Physical Geography

Coal-tar pavement sealant use and polycyclic aromatic hydrocarbon contamination in urban stream sediments

R.T. Pavlowsky[a]

[a] Department of Geography, Geology, and Planning, Missouri State
University, Springfield, MO, USA
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Coal-tar pavement sealant use and polycyclic aromatic hydrocarbon contamination in urban stream sediments

R.T. Pavlowsky*

Department of Geography, Geology, and Planning, Missouri State University, Springfield, MO, USA

Polycyclic aromatic hydrocarbons (PAHs) can occur at levels of environmental concern in stream sediments from urban and industrial watersheds. Recent studies indicate that coal-tar sealant use on parking lots may have been the major source of PAHs to urban streams in the eastern US over the past 40 years. This study evaluates the spatial distribution of PAHs in urban stream and pond sediments in Galloway Creek in Springfield, Missouri by focusing specifically on parking lots with and ithout coal-tar sealants as contamination source areas. Multiple-linear regression analysis is used to evaluate the spatial connectivity of contaminated sediment to potential source areas and compare the relative influence of watershed source factors and reach sediment variability on sediment PAH levels. Sediments from coal-tar sealed parking lots and the streams that drain them are enriched in PAHs at concentrations considered toxic to aquatic life, with concentrations that are, on average, 35 and 480 times greater than those of unsealed asphalt and concrete lots, respectively. Moreover, sediment PAH concentrations are strongly correlated with the percentage of sealed parking lot area within the upstream drainage area of the sampling site, in contrast to total parking lot area or sediment composition. Metal and nutrient contaminants are poorly correlated with sealed lot area indicating a wider range of urban source inputs. Finally, parking lots with coal-tar coatings contribute >80% of the total PAH concentration in urban stream and pond sediments in Galloway Creek. If coal-tar sealant use ended, sediment PAH concentrations would probably decrease over time to levels not harmful to sediment-dwelling organisms.

Keywords: sediment contamination; polycyclic aromatic hydrocarbons; sediment tracers; parking-lot runoff; coal-tar sealant

Introduction

Fluvial geomorphologists have long been concerned with the spatial relationships among sediment sources, transport, and downstream sinks in river systems (Fryirs, 2013; Meade, 1982; Walling et al., 2003). Applications of hydrologic and geomorphic concepts to understand the distribution of sediment contaminants within watersheds have been a subfield within geography since the 1970s (Graf, 1994; Lewin, Davies, & Wolfenden, 1977; Lewin & Wolfenden, 1978; Marcus, 1989; Miller & Orbock-Miller, 2007). For the most part, geomorphic research has focused mainly on the transport of sediment-borne metals from mining and urban sources (Graf, 1994; Miller & Orbock-Miller, 2007). The transport of polycyclic aromatic hydrocarbons (PAHs) in

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*Email: bobpavlowsky@missouristate.edu

urban stream sediments is a relatively new research area for fluvial geomorphologists and physical geographers (Beasley & Kneale, 2002, 2004; Symader, Schorer, & Bierl, 1995, 1997). 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, Stout, & Gunster, 2005). 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 stream and pond sediments over relatively long distances downstream from the source (Hwang & Foster, 2006; Shi et al., 2005; Van Metre, Mahler, & Furlong, 2000; Wilson, Clarke, Arcy, Heal, &Wright, 2005).

Stream water and sediments in many urban and industrial areas contain PAHs at levels of environmental concern (Beasley & Kneale, 2004; Hwang & Foster, 2006; Scoggins, McClintock, Gosselink, & Breyer, 2007; Selbig, 2009; Van Metre & Mahler, 2005; Wilson et al., 2005). PAH contamination of stream bed sediment has been associated with degraded macroinvertebrate communities in streams affected by urban runoff (Beasley & Kneale, 2004; Neff et al., 2005; Scoggins et al., 2007). Further, PAH bioaccumulation can occur in other freshwater organisms such as water fleas (*Daphnia pulex*) and zebra mussels (*Dreissena polymorpha*) (Roper, Cherry, Simmers, & Tatum, 1997; Southworth, Beauchamp, & Schmieder, 1978). Acute or chronic exposure to some PAHs in contaminated soils, dusts, and aerosols may cause cancer, genetic damage, and newborn development problems in humans (ATSDR, 1995; Crane, Grosenheider, & Wilson, 2010).

Stream and pond sediments provide an excellent medium for sampling and spatial analysis of PAHs in urban watersheds. At first, PAHs are typically released to the urban environment in particulate form by the ignition of petroleum products and wood, weathering of asphalt pavements, and abrasion of parking lot sealcoats (Neff et al., 2005; Van Metre & Mahler, 2010; Yang, Ligouis, Pies, Grathwohle, & Hofmann, 2008). Since most PAHs are not very soluble in water, dissolved PAHs tend to bind rapidly to fine-grained and/or organic-rich suspended or bed sediments upon entering a water body (Evans, Gill, & Robotham, 1990; Ghosh & Hawthorne, 2010; Neff et al., 2005; Schorer, 1997; Shi, Tao, Pan, Liu, & Shen, 2007). Therefore, PAHs become more concentrated in suspended and bed sediments in urban streams compared to the dissolved phase. For example, Hwang and Foster (2006) showed that the particulate or suspended phase accounted for 68%–97% of the total PAH transport during storm runoff events in urban streams in Washington DC. Bed and lake bottom sediment surveys have been shown to be effective tools for PAH source monitoring since PAH concentrations are (1) readily detectable at levels of concern in urban and commercial watersheds; (2) persistent within sediment deposits for relatively long periods of time > 50 years; and (3) less affected by local factors compared to water and suspended sediment samples (Satori, Wade, Sericano, Mohanty, & Smith, 2010; Shi et al., 2005; Van Metre & Mahler, 2005).

PAH concentrations in urban sediments can vary greatly since different land-use configurations and combustion and industrial processes can yield different amounts and compositions of PAHs. Nonpoint sources of PAHs can be widespread and specific input locations may be hard to pinpoint within urbanized areas. Urban runoff typically includes PAHs from automobile exhaust, lubricating oils, gasoline, tire particles, pavement particles, wood and coal smoke, and soot in both dissolved and particulate forms (Ahrens & Depree, 2010; Mahler et al., 2012; Van Metre et al., 2000). Point source discharges from industrial sites, such as wood-treatment facilities where creosote

is used, can also produce elevated PAH levels in stream sediments (Brenner et al., 2002; Walker & Dickhut, 2001). Diagnostic ratios between dominant PAH compounds have been used to identify specific source characteristics of PAH contamination in urban streams (Ahrens & Depree, 2010; Mahler, Van Metre, Bashara, Wilson, & Johns, 2005; Yunker et al., 2002). However, PAH ratio precision 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 (Crane et al., 2010; Katsoyiannis, Terzi, & Cai, 2007; Tobiszewski & Namiesnik, 2012; Zhang et al., 2005).

As with other sediment-associated contaminants, PAH concentrations in channel sediments are expected to decrease with distance from source due to sediment dilution and mixing with tributary or bank erosion inputs (Graf, 1990; Lewin et al., 1977; Marcus, 1987). In general, PAH concentrations in stream sediments tend to decrease downstream from core urban source areas due to (1) dilution by lower PAH sediment loads from suburban and rural areas; (2) release of PAHs by decomposition and volatilization; and (3) sedimentation and long-term storage of PAH contaminated particles within alluvial and lake deposits (Van Metre & Mahler, 2010; Zhang et al., 2005). In addition, hydraulic forces that control sediment transport rates and settling velocities can influence where and at what concentrations sediment PAHs are deposited in a channel or pond (Bentzen & Larsen, 2009). Typically, stream power is negatively related to the deposition rate of contaminated sediment within channels and on floodplains (Graf, 1990). However, PAHs tend to be concentrated in both the fine (<63 μm) sediment fraction and the larger floatable organic fraction in urban streams (Bathi, Pitt, & Clark, 2012). Hence, sediment PAH concentrations can range greatly from site to site in different terrains, land-use areas, and watershed sizes.

