Sediment Contamination of Residential Streams in the Metropolitan Kansas City Area, USA: Part I. Distribution of Polycyclic Aromatic Hydrocarbon and Pesticide-Related Compounds

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Abstract This is the first part of a study that evaluates the influence of nonpoint-source contaminants on the sediment quality of five streams within the metropolitan Kansas City area, central United States. Surficial sediment was collected in 2003 from 29 sites along five streams with watersheds that extend from the core of the metropolitan area to its development fringe. Sediment was analyzed for 16 polycyclic aromatic hydrocarbons (PAHs), 3 common polychlorinated biphenyl mixtures (Aroclors), and 25 pesticide-related compounds of eight chemical classes. Multiple PAHs were detected at more than 50% of the sites, and concentrations of total PAHs ranged from 290 to 82,150 μg/kg (dry weight). The concentration and frequency of detection of PAHs increased with increasing urbanization of the residential watersheds. Four- and five-ring PAH compounds predominated the PAH composition (73–100%), especially fluoranthene and pyrene. The PAH composition profiles along with the diagnostic isomer ratios [e.g., anthracene/(anthracene + phenanthrene), 0.16 ± 0.03; fluoranthene/(fluoranthene + pyrene), 0.55 ± 0.01)] indicate that pyrogenic sources (i.e., coal-tar-related operations or materials and traffic-related particles) may be common PAH contributors to these residential streams. Historical-use organochlorine insecticides and their degradates dominated the occurrences of pesticide-related compounds, with chlordane and dieldrin detected in over or nearly 50% of the samples. The occurrence of these historical organic compounds was associated with past urban applications, which may continue to be nonpoint sources replenishing local streams. Concentrations of low molecular weight (LMW; two or three rings) and high molecular weight (HMW; four to six rings) PAHs covaried along individual streams but showed dissimilar distribution patterns between the streams, while the historical pesticide-related compounds generally increased in concentration downstream. Correlations were noted between LMW and HMW PAHs for most of the streams and between historical-use organochlorine compounds and total organic carbon and clay content of sediments for one of the streams (Brush Creek). Stormwater runoff transport modes are proposed to describe how the two groups of contaminants migrated and distributed in the streambed.

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Sediment contamination from anthropogenic organic compounds has been widely reported for urban water

bodies. Thorough investigations have been conducted for watersheds with a long-established industrial history (e.g., Huntley et al. 1995; Marvin et al. 2000; MacDonald et al. 2002; Bender et al. 2006; Kannan et al. 2008). Nevertheless, residential and commercial land uses comprise the largest extent of land use within a number of metropolitan areas in the United States and may contribute a proportion of contaminant loads to urban streams (Robinson 2002). Streams draining residential and commercial urban watersheds may be contaminated by a number of organic pollutants from various nonpoint sources (Romanok et al. 2006).

While the impact of point sources or industrial discharges on sediment contamination can be identified, characterization of nonpoint source contribution in urban watersheds is more challenging (Zeng and Vista 1997; Dickhut et al. 2000; Stark et al. 2003). A wide range of nonpoint sources (e.g., vehicular emissions, lawn care) can contribute organic contaminant influx into urban streams, as their spatial and temporal release is complicated by their dynamic discharge rates via stormwater runoff, atmospheric deposition, weathering and erosion processes, and spills (Huntley et al. 1995; Zakaria et al. 2002).

We selected five adjacent streams to evaluate the influence of nonpoint sources on the sediment contamination (Tao 2005). These streams are located in the Lower Missouri–Crooked subbasin and the Lower Kansas River basin within the metropolitan Kansas City area, which straddles the states of Kansas and Missouri in the central United States. In contrast to the familiar midwestern agricultural landscape, the Kansas City metropolitan area has experienced rapid population growth and urban sprawl in recent decades, with an increase of 18% in population and 37% in urbanized land from 1982 to 1997 (Fulton et al. 2001). The landscape transformation concurrent with socioeconomic changes has likely influenced the pollutant influx into receiving streams (Giddings et al. 2007; Bryant and Goodbred 2008). The adjoining watersheds (38°52′– 39°04′N, 94°31′–94°54′W; Fig. 1) represent a continuum of urban development from residential watersheds to areas with rural agricultural landscape southwestward. Few point sources except for five Publicly Owned Treatment Works (POTWs) and one Combined Sewer System (CSS) are located along these streams (Fig. 1). The limited number of major industrial sources allowed an examination of the influence of nonpoint source contaminants on sediment quality of urban streams, and similar physiographic conditions between the watersheds provided a base for such comparisons. This paper characterizes distributions of the organic contamination in sediments and discusses the environmental implications of these contaminants in sediment. The companion paper describes the toxicity of these sediments to the amphipod *Hyalella azteca* (Tao et al. 2010).

Fig. 1 Study area and sampling sites
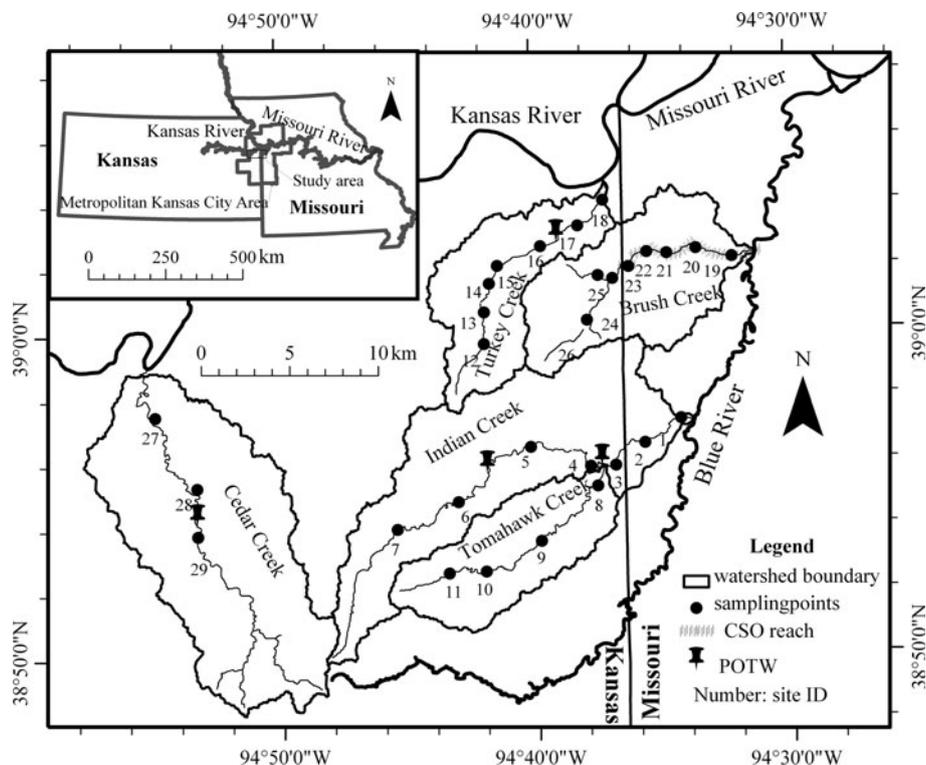
Materials and Methods

