indeno[1,2,3-cd]pyrene	InP	193-39-5	6			33	48	280	670
15) Dibenz[a,h]anthracene*	DahA	53-70-3	5	33	140	33	48	435	1,200
16) Benzo[g,h,i]perylene	BghiP	191-24-2	6			33	48	435	1,200
Total PAHs, sum of above 16	PAH_{16}			1,610	22,800				

Metal		Sediment Toxcity Guidelines[#] ^{m}g/kg		Detection Limit[!] mg/kg
		TEC[$]	PEC[%]	
Arsenic	As	9.8	33	2
Cadmium	Cd	0.99	4.98	0.5
Chromium	Cr	43	111	1
Copper	Cu	31.6	149	1
lead	Pb	35.8	128	2
Mercury	Hg	0.18	1.06	0.01
Nickel	Ni	22.7	48.6	1
Zinc	Zn	121	459	2

* U.S. EPA Group B2, Probable Human Carcinogen

Reported by MacDonald et al. (2000) for sediment-dwelling organisms in freshwater ecosystems.

$ Threshold effect concentration (TEC) is the value below which harmful effects are unlikely to occur. Testing showed that 70-80% of the samples were correctly classified as "Non-toxic."

% Probable effects concentration (PEC) is the value above which harmful effects are likely to occur. Testing showed that >90% of the samples were correctly classified as "toxic."

[&] Detecton limits for rural control stream and pond sediments reported by commercial laboratory.

[+] Detection limit for samples with high PAH16 concentrations (>1,000,000 ug/kg) reported by commerical laboratory. Sample dilution for analytical reasons increases the detection limit accordingly.

[!] Reported detection limit by commercial laboratory

Table 2. PAH Concentrations by Sediment Class

	Nap	**Any**	**Ace**	**Flu**	**Phe**	**Ant**	**Fth**	**Py**	**BaA**	**Chr**	**BbF**	**BkF**	**BaP**	**InP**	**DahA**	**BghiP**	**PAH$_{16}$**
Geo-mean (ug/kg)																	
CT lot (n=4)	73	609	2,995	3,113	96,979	8,107	352,256	236,527	95,199	188,893	262,820	63,013	125,268	37,757	6,455	29,813	1,538,736
Mixed lot (n=4)	53	200	1,164	1,520	44,626	4,759	165,770	106,264	51,506	86,748	131,674	31,453	74,874	33,052	6,508	28,496	782,840
Asphalt lot (n=60	U	30	49	54	2,460	244	7,583	4,993	2,261	4,061	5,699	1,877	3,200	2,006	223	1,665	37,182
Concrete lot (n=4)	U	24	35	40	722	69	2,291	1,225	563	1,128	1,920	568	881	397	71	316	10,368
VS stream (n=5)	18	83	170	186	6,414	745	24,071	15,094	6,820	11,134	15,596	5,264	9,496	6,389	1,216	5,943	111,849
S stream (n=2)	27	115	220	277	8,270	745	23,875	14,859	6,465	11,593	16,432	5,340	8,626	3,723	836	3,441	107,021
S pond (n=8)	U	19	U	U	206	26	752	435	212	412	659	176	362	304	57	227	3,965
M stream (n=8)	24	51	39	41	484	98	1,145	1,001	503	837	1,371	380	790	467	57	333	8,189
L stream (n=6)	19	36	35	37	145	59	433	305	208	242	495	100	340	138	32	117	3,089
Maximum (ug/kg)																	
CT lot	370	2,300	8,500	9,900	210,000	20,000	830,000	560,000	270,000	460,000	730,000	250,000	360,000	77,000	19,000	67,000	3,712,640
Mixed lot	270	730	2,100	2,600	69,000	6,700	240,000	230,000	79,000	130,000	220,000	50,000	120,000	74,000	12,000	66,000	1,092,520
Asphalt lot	U	140	200	240	8,500	1,100	31,000	19,000	9,500	16,000	23,000	7,900	13,000	6,000	1,000	4,900	141,495
Concrete lot	U	49	90	120	2,400	200	8,600	4,800	2,100	4,000	7,600	2,300	3,400	1,300	160	1,100	38,185
VS stream	38	330	850	800	21,000	2,100	87,000	53,000	23,000	44,000	70,000	16,000	46,000	18,000	3,700	16,000	386,975
S stream	47	120	550	640	18,000	1,500	38,000	24,000	11,000	16,000	18,000	6,200	12,000	4,200	970	3,700	154,917
S pond	U	39	U	U	790	97	2,600	1,300	660	1,300	1,900	530	1,000	800	260	660	11,981
M stream	340	460	530	590	9,000	1,500	17,000	11,000	6,100	7,900	11,000	3,100	6,900	2,700	420	2,100	80,640
L stream	56	150	300	280	3,300	820	5,100	3,700	2,100	2,100	2,400	840	1,800	1,100	230	920	24,986
PAH$_{16}$ Fraction (%)																	
CT lot	0.00	0.04	0.19	0.20	6.3	0.53	22.9	15.4	6.2	12.3	17.1	4.1	8.1	2.5	0.4	1.9	100
Mixed lot	0.01	0.03	0.15	0.19	5.7	0.61	21.2	13.6	6.6	11.1	16.8	4.0	9.6	4.2	0.8	3.6	100
Asphalt lot	0.04	0.08	0.13	0.15	6.6	0.66	20.4	13.4	6.1	10.9	15.3	5.0	8.6	5.4	0.6	4.5	100
Concrete lot	0.14	0.24	0.34	0.39	7.0	0.66	22.1	11.8	5.4	10.9	18.5	5.5	8.5	3.8	0.7	3.0	100
VS stream	0.02	0.07	0.15	0.17	5.7	0.67	21.5	13.5	6.1	10.0	13.9	4.7	8.5	5.7	1.1	5.3	100
S stream	0.02	0.11	0.21	0.26	7.7	0.70	22.3	13.9	6.0	10.8	15.4	5.0	8.1	3.5	0.8	3.2	100
S pond	0.38	0.47	0.38	0.38	5.2	0.66	19.0	11.0	5.4	10.4	16.6	4.5	9.1	7.7	1.4	5.7	100
M stream	0.30	0.63	0.47	0.51	5.9	1.2	14.0	12.2	6.1	10.2	16.7	4.6	9.7	5.7	0.7	4.1	100
L stream	0.60	1.2	1.1	1.2	4.7	1.9	14.0	9.9	6.7	7.8	16.0	3.2	11.0	4.5	1.0	3.8	100

Table 3. Frequency Distribution of Relative Difference between Field Duplicates

Percentile	Mean Dia.	D10 Dia.	Median Dia.	D90 Dia.	Sand	Silt	Clay	Ctot	Corg	Cin	N	S	P
n	*13*	*13*	*13*	*13*	*13*	*12*	*12*	*13*	*13*	*13*	*13*	*13*	*13*
90%	44	70	44	50	64	42	51	58	74	131	38	124	5.9
75%	41	37	27	36	39	15	18	33	33	54	26	45	4.9
median	**26**	**10**	**14**	**23**	**15**	**6.1**	**10**	**21**	**26**	**18**	**14**	**19**	**1.5**
25%	12	4.9	3.3	15	4.3	2.4	4.3	1.8	12	9.6	6.7	7	0
10%	7.9	0.5	1.4	10	1.7	0.7	1.5	0.5	4.9	6.2	3.2	6	0

Percentile	Al	Ca	Fe	Mn	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn	pH
n	*13*	*13*	*13*	*13*	*12*	*11*	*13*	*13*	*13*	*13*	*13*	*13*	*13*
90%	8.4	7.0	5.5	9.6	35	18	26	30	20	21	24	9.9	1.4
75%	5.4	5.6	3.5	5.2	24	17	14	24	13	15	8.0	8.8	1.4
median	**1.9**	**2.4**	**1.5**	**3.3**	**13**	**12**	**8.1**	**13**	**8.8**	**0**	**7.4**	**5.3**	**0**
25%	0.9	1.4	0.7	1.7	0	4.2	2.1	9.7	2.8	0	0	2.1	0
10%	0.7	0.3	0.1	1.0	0	0	1.1	8.9	1.9	0	0	0.9	0

Percentile	Nap	Any	Ace	Flu	Phe	Ant	Fth	Py	BaA	Chr	BbF	BkF	BaP	InP	DahA	BghiP	PAH16
n	*2*	*6*	*6*	*5*	*11*	*9*	*11*	*11*	*11*	*11*	*11*	*11*	*11*	*11*	*10*	*11*	*11*
90%	32	63	71	79	55	43	48	48	48	52	49	48	46	43	63	50	46
75%	28	35	24	22	27	22	24	38	42	40	41	26	34	32	46	42	33
median	**19**	**27**	**17**	**21**	**17**	**21**	**22**	**21**	**23**	**17**	**24**	**17**	**15**	**8**	**29**	**26**	**16**
25%	11	19	13	20	13	15	14	13	10	15	13	7.2	11	6.8	4.3	7.4	8.5
10%	6.0	11	6.3	11	6.6	9.1	6.5	10	5.7	5.6	4.3	3.1	3.9	4.5	1.9	2.9	5.2
Analytical Error*	9.7	2.7	3.4	2.8	1.5	2.8	2.1	2.9	2.3	8.0	6.7	1.0	1.5	1.4	5.8	1.2	4.9

* Analytical error for replicate analyses of coal tar standard SRM 1597a reported by Wise et al. (2010)

Table 4. Sediment Toxicity by Sediment Class

Total PAHs (PAH_{16})

Sediment Class	n	Percent of samples in each category			
		<TEC	TEC-PEC	PEC-5xPEC	>5xPEC
Sealed lot	4				100
Mixed lot	4				100
Asphalt lot	6		33	50	17
Concrete lot	4	25	25	50	
VS/S stream	7			57	43
S pond	8	12	88		
M stream	8	12	63	25	
L stream	6	50	33	17	
Total:	47	13	36	26	26

Chrysene (Chr)

Sediment Class	n	Percent of samples in each category				
		<DL	DL-TEC	TEC-PEC	PEC-5xPEC	>5xPEC
Sealed lot	4					100
Mixed lot	4					100
Asphalt lot	6				67	33
Concrete lot	4		25	25	50	
VS/S stream	7				29	71
S pond	8		13	74	13	
M stream	8		13	50	24	13
L stream	6	17	33	17	33	
Total:	47	2	11	26	27	34

Dibenz[a,h]anthracene (DahA)

Sediment Class	n	Percent of samples in each category				
		<DL	DL-TEC	TEC-PEC	PEC-5xPEC	>5xPEC
Sealed lot	4					100
Mixed lot	4					100
Asphalt lot	6	17			66	17
Concrete lot	4	25		50	25	
VS/S stream	7					100
S pond	8	50			50	
M stream	8	50			50	
L stream	6	66		17	17	
Total:	47	30	0	6	30	34

Table 5. Particle Size Trends

Sediment Class	Mean Dia. um	D10 Dia. um	Median Dia. um	D90 Dia. um	Sand %	Silt %	Clay %
Geo-mean							
CT lot	89	2.2	24	278	25.1	53.5	17.5
Mixed lot	288	4.5	142	780	58.4	31.0	9.0
Asphalt lot	188	5.7	99	487	41.6	34.8	7.9
Concrete lot	280	13.0	185	596	52.6	20.1	5.5
VS stream	128	9.7	95	273	20.7	21.4	6.8
S stream	316	6.3	154	807	53.8	31.9	10.6
S pond	53	2.3	19	138	15.5	64.3	16.7
M stream	160	9.0	70	400	35.5	17.9	8.0
L stream	333	12.6	276	690	60.1	17.3	5.6
Maximum							
CT lot	207	3.0	55	588	48.4	67.7	21.2
Mixed lot	359	6.2	275	965	66.6	42.0	13.3
Asphalt lot	375	12.8	335	922	78.8	74.9	17.9
Concrete lot	696	389	660	1092	96.1	65.7	16.2
VS stream	841	469	814	1253	100	77.3	22.6
S stream	554	14.8	600	1000	69.0	43.7	14.3
S pond	152	3.2	25	576	31.0	72.5	24.9
M stream	870	539	835	1250	100	71.1	23.1
L stream	674	234	623	1190	93.4	67.4	17.5

Table 6. Carbon, Nutrients, and pH Trends

Sediment Class	Ctot	Corg	Cin	N	S	P	Corg:N	N:P	pH 50:50 v/v
	loi-%	loi-%	loi-%	loi-%	loi-%	AQ-%	ratio	ratio	pH units
Geo-mean									
CT lot	13.56	12.11	1.40	0.47	0.16	0.07	26	7.2	7.3
Mixed lot	10.24	8.74	1.00	0.26	0.14	0.06	33	4.6	7.3
Asphalt lot	9.88	7.16	2.54	0.20	0.12	0.04	36	5.0	7.5
Concrete lot	4.91	3.88	0.60	0.16	0.23	0.04	24	3.8	7.8
VS stream	3.65	3.18	0.31	0.16	0.07	0.05	20	3.5	7.7
S stream	6.90	6.01	0.81	0.21	0.08	0.07	29	3.2	7.5
S pond	7.67	6.36	1.20	0.35	0.18	0.05	18	6.4	7.3
M stream	4.43	3.87	0.48	0.13	0.09	0.05	29	2.7	7.4
L stream	2.74	2.15	0.50	0.09	0.05	0.07	23	1.4	7.5
Maximum									
CT lot	19.16	16.67	2.49	0.61	0.23	0.09	38.9	10.2	7.4
Mixed lot	15.12	14.81	2.30	0.54	0.19	0.09	42.4	8.4	7.5
Asphalt lot	15.16	11.00	4.43	0.33	0.19	0.05	46.6	7.4	7.6
Concrete lot	7.12	6.91	2.81	0.48	2.04	0.08	48.0	6.3	8.0
VS stream	7.92	6.16	1.76	0.34	0.13	0.07	32.9	7.6	8.2
S stream	7.72	7.12	1.09	0.41	0.08	0.12	46.9	3.6	7.7
S pond	11.03	9.73	2.87	0.66	0.46	0.08	24.5	8.8	7.5
M stream	7.43	6.98	0.64	0.38	0.36	0.09	91.1	8.2	8.0
L stream	5.45	4.84	0.75	0.35	0.16	0.11	53.7	5.1	7.7

Table 7. Sediment Metal Trends

Sediment Class	Al %	Ca %	Fe %	Mn ppm	As ppm	Cd ppm	Cr ppm	Cu ppm	Pb ppm	Hg ppm	Ni ppm	Zn ppm
Geo-mean												
CT lot	0.75	10.6	1.27	458	5	0.9	45	48	77	0.11	12	409
Mixed lot	0.68	12.3	1.12	488	4	0.8	96	32	190	0.05	9	390
Asphalt lot	0.35	20.0	0.86	400	4	0.9	47	31	87	0.03	10	327
Concrete lot	0.56	7.56	1.16	556	3	0.3	77	31	136	0.02	14	180
VS stream	0.99	3.08	1.53	688	3	0.4	43	20	54	0.03	7	260
S stream	1.64	6.44	4.07	3,786	18	0.7	94	28	181	0.04	28	274
S pond	0.99	11.4	1.20	575	4	0.9	28	43	50	0.06	12	169
M stream	1.03	8.03	2.11	1,228	6	1.1	43	32	64	0.07	21	214
L stream	0.82	5.55	2.31	1,459	7	1.4	65	20	91	0.07	24	306
Maximum												
CT lot	1.23	16.2	1.94	1,280	9	1.2	59	65	131	0.20	14	692
Mixed lot	0.86	16.1	1.96	982	5	2.8	513	36	1,875	0.06	11	1235
Asphalt lot	0.5	24.2	1.31	682	5	1.6	117	43	288	0.07	15	463
Concrete lot	1.22	14.6	1.69	1,295	7	0.5	150	51	443	0.06	18	345
VS stream	1.34	12.3	1.87	813	6	0.8	98	54	249	0.07	12	720
S stream	2.26	11.9	7.78	13,850	36	1.7	129	38	204	0.05	58	324
S pond	1.37	19.5	1.68	1,820	7	2.4	46	264	60	0.07	18	297
M stream	1.81	18.6	5.29	5,970	26	2.6	105	67	147	0.13	39	559
L stream	1.3	9.2	4.29	4,720	19	18.9	137	36	224	0.14	52	2,800