Sediment PAH studies usually evaluate the single quantity of the total sum of individual PAHs measured in a sediment sample, typically ranging from 10 to 16 in number (MacDonald, Ingersoll, & Berger, 2000; Mahler et al., 2012). In several studies of urban stream sediment contamination, the average and maximum total PAH concentrations were (1) 2000 and 50,000 μg/kg or ppb for relatively small watersheds in Scotland (Wilson et al., 2005), (2) 11,000 and 19,00,000 μg/kg in small- to medium-sized watersheds in Tianjin, China (Shi et al., 2005), and (3) 100 and 900 μg/kg in the middle and lower Yellow River in China (Li, Xia, Yang, Wang, & Voulvoulis, 2006). Total PAH concentrations were typically 10,000–50,000 μg/kg in 10 reservoirs and lakes from six different metropolitan areas in the United States, ranging from 2790 to 224,000 μg/kg (Van Metre & Mahler, 2005, 2010). Urban and suburban sediment total PAH concentrations tend to be an order of magnitude or higher than those found in undeveloped areas. For comparison, relatively undisturbed lake sediments from Grand Teton National Park, Wyoming, yielded a maximum total PAH concentration of 480 μg/kg (Rhea et al., 2005). MacDonald et al. (2000) reported that total sediment PAH concentrations above 22,800 μg/kg are probably toxic to sediment-dwelling organisms in streams and lakes.

Sediment composition can also affect the transport and environmental fate of PAHs in watersheds. Sediment organic carbon content is often correlated with PAH concentration, regardless of particle size (Ghosh & Hawthorne, 2010; Schorer, 1997; Shi et al., 2007; Yang et al., 2008, 2010). Accordingly, 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 (Ghosh & Hawthorne, 2010; Yang et al., 2008). The low-density fraction may account for only 3–5% of total sediment mass, but contain from 50 to 80% of the PAHs within contaminated channel and floodplain deposits

(Rockne, Schor, Young, Taghon, & Kosson, 2002; Yang et al., 2008). However, more bioavailable PAH forms may preferentially bind to both mineral and organic particles in the silt- and clay-size sediment fractions, and these contaminated sediments may be of greater environmental concern where higher suspended sediment loads or sedimentation rates occur in urban streams (Bentzen & Larson, 2009; Talley, Ghosh, Tucker, Furey, & Luthey, 2002).

Recent studies have raised questions about coal-tar sealant use as a major source of PAH contamination to stream sediments in urban watersheds (Mahler et al., 2012). While concentrations of some point and nonpoint pollutants such as metals and DDT/DDE have been decreasing in United States 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, probably as the result of increased use of coal-tar sealants on parking lots (Van Metre et al., 2000, Van Metre & Mahler, 2005, 2010). Coal-tar is similar in appearance to asphalt but is produced as a byproduct of bituminous coal processing during the production of metallurgical coke. Coal-tar is mixed into an emulsion comparable to asphalt emulsions and is then applied to asphalt pavements on roads, driveways, parking lots, gas stations, and airport taxiways. High concentrations of PAHs can be released to streams both immediately after application before the sealant coat fully sets (Van Metre, Mahler, & Wilson, 2009; USEPA, 2011) and then by the progressive release of weathered and abraded sealant particles over time (Ahrens & Depree, 2010; Mahler et al. 2005, 2012; Van Metre & Mahler, 2010). Unsealed asphalt pavements generally contain total PAH concentrations at concentrations ranging from 10,000 (0.001) to 30,000 μg/kg (0.003%) (Ahrens & Depree, 2010; Blackburn, Kriech, Kurek, & Osborn, (n.d.)). Average PAH concentrations in suspended particulates in runoff from parking lots in Austin, Texas, were 54,000 μg/kg (0.0054%) for unsealed asphalt and concrete lots, 620,000 μg/kg (0.062%) for asphalt sealed lots, and 3500,000 μg/kg (0.35%) for coal-tar sealed lots (Mahler et al., 2012). In comparison, total PAH concentrations in asphalt-based sealants ranged from 0.3 to 6.6% and coal-tar based sealants from 3.4 to 20% (Mahler et al., 2005). A coal-tar content of 0.01% total sediment mass can account for >90% of the total PAH concentration in stream sediments (Ahrens & Depree, 2010). Moreover, coal-tar sealcoat sources have been reported to contribute more than one-half of the PAH contamination or more to stream and lake sediments in some urban drainage basins in central, southern, and eastern United States. (Van Metre & Mahler, 2010).

To advance our understanding of PAH transport at different spatial scales, empirical field studies are needed to help explain the spatial distribution of PAH contaminated stream sediments within watersheds and assess its toxic effects on aquatic life (Beasley & Kneale, 2002, 2004). Since the residence time of fine-grained sediment in alluvial channels is typically <5 years (Walling et al., 2003), a quantitative process-based approach aimed at linking contemporary pollution sources to downstream sediment quality can be useful (Ahrens & Depree, 2010; Beasley & Kneale, 2004; Yunker et al., 2002). Such an approach to PAH assessment may be particularly important in urban watersheds where sediment composition and transport varies due to downstream changes in hydrology, land use, and contaminant inputs (Marcus, 1989).

The purpose of this study is to quantify and evaluate the spatial patterns of PAH concentrations and source–sink relationships in stream and pond sediments in an urban watershed in the City of Springfield, Missouri. The City is concerned about the negative effects that PAHs may have on water and sediment quality and aquatic life. Indeed, several other United States cities and states have already banned the use of coal-tar seal

coat products to prevent excessive PAH contamination (Crane et al., 2010; Mahler et al., 2012). This study addresses two main questions. First, are PAHs found in urban stream and pond sediments at concentrations high enough to raise environmental concerns? Second, if there are concerns, to what degree are coal-tar sealants the source?

To evaluate the influence of several factors on sediment contamination, multivariate-regression analysis was used to relate urban source areas and transport processes to sediment properties at two spatial scales. This method quantifies the combined influences of both parking lot sources within the watershed and sediment composition variability within the reach to predict sediment PAH concentrations within the channel drainage network. This method has been used previously to model downstream variations in mining-related contamination in a North Carolina Piedmont stream (Pavlowsky, Lecce, Bassett, & Martin, 2010). If this approach is successful, then it may have broader application for source–sediment connectivity analysis in other watersheds with different land-use and geological characteristics. Further, this study also informs the potential use of PAHs as a sediment tracer to determine sediment source and stratigraphic age of floodplain and impoundment deposits in urban watersheds where the timing of urban development and coal-tar sealant use is known (Van Metre & Mahler, 2005, 2010). PAH source signatures have been shown to persist in channel and floodplain deposits and soil profiles for 60 years or more (Satori et al., 2010; Vulava, McKay, Driese, Menn, & Sayler, 2007; Walker & Dickhut, 2001).

Study Area

The study area is located on the southeast side of Springfield, Missouri, in the Galloway Creek watershed (18.2 km^2) (Figure 1). Springfield is the third largest city in Missouri and the population has been increasing at nationally high rates since the 1980s. Galloway Creek drains the Springfield Plateau in the western Ozark Highlands, which is underlain mainly by horizontally bedded limestone in which a well-developed karst system of sinkholes, caverns, and springs has formed. Galloway Creek is a losing stream and largely ephemeral, except for three constructed ponds in a residential community located in the middle of the watershed and perennial discharge from Sequiota Spring in the lower segment of the creek above Lake Springfield. Galloway Creek flows into the James River at Lake Springfield, which was formed by dam construction in 1957 to provide a cooling water source for a coal-fired power generation plant. Rapid urban residential and commercial expansion occurred in the Galloway Creek watershed beginning in the late 1970s, peaked in the 1990s and early 2000s, and has continued at a reduced rate until present. At present, the watershed is almost entirely within the city limits of Springfield and is considered urban, with >80% urban land use within the subwatersheds evaluated for this study (Table 1; Figure 1).