Sample Collection

The study streams are located southeast of the confluence of the Kansas and Missouri rivers within the Kansas City metropolitan area (Fig. 1). Turkey and Cedar creeks are north-flowing tributaries to the Lower Kansas River. Brush Creek and Indian Creek with its major tributary, Tomahawk Creek, discharge eastward into the Blue River. Both the Kansas and the Blue rivers enter the Missouri River. These fourth- to fifth-order streams range from 17 to 37 km in length and drain medium-sized watersheds (60 to 193 km^2). Twenty-nine sites along the study streams were selected for sampling to represent sediment quality due to diverse socioeconomic conditions and landscapes within the drainage areas (Fig. 1; Tao 2005). Additional considerations for site selection included (1) the presence of expected contamination sources along the streams (e.g., golf courses, outfalls of POTWs), (2) the accessibility of channel reaches due to private ownership, (3) the absence of sedimentation in the stream bed due to natural fluvial processes or channel management, and (4) localized human disturbances (e.g., construction activities) (Tao 2005).

Sediment sampling was conducted in late June 2003. The month of June was the driest month at the study area in 2003, with one single precipitation event of 0.5–2.2 cm rainfall occurring in early June. The water level at the sampling sites reached the lowest, from <0.6 up to 14.3 m in depth. Water quality parameters were measured in situ using a Horiba U-10 Water Quality Checker.

Each sediment sample, including a field duplicate at site 28, was a composite of fine-grained surficial sediment collected from multiple deposition zones along a 30-m reach at each sampling site. At wadeable reaches, clean stainless-steel spoons and aluminum pans were used to collect sediment to a depth of about 2 to 3 cm. At unwadeable reaches, a precleaned petite Ponar sampler was used to collect sediment to a depth of 5 to 10 cm. Sediments retrieved from multiple zones were homogenized in the field and subsampled in containers for various physicochemical characterizations or for toxicity testing (Tao et al. 2010). Samples for analysis of total organic carbon (TOC) and organic compounds were provided to the U.S. Environmental Protection Agency (EPA) Region 7 laboratories, Kansas City, KS, at the end of each sampling day. Samples were refrigerated, processed within 7 days of collection, and analyzed within 30 days after extraction. Particle size and sediment toxicity were evaluated at the U.S. Geological Survey (USGS) Columbia Environmental Research Center in Columbia, MO (Tao et al. 2010).

Sediment Analysis

Particle size was analyzed following Poppe et al. (2000). Plant debris and shell fragments were manually removed before analysis. TOC was measured using a solid-state module and TOC analyzer (Shimadzu), after the sample was acidified for carbonate removal (Rlab 3152.2A 2003). Sixteen polycyclic aromatic hydrocarbons (PAHs) were analyzed including two- to three-ring low molecular weight (LMW) PAHs [i.e., naphthalene (Naph), acenaphthene (Aen), acenaphthylene (Ayl), fluorene (Fle), phenanthrene (Pn), and anthracene (An)], and four- to six-ring high molecular weight (HMW) PAHs [i.e., fluoranthene (Fla), pyrene (Py), benzo[a]anthracene (BaA), chrysene (Ch), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), and benzo[g,h,i]perylene (Bghi)], along with 2-methylnaphthalene (2-MN). Samples were dried with sodium sulfate and extracted with methylene chloride (Webb 1999). Compounds were identified and quantified using a Hewlett-Packard 5890 Series II capillary gas chromatograph (GC; 60 m × 0.25-mm i.d., 0.25-μm film DB-5 ms silica/alumina columns) equipped with a 5971 mass spectrometer (MS). Concentrations of PAHs are expressed as micrograms per kilogram (dry weight). The reporting limit for individual PAHs was 80 μg/kg.

This study analyzed 28 pesticides and their isomers and degradates representing eight compound classes (Table 1). Sediments were also analyzed for polychlorinated biphenyl (PCB) Aroclor mixtures (Aroclor 1248, Aroclor 1254, and Aroclor 1260). For analyses of 2,4-D, 2,4,5-T, bentazon, dicamba, and pentachlorophenol, samples were acidified and extracted with successive acetone and ether steps. The ether extract was then hydrolyzed with potassium hydroxide and re-extracted prior to methlyation (Roberdes 2003a). For analysis of the remaining pesticide-related compounds and PCBs, samples were dried with anhydrous sodium sulfate and extracted with methylene chloride (Roberdes 2003b). The instrumental analysis of pesticides and PCBs was performed using a Varian GC (30 m × 0.32-mm i.d., 0.25-μm film DB-5, and 30 m × 0.32-mm i.d., 0.25-μm film DB-1701, dual capillary columns) coupled with a ^{63}Ni electron capture detector (ECD). The quantification of technical chlordane is based on three isomer peaks: trans-chlordane, cis-chlordane, and trans-nonachlor. Pesticide concentrations are expressed as micrograms per kilogram (dry weight). Table 1 lists reporting limits.

For quality control, instruments for PAHs and pesticide analysis were calibrated with five concentration levels of external standards. The percentage relative standard deviation (RSD) between the five-point calibration and the daily continuing calibration checks was <15% for target

Table 1 Method reporting limits for pesticides and polychlorinated biphenyl mixtures

Chemical class	Common/trade name	µg/kg (dry wt)	No. of sites with detection (%) (data from 29 sites)
Amides	Alachlor	3	ND
	Bentazon	6.6	ND
Chlorophenoxy acids	2,4,5-T	3.3	ND
	2,4-D	6.6	ND
Dinitroanilines	Benefin	6[a]	ND
	Pendimethalin	2[a]	8 (27.6)
	Trifluralin	0.6	ND
Organochlorines	B-/G-HCH	1/0.4	ND
	cis-/trans-Chlordane	0.6/0.6	18 (62.1)/18 (62.1)
	Chlordane, technical	4	18 (62.1)
	$o,p'/p,p'$-DDT	1[a]/1	1 (3.4)/7 (24.1)
	$o,p'/p,p'$-DDD	1[a]/0.8	6 (20.1)/8(27.6)
	$o,p'/p,p'$-DDE	1[a]/1	ND/9 (31.0)
	Dieldrin	0.6	14 (48.3)
	Endrin	0.8	ND
	Heptachlor	0.6	ND
	Heptachlor epoxide	0.6	1 (3.4)
	Pentachlorophenol	0.7	5 (17.2)
Organophosphates	Chlorpyrifos	2	ND
	Diazinon	6	ND
Triazines	Atrazine	60	ND
	Metribuzin	1	ND
Miscellaneous	Dicamba	3.3	ND
Industrial pollutants	Aroclors 1248, 1254, 1260	20/10/10	ND/ND/3 (10.3)