Table 8. Pearson Correlation Matrixes (Log_{10} x Log_{10}) for Selected PAHs

Parking Lot Sediment (n=23)

	d50	Sd	OC	P	Al	Ca	Fe	Mn	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
Fth	-0.40	-0.07	**0.66**	**0.54**	0.38	0.14	0.17	0.00	0.18	0.41	0.02	0.43	0.03	**0.73**	0.10	**0.49**
Py	-0.40	-0.08	**0.67**	**0.51**	0.35	0.14	0.14	-0.02	0.16	0.39	0.02	0.41	0.03	**0.71**	0.08	0.45
Chr	-0.43	-0.10	**0.68**	**0.54**	0.36	0.14	0.15	-0.02	0.17	0.40	0.01	0.43	0.03	**0.73**	0.10	**0.47**
BaP	-0.43	-0.11	**0.66**	**0.55**	0.40	0.12	0.17	0.00	0.17	0.40	0.02	0.42	0.03	**0.74**	0.10	**0.49**
InP	-0.40	-0.14	**0.65**	**0.54**	0.38	0.09	0.17	0.00	0.19	0.37	-0.04	0.37	-0.04	**0.69**	0.02	0.47
BghiP	-0.39	-0.15	**0.63**	**0.55**	0.40	0.07	0.18	0.01	0.19	0.36	-0.05	0.35	-0.05	**0.67**	-0.01	0.47
PAH16	-0.42	-0.10	**0.67**	**0.54**	0.38	0.13	0.16	-0.01	0.18	0.40	0.01	0.42	0.02	**0.73**	0.09	**0.47**

Stream and Pond Sediment (n=24)

	d50	Sd	OC	P	Al	Ca	Fe	Mn	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
Fth	0.34	0.23	0.28	-0.12	-0.14	0.08	0.25	0.18	0.24	-0.09	0.25	0.25	0.23	0.13	0.18	0.10
Py	0.38	0.31	0.17	-0.04	-0.06	0.00	0.44	0.34	0.44	-0.09	0.40	0.26	0.32	0.01	0.33	0.13
Chr	0.34	0.27	0.21	-0.06	-0.04	0.03	0.41	0.31	0.41	-0.09	0.37	0.28	0.30	0.02	0.31	0.12
BaP	0.45	0.37	0.13	-0.11	-0.04	-0.05	**0.48**	0.36	**0.48**	0.10	0.42	0.22	**0.49**	-0.01	0.35	0.35
InP	0.24	0.18	0.27	0.00	0.04	-0.01	0.43	0.33	**0.47**	-0.09	0.34	0.34	0.26	-0.07	0.30	0.11
BghiP	0.27	0.20	0.29	-0.01	0.02	0.00	0.42	0.33	0.45	-0.07	0.34	0.34	0.31	-0.04	0.30	0.14
PAH16	0.42	0.33	0.17	-0.08	-0.06	-0.01	0.44	0.34	0.44	0.01	0.40	0.24	0.40	0.01	0.33	0.24

* Underline= significant at >0.1 level

Bold= significant at >0.02 level

Table 9. Log PAH16 Regression Equations

Model*	**R^2**	**s.e.** (Error of Y est.)	**F_R**	**bo** (Y-int)	**Log SLA%$^\#$** b1	p-value	**Log TLA%** b2	p-value	**Log OC%** b3	p-value	**Log D50$_{<2mm}$** b4	p-value
For sites with Sealed Lot Area >0% (n=19)												
1-p	0.790	0.549	64.1	2.05	2.26	0.000	X	X	X	X	X	X
2-p	0.827	0.514	38.3	1.29	2.12	0.000	X	X	1.06	0.084	X	X
3-p	0.851	0.492	28.6	0.90	1.97	0.000	X	X	1.01	0.088	0.395	0.139
All sites (n=22) (note: value of 1% for sealed lot area % was used for the 3 "0%" sites to calculate log value)												
1-p	0.655	0.701	38	3.09	1.53	0.000	X	X	X	X	X	X
1-p	0.422	0.907	14.6	1.96	X	X	1.88	0.001	X	X	X	X
2-p	0.803	0.545	38.4	1.62	1.24	0.000	1.19	0.001	X	X	X	X
3-p	0.855	0.479	35.4	0.77	1.05	0.000	1.23	0.001	1.19	0.019	X	X
4-p	0.860	0.484	26.2	0.57	1.08	0.000	1.09	0.005	1.28	0.016	0.178	0.439

* Form of the equation: Log PAH_{16} ug/kg = b0 + (b1 x Log SLA%) + (b2 x Log TLA%) + (b3 x Log OC%) + (b4 x Log D50)

\#

SLA%= Sealed lot area in the drainage area above the sample point (km^2) / drainage area above the sample point (km^2) x 100
TLA%= Total lot area in the drainage area above the sample point (km^2) / drainage area above the sample point (km^2) x 100
OC%= Organic carbon content of the <2 mm fraction of the sediment (%)
$D50_{<2mm}$ = median particle size of the <2 mm fraction in microns