Methods

Field sampling

Urban sediment samples were collected from stream channel beds and bar surfaces, wet detention pond and shallow lake bottom deposits, and parking lot edges and drainageways within Galloway Creek watershed to evaluate the spatial variability of PAH contamination, sources, and transport patterns. Contemporary fine-grained (<2 mm in diameter) sediment deposits were targeted for sampling to improve correlations between contaminant signatures and contemporary pollution sources. Recent deposits for
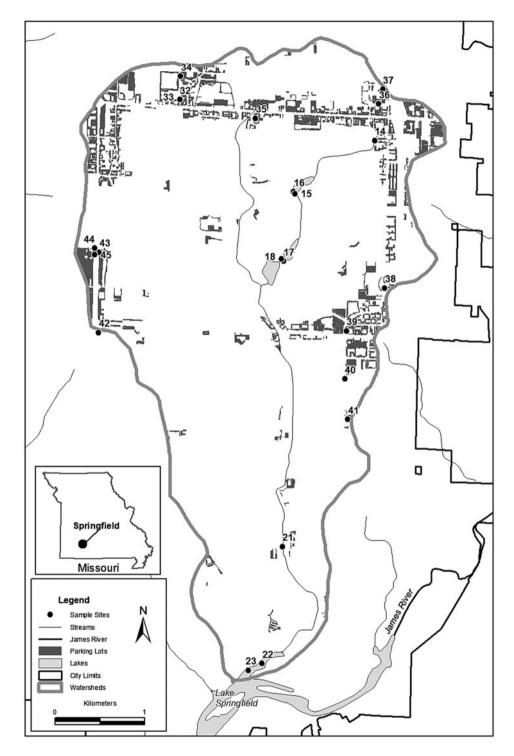
Figure 1.   Galloway Creek watershed and parking lot distribution.
Notes: (1) Sampling site numbers refer to Tables 1 and 3 and (2) The entire study watershed is within the city limits of Springfield, Missouri.

Table 1. Sample site characteristics and sediment properties.

Site[a]		A^b	Land Use Cover (%)[c]				Source Variables[d]			D50[e]	TOC[f]	PAH$_{16}$[g]
No.	Type	(km^2)	Urban	Grass	Crops	Forest	IA%	TLA%	SLA%	(um)	(%)	(ppb)
Urban sediments from galloway creek watershed												
41	lot	0.003	100	0.0	0.0	0.0	100	100	100	55	14.7	2783,715
32	lot	0.004	100	0.0	0.0	0.0	64.5	64.5	64.5	19	6.1	204,510
42	lot	0.006	100	0.0	0.0	0.0	77.4	77.4	74.2	18	16.7	2652,370
36	lot	0.022	100	0.0	0.0	0.0	33.3	33.3	25.9	17	14.3	3712,640
37	lot	0.004	100	0.0	0.0	0.0	36.4	36.4	36.4	206	14.8	1008,430
35	lot	0.008	100	0.0	0.0	0.0	50.0	50.0	50.0	42	8.2	1076,100
44	lot	0.010	100	0.0	0.0	0.0	100	100	27.8	172	6.3	316,785
45	lot	0.038	100	0.0	0.0	0.0	84.5	84.5	80.6	275	7.6	1092,520
38	lot	0.001	100	0.0	0.0	0.0	82.1	82.1	0.0	17	11.0	26,705
34	lot	0.053	100	0.0	0.0	0.0	41.7	38.9	8.3	190	8.8	70,840
39	lot	0.011	100	0.0	0.0	0.0	50.0	50.0	0.0	472	3.5	7634
43	lot	0.024	100	0.0	0.0	0.0	66.7	66.7	0.0	660	2.1	1324
33	stream	0.080	100	0.0	0.0	0.0	40.4	38.5	18.0	13	4.5	59,990
40	stream	0.138	100	0.0	0.0	0.0	46.0	38.0	32.8	23	2.0	80,408
14	stream	0.5	95.3	3.7	0.0	1.0	37.1	26.1	17.8	223	6.2	266,355
15	pond	2.1	92.4	4.1	0.0	2.6	24.4	13.4	8.3	12	6.8	4605
16	pond	2.1	92.4	4.1	0.0	2.6	24.4	13.4	8.3	24	7.4	4611
17	pond	2.5	91.3	4.1	0.0	2.5	22.4	11.3	7.0	23	8.4	2570
18	pond	2.5	91.3	4.1	0.0	2.5	22.4	11.3	7.0	12	9.7	3140
21	stream	16.1	86.2	6.4	0.0	6.3	16.0	6.9	4.9	15	6.7	2113
22	lake	17.7	83.3	8.2	0.0	7.5	15.4	6.4	4.6	17	7.0	7611
23	lake	17.8	82.9	8.3	0.0	7.7	15.4	6.4	4.5	21	4.2	4497
Rural sediments from spring creek watershed												
51	pond	0.0	0.0	100	0.0	0.0	0[h]	nd[i]	nd	26	6.1	<DL[j]
52	pond	0.4	5.7	89.5	0.5	4.3	5.0	nd	nd	12	4.2	<DL
53	pond	0.0	0.0	87.7	0.0	13.3	0.0	nd	nd	533	1.6	<DL
54	pond	0.04	9.7	80.5	0.0	9.8	0.8	nd	nd	17	5.0	<DL
55	stream	8.7	0.3	77.9	12.0	9.8	1.1	nd	nd	22	1.8	<DL
56	stream	42.8	1.0	75.7	6.3	16.9	1.7	nd	nd	24	8.2	450[k]
57	stream	43.4	1.4	76.3	6.0	16.1	1.8	nd	nd	25	4.2	<DL
58	stream	91.1	1.1	74.5	5.8	18.4	1.7	nd	nd	51	3.2	77[k]

[a]Site numbers for Galloway Creek are indicated on Figure 2 and site types are described in text;
[b]Drainage area above the sampling site;
[c]Land use/cover above sampling site in percent area: urban/dense suburban, grassland/pasture, rowcrops/fields, and forest/woodlands;
[d]Percent source area in drainage area: IA%, IA as total commercial lots + road area; TLA%, total commercal lot area; and SLA%, sealed lot area;
[e]Median particle size diameter in the < 2 mm fraction;
[f]Total organic carbon;
[g]Sum of 6 PAHs;
[h]Only road area included, parking lot areas not measured;
[i]not determined;
[j]Below detection, no quantitative analysis reported;
[k]only detected concentrations reported.

sampling were found in depositional areas that shift or erode often so as to "reset the clock" after one or several storm runoff events. The deposits were typically unconsolidated, lacked vegetation growth, and occurred as distinct layers overlying older soils, artificial surfaces, or seasonal leaf litter.

Sediment samples were collected from a total of 22 sites within the Galloway Creek watershed during the summer of 2011. Twelve "parking lot" sites were located near outlets of small storm water catchments (<0.05 km^2) below relatively large parking lot areas, ranging from 36 to 100% of the contributing drainage area (Table 1). Parking lot sampling sites were distributed across a gradient from high to low source influence by coal-tar sealed lots, with percent sealed lot area within site catchments ranging from 0 to 100% (Table 1). Three sites drained only unsealed lot areas (i.e., 0% sealed lot area), including one unsealed asphalt lot (site 38) and two concrete lots (sites 39 and 43) (Table 1 and Figure 1). While concrete lots occur relatively infrequently in the Springfield area, two concrete-only lot sampling sites were included in the study to provide a sediment quality control between unsealed asphalt and concrete pavement surfaces. Parking lot sampling sites were selected based on visual interpretation of the drainage system and lot characteristics present on high resolution 2009 aerial photography. Subsequent field inspections in 2011 identified seal-coated (shiny dark blue-black colored), unsealed asphalt (dull gray colored), and concrete (white-yellow brown colored) parking lots. All parking lots selected for sampling had several common characteristics: (1) good public and open access; (2) drainage areas with clearly identified parking lot types and well-defined source areas; and (3) areas indicative of recent sedimentation, such as in flat areas along lot edges, at breaks in slope below outfalls, or in trickle channels within adjacent storm water basins.