ND not detected

[a] No method detection limits are established for these compounds. The reporting limits are set at the lowest-level calibration standards

analytes. Multiple sets of method blank (MB), matrix spike (MS), matrix spike duplicate (MSD), laboratory-fortified blank (LFB), and laboratory control standard (LCS) were run with the field samples. Surrogates were also used which included phenol-d$_6$, 2,4,6-tribromophenol, 2-fluorophenol, nitrobenzene-d$_5$, p-terphenyl-d$_{14}$, and 2-fluorobiphenyl for PAHs; 2,4-dichlorophenylacetic acid for organochlorine herbicides; and decachlorobiphenyl for organochlorine pesticides and PCBs. Quality control results, including MBs, relative percentage differences (RPD) between the sample and its field duplicate and between MS and MSD, surrogate recoveries (for MB, MS, MSD, and LCS), LFBs, and LCSs, were within the acceptance limits.

Statistical Analysis

Components of PAHs were grouped into LMW PAHs (two or three rings) or HMW PAHs (four or more rings). The sum concentration of each group and total concentration of the two groups for each site were calculated. Isomer ratios of Pn/An, Fla/Py, An/(An + Pn), Fla/(Fla + Py), IP/(IP + Bghi), BbF/BkF, IP/Bghi, and BaA/Ch, were compared with ratios of known PAH sources (Baumard et al. 1998; Dickhut et al. 2000; Sanders et al. 2002; Mahler et al.

2005). Pesticide concentrations across the streams were compared, and their component ratios were calculated.

Statistical analysis included ANOVA (analysis of variance), hierarchical cluster analysis, and Pearson correlation using PASW (Predictive Analytics Software) Statistics 17.0 (SPSS Inc. 2009). ANOVA was performed to examine the differences among the mean PAH variables for three streams with high PAH detection frequencies (Indian, Turkey, and Brush creeks). PAH data were transformed to the base-10 logarithm and tested for normality and homogeneity of variance prior to the statistical analysis. Hierarchical cluster analysis (Diekhoff 1996) based on the 16 target PAH analytes was used to evaluate the degree of similarities or dissimilarities between individual samples with regard to individual PAH concentrations. Every analyte concentration was logarithmically transformed. The complete linkage clustering method was adopted to compute the distance between the most distant pair of samples, one from each cluster (farthest neighbors, Diekhoff 1996). The squared Euclidean distance, which places progressively greater weight on samples farther apart (Diekhoff 1996), was then calculated. Pearson correlation was used to evaluate the linear relationship between paired variables. The corresponding coefficient was calculated to examine

the relationships within and between PAH parameters, pesticide concentrations, and both TOC and fine particles.

Two approaches were used to treat concentrations of PAHs and pesticide-related compounds below detection limits. In the statistical analysis involving ANOVA, hierarchical cluster, and Pearson correlation, half of the reporting limits were used, a common practice in treating values identified as lower than the detection limit values (Gillis et al. 1995; Eitzer et al. 2001). In ratio or composition calculation, nondetections were treated as zero values to be comparable to the results of previous studies (e.g., Sanders et al. 2002; Yunker et al. 2002).

Results and Discussion

Minor variations were observed in overlying water quality at the sediment sampling sites. Mean values (standard deviations) were pH 8.3 (0.3); conductivity, 939 (80) µS/cm; turbidity, 15 (7) NTU; and dissolved oxygen, 7.6 (2.8) mg/L. The clay content of the sediments ranged from 16% to 53%, with an average of 38%; and the TOC content was between 0.2% and 5.1%, with an average of 1.2%.

PAHs: Occurrence, Concentration, and Composition

Twenty-one samples contained one or more of the target PAHs above the detection limits (Fig. 2). Sediments with no PAH detected were mostly collected from sites on Cedar and Tomahawk creeks and along the upstream portion of Indian Creek (Fig. 2). The total concentration of detected PAHs varied considerably, from 290 µg/kg at site 28 on Cedar Creek to 82,150 µg/kg at site 26 on Brush Creek, with a median value of 14,990 µg/kg.

The magnitude of PAH contamination in the present study was comparable to that of other urban water bodies in North America, with the majority of the concentrations of total PAHs biased slightly toward the high range of the compiled data (Fig. 3). About 85% of the concentrations of total PAHs in the present study exceeded 5,000 µg/kg, and more than 50% of the concentrations of total PAHs exceeded 10,000 µg/kg. Other urban aquatic systems (e.g., Hamilton Harbor, Ontario, Canada, and Dorchester Bay, MA, USA) either receive outflows from or flow through urban drainage basins. Some drainage basins, such as that of Newark Bay Estuary, host heavy industrial activities including shipping, chemical manufacturing, and metal refineries. Sediment PAH contamination in these urban systems was severe (Huntley et al. 1995; Marvin et al. 2000; Sanders et al. 2002). Note that the concentration of the 16 PAHs measured in the present study was considered for the comparison (Fig. 3), except for the cited concentrations in Hamilton Harbor, which included dibenzo[a,h]anthracene (Marvin et al. 2000), and cited concentrations in the Savannah River, which included another nine parent and alkyl-PAHs (Sanders et al. 2002).