FIGURES

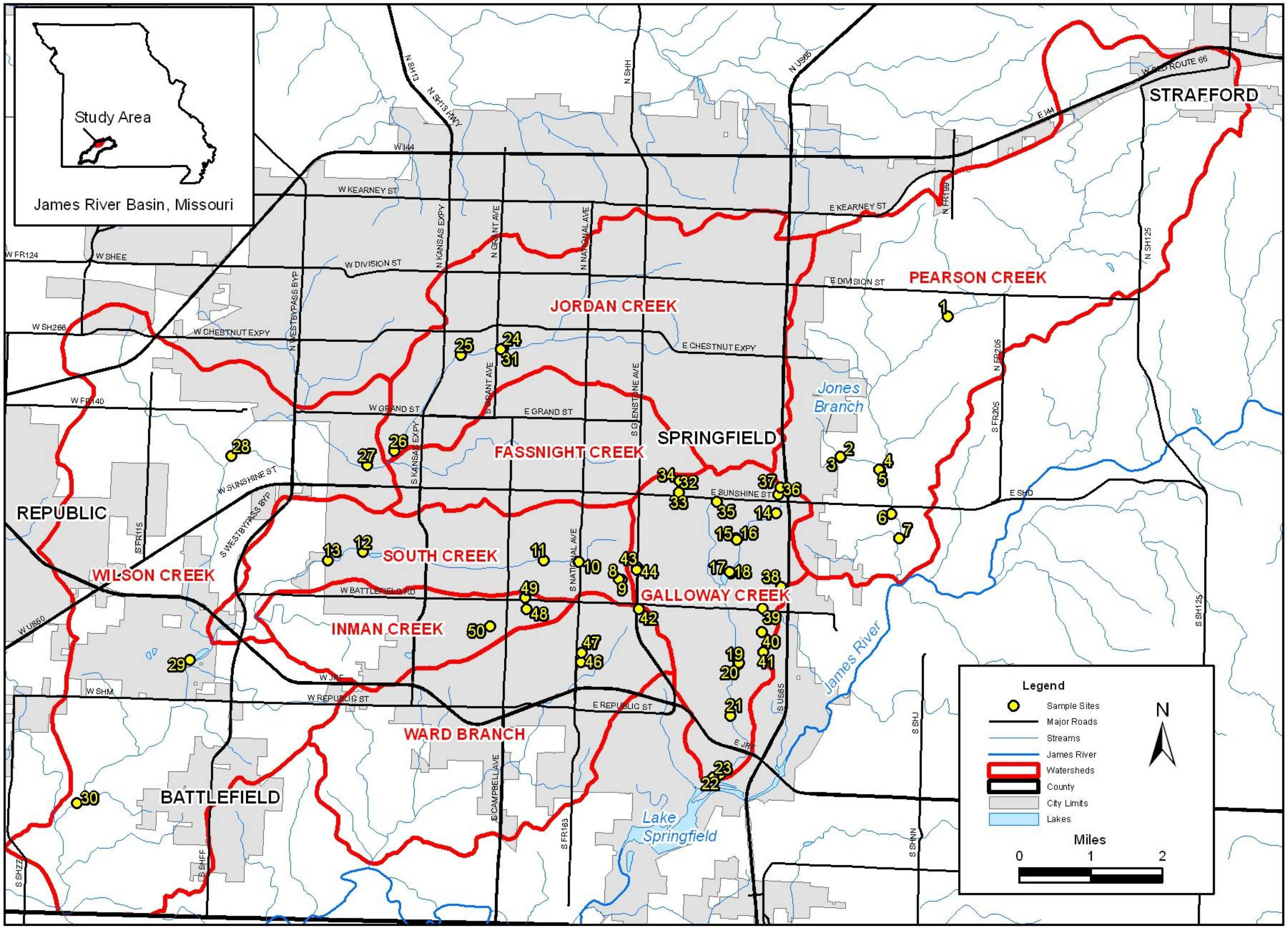


Figure 1. Urban Samples Sites in the Springfield Area

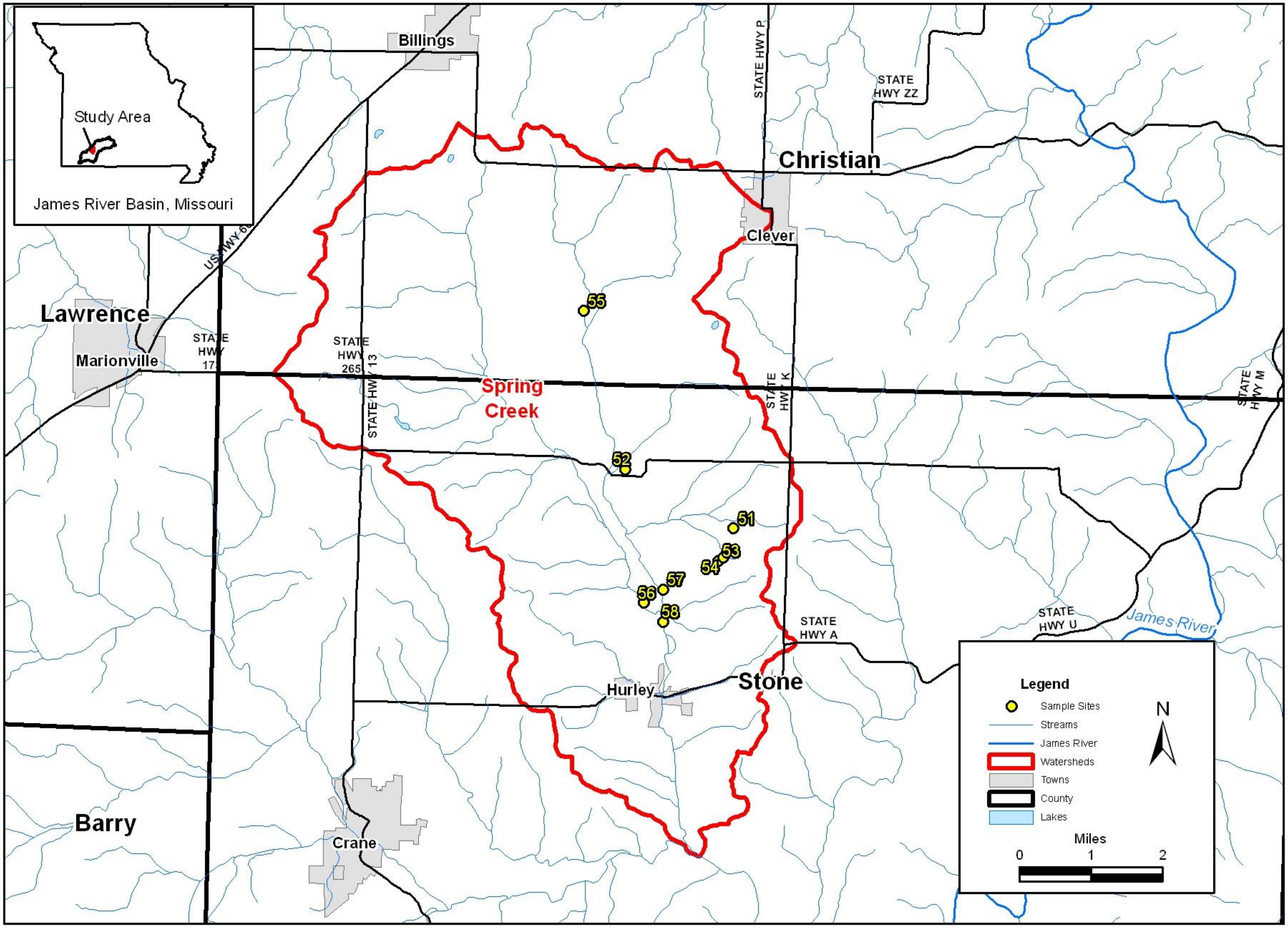


Figure 2. Rural Sample Sites in Christian and Stone Counties

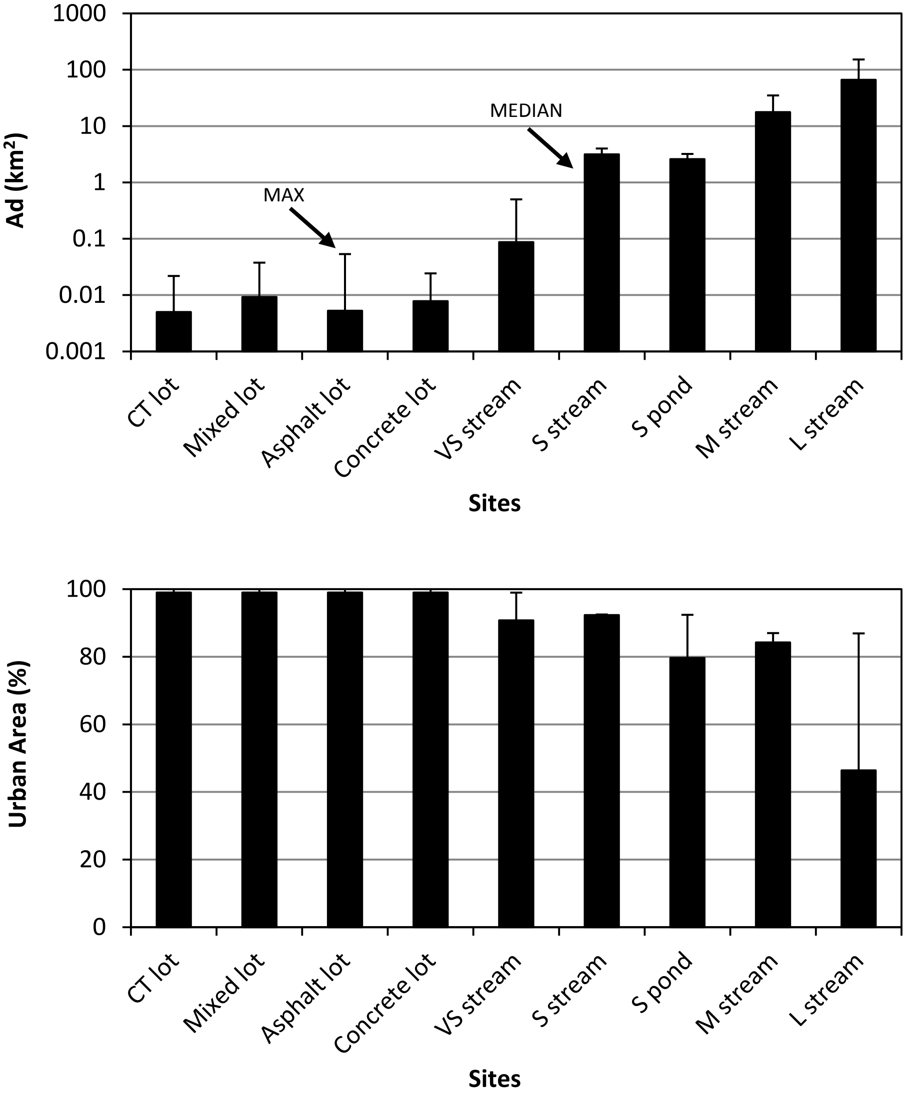


Figure 3. Watershed Characteristics by Sediment Class

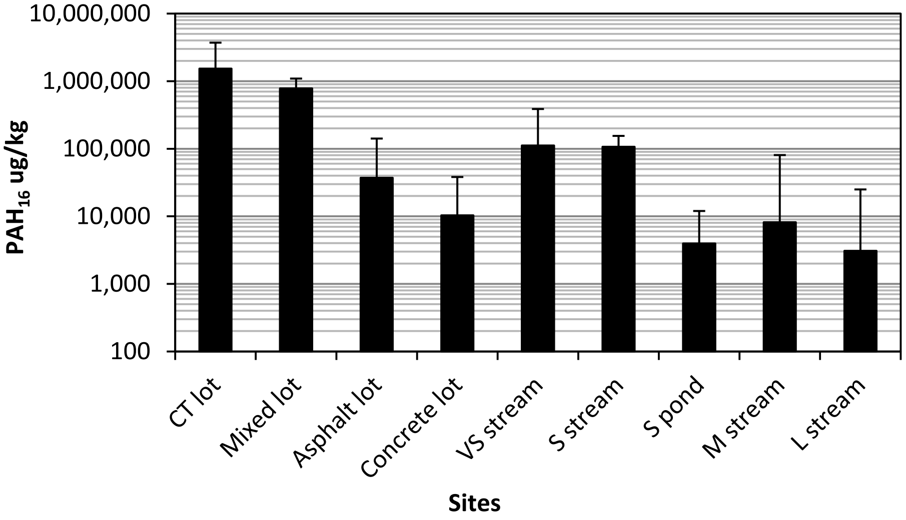


Figure 4. PAH$_{16}$ Trends by Sediment Class

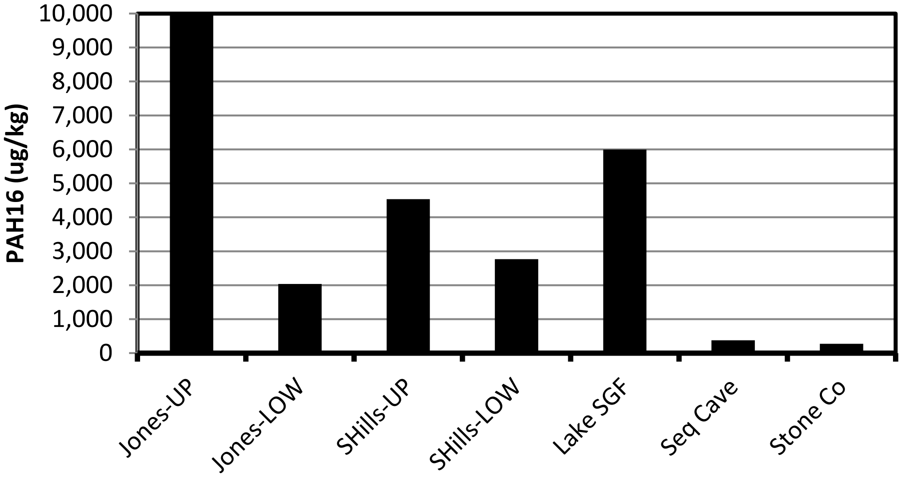


Figure 5. Average PAH$_{16}$ Concentrations in Pond Samples

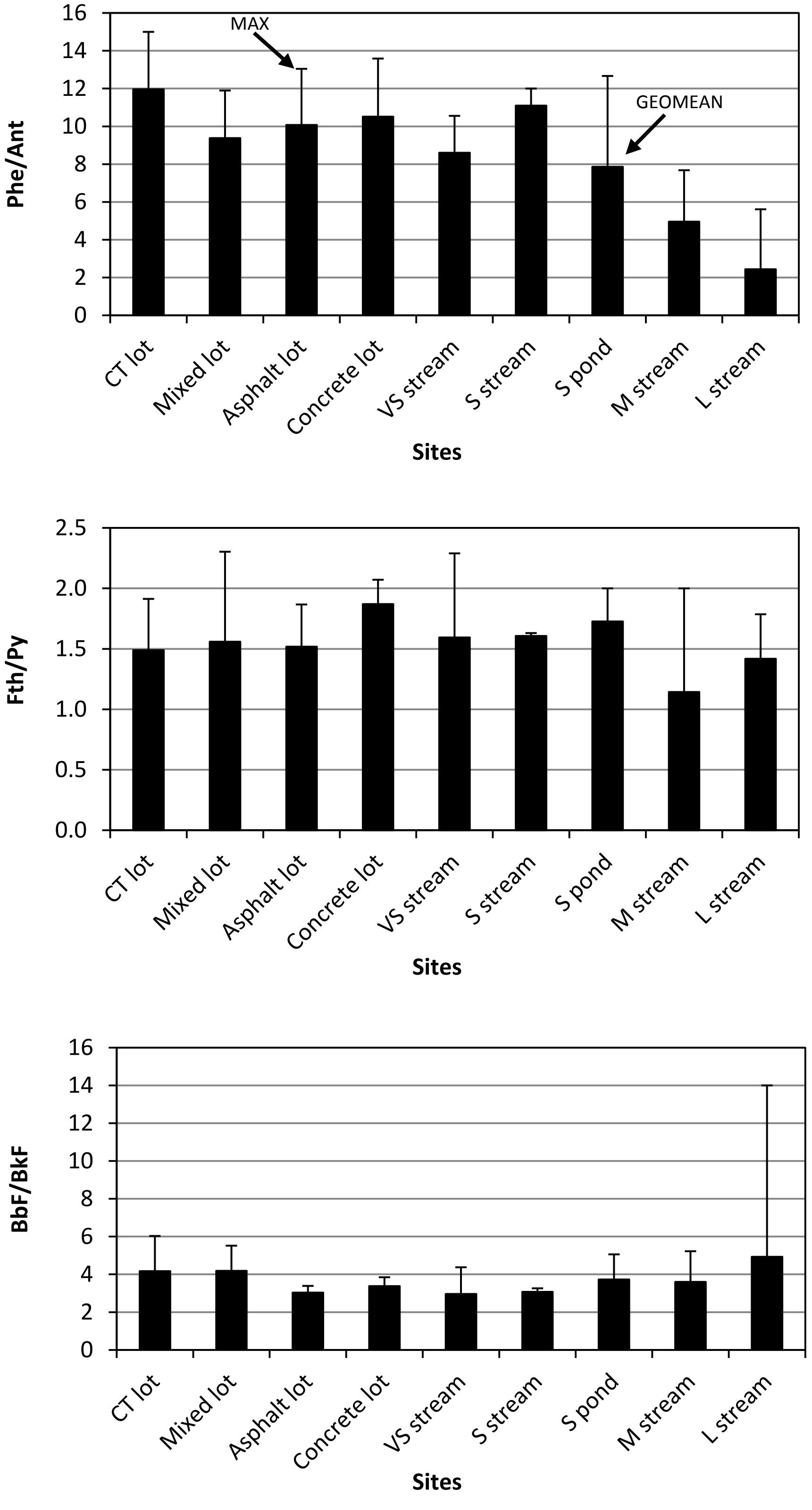


Figure 6. Selected PAH Ratios

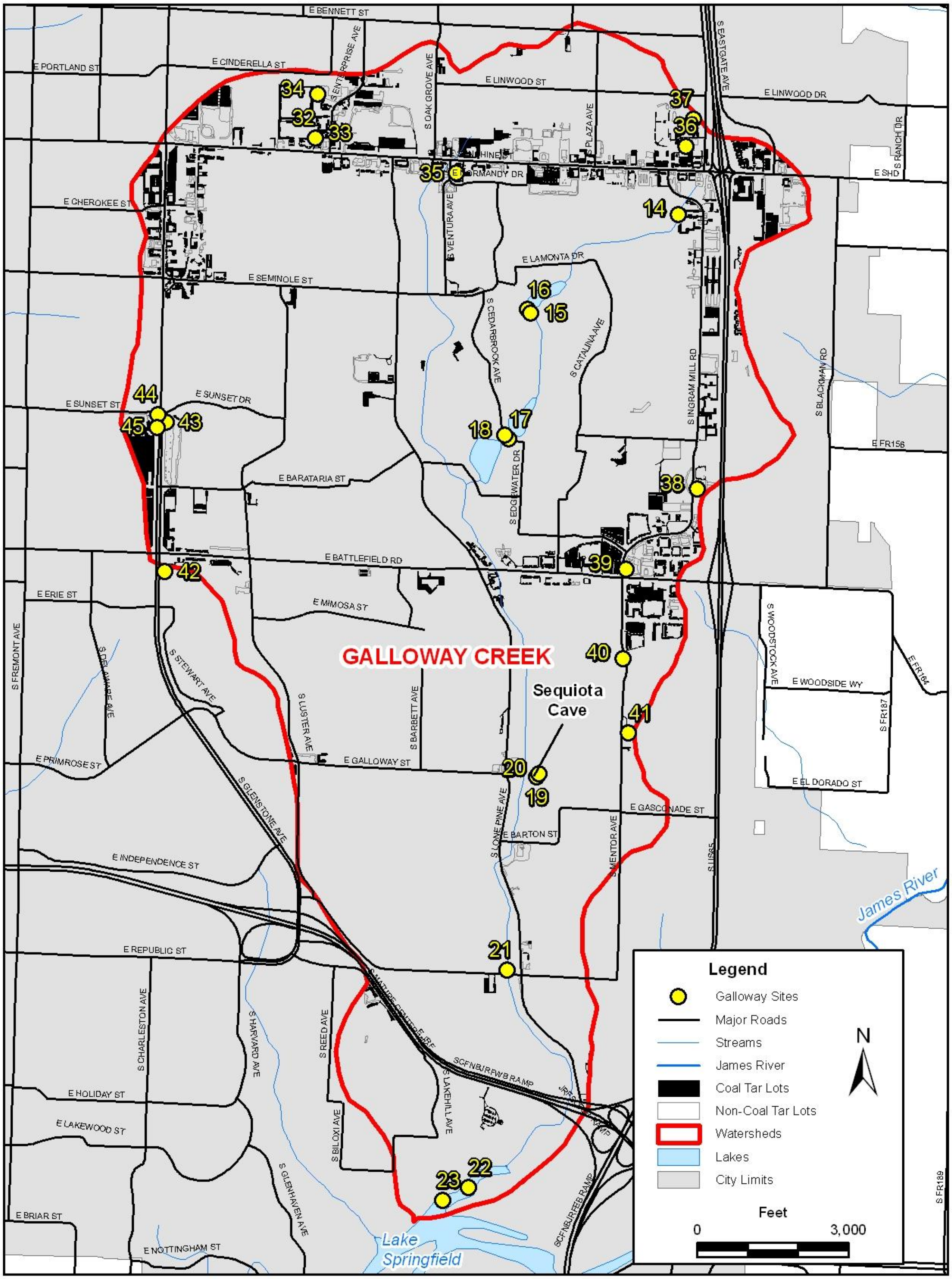


Figure 7. Galloway Creek Sample Sites

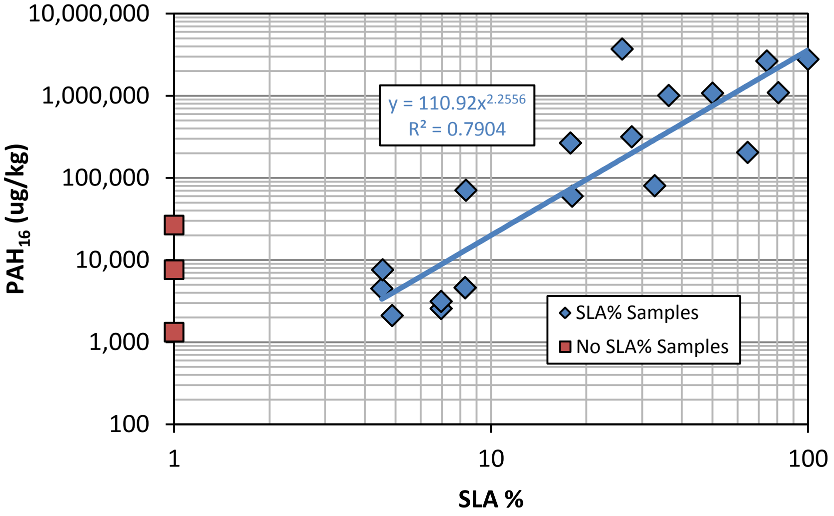


Figure 8. PAH$_{16}$ Relationships to Seal-Coated Lot Area

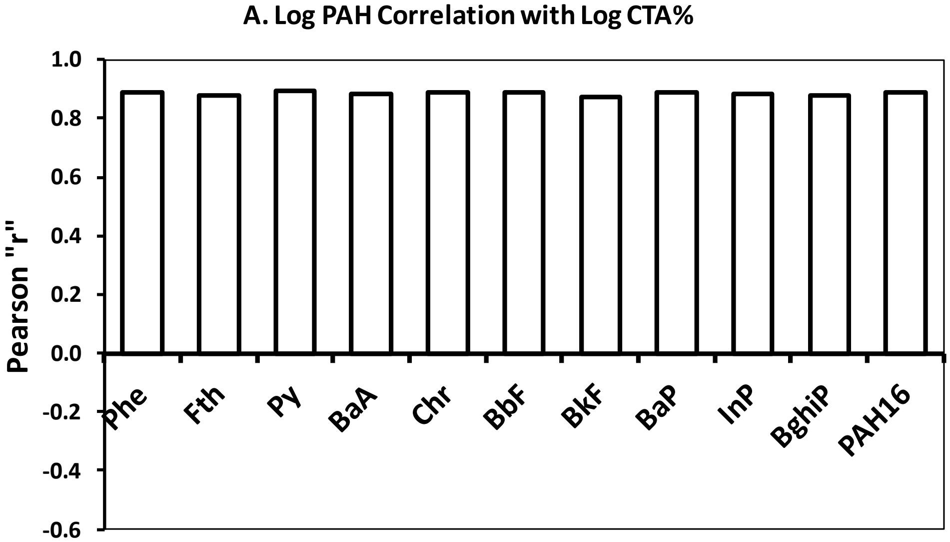


Figure 9. Correlation of Sealed-Coated Lot Area with PAHs.

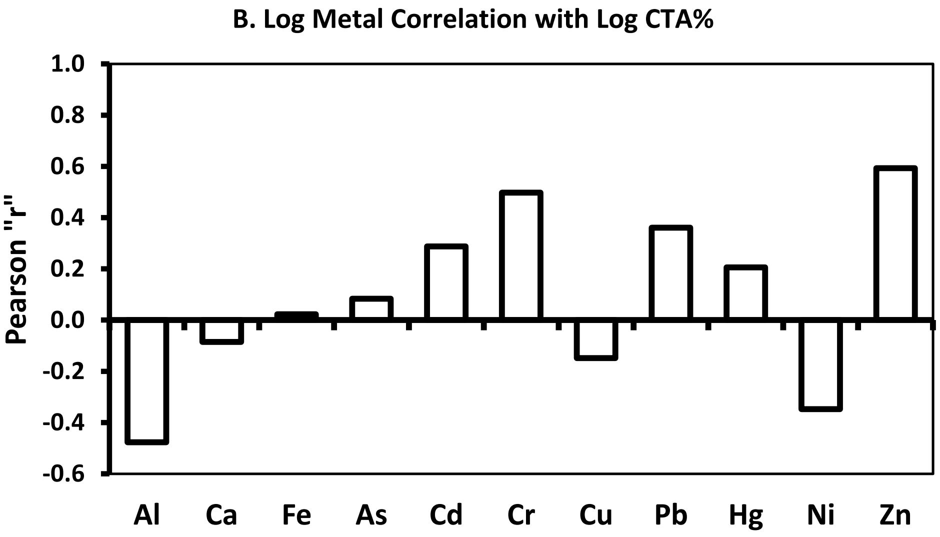


Figure 10. Correlation of Sealed-Coated Lot Area with Metals

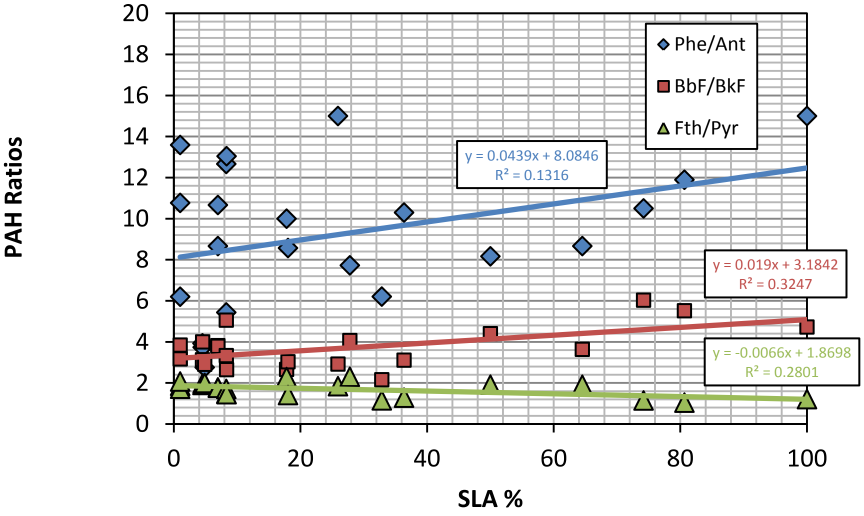
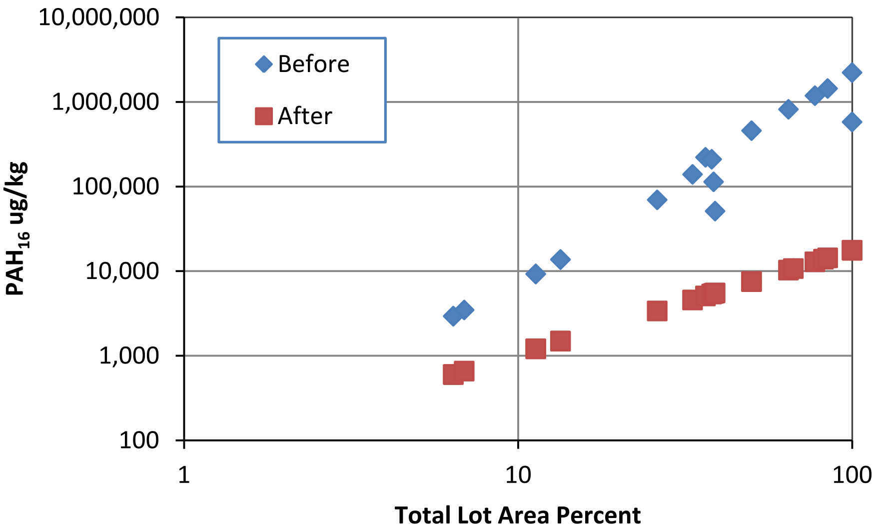


Figure 11. PAH Relationships to Seal-Coated Lot Area

A.) Predicted change in sediment PAH concentration assuming no sealed lots



B.) Percent decrease in PAH_{16} concentrations assuming 0 parking lot area.