Additional sampling sites were selected to provide a distribution of sites along an urban core-suburban-rural area gradient. Stream and pond samples were collected at 10 sites below parking lot sites with good public access and availability of recent sediment deposits, including stream channel ($n = 4$), residential ponds ($n = 4$), and impounded lake ($n = 2$) locations. These samples spanned a range of downstream drainage area from about 0.1 to almost 18 km^2 (Table 1). Rural land-use samples were collected at four stream channel and four pond sites from the Spring Creek watershed, located 20 km southwest from Galloway Creek in Stone and Christian Counties, Missouri, to provide information on PAH levels present in forested and agricultural areas, since PAHs are known to form naturally through organic matter decomposition and forest fires (Denis et al., 2012; Rhea et al., 2005). The spatial distribution of rural sediment PAH concentrations and other characteristics is not evaluated in this study. However, analytical results from these samples are used to provide information for analytical quality control purposes to evaluate potential sampling contamination effects and different rural and urban land-use effects on PAH levels (Tables 1 and 2).

Sediment samples were collected in the field at each site with a shovel and then transferred to a clean 8-inch (20.3 cm) stainless steel pan for mixing and removal of

Table 2. Pearson correlations among source variables and sediment properties[a]. (A) Source variable covariation[a].

	A_d[a,b,c]	U%	IA%	TLA%
U%	−0.91			
IA%	−0.56	0.71		
TLA%	−0.57	0.74	0.99	
SLA%	−0.36	0.47	0.63	0.63

[a]$N = 22$; analysis of arithmetic values.
[b]See Tables 1 & 3 and text for definitions.
[c]Underlined values are significant at $p = 0.05$.

large particles and organic debris by hand. Care was taken to only collect grab material that did not contact the shovel surface. For PAH analysis, a 50-g portion of field-prepped sediment was immediately placed into a pesticide-grade, pre-cleaned, amber-colored glass jar with a Teflon-lined lid. 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, organic carbon, and particle-size analysis.

Sediment analysis

Sediment samples for PAH analysis were processed wet and put into glass jars, packed in a cooler with ice in the field, and mailed "overnight" to a commercial laboratory for analysis. All sediment samples were analyzed for USEPA's 16 Priority PAHs using gas chromatography and mass spectrometry according to USEPA standard method 8270C by a certified commercial laboratory (EMSL Analytical, Inc., Westmont, NJ). Analytical error for the method was reported by the laboratory to be <20% difference from sample duplicates. It is common practice in environmental studies of PAHs to focus investigation on the total PAH burden in the sediment (Mahler et al., 2012). In this study, analysis focused primarily on the sum of 16 different PAH concentrations (hence referred to as total PAHs or PAH$_{16}$). The 16 PAHs tested for in this study and the number of benzene rings incorporated within each molecule are as follows: naphthalene (2), acenaphthylene (3), acenaphthene (3), fluorene (3), phenanthrene (3), anthracene (3), fluoranthene (4), pyrene (4), benzo[a]anthracene (4), chrysene (4), benzo[b]fluoranthene (5), benzo[k]fluoranthene (5), benzo[a]pyrene (5), indeno[1,2,3-cd]pyrene (6), dibenz[a,h,anthracene (5), and benzo[g,h,i]perylene (6). The most abundant PAHs in urban sediments have relatively high molecular weights and contain 4--6-rings (i.e., H-PAHs), particularly the fluoranthene and pyrene isomers (Crane et al., 2010). The most common low molecular weight PAHs with 2--3-rings (i.e., L-PAHs) in urban sediments are the anthracene and phenanthrene isomers. L-PAHs degrade more rapidly and are washed downstream at a faster rate compared to H-PAHs (USEPA, 2011; Van Metre & Mahler, 2010). H-PAHs tend to be less soluble in water, bind more strongly to sediment particles, and last longer in the environment (Neff et al., 2005).

Sediment sample preparation and all analyzes except for metals, phosphorus, and PAHs were completed at the Ozarks Environmental and Water Resources Institute at Missouri State University (MSU) campus in Springfield. Sample splits for textural and geochemical analysis were dried in an oven at 60 °C, disaggregated with mortar and pestle, and put through a 2 mm sieve to remove oversized material. Dried samples were stored in plastic bags until subsequent analysis. All samples were analyzed for phosphorus (P) and metals, including copper (Cu), lead (Pb), mercury (Hg), and zinc (Zn), by hot strong acid (i.e., aqua-regia) extraction and inductively coupled plasma atomic emission spectroscopy analysis (ICP-AES) at a certified commercial laboratory (ALS Minerals, Winnemucca, NV using method ME-ICP41 m). Geochemical standards were routinely analyzed during sample runs, and analytical errors for the method were reported by the laboratory to be <20% difference for sample duplicates for all metals and P. Information on the geochemical trends of major and trace metals in sediment and soil samples can help to better understand source locations and transport pathways of PAHs in urban sediments (Bentzen & Larsen, 2009; Schorer, 1997; Wilson et al., 2005).

Sediment size, organic carbon (TOC), and nitrogen (N) analyses were completed at the water and sediment laboratory at MSU (see standard operating procedures at

http://oewri.missouristate.edu/80056.htm). Particle-size distribution including the median diameter (D50) for the <2 mm fraction was determined for each sample using a Beckman-Coulter LS 13–320 laser diffraction particle size analyzer. Prior to analysis, samples were pretreated with hydrogen peroxide to remove organic matter and then dispersed by sodium hexa-metaphosphate solution using a sonicator. Analytical errors for calculated D_{50} values were typically within 5–15% difference for sample duplicates. In addition, all samples were analyzed for total and organic carbon and N by combustion in an Elementar Vario EL III CNS Analyzer. The analytical error for total organic carbon (TOC) was typically within 5–20% relative difference for sample duplicates.

Geospatial data and analysis

All geospatial information science (GIS) database operations and analysis were completed in the geospatial technology laboratory at MSU. The City of Springfield provided the 2009 aerial photographs and GIS layers describing the stormwater infrastructure network of the study area. Additional GIS databases, including land use, roads, and hydrology layers, were obtained from the MSU database or retrieved from the Missouri spatial data information service. Each sampling site was marked by a hand-held geographic positioning system receiver. Parking lot locations, drainage divides, surface type, and sampling site locations were verified for a second time by field inspection and corrected, if necessary, using high-resolution 2009 aerial photography. Each parking lot was attributed by type (i.e., sealed, unsealed asphalt, and unsealed concrete) and surface area (km^2), which was used to calculate percent coverage of the watershed by each lot type. Upstream drainage areas were delineated using the Arc Hydro Tools extension within ESRI's ArcMap 10 GIS software with a 10-m digital elevation model. In this study, impervious area (IA%) above each sampling point was determined as the sum of two urban surface areas: large commercial and residential parking lot areas and road areas as estimated by the length of all mapped roads multiplied by an assumed 10 m average roadway width.

Source-sediment quality regression modeling approach

Multiple regression analysis was used to evaluate pollution source effects on the spatial patterns of sediment PAH, metal, and nutrient concentrations in urban sediments. The regression models developed included parameters that quantify contamination trends based on the influence of both source input magnitude (Y-intercept) and downstream decay rate due to dilution/mixing, sedimentation, and removal by uptake and volatilization (slope coefficients) (Marcus, 1987; Phillips, 1988). Because the primary goal was to determine the source contributions of coal-tar lots to PAH contamination compared to unsealed asphalt and concrete parking lots and other nonpoint urban sources, the regression modeling approach focused on testing the relative strength of two spatial variables on PAH transport patterns: (1) percent coal-tar sealed lot area within the upstream drainage area above the sampling point (SLA%) and (2) percent total parking lot area above the sampling point (TLA%). The first variable focuses on the direct source effect of coal-tar lots which have been reported to be major sources of PAHs in urban watersheds nationally (Mahler et al., 2012). The second variable evaluates the influence of broader sources of contaminants in urban watersheds in addition to coal-tar sealant sources, including unsealed lot weathering, vehicular exhaust and tire wear,

atmospheric deposition, and runoff from other impervious surfaces such as roads, drive-ways, walkways, and roofs (Wilson et al., 2005). It was hypothesized that contaminants originating directly from coal-tar sealed lots would correlate more significantly with the SLA% variable, while contaminants being released from a wider range of urban sources would correlate more with the TLA% variable.