Fig. 2 Occurrences and concentrations of low and high molecular weight PAHs
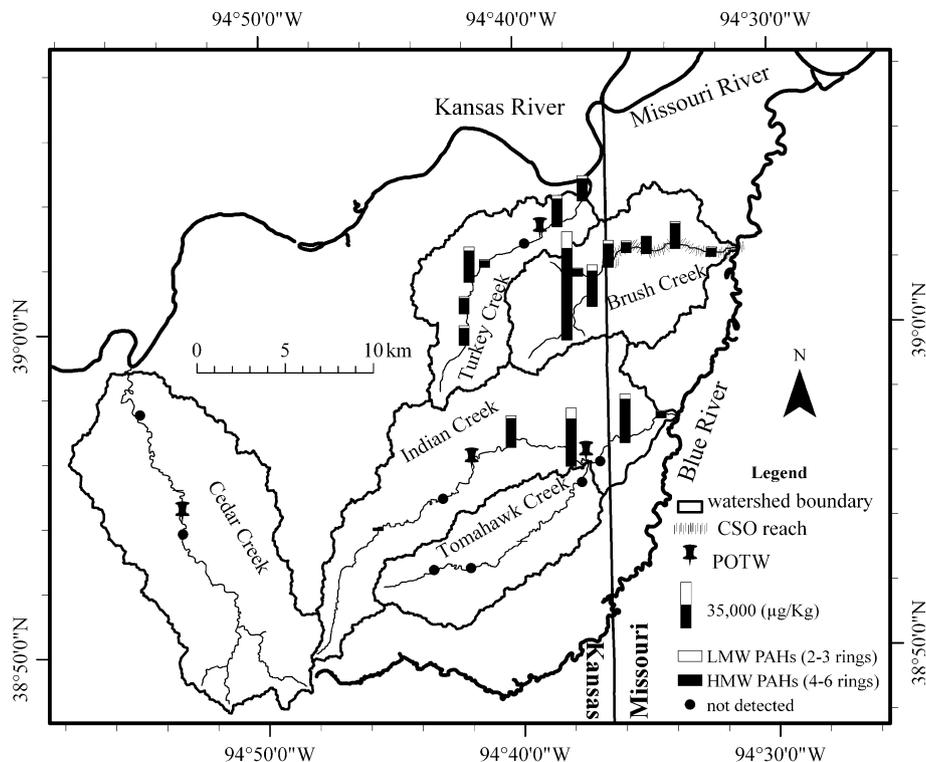
Fig. 3 A comparison of concentrations of total PAHs in sediments from the metropolitan Kansas City area to those in other locations in North America
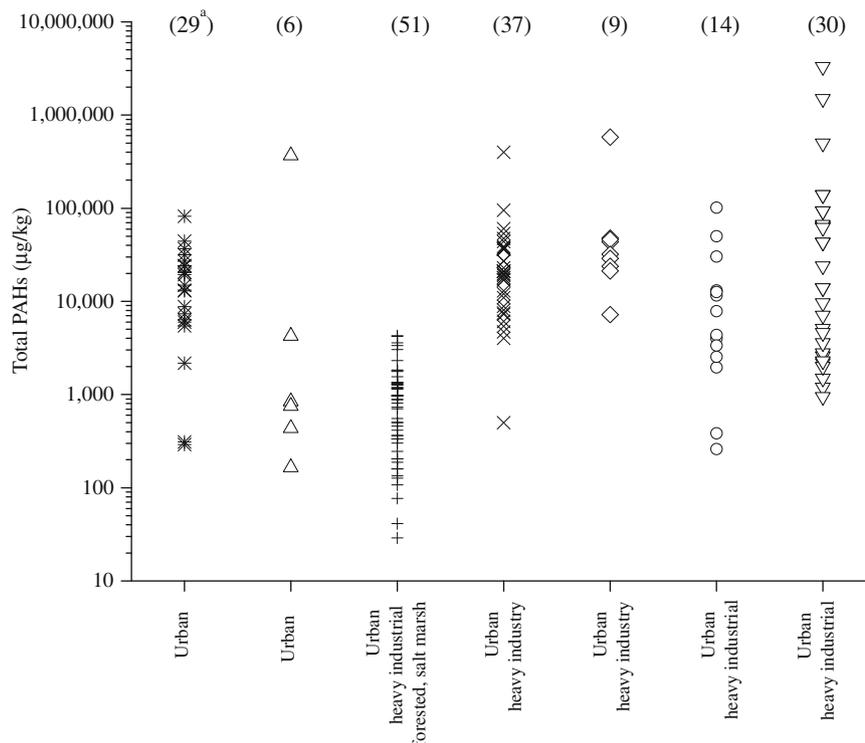
[a] Values in parentheses indicate the number of samples.

∗ This study   △ St. Lawrence River, Ontario/NY (Based on Fig. 8 by Stark et al. 2003)
+ Savannah River, SC/GA (Sanders et al. 2002)   × Newark Bay Estuary, NJ (Huntley et al. 1995)
◇ Hamilton Harbor, Ontario (Marvin et al. 2000)   ○ Dorchester Bay, MA (Lefkovitz et al. 2000)
▽ The Grand Calumet River and Indiana Harbor Canal, IN (Ingersoll et al. 2002)

The individual difference in PAHs included for comparison should not affect the overall evaluation result, since dibenzo[*a,h*]anthracene either was not detected or was present only at low μg/kg levels, while the other PAHs were detected at the milligram per kilogram level for Hamilton Harbor (Chris Marvin, personal communication, September 28, 2004), and the values of Savannah River were similar to those of the other groups used for comparison.

Compositions of PAHs were generally uniform at sites with measured concentrations of PAHs across the five streams. Most sites fell into one distinct and dominant group on ternary plots based on the number of PAH benzene rings (i.e., two and three rings, four and five rings, six rings). Sites that failed to cluster (e.g., site 9 and site 28) are those that had the fewest detections biasing their locations in the plots. Four- and five-ring members dominated individual PAH profiles, ranging from 73% to 100% of the concentration of total PAHs at each site except for site 28, with only benzo[*ghi*]perylene detected in the sample. Four-ring component—fluoranthene and pyrene—were most abundant, contributing to more than 40% of HMW PAH concentrations for most samples. Concentrations of LMW PAHs accounted for <20% of the total PAH concentrations. Concentrations of phenanthrene dominated

the concentrations of LMW PAHs by 66% to 100%. Hierarchical cluster analysis of individual PAH concentrations indicates that sites across these streams tended to display more similarity than sites within a stream. Two major clusters were identified: one dominated by sites on Indian, Tomahawk, and Cedar creeks, with relatively low PAH concentrations; the other comprising sites on Indian, Turkey, and Brush creeks, with higher PAH concentrations (Fig. 2). Within each cluster, the sites did not separate into subclusters corresponding to the streams. For example, site 4 on Indian Creek and site 26 on Brush Creek form a subcluster separate from the subcluster consisting of sites 2 and 5 on Indian Creek, sites 24 and 23 on Brush Creek, and sites 18, 14, and 17 on Turkey Creek. Site PAH composition and concentration did not group by streams, indicating that there were similar types of PAH sources across the streams.