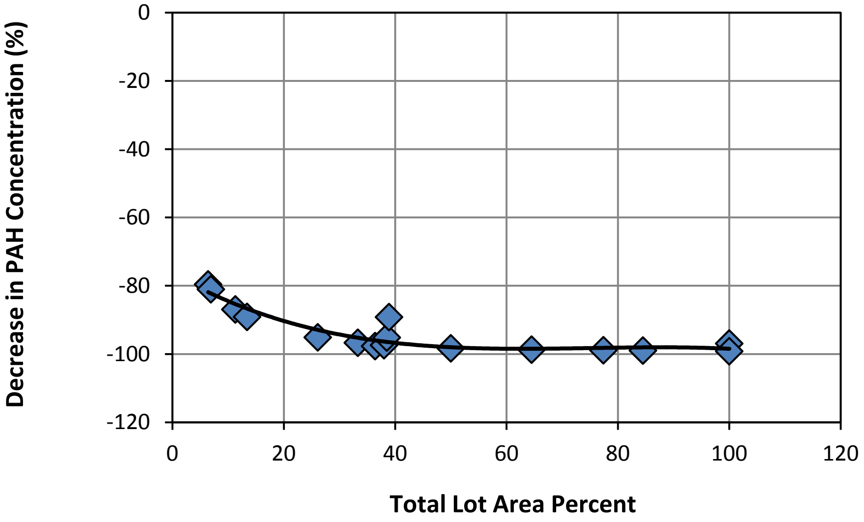


Figure 12. Reduction in Sediment PAH Concentrations Assuming No Sealed Parking Lots.

Appendix A. Sample Site Characteristics

Sample ID	Sample Location			GPS Point		Description	
	Watershed	County	Site	Latitude	Longitude	Sediment Class	Deposit
001	Pearson Creek	Greene	FR 199 crossing	37.21799	-93.18448	U stream	bar
001-FD	Pearson Creek	Greene	FR 199 crossing	37.21799	-93.18448	U stream	bar
002	Pearson Creek	Greene	Jones Br-upper pond	37.18940	-93.21137	S pond	bed
002-FD	Pearson Creek	Greene	Jones Br-upper pond	37.18940	-93.21137	S pond	bed
003	Pearson Creek	Greene	Jones Br-upper pond	37.18952	-93.21144	S pond	bed
004	Pearson Creek	Greene	Jones Br-lower pond	37.18698	-93.20147	S pond	bed
005	Pearson Creek	Greene	Jones Br-lower pond	37.18692	-93.20163	S pond	bed
006	Pearson Creek	Greene	FR 148 @ USGS Gage	37.17801	-93.19839	L stream	bench
007	Pearson Creek	Greene	Near railroad bridge	37.17298	-93.19631	L stream	bar
008	South Creek	Greene	N of Battlefield Mall	37.16424	-93.26665	VS stream	bed
008-FD	South Creek	Greene	N of Battlefield Mall	37.16424	-93.26665	VS stream	bed
009	South Creek	Greene	N of Battlefield Mall	37.16433	-93.26736	VS stream	bed
010	South Creek	Greene	Between National-Campbell	37.16776	-93.27748	S stream	bar
011	South Creek	Greene	Between National-Campbell	37.16802	-93.28635	S stream	bench
012	South Creek	Greene	Below Close Park lake	37.16937	-93.33227	M stream	bench
013	South Creek	Greene	Golden Ave crossing	37.16758	-93.34099	M stream	bench
013-FD	South Creek	Greene	Golden Ave crossing	37.16758	-93.34099	M stream	bench
014	Galloway Creek	Greene	Linden/Latoka basin	37.14523	-93.22747	VS stream	bed
014-FD	Galloway Creek	Greene	Linden/Latoka basin	37.14523	-93.22747	VS stream	bed
015	Galloway Creek	Greene	Southern Hills- upper pond	37.12636	-93.23698	S pond	bed
015-FD	Galloway Creek	Greene	Southern Hills- upper pond	37.12636	-93.23698	S pond	bed
016	Galloway Creek	Greene	Southern Hills- upper pond	37.17004	-93.23751	S pond	bed
017	Galloway Creek	Greene	Southern Hills- middle pond	37.16570	-93.23893	S pond	bed
018	Galloway Creek	Greene	Southern Hills- middle pond	37.16591	-93.23921	S pond	bed
019	Galloway Creek	Greene	Sequiota Cave pond	37.14733	-93.23683	U pond	bed

Sample ID	Sample Location			GPS Point		Description	
	Watershed	County	Site	Latitude	Longitude	Sediment Class	Deposit
020	Galloway Creek	Greene	Sequiota Cave pond	37.14753	-93.23668	U pond	bed
021	Galloway Creek	Greene	Above James River Expressway	37.13683	-93.23877	M stream	bed
022	Galloway Creek	Greene	Lake Springfield (arm)	37.12499	-93.24124	M stream	bed
023	Galloway Creek	Greene	Lake Springfield (arm)	37.12428	-93.24298	M stream	bed
024	Wilson-Jordan Creek	Greene	West Meadows	37.21081	-93.29716	M stream	bed
025	Wilson-Jordan Creek	Greene	Fort Ave crossing	37.20941	-93.30791	M stream	bar
026	Wilson-Jordan Creek	Greene	Bennett St crossing	37.18987	-93.32441	M stream	bar
027	Wilson-Jordan Creek	Greene	Scenic Ave @ USGS gage	37.18693	-93.33141	L stream	bar
028	Wilson-Jordan Creek	Greene	MS4 site above WWTP	37.18855	-93.36577	L stream	bar
028-FD	Wilson-Jordan Creek	Greene	MS4 site above WWTP	37.18855	-93.36577	L stream	bar
029	Wilson-Jordan Creek	Greene	Below WWTP @ USGS gage	37.14721	-93.37577	L stream	bar
029-FD	Wilson-Jordan Creek	Greene	Below WWTP @ USGS gage	37.14721	-93.37577	L stream	bar
030	Wilson-Jordan Creek	Greene	Above National Park	37.11796	-93.40410	L stream	bar
031	Wilson-Jordan Creek	Greene	West Meadows	37.21070	-93.29767	Asphalt lot	edge
031-FD	Wilson-Jordan Creek	Greene	West Meadows	37.21070	-93.29767	Asphalt lot	edge
032	Galloway Creek	Greene	Chinese Chef @ Enterprise	37.18198	-93.25220	Sealed lot	inlet
033	Galloway Creek	Greene	Chinese Chef @ Enterprise	37.18198	-93.25220	VS stream	bed
033-FD	Galloway Creek	Greene	Chinese Chef @ Enterprise	37.18198	-93.25220	VS stream	bed
034	Galloway Creek	Greene	Enterprise Park Lanes	37.18436	-93.25211	Asphalt lot	edge
034-FD	Galloway Creek	Greene	Enterprise Park Lanes	37.18436	-93.25211	Asphalt lot	edge
035	Galloway Creek	Greene	Walgreens (Sunshine & Ventura)	37.18014	-93.24261	Mixed lot	basin
036	Galloway Creek	Greene	Apartments/Ingram Mill	37.18169	-93.22703	Sealed lot	basin
037	Galloway Creek	Greene	Commercial/Ingram Mill	37.18318	-93.22653	Mixed lot	edge
038	Galloway Creek	Greene	Glendale Park Apartments	37.16306	-93.22609	Asphalt lot	edge
039	Galloway Creek	Greene	Bancorp South	37.15868	-93.23089	Concrete lot	inlet
040	Galloway Creek	Greene	Below Spfld 8/Ingram Mill	37.15381	-93.23106	VS stream	bed

Sample ID	**Sample Location**			**GPS Point**		**Description**	
	Watershed	County	Site	Latitude	Longitude	Sediment Class	Deposit
041	Galloway Creek	Greene	Basin @ Sequiota Elem.	37.14975	-93.23064	Sealed lot	edge
042	Galloway Creek	Greene	Entertain Mart	37.15834	-93.26222	Sealed lot	edge
042-FD	Galloway Creek	Greene	Entertain Mart	37.15834	-93.26222	Sealed lot	edge
043	Galloway Creek	Greene	Brentwood Center	37.16645	-93.26223	Concrete lot	edge
044	Galloway Creek	Greene	Nakato	37.16687	-93.26280	Mixed lot	inlet
045	Galloway Creek	Greene	Nakato	37.16619	-93.26282	Mixed lot	inlet
046	Ward Branch	Greene	Culpepper @ Mattax Neu	37.14752	-93.27679	Concrete lot	edge
047	Ward Branch	Greene	Culpepper @ MN Bank	37.14942	-93.27649	Concrete lot	edge
048	Inman Creek	Greene	Apts off Battlefield	37.15815	-93.29070	Asphalt lot	edge
049	Inman Creek	Greene	Aldi's	37.16036	-93.29096	Asphalt lot	basin
050	Inman Creek	Greene	Wal-Mart	37.15460	-93.29990	Asphalt lot	edge
051	Spring Creek	Stone	Silver Lake Rd, Billings	36.96537	-93.47959	U pond	bed
052	Spring Creek	Stone	Hwy M, Billings	36.97710	-93.50704	U pond	bed
052-FD	Spring Creek	Stone	Hwy M, Billings	36.97710	-93.50704	U pond	bed
053	Spring Creek	Stone	Beaver Dam Rd, Billings	36.95877	-93.48334	U pond	bed
054	Spring Creek	Stone	Beaver Dam Rd, Billings	36.95945	-93.48217	U pond	bed
055	Spring Creek	Christian	Spring Creek Rd, Billings	37.00913	-93.51796	U stream	bed
056	Spring Creek	Stone	Gideon Cave Rd, Billings	36.95011	-93.50204	U stream	bar
056-FD	Spring Creek	Stone	Gideon Cave Rd, Billings	36.95011	-93.50204	U stream	bar
057	Spring Creek	Stone	Gideon Cave Rd, Billings	36.95280	-93.49721	U stream	bar
058	Spring Creek	Stone	Beaver Dam Rd, Billings	36.94626	-93.49719	U stream	bar

Appendix B. Particle Size Distribution and Carbon, Nitrogen, and Sulfur (CNS) Analysis

Sample ID	Laser Sizer							CNS Analyzer				
	Mean	D10	Median	D90	Sand	Silt	Clay	Ctot	Corg	Cin	N	S
	um	um	um	um	%	%	%	%	%	%	%	%
001	125	3	25	505	27.0	58.1	14.9	4.93	4.45	0.47	0.36	0.15
001-FD	163	3	29	633	32.4	54.0	13.5	3.98	3.55	0.43	0.31	0.12
002	55	2	21	138	17.3	67.5	15.2	5.34	4.19	1.15	0.23	0.11
002-FD	60	2	21	112	16.7	67.9	15.4	5.44	4.35	1.09	0.24	0.10
003	34	2	19	73	11.5	72.2	16.2	5.67	4.86	0.81	0.25	0.11
004	66	3	25	179	22.2	65.9	11.8	6.30	5.17	1.13	0.22	0.10
005	47	3	22	106	19.5	66.8	13.7	9.01	6.14	2.87	0.25	0.14
006	45	2	20	100	15.2	67.4	17.5	5.45	4.84	0.60	0.35	0.09
007	341	5	282	829	65.0	27.2	7.8	3.17	2.42	0.75	0.13	0.13
008	841	469	814	1,253	100.0	0.0	0.0	1.89	1.77	0.11	0.06	0.07
008-FD	1,089	678	1,063	1,574	100.0	0.0	0.0	0.55	0.45	0.10	0.04	0.04
009	327	7	149	863	64.0	29.4	6.6	4.46	3.35	1.12	0.13	0.07
010	554	15	600	1,000	69.0	23.2	7.8	6.16	5.07	1.09	0.11	0.07
011	180	3	39	651	41.9	43.7	14.3	7.72	7.12	0.61	0.41	0.08
012	188	2	27	650	38.5	42.5	19.0	2.28	1.71	0.57	0.15	0.04
013	150	2	23	615	29.2	52.0	18.8	3.80	3.61	0.19	0.30	0.06
013-FD	97	2	21	362	25.2	55.3	19.5	4.26	4.06	0.20	0.32	0.07
014	289	6	223	722	67.1	25.6	7.2	7.92	6.16	1.76	0.19	0.13
014-FD	326	8	220	836	68.0	25.6	6.4	7.81	7.46	0.34	0.17	0.12
015	25	2	12	51	7.2	67.8	24.9	7.52	6.78	0.74	0.46	0.21
015-FD	37	2	15	103	14.1	63.7	22.1	10.88	9.86	1.02	0.51	0.27
016	152	2	24	576	31.0	51.6	17.4	8.45	7.45	1.00	0.33	0.18
017	137	2	23	546	30.8	53.4	15.8	9.95	8.44	1.51	0.63	0.37

Sample ID	**Laser Sizer**							**CNS Analyzer**				
	Mean	D10	Median	D90	Sand	Silt	Clay	Ctot	Corg	Cin	N	S
	um	um	um	um	%	%	%	%	%	%	%	%
018	21	2	12	44	5.5	72.5	22.0	11.03	9.73	1.30	0.66	0.46
019	323	3	249	792	59.1	27.8	13.1	1.88	1.45	0.43	0.07	0.06
020	118	2	37	337	43.7	36.6	19.7	1.66	1.28	0.39	0.09	0.04
021	77	2	15	307	18.5	58.3	23.1	7.25	6.65	0.60	0.12	0.09
022	28	2	17	63	9.9	71.1	19.0	7.43	6.98	0.45	0.38	0.36
023	38	2	21	94	16.2	66.7	17.1	4.89	4.25	0.64	0.22	0.06
024	666	337	591	1,140	100.0	0.0	0.0	4.50	4.09	0.41	0.04	0.15
025	870	539	835	1,250	100.0	0.0	0.0	2.97	2.35	0.62	0.07	0.06
026	330	9	330	634	76.7	17.3	6.1	4.87	4.33	0.54	0.07	0.09
027	674	234	623	1,190	93.4	6.6	0.0	2.34	1.87	0.46	0.04	0.02
028	577	12	583	1,089	82.4	11.9	5.7	3.02	2.80	0.21	0.05	0.16
028-FD	830	258	854	1,356	92.3	7.7	0.0	2.23	2.06	0.18	0.08	0.03
029	484	5	498	1,031	72.0	19.6	8.4	2.49	1.82	0.67	0.07	0.01
029-FD	759	11	795	1,378	82.4	12.7	4.9	4.82	4.44	0.38	0.10	0.08
030	475	27	430	978	86.1	9.4	4.5	1.40	0.89	0.52	0.09	0.07
031	269	11	125	756	62.5	32.5	5.0	9.95	5.52	4.43	0.14	0.12
031-FD												
032	106	2	19	449	24.8	55.7	19.5	6.97	6.15	0.82	0.36	0.08
033	16	2	13	36	1.0	76.4	22.6	4.59	4.49	0.10	0.34	0.07
033-FD	19	2	13	42	3.8	74.6	21.6	4.51	4.44	0.07	0.33	0.05
034	336	5	190	922	59.7	31.6	8.7	12.01	8.77	3.24	0.31	0.08
034-FD	191	3	36	641	40.3	46.9	12.8	12.02	11.44	0.58	0.40	0.07
035	200	3	42	610	44.7	42.0	13.3	8.92	8.18	0.74	0.27	0.19
036	36	2	17	87	14.2	67.7	18.1	15.24	14.29	0.96	0.61	0.18