An important element of this study was the evaluation of the interaction of total and coal-tar lot area variables during regression analysis. By including both variables in the regression analysis, it was anticipated that the effects of PAH contributions from coal-tar lots could be distinguished from PAH contributions from unsealed lots and other urban nonpoint sources based on the relative significance of one variable com-pared to the other. However, the two variables are not completely independent of one another because SLA% is a subset of TLA% and is equal to or less than total lot area. As a control to check for the overlapping influence of the two lot area variables, the spatial patterns of other urban sediment contaminants such as metals and nutrients were also evaluated using the same regression approach as for PAHs. If PAH regression models were similar to those developed for contaminants released from a wider range of urban sources, not specific to coal-tar lots, then the importance of PAH contributions from urban nonpoint sources could be inferred. Further, in the final analysis, two differ-ent regression model scenarios were compared to quantify the relative source contribu-tions of PAHs from coal-tar sealed lots: (1) predicted PAH_{16} concentrations, assuming present parking lot conditions, and (2) predicted PAH_{16} concentrations after setting the effect of the coal-tar lot area parameter in the regression equation to zero. The predicted contribution of coal-tar lot area on PAH concentrations in urban sediments was simply calculated by subtraction of predicted PAH values between model scenarios 1 and 2 above.

In addition to the influence of watershed-scale factors, like the parking lot area vari-ables described above, the influence of local- or reach-scale erosion/deposition factors on geochemical variability also needed to be considered during the spatial analysis of stream sediment contaminants (Pavlowsky et al., 2010). Multiple-linear regression anal-ysis was used to test for additional effects of fluvial transport and geochemical substrate variability on PAH, metal, and nutrient concentrations in urban sediments (Horowitz, 1991; Miller & Orbock-Miller, 2007). In this study, hydraulic sorting effects were assessed in the regression analysis using median diameter of the < 2 mm fraction (D_{50}) to evaluate particle size effects with smaller particles assumed to have higher surface area and binding capacity (Talley et al., 2002). In addition, the effect of organic matter deposition on contaminant concentration was evaluated using percent TOC to test for preferential binding and incorporation of PAHs and other contaminants within the organic particle fraction (Schorer, 1997).

Results and discussion

Parking lot type and location

The spatial characteristics of parking lot types and locations were needed to base field sampling and evaluate PAH source effects (Figure 1). In 2009, the watershed contained a total of 383 individually mapped large commercial and residential parking lots cover-ing 1.218 km^2 of land area (i.e., 6.7% of the total watershed area) including 245 coal-tar sealed parking lots covering 0.865 km^2 which comprised 71.0% of the total parking lot area or 4.8% of the total watershed area. By comparison, unsealed parking lot areas covered 0.353 km^2 of the watershed as: (1) 105 unsealed asphalt pavement lots,

covering 0.268 km^2 or 1.4% of the watershed; (2) concrete pavement lots, covering 0.073 km^2 or 0.4% of the watershed; and (3) six gravel or gravel mixed with asphalt or concrete lots, covering 0.012 km^2 or 0.1% of the watershed. The spatial distribution of parking lots within the Galloway Creek watershed shows significant clustering along linear road corridors typically located along upland basin boundaries (Figure 1). A market study in 2009 on pavement sealer use by the City of Springfield indicated that 85% of all pavement sealant sales were coal-tar sealants and 15% were asphalt-based sealants (Lamb, 2009). The largest commercial lot applicator in town reported that they applied 95% coal-tar sealant, and two other large applicators used coal-tar sealant >98% of the time (Lamb, 2009). Hence, the sealed parking lots evaluated by this study were assumed to be primarily, if not entirely, coated with coal-tar sealants.

Sediment PAH_{16} concentrations

Sediments from all parking lot types and the stream channels that drain them are highly enriched in PAH_{16} and other relative to rural sediments (Table 1). Indeed, none of the four rural pond sediment samples tested, with concentrations ranging from 18 to 48 μg/kg and a median of 33 μg/kg (0 detections in 64 tests), exceeded laboratory detection limits for individual PAHs. Moreover, only three individual PAHs were detected for the four rural stream sediment samples (3 detections in 64 tests). Multiplying the median detection limit above by 16 different PAHs, the detection limit for sediment PAH_{16} in concentrations in Galloway Creek is about 500 μg/kg. Given that the actual PAH concentrations in rural sediments are probably below the reported detection limit, it appears that total PAH concentrations in urban sediments in Galloway Creek are at least 5–10 times higher than those found in rural sediments. Further, the gap between the detection limit for PAH analyses and elevated urban background PAH concentrations indicates that the sampling and analytical methods used to determine PAH concentrations in this study are sufficiently precise to measure urban source effects in Galloway Creek sediments.

Urban sediment PAH_{16} concentrations in Galloway Creek ranged over three orders of magnitude. The lowest urban sediment PAH_{16} concentrations were associated with site locations furthest from the urban core or lacking asphalt pavement or sealant coatings, including 1324 μg/kg at a concrete lot (site 43), 2113 μg/kg in a lower segment stream (site 21), and 2570 μg/kg in a residential pond (site 17) (Table 1). In general, the highest sediment PAH_{16} concentrations were associated with site locations below small stormwater catchments that drained > 25% coal-tar lot area, with a maximum of 3712,640 μg/kg PAH_{16} measured at a residential apartment complex (Table 1). Six of the 10 sites draining asphalt and/or sealed parking lots yielded sediment PAH_{16} concentrations >1000,000 μg/kg (Table 1). Stream sediments collected from three different storm water channels, each draining several commercial and residential developments, contained lower PAH concentrations ranging from 59,900 to 266,355 μg/kg PAH_{16} (Table 1). The highest PAH_{16} concentration measured in a pond or lake sediment sample was 7611 μg/kg in the Galloway Creek arm of Lake Springfield, with a drainage area of 17.7 km^2 (Table 1).

Most parking lot sediments and some stream sediments in Galloway Creek are contaminated to levels considered toxic to sediment-dwelling organisms (Table 1). MacDonald et al. (2000) reported the threshold effect concentration (TEC) of 1610 μg/kg and probable effects concentration of 22,800 μg/kg for total PAHs in aquatic sediments. The "TEC" is the value below which harmful effects are unlikely to occur. The "probable effects concentration" (PEC) is the value above which harmful effects are

likely to occur. Except for one concrete lot site (#43), all other sites produced sediment PAH_{16} concentrations at levels above the TEC limit of 1610 μg/kg PAH_{16} (Table 1). Further, 59% of all sites (13 out of 22) produced total PAH concentrations in excess of the PEC value of 22,800 μg/kg PAH_{16}. Total PAH concentrations in stream and pond sediments decreased rapidly below urban and commercial core areas, generally dropping below the PEC along the main stem of Galloway Creek where drainage area exceeds 2 km^2 (Table 1 & Figure 1). PAH deposition in pond, bar, and floodplain deposits may partially account for reduction in PAH concentrations downstream. Indeed, almost 1 m of contemporary sediment is trapped within residential ponds located along the east branch of Galloway Creek (sites 16–18) (Wright Water Engineers, 2001).

Comparison of PAH_{16} among different parking lot types

There were large differences in PAH levels among the three different parking lot types evaluated in this study. Three of the four sealed lot samples contained PAH concentrations over 100 times the PEC for toxicity to aquatic life at >2600,000 μg/kg or > 0.26% dry weight total PAHs. These levels are much higher than those found in unsealed asphalt and concrete parking lot samples (Table 1). On average, sealed parking lots yielded sediments with PAH_{16} concentrations 484 times higher than concrete parking lots, and 35 times higher than unsealed asphalt parking lots (Table 1). Admittedly, these results are from a small sample. However, the relative difference in PAH concentrations of sealed lots compared to unsealed lots found in this study is similar to that of other sediment PAH studies of parking lot effects in other urban areas (Mahler et al., 2005, 2012; Van Metre et al., 2009).