Pesticides: Occurrence, Concentration, and Profile

Pesticide-related compounds were detected at 21 of the 29 sampling sites (Fig. 4). Historical-use organochlorine insecticides and their degradates were far more frequently detected than any other pesticide-related compounds. For instance, at site 17 on Turkey Creek, five occurrences were

Fig. 4 Occurrences of pesticide-related compounds and polychlorinated biphenyls
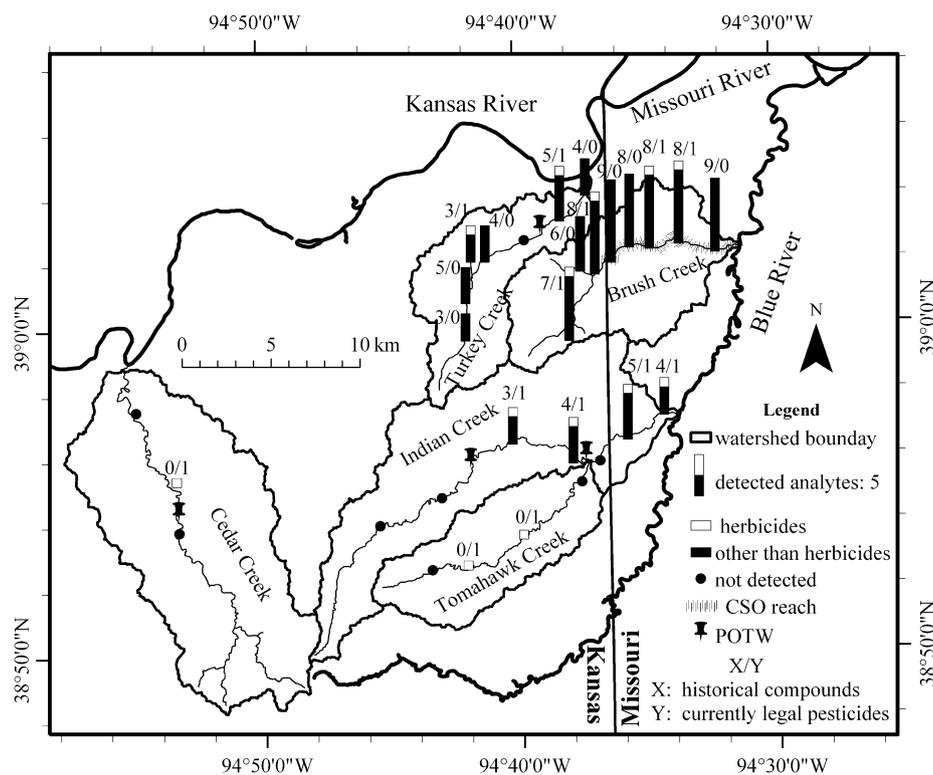
associated with historical insecticides, and the sixth detected pesticide was pentachlorophenol, which could have originated from both historical and current sources. Twelve pesticide-related compounds along with one PCB mixture (Aroclor 1260) were detected among the 28 targeted analytes (Table 1). All detected compounds belong to the organochlorine class of historical sources, except for pendimethalin of the dinitroaniline group and pentachlorophenol of the organochlorine class (Table 1). Pendimethalin and pentachlorophenol were detected in four of the five study streams, while all the other historical organochlorine compounds were detected at up to three streams: Brush Creek, Turkey Creek, and Indian Creek. Detection of DDT isomers and their degradation products was nearly confined to Brush Creek sites, and all the historical compounds detected in this study, except for heptachlor epoxide, were also detected in Brush Creek. In all, chlordane components (cis-, trans-, and technical chlordanes) had the highest detection frequencies, each occurring at over 60% of the sampling sites, followed by dieldrin, at nearly 50% of the sites.

Chlordane and its components were detected in samples collected from Turkey Creek, Brush Creek, and lower Indian Creek (Fig. 5). The relative proportion of chlordane components varied slightly from site to site, albeit the remarkable variation in chlordane concentrations. The ratios of cis- and trans-chlordane to technical chlordane ranged from 0.10 to 0.24; the trans-/cis-chlordane ratios ranged from 1.1 to 2.3 for all sites, except for site 15 on Turkey Creek which had a

ratio of 0.84. In contrast to the relatively extensive distribution of chlordanes, detection of DDT compounds was limited to Brush Creek and one site on lower Indian Creek. But similarly to the chlordanes, total DDTs, though the concentration varied considerably among different sites, displayed a common composition profile: DDE dominated the DDT compounds, comprising 54% to 100% of the concentration of total DDTs, followed by DDD, which comprised less than 37% of the concentration of total DDTs (Fig. 5). Concentrations of sum parent DDTs were less than 20% of the total DDTs. The ratio of sum DDEs to sum DDTs ranged from 3.1 to 8.6. Of the DDT isomers, the o,p'-isomers were distinctly lower in concentration than their corresponding p,p'-isomers. Concentrations of both o,p'-DDE and o,p'-DDT were below the detection limit at all sites except site 23 (o,p'-DDT, 4.4 µg/kg). The concentration of o,p'-DDD detected at Brush Creek sites was mostly less than 50% that of p,p'-DDD. Remarkably, p,p'-DDE prevailed in DDT compounds, contributing >50% of total DDTs at the sites with detected DDT compounds.

PAHs and Pesticides: Spatial Distribution and Correlation with Clay or TOC in Sediment

The five streams can be divided into two groups based on the occurrence and concentration of PAHs and pesticides: the group of sites on Tomahawk, Cedar, and upper Indian Creeks, with low detection frequencies and low concentrations; and the group of sites on Turkey and Brush creeks