Sample ID	**Laser Sizer**							**CNS Analyzer**				
	Mean	D10	Median	D90	Sand	Silt	Clay	Ctot	Corg	Cin	N	S
	um	um	um	um	%	%	%	%	%	%	%	%
037	359	6	206	965	64.0	28.9	7.0	15.12	14.81	0.31	0.54	0.14
038	28	2	17	54	7.2	74.9	17.9	15.16	11.00	4.16	0.33	0.19
039	460	4	472	1,005	70.4	20.9	8.8	6.34	3.53	2.81	0.14	0.07
040	26	2	23	53	8.9	77.3	13.8	2.12	1.98	0.13	0.18	0.04
041	207	3	55	588	48.4	39.0	12.6	16.61	14.67	1.94	0.53	0.20
042	79	2	18	261	23.2	55.7	21.2	19.16	16.67	2.49	0.43	0.23
042-FD	76	2	18	238	22.2	57.6	20.2	19.12	18.45	0.67	0.43	0.22
043	696	389	660	1,092	96.1	3.9	0.0	2.68	2.12	0.56	0.04	0.04
044	312	4	172	902	61.0	30.3	8.8	8.20	6.31	1.89	0.18	0.13
045	307	5	275	699	66.6	25.3	8.1	9.94	7.64	2.30	0.18	0.10
046	285	7	161	709	62.5	31.1	6.4	4.79	4.39	0.40	0.23	2.04
047	67	2	24	162	18.1	65.7	16.2	7.12	6.91	0.21	0.48	0.55
048	156	3	35	573	36.4	51.8	11.8	9.32	7.68	1.64	0.26	0.14
049	299	8	190	762	67.4	26.5	6.1	8.80	6.61	2.19	0.14	0.12
050	375	13	335	813	78.8	16.7	4.5	6.24	4.99	1.25	0.12	0.10
051	151	2	26	591	33.9	49.2	17.0	6.12	6.05	0.07	0.58	0.11
052	18	2	12	39	3.8	72.6	23.6	4.29	4.21	0.08	0.40	0.06
052-FD	17	2	12	38	1.9	74.4	23.6	5.97	5.88	0.09	0.49	0.07
053	550	4	533	1,270	68.9	20.9	10.2	1.82	1.62	0.21	0.12	0.03
054	23	2	17	50	6.4	74.0	19.6	5.02	4.95	0.07	0.44	0.05
055	206	2	22	754	33.5	45.8	20.8	1.91	1.79	0.12	0.19	0.12
056	101	2	24	399	25.1	59.2	15.8	8.25	8.19	0.06	0.54	0.16
056-FD	153	3	27	606	30.2	55.7	14.1	6.06	6.00	0.07	0.44	0.06
057	61	3	25	141	20.3	65.5	14.2	4.26	4.18	0.08	0.33	0.09
058	236	4	51	752	47.0	42.8	10.3	3.37	3.22	0.15	0.25	0.08

Appendix C. Sample pH and Aqua Regia (AQ) Extraction and ICP-AES Analysis (Ag-Cu)

Sample ID	50:50 v/v	**Ag**	**Al**	**As**	**B**	**Ba**	**Be**	**Bi**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**
	pH units	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm
001	7.3	<0.2	1.02	3	<10	180	0.8	<2	3.26	0.5	8	30	12
001-FD	7.2	0.2	1.04	3	<10	120	0.8	<2	3.25	0.5	8	26	11
002	7.4	0.2	1.14	4	<10	100	0.8	<2	8.6	2.3	10	21	17
002-FD	7.4	<0.2	1.13	5	<10	100	0.8	<2	8.4	2.5	10	21	15
003	7.4	<0.2	1.06	4	<10	90	0.8	<2	8.6	2.4	9	26	19
004	7.5	<0.2	0.71	3	<10	70	0.5	<2	13.1	1.6	6	19	9
005	7.4	0.2	0.74	2	<10	110	0.5	<2	19.5	1.8	5	14	14
006	7.3	<0.2	1.3	4	<10	120	0.8	<2	5.44	0.8	11	22	22
007	7.7	<0.2	0.93	5	<10	70	0.6	<2	5.53	18.9	10	35	13
008	8.2	<0.2	1.34	2	10	80	1.2	<2	2.12	<0.5	2	26	7
008-FD	7.6	<0.2	1.27	<2	10	70	1.2	<2	1.97	<0.5	1	29	10
009	7.7	<0.2	1.14	2	20	110	0.8	<2	8.9	0.7	8	98	32
010	7.7	<0.2	1.19	9	<10	130	0.6	<2	11.9	<0.5	12	68	21
011	7.3	<0.2	2.26	36	<10	1520	2.8	<2	3.48	1.7	117	129	38
012	7.6	<0.2	1.72	26	<10	610	1.7	<2	6.23	0.8	45	105	26
013	7.4	<0.2	1.81	10	<10	270	1.1	<2	2.65	0.6	18	48	24
013-FD	7.4	<0.2	1.83	7	<10	270	1.1	<2	2.66	0.7	18	47	25
014	7.7	<0.2	0.63	5	10	180	<0.5	<2	12.3	0.8	9	56	54
014-FD	7.6	<0.2	0.72	3	10	190	<0.5	<2	12.6	0.9	9	57	49
015	7.1	<0.2	1.37	7	<10	110	0.7	<2	7.42	0.6	15	36	264
015-FD	7.2	<0.2	1.38	6	<10	110	0.7	<2	7.6	0.5	14	35	239
016	7.2	<0.2	1.05	7	<10	80	0.6	<2	11	<0.5	17	46	195
017	7.1	<0.2	1.01	5	<10	140	0.6	<2	12	0.5	15	43	70
018	7.2	<0.2	1	6	<10	150	0.5	<2	15.2	<0.5	13	34	79
019	7.7	<0.2	3.42	14	<10	120	1.9	<2	5.31	0.7	17	61	26

Sample ID	50:50 v/v	Ag	Al	As	B	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu
	pH units	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm
020	7.8	<0.2	3.55	10	<10	110	2	<2	5.17	0.6	15	56	31
021	7.3	<0.2	0.98	2	<10	70	0.5	<2	18.6	0.6	7	18	25
022	6.8	<0.2	1.25	4	<10	90	0.7	<2	9.7	0.8	8	23	23
023	7.5	<0.2	1.41	3	<10	110	0.8	<2	7.6	0.6	9	24	23
024	8	<0.2	0.61	8	<10	220	0.5	<2	7.9	2.6	15	74	67
025	7.5	<0.2	0.46	5	<10	220	<0.5	<2	10.5	2.1	14	51	45
026	7.4	0.2	0.85	9	<10	340	0.7	<2	9.2	2	13	63	43
027	7.3	<0.2	0.53	9	<10	350	0.7	<2	9.2	1.5	17	73	36
028	7.6	<0.2	0.69	19	<10	300	1.2	<2	3.3	1	24	137	24
028-FD	7.6	<0.2	0.74	17	<10	260	1.2	<2	3.49	1.1	25	134	21
029	7.5	0.2	1.16	14	<10	460	1.2	<2	8.7	1.2	38	114	25
029-FD	7.5	0.3	1.14	14	<10	500	1.2	<2	9.2	1.4	40	115	21
030	7.7	0.3	0.58	2	<10	50	0.5	<2	3.69	<0.5	10	83	10
031	7.6	<0.2	0.32	5	<10	60	<0.5	<2	24.2	1.6	5	33	40
031-FD													
032	7.4	<0.2	1.23	9	<10	150	0.6	<2	6.53	0.9	15	44	48
033	7.2	<0.2	1.34	6	<10	130	0.7	<2	0.89	0.5	10	40	27
033-FD	7.2	<0.2	1.33	6	<10	130	0.7	<2	0.84	0.5	11	30	35
034	7.5	<0.2	0.41	4	<10	80	<0.5	<2	21.5	0.6	5	34	23
034-FD	7.4	0.2	0.39	4	<10	80	<0.5	<2	21.2	0.5	5	39	18
035	7.3	0.4	0.86	5	<10	160	0.5	<2	8.2	0.6	13	51	36
036	7.3	0.4	0.91	3	<10	100	0.5	<2	9.3	1.1	6	49	49
037	6.9	<0.2	0.43	4	<10	80	<0.5	<2	16.1	<0.5	5	25	25
038	7.4	0.2	0.31	4	<10	70	<0.5	<2	20.4	0.8	4	29	43
039	7.9	<0.2	0.43	<2	<10	140	<0.5	<2	14.6	<0.5	5	47	26
040	7.6	<0.2	0.75	3	<10	100	<0.5	<2	1.35	<0.5	8	25	11

Sample ID	50:50 v/v	**Ag**	**Al**	**As**	**B**	**Ba**	**Be**	**Bi**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**
	pH units	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm
041	7.1	0.2	0.47	6	<10	80	<0.5	<2	12.8	0.6	6	33	35
042	7.4	0.3	0.6	3	<10	160	<0.5	<2	16.2	1.2	5	59	65
042-FD	7.4	0.2	0.55	4	<10	130	<0.5	<2	16.2	1.2	4	64	58
043	8.0	<0.2	0.29	4	<10	170	<0.5	<2	6.67	<0.5	9	150	15
044	7.4	0.3	0.78	4	<10	80	<0.5	<2	12.8	2.8	4	128	34
045	7.5	0.2	0.73	3	<10	320	<0.5	<2	13.4	1.1	9	513	33
046	7.9	0.2	0.66	3	10	170	<0.5	<2	7.8	<0.5	5	56	46
047	7.5	0.3	1.22	7	10	230	0.6	<2	4.3	0.5	14	90	51
048	7.5	0.2	0.5	5	<10	90	<0.5	<2	18.6	0.8	8	75	32
049	7.5	<0.2	0.26	4	<10	40	<0.5	<2	23	0.5	3	39	28
050	7.3	0.3	0.33	3	<10	110	<0.5	<2	14.3	1.3	4	117	27
051	6.6	<0.2	0.83	3	<10	90	<0.5	<2	0.48	<0.5	6	41	13
052	7.0	<0.2	1.26	5	<10	140	0.8	<2	1.24	<0.5	11	24	15
052-FD	7.0	<0.2	1.23	6	<10	130	0.8	<2	1.06	<0.5	10	21	11
053	6.9	0.2	0.67	14	<10	100	0.9	<2	2.2	<0.5	16	98	12
054	6.3	<0.2	0.77	3	<10	110	<0.5	2	0.48	<0.5	5	26	12
055	7.1	<0.2	1.73	8	<10	140	1	<2	1.68	0.6	16	35	14
056	6.8	<0.2	0.78	3	<10	70	0.7	<2	0.98	0.5	7	37	10
056-FD	6.9	<0.2	0.78	3	<10	70	0.7	<2	0.96	0.6	7	26	11
057	7.0	<0.2	0.81	2	<10	80	0.7	<2	1.26	0.8	7	22	9
058	7.3	<0.2	0.66	4	<10	70	0.6	<2	2.29	0.7	7	26	11

Appendix D. Sample Aqua Regia (AQ) Extraction and ICP-AES Analysis (Fe-S)

Sample ID	**Fe**	**Ga**	**Hg**	**K**	**La**	**Mg**	**Mn**	**Mo**	**Na**	**Ni**	**P**	**Pb**	**S**
	AQ-%	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-%
001	1.24	<10	0.06	0.1	20	0.22	559	1	0.01	13	490	21	0.07
001-FD	1.24	<10	0.06	0.1	20	0.22	554	1	0.01	12	500	17	0.07
002	1.38	<10	0.06	0.1	20	0.27	584	1	0.02	14	530	54	0.09
002-FD	1.37	<10	0.07	0.1	20	0.26	565	1	0.02	13	520	55	0.09
003	1.27	<10	0.06	0.09	20	0.26	499	1	0.01	13	490	51	0.1
004	0.76	<10	0.06	0.07	20	0.27	223	<1	0.02	8	340	38	0.11
005	0.7	<10	0.04	0.07	10	0.31	313	<1	0.02	7	420	53	0.22
006	1.48	<10	0.05	0.13	20	0.28	625	1	0.02	20	700	94	0.08
007	1.63	<10	0.06	0.09	20	0.9	849	1	0.01	15	380	224	0.19
008	1.87	<10	0.01	0.25	60	0.17	745	5	0.79	2	690	24	0.05
008-FD	1.77	<10	0.01	0.23	50	0.15	708	5	0.76	3	650	39	0.04
009	1.76	<10	0.07	0.14	30	0.33	813	4	0.35	11	560	249	0.05
010	2.13	<10	0.03	0.08	10	0.39	1,035	2	0.07	14	370	160	0.05
011	7.78	10	0.05	0.11	70	0.24	13,850	5	0.02	58	1,150	204	0.05
012	5.29	10	0.03	0.1	40	0.15	5,970	2	0.02	39	870	77	0.03
013	2.7	<10	0.08	0.12	40	0.16	2,490	1	0.02	22	750	36	0.05
013-FD	2.69	10	0.08	0.12	50	0.16	2,500	1	0.02	22	760	35	0.05
014	1.46	<10	0.04	0.06	10	0.73	758	2	0.04	12	410	89	0.12
014-FD	1.54	<10	0.03	0.06	10	0.71	687	3	0.04	13	410	78	0.15
015	1.42	<10	0.07	0.13	20	0.13	324	1	0.06	15	570	51	0.26
015-FD	1.39	<10	0.06	0.13	20	0.12	284	1	0.06	14	540	45	0.27
016	1.34	<10	0.05	0.11	10	0.12	572	<1	0.02	12	610	60	0.21
017	1.68	<10	0.07	0.09	10	0.09	1,740	1	0.02	18	790	50	0.33
018	1.43	<10	0.07	0.1	10	0.1	1,820	1	0.02	17	750	49	0.42
019	3.83	10	0.05	0.17	70	0.13	1,625	1	0.02	25	450	42	0.01

Sample ID	**Fe**	**Ga**	**Hg**	**K**	**La**	**Mg**	**Mn**	**Mo**	**Na**	**Ni**	**P**	**Pb**	**S**
	AQ-%	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-%
020	4.25	10	0.06	0.18	70	0.16	1,660	1	0.02	32	550	37	0.01
021	0.92	<10	0.06	0.09	10	0.14	507	1	0.02	12	370	43	0.14
022	1.18	<10	0.07	0.11	20	0.15	152	<1	0.02	13	460	41	0.35
023	1.65	<10	0.05	0.13	20	0.19	741	<1	0.02	13	500	36	0.05
024	2.49	<10	0.08	0.05	10	0.19	1,695	6	0.03	32	380	147	0.06
025	2.31	<10	0.1	0.04	10	0.2	1,525	4	0.03	26	410	78	0.05
026	2.72	<10	0.13	0.07	20	0.17	2,350	2	0.02	25	480	141	0.04
027	2.8	<10	0.06	0.04	20	0.13	2,710	2	0.02	23	430	72	0.03
028	4.29	<10	0.07	0.04	70	0.05	2,650	1	0.01	33	1,010	61	0.01
028-FD	4.36	<10	0.07	0.04	60	0.06	2,520	1	0.01	33	940	64	0.01
029	3.64	10	0.14	0.08	30	0.14	4,720	3	0.02	52	1,060	93	0.01
029-FD	3.64	<10	0.15	0.08	30	0.14	4,970	3	0.02	53	1,060	107	0.01
030	1.44	<10	0.1	0.03	20	0.05	537	1	0.02	18	760	65	0.02
031	1.08	<10	0.07	0.03	10	0.38	546	2	0.02	15	250	67	0.08
031-FD													
032	1.94	<10	0.2	0.12	10	0.16	1,280	1	0.03	13	600	77	0.05
033	1.74	<10	0.05	0.11	20	0.13	713	1	0.01	12	450	45	0.04
033-FD	1.68	<10	0.05	0.12	20	0.13	696	1	0.02	13	450	46	0.04
034	0.68	<10	0.05	0.06	10	0.19	430	1	0.03	7	420	81	0.05
034-FD	0.69	<10	0.04	0.06	10	0.22	468	1	0.03	9	400	78	0.05
035	1.96	<10	0.05	0.08	10	0.28	982	2	0.03	11	460	76	0.07
036	1.03	<10	0.11	0.14	10	0.36	245	1	0.03	14	880	116	0.1
037	0.69	<10	0.05	0.07	10	0.51	465	1	0.04	6	640	24	0.08
038	0.62	<10	0.03	0.05	10	0.59	332	3	0.03	11	450	25	0.1
039	0.62	<10	0.02	0.05	10	0.25	255	1	0.04	11	340	101	0.04
040	1.01	<10	0.02	0.09	10	0.09	472	<1	0.02	7	260	19	0.02