PAH levels in sediments collected below concrete parking lots can be used to evaluate the magnitude of other nonpoint PAH emissions to urban parking lots in addition to asphalt pavements and sealants. It is probable that the levels of PAHs observed in sediments from concrete lots will approximate the effects of other nonpoint sources on PAH levels if three conditions are generally true. First, there is little difference in PAH source rates among the parking lots sampled related to vehicular traffic use and external inputs, such as roof runoff releases and atmospheric deposition rates. Second, concrete materials contain low amounts of PAHs so that the effective contribution of PAHs to sediments from concrete wear is negligible. Third, PAH inputs from tire tracking and wind in delivering asphalt and coal-tar particles from adjacent lots other lots is also negligible. Field observations indicated that some concrete lots turned a grayish-blue color from the tracking of coal-tar and asphalt from nearby parking lots or roads. This suggests that assumption three may not hold true in all cases and that PAH concentrations in sediments from concrete lots may vary in response to tracking inputs.

Concrete parking lot sediments yielded the lowest PAH_{16} concentrations of the three lot types tested (<8000 μg/kg) (Table 1, sites 39 & 43). This finding suggests that PAH contamination rates from urban nonpoint sources, including vehicular wear, exhaust emissions, and atmospheric fallout, are relatively low compared to PAH emissions from the weathering and abrasion of asphalt pavements and coal-tar sealant coatings. Concrete pavement materials typically contain <<100 μg/kg total PAHs (Leblanc, Durant, Swan, Weaver, & Jansen, 2000). However, if fly ash produced by coal-burning power plants is used as a substitute for Portland cement in the mix, then total PAH concentrations in the concrete could approach 2000 μg/kg (Openshaw, 1992). Moreover, the supply rate of concrete particles to parking lot sediments is relatively low since concrete pavements break down more slowly and last longer than both asphalt
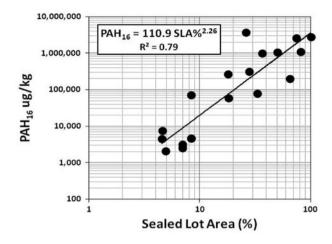
Figure 2.   Relationship between sealed parking lot area and total PAH concentration.

pavements and pavement sealants. For example, the replacement period decreases in the following order: (1) concrete, 13–30 years; (2) asphalt, 6–20 years; and (3) parking lot sealants, 3– 5 years (Gadja & Van Geem, 2001; Mahler et al., 2012; Scoggins, Ennis, Parker, & Herrington, 2006). Given that concrete contains relatively low concentrations of PAHs, the urban nonpoint contributions of PAHs to contaminated sediments, not including asphalt pavement or coal-tar sealant sources, are probably < 10,000 μg/kg PAH_{16} and may even approach the TEC of 1610 μg/kg if tracking, oil and gas spillage, and atmospheric inputs are minimal (MacDonald et al., 2000) (Table 1).

Sealed parking lot influence on PAH_{16} trends

In the Galloway Creek watershed, there is a strong relationship between SLA% and sediment PAH_{16} (Figure 2). Using data from only sites draining mapped sealed parking lot areas ($n = 19$), a regression equation using Log_{10} SLA% to predict Log_{10} PAH_{16} concentration explains 79% of the variance in PAH_{16} concentration (Figure 2). Adding Log_{10} TOC reduces the error by 4% and adding Log D50 reduces the error an additional 2% (results not shown). Thus, sealed lot area, organic carbon, and grain size explains 85% of the variance in PAH_{16} concentrations with Log SLA% contributing to 93% of explained variance in the three-parameter equation. Extrapolating from the PAH-SLA% regression model (Figure 2), TEC levels are exceeded where SLA% reaches 3% and PEC levels are exceeded where at SLA% reaches 10%. These ecologically based thresholds for stream sediment PAH contamination can be used to identify potentially contaminated streams in other urban watersheds in the Springfield area.

Urban source indicator relationships

Evaluation of the relationships between different urban source variables and downstream changes in sediment properties can be used to evaluate different source influences on PAHs and other pollutants in the Galloway Creek watershed (Tables 2, 3). Pearson correlation analysis among drainage area, urban land use, IA, TLA, and SLA% indicates that urban influence decreases downstream in the watershed (Table 2A). This result was expected since core urban development is mainly located

Table 2. (B) Source to sediment relationships.

Sediment property	Source variables				
	A_d	U%	IA%	TLA%	SLA%
D50	−0.28	0.35	0.28	0.30	−0.14
TOC	−0.22	0.21	0.22	0.24	0.47
N	−0.14	−0.06	−0.20	−0.20	0.15
P	−0.14	−0.02	0.00	0.00	0.10
Cu	−0.10	−0.20	−0.27	−0.31	−0.15
Pb	−0.16	0.22	0.41	0.40	0.38
Hg	−0.02	0.02	0.08	0.09	0.46
Zn	−0.31	0.40	0.62	0.62	0.31
Phe	−0.28	0.38	0.42	0.44	0.71
Fth	−0.27	0.37	0.38	0.40	0.66
Chr	−0.27	0.37	0.36	0.39	0.65
BbF	−0.26	0.36	0.29	0.33	0.57
InP	−0.32	0.44	0.32	0.37	0.66
PAH16	−0.28	0.38	0.36	0.39	0.65

in the upper and middle portions of the watershed (Table 1; Figure 1). There is significant autocorrelation between source variables. For example, IA (i.e., roads + parking lots) and TLA% basically represent the same quantity, since road areas are not large in relative comparison to parking lot areas ($r = 0.99$) (Table 2A). SLA% typically exhibits the weakest relationship with the other source variables and is most strongly related to TLA% ($r = 0.63$). These results support the use of TLA% and SLA% to investigate source relationships for PAHs in Galloway Creek watershed.

Correlation analysis of the spatial relationships between source variables and downstream variability of sediment properties and contaminants can be used to evaluate difference in transport among different sediment contaminants (Table 2B). Again, urban influence on sediment contamination decreases downstream since all correlations indicate weak negative relationship and decreasing trend in concentration downstream from urban sources due to sedimentary dilution, mixing, and deposition (Table 2B). Sediment D_{50} also decreases downstream, possibly due to coarser sediment inputs from eroding construction materials and higher flow velocities associated with storm water runoff practices. Individual PAH and PAH_{16} concentrations tend to be strongly related to SLA%, with r-values ranging from 0.57 to 0.71. PAHs exhibit weaker relationships with other source variables, including TLA%, with r-values <0.45 (Table 2B). TOC is significantly correlated with SLA%, possibly indicating the effect of high carbon content (>80%) in coal-tar particles. Mercury is also significantly related to SLA% perhaps because it is often enriched in coal, which is used to manufacture coal-tar. Sediment properties that occur at concentrations in urban sediments that are similar in magnitude to those found in rural sediments tend to exhibit poor correlations over all and are not related to the urban pollution sources being evaluate here (e.g., D_{50}, TOC, N, P, and Cu) (Tables 1, 2, and 3). As expected, PAH concentrations generally appear to be better linked to SLA% compared to TLA%. In addition, it appears that TLA% increases in relative significance for contaminants that are expected to be emitted from a wide range of nonpoint sources in urban areas.

Table 3. Selected sediment contaminant concentrations[a].