flow direction for each creek ⟶
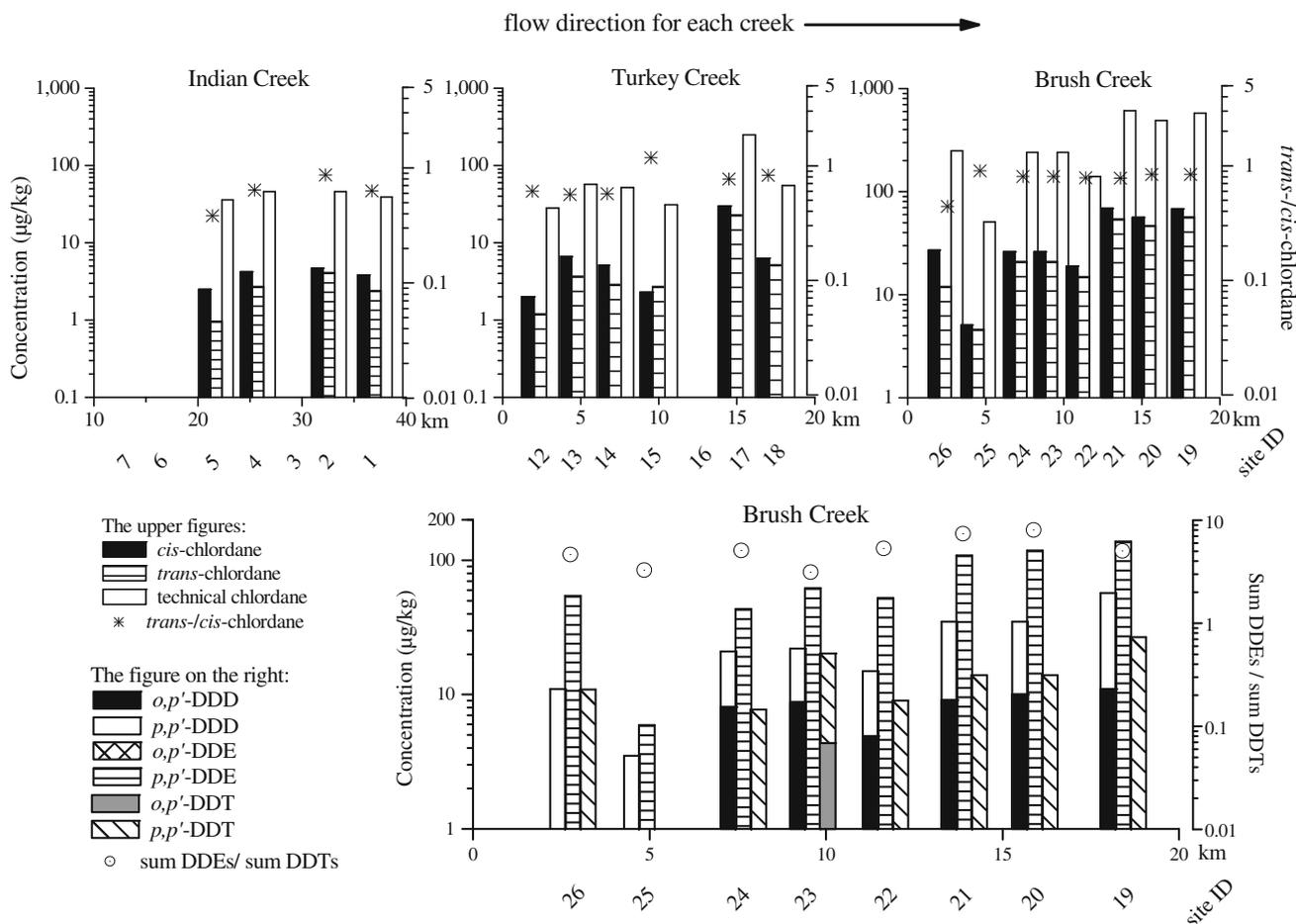
Fig. 5 Compositional profiles of chlordane and DDTs

and lower Indian Creek, distinguished by relatively high detection frequencies and high concentrations (Fig. 2). For instance, in the first group, only benzo[*g,h,i*]perylene (290 µg/kg) and pentachlorophenol (2.9 µg/kg) were detected at site 28 on Cedar Creek. The majority of sites in the second stream group had 4 to 13 PAHs and 2 to 9 pesticide-related compounds detected (Figs. 6, 7). An example is site 4 on Indian Creek, with 13 PAHs detected and a concentration of total PAHs of 44,200 µg/kg, and five pesticide compounds detected, individually ranging between 1.7 and 46 µg/kg (Figs. 6, 7).

Within the Indian, Turkey, and Brush creek group, there was no significant difference ($p < 0.01$) in the means of the sum concentration of LMW PAHs or HMW PAHs or the total concentration of PAHs. In contrast, concentrations of historical-use organochlorine pesticide compounds and Aroclor 1260 were several times to an order of magnitude higher at Brush Creek sites compared to the Indian Creek or Turkey Creek site (Fig. 7). For example, concentrations of technical chlordane ranged between 20 and 70 µg/kg at Indian Creek sites and at most of the Turkey Creek sites; concentrations of technical chlordane ranged from 200 to

700 µg/kg at more than half of the Brush Creek sites. Additional differences in distribution patterns are noted between concentrations of PAHs and those of pesticides. The streams do not share a common spatial distribution pattern of LMW PAHs or HMW PAHs (Fig. 6). The variation in concentrations of individual PAHs along Indian or Turkey Creek showed no distinct directional trend. For example, concentrations of PAHs peaked at the mid portion of Indian Creek: site 4 (which is farther downstream of one POTW than site 3 and upstream of the other POTW). Concentrations of PAHs peaked at site 14, upstream of the POTW on Turkey Creek. PAH concentrations tended to decline toward downstream along Brush Creek. For example, concentrations of phenanthrene decreased from 9,000 µg/kg at site 26 upstream to 1,200 µg/kg at site 19 downstream; the receiving stream reach where site 23 through site 19 were located is affected by combined sewer overflows (Fig. 1). These general trends also apply to TOC-normalized PAH spatial variation: the change in concentrations of TOC-normalized PAHs was not consistent along Indian or Turkey Creek but generally declined along Brush Creek.
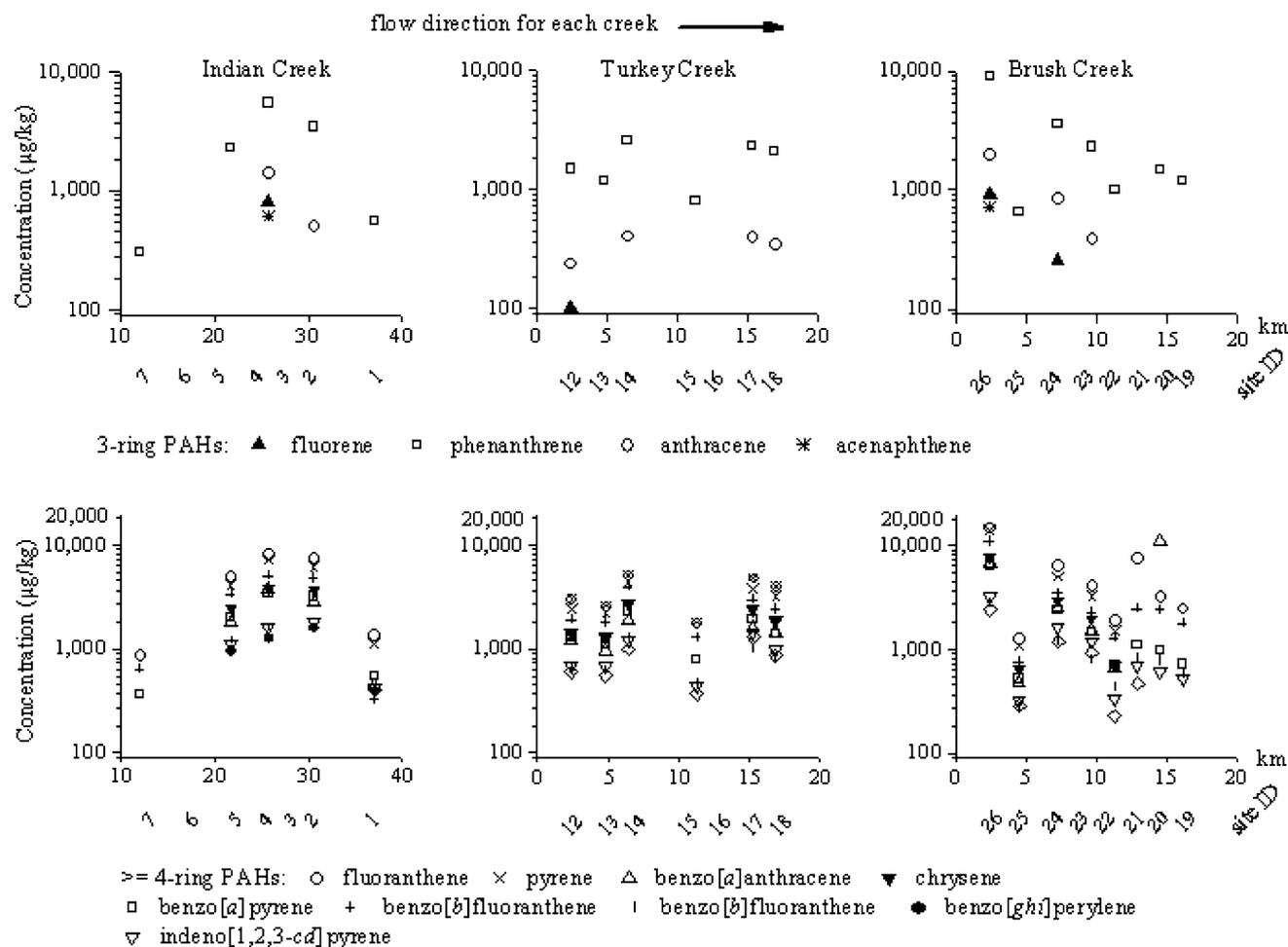
Fig. 6 Distribution of PAH concentrations along the streams