Sample ID	**Fe**	**Ga**	**Hg**	**K**	**La**	**Mg**	**Mn**	**Mo**	**Na**	**Ni**	**P**	**Pb**	**S**
	AQ-%	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-%
041	1.48	<10	0.09	0.06	10	0.29	483	2	0.03	10	520	30	0.15
042	0.89	<10	0.08	0.09	10	0.75	290	1	0.13	12	680	131	0.14
042-FD	0.83	<10	0.08	0.09	10	0.76	285	1	0.12	10	670	143	0.14
043	1.09	<10	0.01	0.05	10	0.28	753	2	0.03	11	260	443	0.02
044	0.91	<10	0.06	0.05	10	1.73	196	1	0.08	11	890	381	0.15
045	1.3	<10	0.06	0.07	10	0.69	636	2	0.05	11	390	1875	0.05
046	1.58	<10	0.03	0.1	10	0.55	383	3	0.04	16	490	37	1.47
047	1.69	<10	0.06	0.14	20	0.33	1295	1	0.03	18	760	207	0.41
048	0.97	<10	0.04	0.08	10	0.32	682	1	0.03	11	510	216	0.09
049	0.71	<10	0.02	0.03	10	0.32	244	1	0.03	7	420	50	0.05
050	1.31	<10	0.01	0.04	10	0.36	318	3	0.04	10	380	288	0.13
051	1.4	<10	0.05	0.14	10	0.08	411	1	0.02	9	1,160	14	0.09
052	1.5	<10	0.05	0.13	30	0.08	761	1	0.02	16	710	19	0.06
052-FD	1.49	<10	0.05	0.13	20	0.08	750	<1	0.02	16	710	19	0.05
053	3.7	<10	0.02	0.04	10	0.82	1715	1	0.02	7	540	33	0.01
054	1.06	<10	0.04	0.1	10	0.14	508	1	0.01	6	760	13	0.05
055	2.41	<10	0.04	0.12	20	0.18	1480	1	0.01	18	350	36	0.01
056	0.95	<10	0.05	0.07	20	0.07	324	<1	0.02	12	460	14	0.07
056-FD	0.94	<10	0.05	0.08	20	0.07	317	<1	0.01	12	460	16	0.07
057	1.01	<10	0.04	0.08	20	0.09	339	<1	0.02	10	530	16	0.05
058	1.02	<10	0.04	0.07	20	0.08	614	<1	0.02	11	410	13	0.03

Appendix E. Sample Aqua Regia (AQ) Extraction and ICP-AES Analysis (Sb-Zn)

Sample ID	Sb	Sc	Sr	Th	Ti	Tl	U	V	W	Zn
	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm
001	<2	2	18	<20	0.02	<10	<10	23	<10	71
001-FD	<2	2	17	<20	0.02	<10	<10	23	<10	65
002	<2	3	33	<20	0.02	<10	<10	24	<10	296
002-FD	<2	3	32	<20	0.02	<10	<10	24	<10	312
003	<2	2	32	<20	0.02	<10	<10	23	<10	297
004	<2	2	39	<20	0.01	<10	<10	16	<10	192
005	<2	2	61	<20	0.01	<10	<10	14	<10	245
006	<2	3	23	<20	0.02	<10	<10	27	<10	126
007	<2	2	34	<20	0.02	<10	<10	26	<10	2,800
008	<2	1	35	<20	0.22	10	<10	24	<10	230
008-FD	<2	<1	38	<20	0.2	<10	<10	22	<10	201
009	<2	1	65	<20	0.09	<10	<10	28	<10	720
010	<2	2	84	<20	0.02	<10	<10	37	<10	231
011	2	4	37	<20	0.02	<10	<10	170	<10	324
012	<2	4	38	<20	0.02	<10	<10	110	<10	146
013	<2	4	25	<20	0.02	<10	<10	50	<10	155
013-FD	<2	4	26	<20	0.02	<10	<10	51	<10	156
014	<2	1	112	<20	0.02	<10	<10	23	<10	403
014-FD	<2	1	116	<20	0.01	<10	<10	22	<10	445
015	<2	2	34	<20	0.02	<10	<10	33	<10	141
015-FD	<2	2	33	<20	0.02	<10	<10	33	<10	131
016	<2	2	47	<20	0.02	<10	<10	33	<10	108
017	<2	2	43	<20	0.02	<10	<10	34	<10	103
018	<2	2	50	<20	0.02	<10	<10	31	<10	104
019	<2	11	25	20	0.03	<10	<10	71	<10	106

Sample ID	Sb	Sc	Sr	Th	Ti	Tl	U	V	W	Zn
	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm
020	2	11	25	20	0.03	<10	<10	72	<10	117
021	<2	2	83	<20	0.02	<10	<10	21	<10	93
022	<2	3	40	<20	0.02	<10	<10	27	<10	131
023	<2	3	36	<20	0.02	<10	<10	29	<10	121
024	2	1	62	<20	0.02	<10	<10	30	<10	559
025	<2	1	65	<20	0.01	10	<10	22	<10	516
026	<2	2	61	<20	0.02	<10	<10	35	<10	463
027	<2	2	59	<20	0.01	<10	<10	43	<10	368
028	<2	3	24	<20	0.02	<10	<10	97	<10	313
028-FD	<2	3	27	<20	0.02	<10	<10	94	<10	325
029	<2	3	45	<20	0.02	<10	<10	82	<10	194
029-FD	<2	3	47	<20	0.02	<10	<10	84	<10	184
030	<2	1	17	<20	0.02	<10	<10	29	<10	104
031	<2	1	121	<20	0.01	<10	10	13	<10	417
031-FD										
032	<2	2	49	<20	0.02	<10	<10	40	<10	335
033	<2	2	14	<20	0.02	<10	<10	35	<10	237
033-FD	<2	2	14	<20	0.02	<10	<10	35	<10	242
034	<2	1	113	<20	0.01	<10	<10	15	<10	280
034-FD	<2	1	111	<20	0.01	<10	10	15	<10	254
035	<2	2	84	<20	0.02	<10	<10	35	<10	400
036	<2	1	57	<20	0.02	<10	<10	21	<10	424
037	<2	1	92	<20	0.01	<10	<10	16	<10	174
038	<2	1	106	<20	0.01	<10	<10	15	<10	380
039	<2	1	180	<20	0.02	<10	<10	10	<10	212
040	<2	1	13	<20	0.02	<10	<10	21	<10	75

Sample ID	Sb	Sc	Sr	Th	Ti	Tl	U	V	W	Zn
	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-%	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm	AQ-ppm
041	<2	1	95	<20	0.01	<10	<10	19	<10	286
042	<2	1	120	<20	0.01	<10	<10	16	<10	692
042-FD	<2	1	119	<20	0.01	<10	<10	16	10	696
043	<2	1	115	<20	0.01	<10	<10	13	<10	58
044	<2	1	112	<20	0.02	<10	<10	14	<10	1235
045	<2	1	133	<20	0.03	<10	<10	22	<10	270
046	<2	1	163	<20	0.03	<10	<10	15	<10	245
047	<2	2	141	<20	0.03	<10	<10	31	<10	345
048	<2	1	90	<20	0.01	<10	<10	19	<10	283
049	<2	1	109	<20	0.01	<10	10	8	<10	211
050	<2	1	120	<20	0.01	<10	<10	11	<10	463
051	<2	1	9	<20	0.02	<10	<10	26	<10	42
052	<2	2	11	<20	0.02	<10	<10	29	<10	71
052-FD	<2	2	10	<20	0.02	<10	<10	28	<10	65
053	<2	1	12	<20	0.03	<10	<10	75	<10	24
054	<2	1	11	<20	0.02	<10	<10	21	<10	30
055	<2	4	11	<20	0.02	<10	<10	47	<10	104
056	<2	2	9	<20	0.02	<10	<10	20	<10	53
056-FD	<2	2	9	<20	0.02	<10	<10	20	<10	54
057	<2	2	9	<20	0.02	<10	<10	18	<10	74
058	<2	1	12	<20	0.01	<10	<10	17	<10	74

Appendix F. Sample X-Ray Fluorescence (XRF) Analysis

Sample ID	**Pb**	**Zn**	**Cu**	**Ti**	**Fe**	**Mn**	**Sr**	**Ca**	**Zr**
	XRF-ppm	XRF-ppm	XRF-ppm	XRF-ppm	XRF-%	XRF-ppm	XRF-ppm	XRF-%	XRF-ppm
001	21	82	ND	3,912	1.72	600	55	3.96	513
001-FD	63	409	ND	3,633	1.90	491	65	8.20	423
002	68	467	ND	3,648	2.07	494	66	9.50	428
002-FD	ND	77	ND	4,096	1.54	588	57	3.23	524
003	64	229	ND	3,231	1.78	433	66	8.46	426
004	ND	162	ND	2,199	1.16	121	67	14.77	381
005	53	249	ND	1,545	1.12	173	81	25.64	194
006	85	121	ND	4,018	1.85	554	61	5.27	483
007	279	1,371	ND	2,456	2.21	1,052	49	5.02	259
008	183	888	46	2,663	2.48	693	248	14.44	338
008-FD	150	967	26	3,196	2.54	538	350	13.67	540
009	494	1,118	ND	3,286	1.98	489	240	12.45	298
010	66	484	12	3,180	3.68	1,091	106	8.53	277
011	179	393	ND	4,293	6.10	14,793	69	3.88	335
012	68	157	ND	4,159	4.09	4,303	61	2.31	370
013	40	150	ND	3,747	2.88	2,712	58	1.92	420
013-FD	46	157	ND	4,202	3.02	3,110	60	1.73	503
014	48	452	26	2,707	1.90	473	164	13.08	231
014-FD	48	172	ND	4,612	3.06	3,249	62	1.76	494
015	51	119	199	2,613	1.47	264	68	8.81	396
015-FD	55	139	201	3,072	1.61	144	64	8.42	351
016	57	133	162	3,482	1.64	231	79	8.24	417
017	ND	106	45	1,556	1.58	1,980	68	17.30	253
018	33	112	33	1,874	1.42	1,793	69	19.53	234
019	63	143	ND	2,912	5.10	2,020	20	3.14	173

Sample ID	**Pb**	**Zn**	**Cu**	**Ti**	**Fe**	**Mn**	**Sr**	**Ca**	**Zr**
	XRF-ppm	XRF-ppm	XRF-ppm	XRF-ppm	XRF-%	XRF-ppm	XRF-ppm	XRF-%	XRF-ppm
020	55	160	ND	3,974	5.94	1,919	50	4.84	227
021	43	105	10	1,957	1.31	449	103	21.06	236
022	52	137	ND	2,685	1.48	25	70	10.74	393
023	39	137	9	3,815	1.99	671	71	7.67	502
024	128	338	28	1,008	4.08	1,455	186	10.55	101
025	149	620	45	1,615	2.94	2,327	118	15.35	139
026	156	375	50	2,487	3.98	2,746	109	12.67	218
027	217	294	ND	1,472	4.24	2,413	104	13.13	99
028	127	322	ND	1,941	3.85	2,461	54	9.91	190
028-FD	85	324	ND	1,653	4.02	2,718	54	8.37	107
029	110	225	ND	3,320	2.87	2,654	68	6.32	305
029-FD	100	241	ND	3,580	4.11	3,758	52	9.11	211
030	53	143	ND	2,415	1.54	896	32	4.26	269
031	65	612	12	2,281	1.83	743	132	26.41	187
031-FD									
032	77	352	24	4,379	1.71	603	69	2.04	493
033	54	248	ND	4,370	1.77	289	60	0.42	537
033-FD	44	256	9	5,018	1.89	322	61	0.50	560
034	88	444	ND	1,783	1.15	405	126	22.17	288
034-FD	97	486	ND	2,157	1.26	350	123	18.93	257
035	101	605	17	5,669	1.90	383	130	7.38	387
036	166	549	26	2,970	1.52	104	103	10.48	301
037	56	340	12	3,274	1.40	438	104	10.00	253
038	29	600	29	825	1.18	246	121	26.86	127
039	86	332	20	621	0.97	290	256	24.75	87
040	14	79	ND	5,099	1.28	431	57	0.75	825

Sample ID	Pb	Zn	Cu	Ti	Fe	Mn	Sr	Ca	Zr
	XRF-ppm	XRF-ppm	XRF-ppm	XRF-ppm	XRF-%	XRF-ppm	XRF-ppm	XRF-%	XRF-ppm
041	44	456	16	3,323	1.70	368	123	10.36	305
042	136	954	37	1,838	1.20	196	138	19.12	163
042-FD	136	917	31	1,604	1.30	175	172	19.50	178
043	79	61	ND	1,616	1.25	187	169	5.76	96
044	323	1,756	14	2,096	1.41	119	149	19.23	149
045	777	395	26	3,619	1.83	668	149	11.96	286
046	32	424	25	2,145	2.30	476	266	11.89	219
047	61	428	13	4,459	2.19	1,033	184	3.67	490
048	157	358	10	2,306	1.35	524	101	18.22	331
049	43	600	13	1,570	1.38	142	134	27.37	133
050	1,529	1,035	ND	1,610	1.62	221	127	18.85	89
051	11	44	ND	3,172	1.46	342	30	0.27	346
052	19	78	ND	4,382	1.69	584	58	1.09	465
052-FD	29	81	ND	4,607	1.71	619	59	0.75	479
053	ND	13	ND	5,136	1.31	1,044	28	0.57	352
054	ND	17	ND	4,809	1.34	1,070	23	0.47	358
055	ND	120	ND	3,438	2.85	1,260	40	0.94	380
056	ND	51	ND	4,366	1.13	108	42	0.67	540
056-FD	16	63	ND	4,159	1.18	201	47	0.70	520
057	17	79	ND	4,253	1.26	230	49	1.13	611
058	ND	70	13	3,814	1.29	538	46	2.25	482

Appendix G. PAH Data (Total Solids - (8) Pyrene)

Sample ID	Total Solids	(1) Naphthalene	(2) Acenaphthylene	(3) Acenaphthene	(4) Fluorene	(5) Phenanthrene	(6) Anthracene	(7) Fluoranthene	(8) Pyrene
	%	ug/kg = ppb	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg
001	56	U	U	U	U	U	U	U	U
001-FD	54	U	U	U	U	U	U	U	U
002	50	U	35	U	U	500	66	1,600	1,000
002-FD	57	U	U	U	U	560	81	1,600	900
003	44	U	39	U	U	790	97	2,600	1,300
004	58	U	U	U	U	49	U	230	140
005	45	U	U	U	U	170	U	510	270
006	47	U	U	U	U	U	U	250	180
007	63	U	U	U	U	U	U	U	U
008	97	U	39	72	81	2,100	250	8,600	4,400
008-FD	96	U	55	94	100	2,900	310	10,000	7,200
009	94	U	330	560	570	19,000	1,800	75,000	53,000
010	67	47	110	550	640	18,000	1,500	38,000	24,000
011	62	U	120	88	120	3,800	370	15,000	9,200
012	73	U	U	U	U	66	U	U	180
013	57	U	U	U	U	94	U	390	320
013-FD	60	U	U	U	U	88	U	300	240
014	69	U	190	850	800	21,000	2,100	87,000	38,000
014-FD	67	U	230	1,000	1,000	26,000	2,600	70,000	47,000
015	36	U	U	U	U	190	U	740	500
015-FD	33	U	U	U	U	160	U	630	380
016	47	U	U	U	U	250	46	940	550
017	28	U	U	U	U	130	U	500	280
018	21	U	U	U	U	160	U	600	340