Site No.	Nutrients (%)		Metals (ppm)				PAHs (ppb)				
	N	P	Cu	Pb	Hg	Zn	Phe	Fth	Chr	BbF	InP
Urban sediments from galloway creek watershed											
41	0.53	0.05	35	30	0.09	286	180,000	680,000	370,000	430,000	69,000
32	0.36	0.06	48	77	0.2	335	13,000	44,000	22,000	40,000	8500
42	0.43	0.07	65	131	0.08	692	210,000	620,000	340,000	380,000	45,000
36	0.61	0.09	49	116	0.11	424	180,000	830,000	460,000	730,000	77,000
37	0.54	0.06	25	24	0.05	174	69,000	180,000	110,000	140,000	74,000
35	0.27	0.05	36	76	0.05	400	49,000	230,000	130,000	220,000	42,000
44	0.18	0.09	34	381	0.06	1235	17,000	76,000	33,000	61,000	12,000
45	0.18	0.04	33	1875	0.06	270	69,000	240,000	120,000	160,000	32,000
38	0.33	0.05	43	25	0.03	380	1400	5600	3300	5400	1300
34	0.31	0.04	23	81	0.05	280	6000	16,000	7400	9800	2900
39	0.14	0.03	26	101	0.02	212	530	1600	870	1300	400
43	0.04	0.03	15	443	0.01	58	93	290	150	250	48
33	0.34	0.05	27	45	0.05	237	2400	9600	6100	9400	6500
40	0.18	0.03	11	19	0.02	75	5400	15,000	8400	11,000	3500
14	0.19	0.04	54	89	0.04	403	21,000	87,000	23,000	25,000	13,000
15	0.46	0.06	264	51	0.07	141	190	740	480	860	430
16	0.33	0.06	195	60	0.05	108	250	940	500	700	360
17	0.63	0.08	70	50	0.07	103	130	500	280	420	210
18	0.66	0.08	79	49	0.07	104	160	600	340	530	260
21	0.12	0.04	25	43	0.06	93	91	500	230	320	94
22	0.38	0.05	23	41	0.07	131	370	1600	850	1400	420
23	0.22	0.05	23	36	0.05	121	220	990	520	720	240
Rural sediments from spring creek watershed											
51	0.58	0.12	13	14	0.05	42	<DL[b]	<DL	<DL	<DL	<DL
52	0.40	0.07	15	19	0.05	71	<DL	<DL	<DL	<DL	<DL
53	0.12	0.05	12	33	0.02	24	<DL	<DL	<DL	<DL	<DL
54	0.44	0.08	12	13	0.04	30	<DL	<DL	<DL	<DL	<DL
55	0.19	0.04	14	36	0.04	104	<DL	<DL	<DL	<DL	<DL
56	0.54	0.05	10	14	0.05	53	<DL	<DL	<DL	240[c]	<DL
57	0.33	0.05	9	16	0.04	74	<DL	<DL	<DL	<DL	<DL
58	0.25	0.04	11	13	0.04	74	<DL	48[c]	<DL	<DL	<DL

[a]See Table 1 for site and data descriptions and text for contaminant descriptions.
[b]Below detection, no quantitative analysis reported.
[c]Only detected concentrations reported.

Comparison of total and sealed parking lot influence

To further evaluate the relative influence of total or sealed lot area variables on sediment PAH concentrations and other sediment properties, a series of logarithmic regression equations were developed using both TLA and SLA% as independent variables (Table 4). Three sampling sites did not contain any mapped sealed lot areas within their drainage area (Table 1; sites 38, 39, & 43). To allow regression modeling with log-transformed variables, a value for sealed lot area of 0.1% was substituted for each of the three zero values. Thus, regression analyses were completed with a sample size of 22 for all sediment properties and contaminants (Table 4). A "lot source index" was used to evaluate the relative strength of influence or variable significance (i.e., *p*-value) of total versus sealed lot area on the dependent variable. The index is calculated as the ratio of the p-value for the SLA% regression parameter (b_2) to the p-value for the TLA

Table 4.   Regression analysis of lot source-area Influence[a].

Sediment Property[b]	R^2	Y-int b_o	X_1-Log TLA% b_1 coef.[c]	X_1-Log TLA% p-value	X_2-Log SLA% b_2 coef.[c]	X_2-Log SLA% p-value	Lot Source Index[d] p-value b_1/p-value b_2
Cu ppm	0.08	1.83	−0.19[c]	0.29118	0.06	0.45200	ns[e]
TOC %	0.17	0.70	0.03	0.83702	0.11	0.07224	11.6[f]
Pb ppm	0.18	1.15	0.49	0.05790	−0.01	0.96325	0.1
P%	0.18	−1.29	−0.05	0.52013	0.07	0.05993	8.7
N%	0.26	−0.45	−0.16	0.26621	0.15	0.02541	10.5
D50 um	0.30	0.76	0.72	0.01730	−0.19	0.14850	0.1
Zn ppm	0.45	1.52	0.47	0.00358	0.11	0.09853	0.04
Hg ppm	0.49	−1.27	−0.14	0.22364	0.21	0.00045	493
Fth ppb	0.78	0.80	1.70	0.00004	0.79	0.00002	1.8
Chr ppb	0.78	0.53	1.69	0.00003	0.78	0.00002	1.6
InP ppb	0.79	0.64	1.40	0.00007	0.74	0.00001	8.8
BbF ppb	0.79	0.71	1.69	0.00002	0.76	0.00002	1.2
PAH16 ppb	0.79	1.52	1.67	0.00003	0.79	0.00001	2.1
Phe ppb	0.79	0.10	1.78	0.00002	0.78	0.00002	0.9

[a]Fitted regression equation : Log $Y = b_0 + b_1 \log X_1 + b_2 \log X_2$.
[b]Dependent (Y) variables arranged in order of increasing R^2 value.
[c]Underlined values indicate a negative lot effect in the equation.
[d]The lot source Index is the ratio of the p-value of the b_1 parameter to the p-value of the b_2 parmeter in each sediment property equation.
[e]Both lot parameters were not significant at $p < 0.1$.
[f]Bold: index value >1.2, indicates greater influence of coal-tar lot source on sediment.

% parameter (b_1) (Table 4). A high index value above 1.2 indicates greater significance of SLA% in the regression model compared to TLA%. The R^2 value is used to evaluate the strength of the regression model as a prediction tool, while the lot source index value is used to indicate the relative influence of total or sealed lot area on PAH concentration and other sediment properties.

The two-parameter regression model with TLA% and SLA% explains about 79% of the variance for individual and total PAHs and typically indicates the relatively high significance of SLA% in the model compared to the TLA% variable (Table 4). Again, sediment Hg and TOC concentrations exhibit a positive relationship with SLA% (index values >11). In addition, P and N concentrations are also linked to sealed lot area by similar high index values >8 (Table 4). This is not surprising since organic matter contains high concentration of C, N, and P. Interestingly, index values for Pb and Zn are low, suggesting that they are released by a wider variety of nonpoint sources compared to PAHs (Table 4). The regression models presented here only explain 10–50% of the variance in sediment properties and contaminants, so care should be taken in judging the significance these results. However, regression modeling has shown that transport patterns of PAHs have different spatial characteristics compared to other nonpoint contaminants in urban stream and pond sediments. While coal-tar sealants on parking lot pavements represent the major source of PAHs to stream sediments, sediment PAH concentrations are probably also elevated to a lesser degree by loadings from asphalt lot runoff and other nonpoint urban sources that are not specifically related to the SLA% parameter.

Source-sediment regression modeling

Source-sediment regression modeling is used to test for the effects of fluvial sorting and geochemical processes on the variability of metal and nutrient concentrations in

Table 5. Source-sediment regression equations[a].