In contrast to the distribution of PAHs, a common pattern that characterizes the distribution of organochlorine pesticide compounds among the three streams was an increase in concentration toward downstream (Fig. 7). For instance, concentrations of dieldrin at the downstream sites of Turkey Creek were 5 to 10 times higher than that at its upstream sites. The spatial distribution pattern was not clear for current pesticides (i.e., pentachlorophenol and pendimethalin) due to their low detection frequencies.

Correlations were observed within concentrations of PAHs and between the concentrations of pesticides and the content of clay or TOC in the sediment samples. When Indian, Turkey, and Brush creeks were included in the analysis, correlations were common between the log-transformed concentrations of various individual PAH members including both LMW and HMW PAHs (r ranged from 0.57 to 0.99; $p < 0.01$). When streams were considered individually, the Brush Creek samples exhibited a positive linear correlation ($p < 0.01$) between the historical-use pesticides and the clay content or TOC (Fig. 8). No such correlations were observed at $p < 0.01$ for either

Turkey or Indian Creek samples, nor were correlations identified between PAH concentrations and clay contents or TOC contents for any individual streams.

PAHs: Inferred Origins

The ternary diagrams of PAH compositions, as well as the cluster analysis based on individual PAH concentrations, indicate a lack of site grouping corresponding to Brush, Indian, and Turkey creeks, where PAHs were commonly detected, suggesting that the sources of PAHs in these stream sediments were similar. It is consistent with the residential nature of these watersheds that nonpoint sources primarily contribute PAHs to local streams.

The predominance of four-ring components—fluoranthene and pyrene (mass 202)—in PAH composition at most sites suggests that pyrolytic processes were the major sources of PAHs, as further confirmed by the PAH isomer ratios (Fig. 9). The Pn/An ratios (3.86–6.67) and Fla/Py ratios (1.07–1.30) were both in the index ranges (Pn/An <10, Fla/Py >1) indicating pyrogenic origins of PAHs
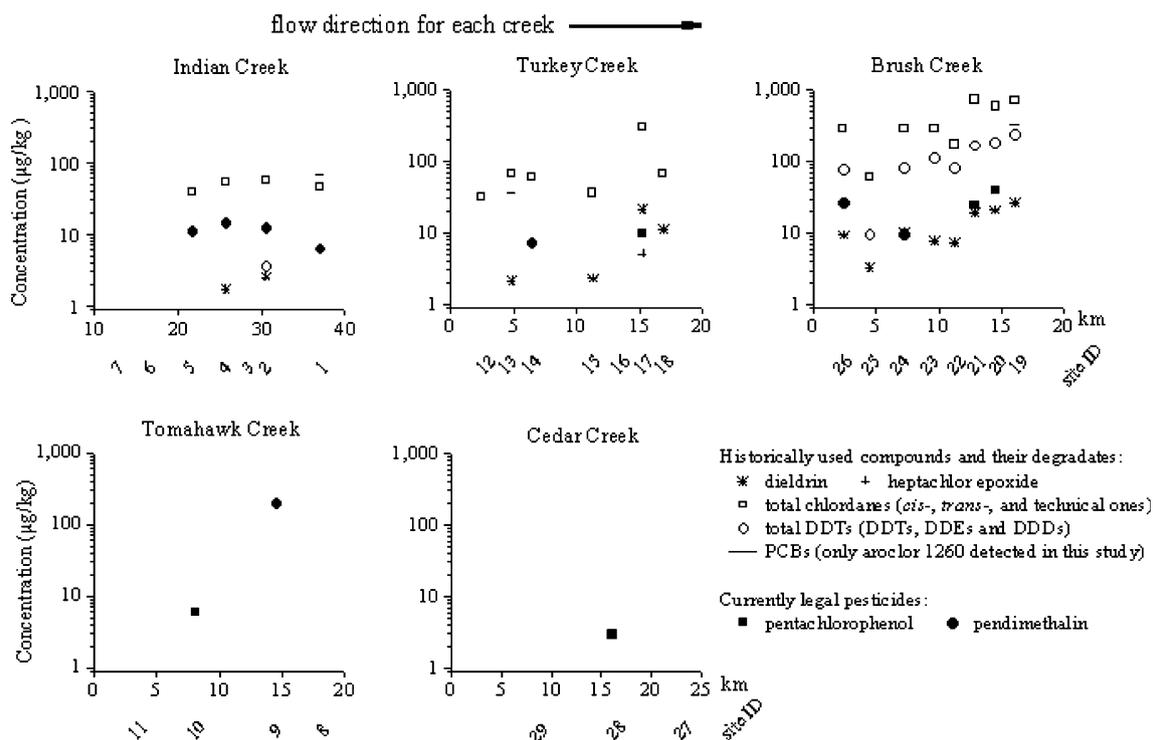
Fig. 7 Distribution of detected pesticide-related compounds and polychlorinated biphenyl mixtures along the streams