Sample ID	**Total Solids**	**(1) Naphthalene**	**(2) Acenaphthylene**	**(3) Acenaphthene**	**(4) Fluorene**	**(5) Phenanthrene**	**(6) Anthracene**	**(7) Fluoranthene**	**(8) Pyrene**
	%	ug/kg = ppb	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg
019	63	U	U	U	U	U	U	74	48
020	56	U	U	U	U	U	U	56	37
021	67	U	U	U	U	91	33	500	250
022	34	U	72	U	U	370	99	1,600	810
023	52	U	51	U	U	220	56	990	520
024	73	31	150	200	230	4,300	560	8,900	5,600
025	81	U	56	64	84	1,700	240	4,200	2,700
026	95	340	460	530	590	9,000	1,500	17,000	11,000
027	76	U	63	130	170	2,300	410	4,600	2,900
028	92	56	150	300	280	3,300	820	5,100	3,700
028-FD	87	39	56	81	74	1,200	180	1,900	1,300
029	91	U	70	U	U	140	39	500	280
029-FD	91	U	68	U	U	120	35	400	260
030	70	U	U	U	U	39	U	150	100
031	93	U	110	130	160	3,400	350	9,400	5,200
031-FD	91	U	91	130	U	2,900	300	8,200	4,400
032	71	U	U	520	480	13,000	1,500	44,000	23,000
033	69	U	U	U	U	2,400	280	9,600	6,800
033-FD	69	U	U	U	U	3,000	350	12,000	7,900
034	74	U	U	150	190	6,000	460	16,000	11,000
034-FD	73	U	U	170	200	6,200	450	15,000	10,000
035	72	270	730	1,300	1,800	49,000	6,000	230,000	120,000
036	56	340	2,000	2,800	2,500	180,000	12,000	830,000	450,000
037	73	U	U	2,100	2,600	69,000	6,700	180,000	140,000
038	73	U	U	U	U	1,400	130	5,600	3,000
039	80	U	U	U	U	530	39	1,600	930

Sample ID	Total Solids	(1) Naphthalene	(2) Acenaphthylene	(3) Acenaphthene	(4) Fluorene	(5) Phenanthrene	(6) Anthracene	(7) Fluoranthene	(8) Pyrene
	%	ug/kg = ppb	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg
040	67	38	110	280	400	5,400	870	15,000	13,000
041	62	U	2,300	6,500	7,900	180,000	12,000	680,000	560,000
042	65	370	2,000	8,500	9,900	210,000	20,000	620,000	540,000
042-FD	63	380	1,400	7,100	8,100	120,000	16,000	380,000	330,000
043	86	U	U	U	U	93	U	290	140
044	76	U	250	420	600	17,000	2,200	76,000	33,000
045	76	130	590	1,600	1,900	69,000	5,800	240,000	230,000
046	63	U	32	90	120	2,300	200	6,900	3,600
047	63	U	49	76	95	2,400	190	8,600	4,800
048	72	U	140	200	240	8,500	1,100	31,000	19,000
049	83	U	U	U	U	1,100	97	2,800	2,500
050	79	U	U	U	U	830	95	2,600	1,900
051	35	U	U	U	U	U	U	U	U
052	51	U	U	U	U	U	U	U	U
052-FD	54	U	U	U	U	U	U	U	U
053	82	U	U	U	U	U	U	U	U
054	51	U	U	U	U	U	U	U	U
055	92	U	U	U	U	U	U	U	U
056	39	U	U	U	U	U	U	U	U
056-FD	36	U	U	U	U	U	U	U	U
057	39	U	U	U	U	U	U	U	U
058	66	U	U	U	U	U	U	48	29

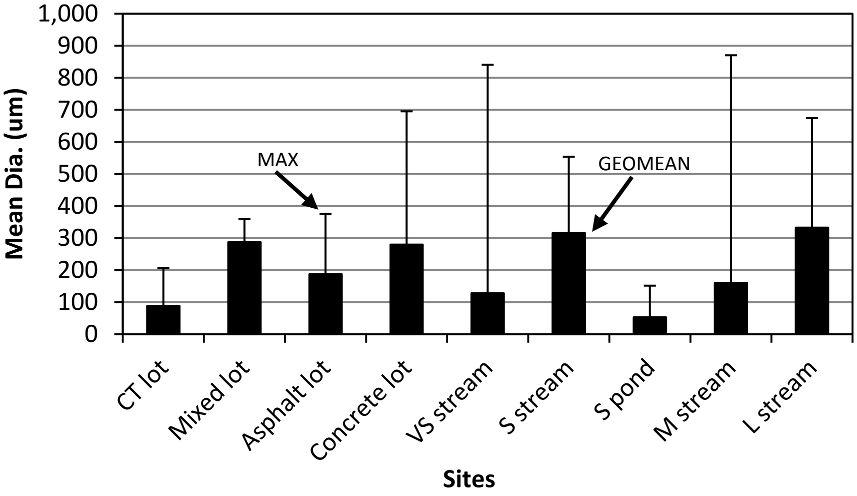
Appendix H. PAH Data ((9)Benzo[a]anthracene - Total 16 PAHs)

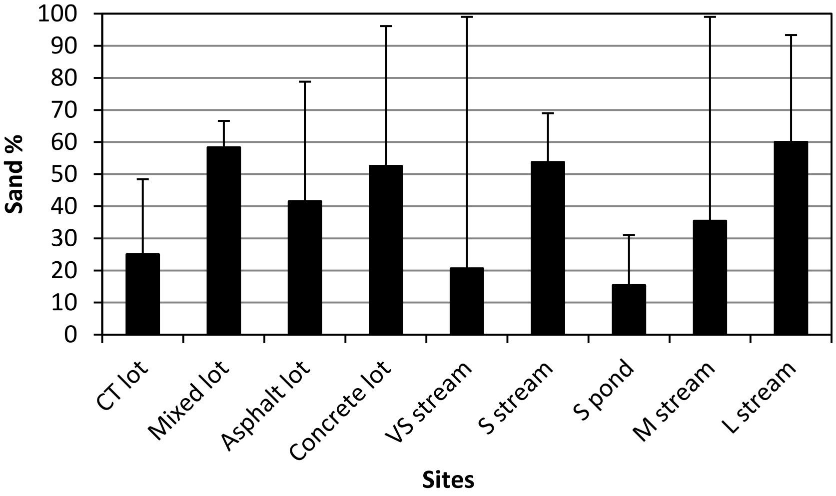
Sample ID	(9) Benzo[a] anthracene	(10) Chrysene	(11) Benzo[b] fluoranthene	(12) Benzo[k] fluoranthene	(13) Benzo[a] pyrene	(14) Indeno[1,2,3-cd]pyrene	(15) Dibenz[a,h] anthracene	(16) Benzo[g,h,i] perylene	Total 16 PAHs
	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg
001	U	U	U	U	U	U	U	U	240
001-FD	U	U	U	U	U	U	U	U	240
002	470	860	1,200	350	720	580	220	450	8,291
002-FD	450	750	1,100	330	630	460	180	340	7,621
003	660	1,300	1,900	530	1,000	800	260	660	12,176
004	62	130	220	71	110	64	U	54	1,370
005	150	250	530	130	340	290	170	130	3,180
006	120	140	210	U	150	120	U	110	1,520
007	U	U	150	U	130	U	U	U	520
008	2,200	3,300	5,100	1,700	2,700	2,000	450	2,200	35,432
008-FD	3,400	5,300	8,300	2,300	4,300	3,100	680	3,200	51,479
009	23,000	44,000	70,000	16,000	46,000	18,000	3,700	16,000	387,200
010	11,000	16,000	18,000	6,200	12,000	4,200	970	3,700	155,157
011	3,800	8,400	15,000	4,600	6,200	3,300	720	3,200	74,158
012	71	130	350	67	200	180	U	75	1,559
013	110	240	610	130	310	290	140	160	3,034
013-FD	83	170	430	80	260	220	130	100	2,341
014	15,000	23,000	25,000	9,400	16,000	13,000	3,000	12,000	266,580
014-FD	17,000	27,000	33,000	9,700	20,000	12,000	3,100	11,000	280,870
015	230	480	860	170	490	430	220	220	4,770
015-FD	150	380	730	170	450	400	220	170	4,080
016	260	500	700	210	380	360	U	340	4,776
017	140	280	420	110	220	210	U	190	2,720
018	170	340	530	140	270	260	U	240	3,290

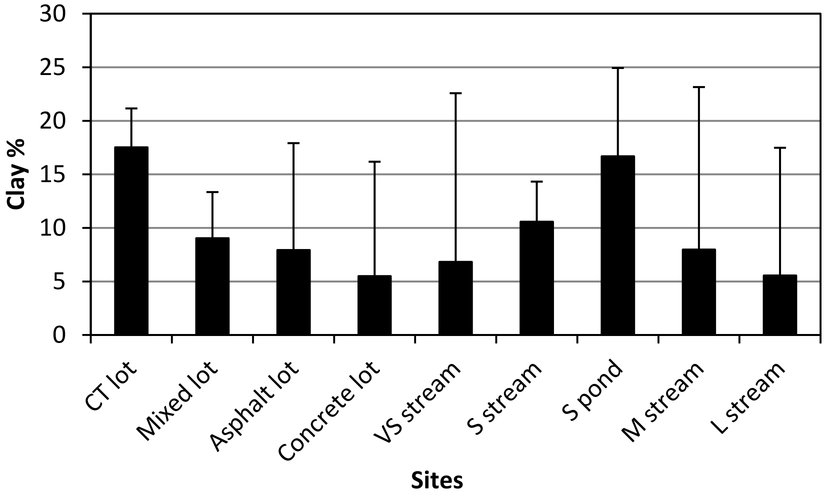
Sample ID	(9) Benzo[a] anthracene	(10) Chrysene	(11) Benzo[b] fluoranthene	(12) Benzo[k] fluoranthene	(13) Benzo[a] pyrene	(14) Indeno[1,2,3-cd]pyrene	(15) Dibenz[a,h] anthracene	(16) Benzo[g,h,i] perylene	Total 16 PAHs
	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg
019	40	33	U	U	28	U	U	U	463
020	30	U	U	U	U	U	U	U	363
021	140	230	320	110	190	94	U	80	2,278
022	490	850	1,400	350	750	420	U	340	7,791
023	290	520	720	230	400	240	U	200	4,677
024	3,300	4,800	6,600	2,100	3,900	1,700	280	1,300	44,191
025	1,300	2,000	2,500	870	1,600	1,000	140	840	19,534
026	6,100	7,900	11,000	3,100	6,900	2,700	420	2,100	80,880
027	1,600	2,000	2,400	840	1,700	790	94	620	20,857
028	2,100	2,100	2,300	730	1,800	1,100	230	920	25,226
028-FD	710	840	1,000	350	760	490	100	420	9,740
029	180	250	470	130	260	97	U	79	2,735
029-FD	170	240	450	110	250	100	U	84	2,527
030	75	91	180	57	100	45	U	34	1,111
031	2,700	4,500	6,700	2,100	3,600	1,600	100	1,200	41,490
031-FD	2,200	3,800	5,500	1,700	3,100	1,500	68	1,200	35,329
032	13,000	22,000	40,000	11,000	20,000	8,500	680	6,800	204,720
033	2,700	6,100	9,400	3,100	5,800	6,500	750	6,500	60,170
033-FD	3,400	7,200	12,000	3,700	6,700	4,500	460	3,900	65,350
034	4,400	7,400	9,800	3,700	5,900	2,900	410	2,500	71,050
034-FD	4,100	7,000	9,800	3,400	5,700	2,700	770	2,200	67,930
035	58,000	130,000	220,000	50,000	120,000	42,000	10,000	37,000	1,076,340
036	270,000	460,000	730,000	250,000	360,000	77,000	19,000	67,000	3,712,880
037	64,000	110,000	140,000	45,000	97,000	74,000	12,000	66,000	1,008,640
038	1,400	3,300	5,400	1,700	2,300	1,300	U	1,100	26,870

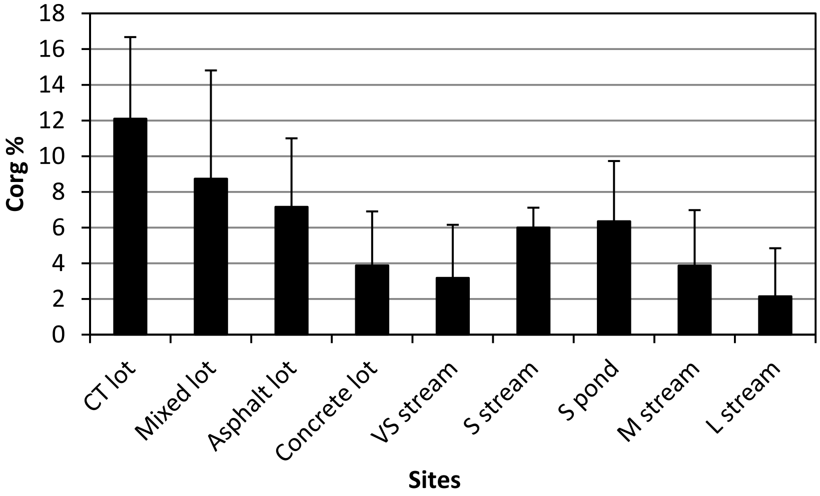
Sample ID	**(9) Benzo[a] anthracene**	**(10) Chrysene**	**(11) Benzo[b] fluoranthene**	**(12) Benzo[k] fluoranthene**	**(13) Benzo[a] pyrene**	**(14) Indeno[1,2,3-cd]pyrene**	**(15) Dibenz[a,h] anthracene**	**(16) Benzo[g,h,i] perylene**	**Total 16 PAHs**
	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg	ug/kg
039	430	870	1,300	410	680	400	95	290	7,814
040	7,200	8,400	11,000	5,100	6,700	3,500	710	2,700	80,648
041	130,000	370,000	430,000	91,000	180,000	69,000	14,000	51,000	2,783,940
042	180,000	340,000	380,000	63,000	190,000	45,000	9,600	34,000	2,652,610
042-FD	110,000	200,000	230,000	55,000	120,000	43,000	9,400	35,000	1,665,620
043	62	150	250	65	100	48	U	36	1,474
044	24,000	33,000	61,000	15,000	30,000	12,000	2,300	10,000	317,010
045	79,000	120,000	160,000	29,000	90,000	32,000	6,500	27,000	1,092,760
046	1,800	3,100	5,500	1,700	2,600	1,000	110	870	30,162
047	2,100	4,000	7,600	2,300	3,400	1,300	160	1,100	38,410
048	9,500	16,000	23,000	7,900	13,000	6,000	1,000	4,900	141,720
049	940	1,700	2,100	710	1,300	1,500	480	1,400	16,867
050	900	1,500	2,000	590	1,300	1,200	420	940	14,515
051	U	U	U	U	U	U	U	U	240
052	U	U	U	U	U	U	U	U	240
052-FD	U	U	U	U	U	U	U	U	240
053	U	U	U	U	U	U	U	U	240
054	U	U	U	U	U	U	U	U	240
055	U	U	U	U	U	U	U	U	240
056	U	U	240	U	210	U	U	U	690
056-FD	U	U	U	U	U	U	U	U	240
057	U	U	U	U	U	U	U	U	240
058	U	U	U	U	U	U	U	U	317

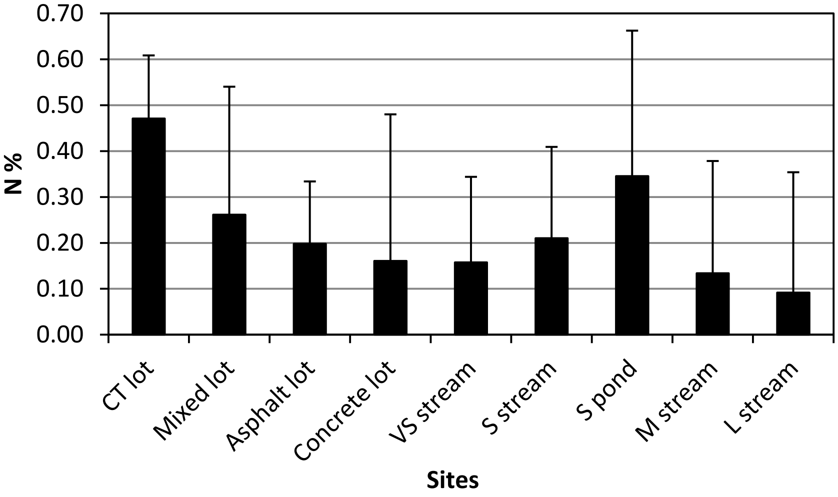
Appendix I. Mean and Max Grain Size, Nutrients and Metals by Sediment Class