Contaminant (Y-variable)[b]	No. of parameters	R^2	s.e. (Er. of Y est.)	F_R	b_o (Y-int)	b_1 coef. Log SLA%	b_2 coef. Log TLA%	b_3 coef. Log TOC	b_4 coef. Log D50
1) PAH_{16}	3	0.85	0.49	33	0.676	0.656 *0.000093*[c]	1.63 *0.000010*	1.20 *0.021768*	X
2) PAH_{16}	4	0.85	0.50	24	0.495	0.678 *0.000119*	1.51 *0.000219*	1.28 *0.019831*	0.16 *0.492599*
3) Zn	2	0.55	0.23	12	1.14	X	0.465 *0.001658*	0.586 *0.010703*	X
4) Hg	3	0.72	0.16	15	−1.53	0.131 *0.005473*	X	0.436 *0.010433*	−0.151 *0.023472*
5) Pb	1	0.31	0.39	9	1.120	X	X	X	0.450 *0.006630*
6) Cu	2	0.27	0.29	4	1.46	X	X	0.478 *0.08758*	−0.163 *0.16705*
7) N	2	0.71	0.16	24	−0.827	X	X	0.734 *0.000070*	−0.203 *0.00396*
8) P	2	0.52	0.11	10	−1.54	X	X	0.391 *0.000997*	−0.054 *0.221113*

[a]Fitted equation: Log $Y = b_o + (b_1 \times$ Log SLA%$) + (b_2 \times$ Log TLA%$) + (b_3 \times$ Log OC%$) + (b_4 \times$ Log D50$)$.
[b]Sample size, $n = 22$.
[c]p-value for specified parameter.

stream sediments in addition to source area effects such as drainage area or, in the case of the present study, parking lot area (Pavlowsky et al., 2010). For Galloway Creek, regression analysis was used to evaluate the degree to which the effects of sediment transport and geochemistry may be clouding the source relationships with SLA% and TLA%. An evaluation of the most significant source-sediment models (highest R^2 and lowest s.e.) indicates different source behaviors and sediment interactions for total PAHs, metals, and nutrients (Table 5). The source-sediment regression equation ($n = 22$) developed for PAH_{16} explained 85% of the variance in concentration and included three parameters: SLA%, TLA%, and TOC (Table 5; equation 1). Both parking lot variables are highly significant in the equation. However, the significance of the TLA% parameter ($p = 0.0.000010$) is about nine times more significant than the SLA% parameter ($p = 0.000093$) (Table 5). This result indicates the interaction of the SLA% variable with TOC in the model and is not interpreted as a stronger effect of TLA% on PAH_{16}. There are three points of support for this conclusion. First, the arithmetic correlation coefficient between PAH_{16} and parking lot area is more significant for SLA% ($r = 0.65$) compared to TLA% ($r = 0.39$) (Table 2). Second, SLA% is two times more significant than TLA% in the two-parameter source model for PAH_{16} (Table 4). Third, the SLA%–TOC relationship is relatively strong, and the co-variation effect reduces the significance of SLA% slightly in the three-parameter model (Table 2B and Table 4, equation 1). While TOC was of secondary significance in the model and only added

6% of the explained variance, the addition of D50 as a fourth parameter did not improve the model further (Table 5; equation 2). The regression approach using total parking lot area, sealed lot area, and organic carbon to predict urban sediment PAH concentrations in Galloway Creek was robust for a variety of PAH compounds. Using the same three variables included in the three-parameter model for PAH_{16} (Table 5), individual regression models were developed for five additional PAHs (Table 2). Similar results were obtained for PAHs across a range of molecular weights as indicated by similar R^2 values as: phenanthrene (3 rings), 0.86; fluoranthene (4), 0.85; chrysene (4), 0.86; benzo[b]fluoranthene (5), 0.86; and indeno[1,2,3-cd]pyrene (6), and 0.84.

It is clear that parking lot area and sealant use distribution are important variables in explaining the spatial distribution of total and individual PAH concentrations in urban stream and pond sediments (Table 4). However, while organic carbon is positively related to PAH concentrations in Galloway Creek, its effect is secondary and only marginally significant for spatial transport modeling (Tables 2 and 5). Nevertheless, the effect of TOC on PAH concentrations is more significant than grain size or the D_{50} variable (Table 5). Carbon content in sediment is often positively correlated with PAH concentration regardless of particle size (Ghosh & Hawthorne, 2010; Schorer, 1997; Shi et al., 2007; Yang et al., 2008; Yang et al., 2010). 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 (Bathi et al., 2012; Evans et al., 1990; Schorer, 1997). Overall, the lack of significance of sediment or geochemical variables in explaining PAH concentrations in urban stream sediments probably indicates that much of the PAH burden in the sediment is in association with flakes and dust particles released directly from coal-tar sealant coatings or asphalt pavements (Ahrens & Depree, 2010; Ghosh & Hawthorne, 2010; Yang et al., 2008, 2010). Generally speaking, sediment sorption processes that reflect dissolved phase transport have been overwhelmed by the particulate phase of PAH transport. In addition, the lack of effect of grain size and sorting effects on PAH trends probably reflects the high variability of sediment sources, sizes, and geochemistry in urban streams (Bathi et al., 2012).

If high PAH levels in stream sediments are related specifically to sealed parking lot sources and not just generally to urban nonpoint sources overall, source-sediment regression equations should differ between PAHs and pollutants that are expected to be more broadly associated with urbanization, such as metals and nutrients. Using a logarithmic transformation for all variables, only the source-sediment regression equation for Hg contained the SLA% parameter, and only the Zn equation contained the TLA% parameter (Table 5; equations 4 and 3, respectively). The source-sediment regression equations for Cu, N, and P contained only two parameters for TOC and D_{50}, with no source variable remaining in the final model (Table 5; equations 6–8). Moreover, the equation for Pb only has one parameter for D_{50} (Table 5; equation 5). The lack of strong link of some metals and nutrients to parking lot sources underscores the nonpoint character of urban contamination in general. Further, concentrations of the metals examined tended to be only marginally contaminated with the percent of samples exceeding the PEC value as: (1) 9% exceeding 149 ppm Cu; (2) 0% exceeding 1.06 ppm Hg; (3) 18% exceeding 128 ppm Pb; and (4) 9% exceeding 459 ppm Zn (MacDonald et al., 2000) (Table 3). At these levels, it is expected that background sediment and diffuse pollution effects would compete with parking lot source relationships. Nevertheless, while sediment-associated and dissolved metals and nutrients may runoff into streams from large commercial sealed parking lots, they are also released from

unsealed lots and other widespread urban sources, so the strong relationship with SLA % is diluted by other sources, and the significance of regression coefficients is weakened.

Contribution of coal-tar sealed lots to sediment PAH levels

Source-sediment modeling can be used to evaluate the contribution of a source to downstream sediment quality. For purposes here, the three-parameter "all-sites" PAH_{16} regression model developed for Galloway Creek (Table 5, equation 4) was manipulated to predict the contribution of coal-tar lot sources to downstream sediment PAH_{16} concentrations. Predicted PAH_{16} sediment concentrations for all sites were compared under two scenarios. One scenario is the present effect of sealed lots on PAH concentrations. The other scenario sets the contribution of sealed lots to "zero" and assumes that there are no coal-tar sealed lots in the watershed. Under both scenarios, the TOC concentration for all the sediment samples was set to a constant 7.12%, the median for all the Galloway Branch samples. In comparing the predicted PAH concentrations for all study sites between the "present" and "no sealed lot" scenarios, the effect of a reduction of sealed parking lots on sediment and pond sediment PAH_{16} levels was dramatic. In general, the percent decrease in total PAH concentrations for parking lot sites with >50% TLA% was typically >96%, and for stream/pond sites with <20% TLA%, the decrease ranged from 80 to 90%. It would be expected that PAH response at more distant sites would be lower, since they are further from the urban core area where lower PAH urban and rural background sources are relatively active.

Conclusions

This study has shown that large commercial and residential parking lots are a major source of PAHs to stream and pond sediments in Springfield, Missouri, 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. In contrast, pavement 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). Banning the use of coal-tar sealants has the potential to eventually reduce sediment PAH levels by 80–99% in urban streams and ponds. If coal-tar sealants are not used in the Galloway Creek watershed in the future, it is predicted that sediment PAH concentrations in most perennial aquatic habitats in the City will drop below the PEC and many below the TEC given enough time for existing sealant coatings to weather away and in-transit or stored contaminated sediment to become depleted. The distinct and strong link between sealed lot area and downstream sediment PAH contamination found in this study suggests that PAH profiles in floodplain and lake cores may be useful for sediment source assessments and stratigraphic dating purposes. This is especially true if the land-use history and timing

of coal-tar sealant applications is generally known (e.g., Satori et al., 2010; Van Metre & Mahler, 2010).

Acknowledgments

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