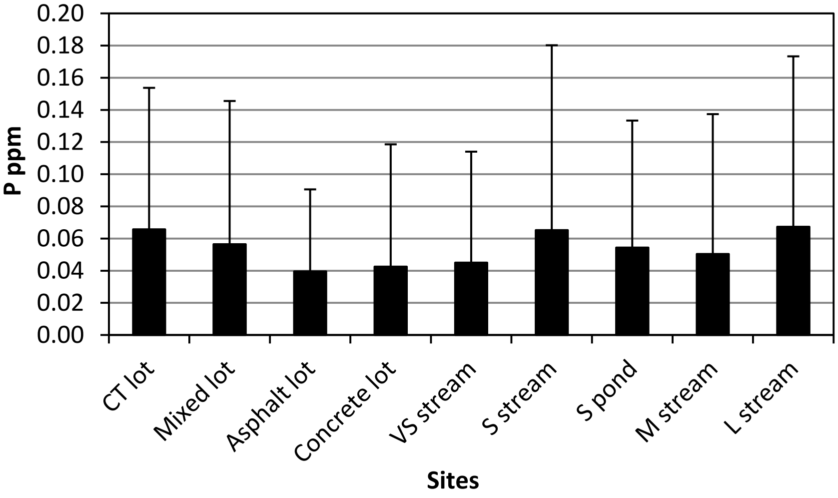


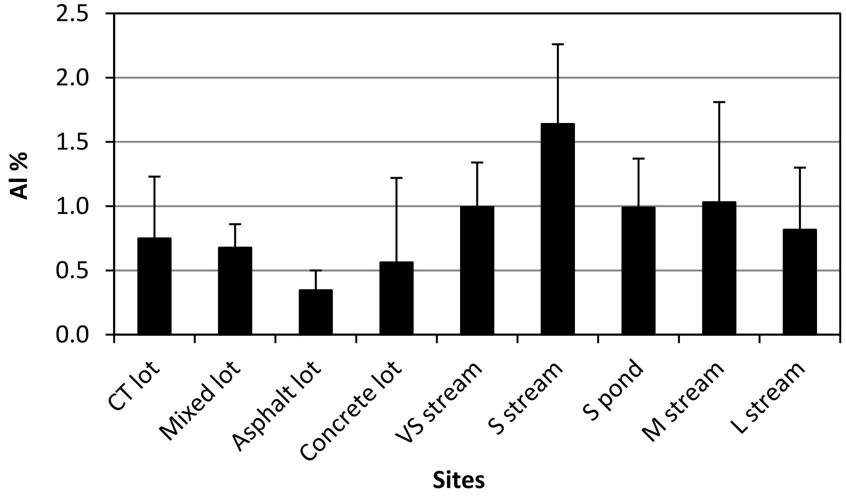




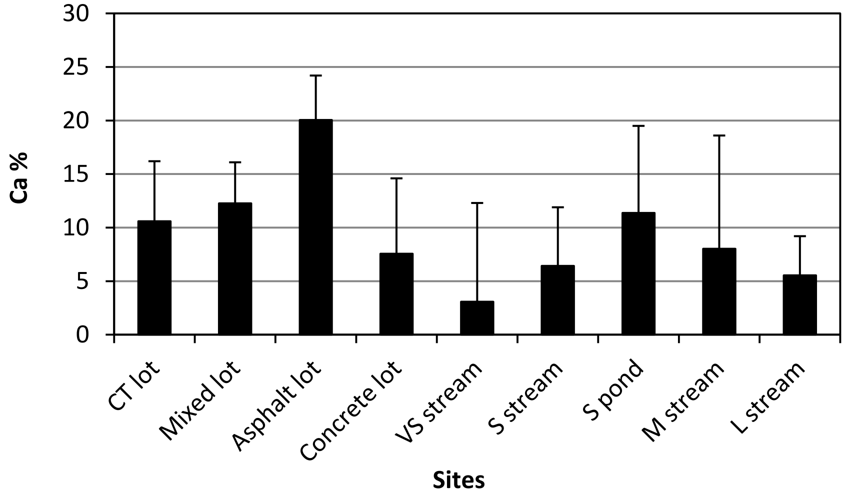

18
16
14
12
10
8
6
4
2
0
Corg %
CT lot
Mixed lot
Asphalt lot
Concrete lot
VS stream
S stream
S pond
M stream
L stream
Sites


0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
N %
CT lot
Mixed lot
Asphalt lot
Concrete lot
VS stream
S stream
S pond
M stream
L stream
Sites

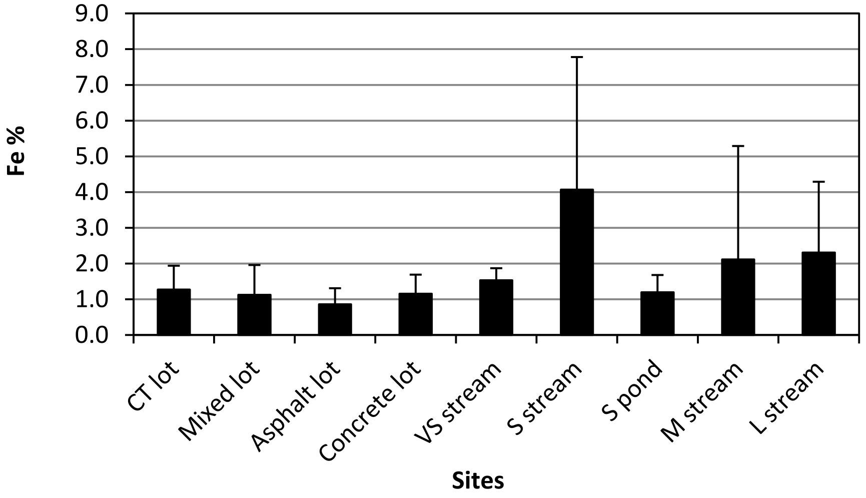

0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
P ppm
CT lot
Mixed lot
Asphalt lot
Concrete lot
VS stream
S stream
S pond
M stream
L stream
Sites



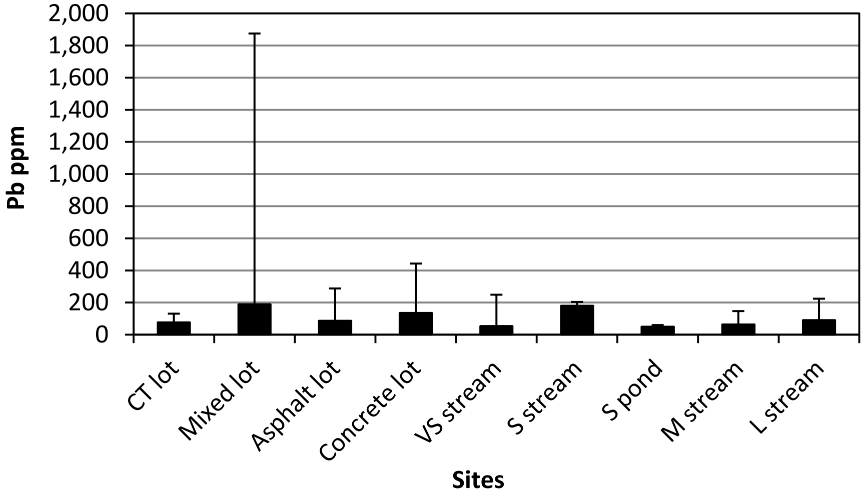
2.5
2.0
1.5
1.0
0.5
0.0
Al %
CT lot
Mixed lot
Asphalt lot
Concrete lot
VS stream
S stream
S pond
M stream
L stream
Sites

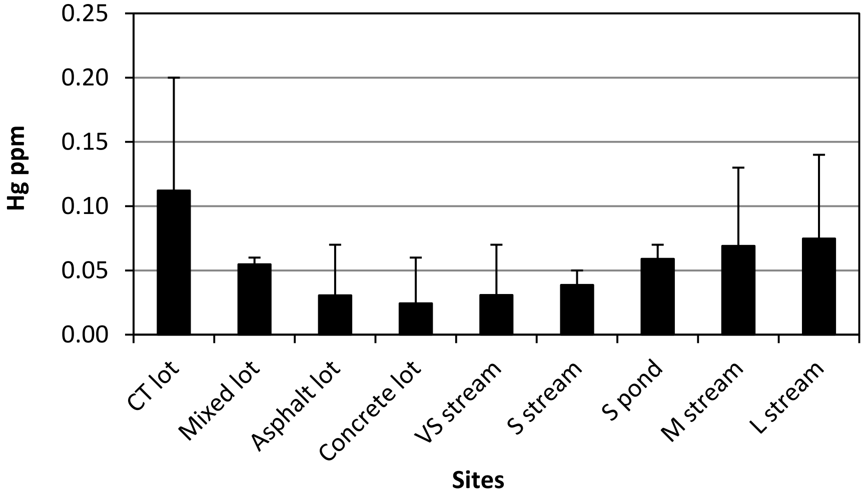


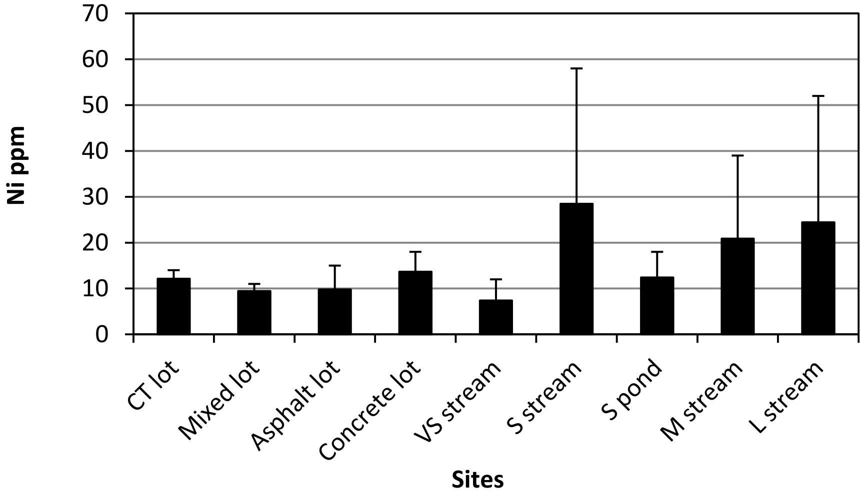
30
25
20
15
10
5
0
Ca %
CT lot
Mixed lot
Asphalt lot
Concrete lot
VS stream
S stream
S pond
M stream
L stream
Sites



9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Fe %
CT lot
Mixed lot
Asphalt lot
Concrete lot
VS stream
S stream
S pond
M stream
L stream
Sites


Pb ppm
2,000
1,800
1,600
1,400
1,200
1,000
800
600
400
200
0
CT lot
Mixed lot
Asphalt lot
Concrete lot
VS stream
S stream
S pond
M stream
L stream
Sites


Hg ppm
0.25
0.20
0.15
0.10
0.05
0.00
CT lot
Mixed lot
Asphalt lot
Concrete lot
VS stream
S stream
S pond
M stream
L stream
Sites


Ni ppm
70
60
50
40
30
20
10
0
CT lot
Mixed lot
Asphalt lot
Concrete lot
VS stream
S stream
S pond
M stream
L stream
Sites

Appendix J. Parking lot sampling locations

Parking Lot above sample 31

Sample 31- Lot edge

Parking Lot near outfall above samples 32 and 33

Sample 32- outfall edge

Sample 33- stream bed above spillway

Parking lot and outfall above sample 34

Sample 34- channel bed

Parking lot and outfall above sample 35

Sample 35- channel bed

Parking lot and outfall above sample 36

Sample 36- channe bed above spillway

Parking lot and outfall above sample 37

Sample 37- lot edge

Parking lot and outfall near sample 38

Sample 38- lot edge

Parking lot outfall above sample 39

Sample 39- bed sample at basin inlet

Sample 40- bed sediment accumulate at culvert outlet

Parking lot above sample 41

Sample 41- lot edge

Sample 42- lot edge at outlet

Sample 43- lot edge on outlet

Parking lot outfall above sample 44

Sample 44- bed sample at basin inlet

Parking lot outfall above sample 45

Sample 45- outfall edge

Parking lot above sample 46

Sample 46- lot edge at outfall

Parking lot above sample 47

Sample 47- lot edge

Parking lot above sample 48

Sample 48- lot edge

Parking lot above sample 49

Sample 49- basin channnel bed

Parking lot above sample 50

Sample 50- lot edge outlet

Appendix K. Examples of different parking lot surfaces

Mixed sealed and asphalt parking lot

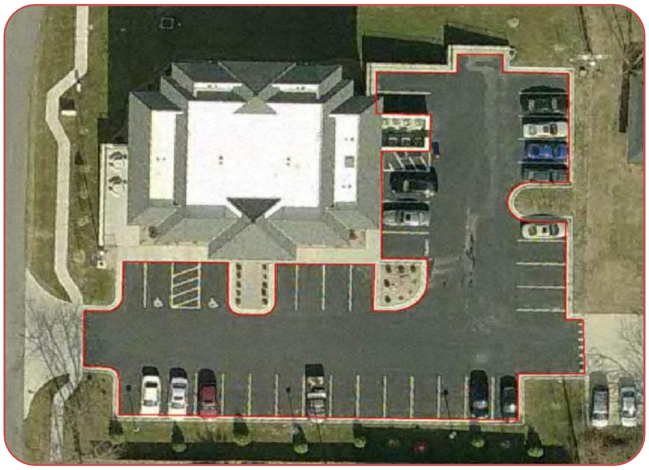
Seal-coated Lot

Mixed Asphalt(unsealed) and Seal-coated Lot

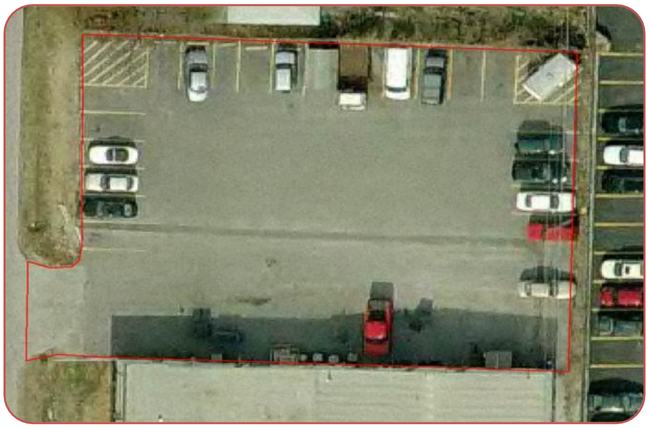
Asphalt Lot (Unsealed)

Concrete Lot (Unsealed)

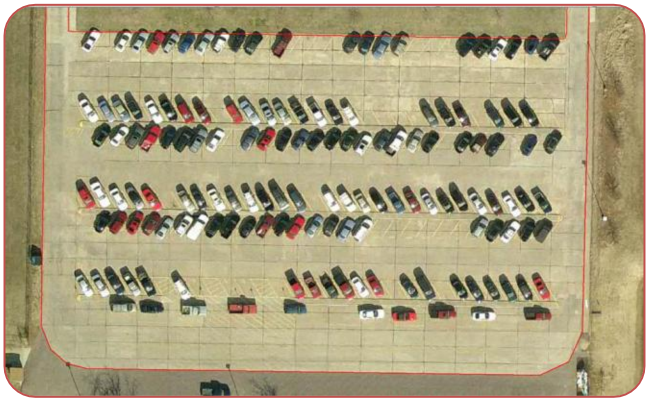
Appendix L. Examples from aerial photo classification



Sealant-coated Lot (probably coal-tar) on 2009 Aerial Photograph



Asphalt Lot (unsealed) on 2009 Aerial Photograph



Concrete Lot (unsealed) on 2009 Aerial Photograph