(Baumard et al. 1998; Sanders et al. 2002). Further discrimination in pyrolytic origins was reflected by the isomer ratios: An/(An + Pn), 0.16(±0.03); Fla/(Fla + Py), 0.55(±0.01); and IP/(IP + Bghi), 0.55(±0.01). These index values coincided with the respective ratios characteristic of coal tar [standard reference material (SRM) 1597], while the ratios of Fla/Py and IP/Bghi of the sediment were similar to those of coal tar and coal-tar-related material as well (Table 2; Fig. 9). Consistent indication from isomer ratios suggests that coal-tar-related operations or materials may have been a primary source of PAHs in the study streams. One example of this source is coal-tar emulsion-based sealcoat. This sealcoat and asphalt emulsion-based sealcoat are the two primary types used in the United States. The former product has recently captured public attention with its environmental impact due to coal tar's enrichment in PAHs as a by-product of coking and the potential of being carried into streams via surface runoff (Grosenheider et al. 2005; Mahler et al. 2005). According to our survey of the regional major sealcoat suppliers and municipal public works departments, coal-tar-based sealant is popular in the regional sales market. It is commonly used on domestic driveways and various parking lots in the metropolitan Kansas City area. Consequently, this PAH source may be significant in the study watersheds.

Other PAH sources may also have contributed to sediment contamination, though further evidence is needed.

For example, the BbF/BkF ratio (2.90 ± 0.53) was in a range typical of smelters (2.69 ± 0.20), which were not a known source in the study area. Another example was associated with the ratios of IP/Bghi (1.22 ± 0.13), BaA/Ch (0.78 ± 0.10), and BbF/BkF (2.90 ± 0.53), which did not reflect vehicular emissions, a primary source of fossil-fuel combustion-derived PAHs in the United States (Dickhut et al. 2000), as a locally prevalent PAH source (Fig. 9). This does not necessarily exclude traffic as a significant local PAH source. Among the 39 U.S. urbanized areas with a population of more than 1 million, the Kansas City area ranked fifth in per capita vehicle miles and first in freeway equivalent lane miles per 1,000 population in 1999 (Wendell Cox Consultancy 2002). Numerous roadways across the watersheds may have provided transportation-related nonpoint source pollutants into the streams. Dickhut and coworkers' (2000) study of particulate matter in the Chesapeake Bay region noted that the PAHs in aerosol, rain, and surface water may represent predominant automotive sources, while PAHs in surface sediments of the bay area were primarily coal derived. Such inconsistent indications of PAH sources were attributed to PAH photodegradation occurring between PAH release from vehicular-related sources and deposition to the sediments or to dilution by recently deposited coal-derived PAHs (Dickhut et al. 2000). In the present study area, the possible presence of other PAH sources and the degradation of
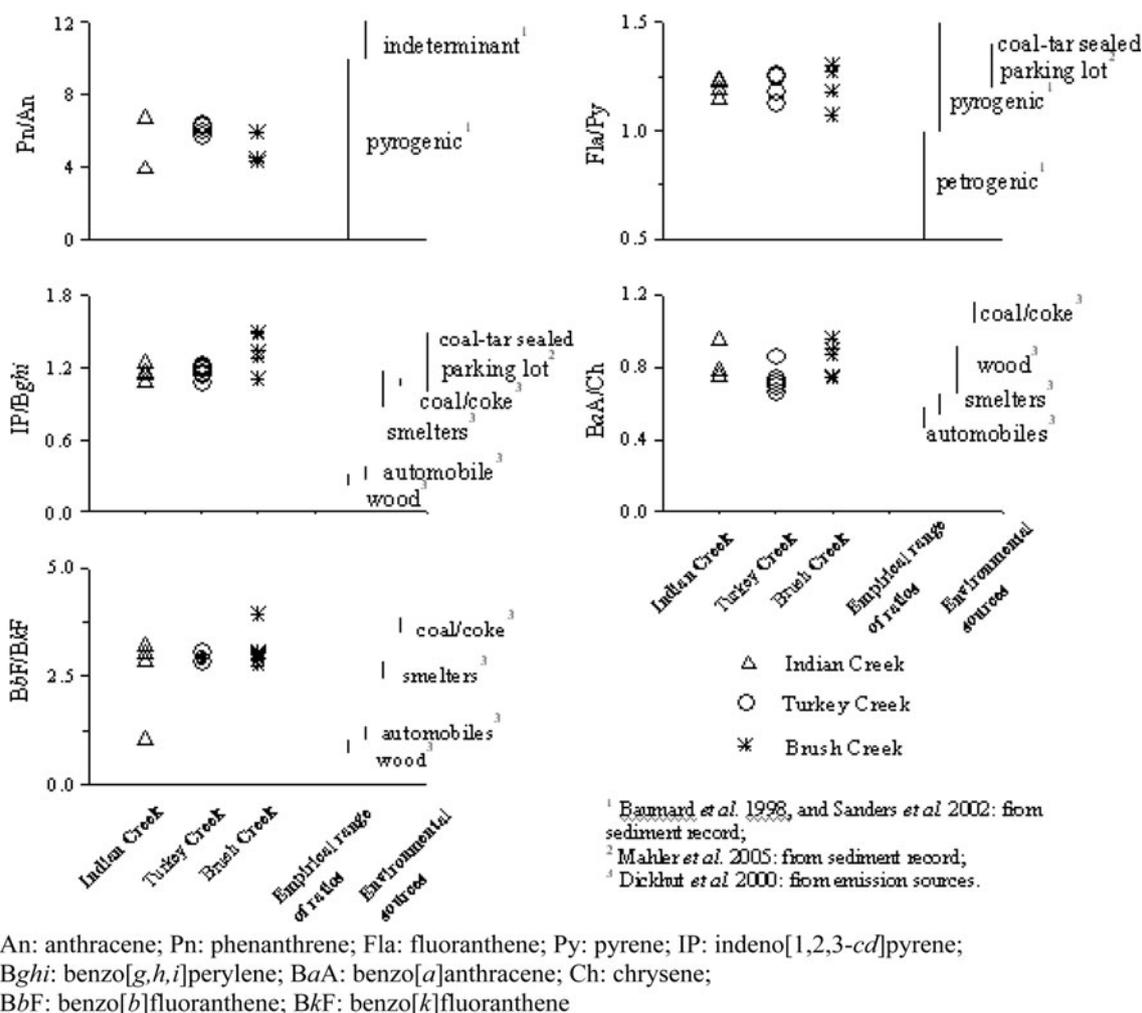
Fig. 8 Correlations among concentrations of PAHs, historical pesticides, and both clay and TOC content
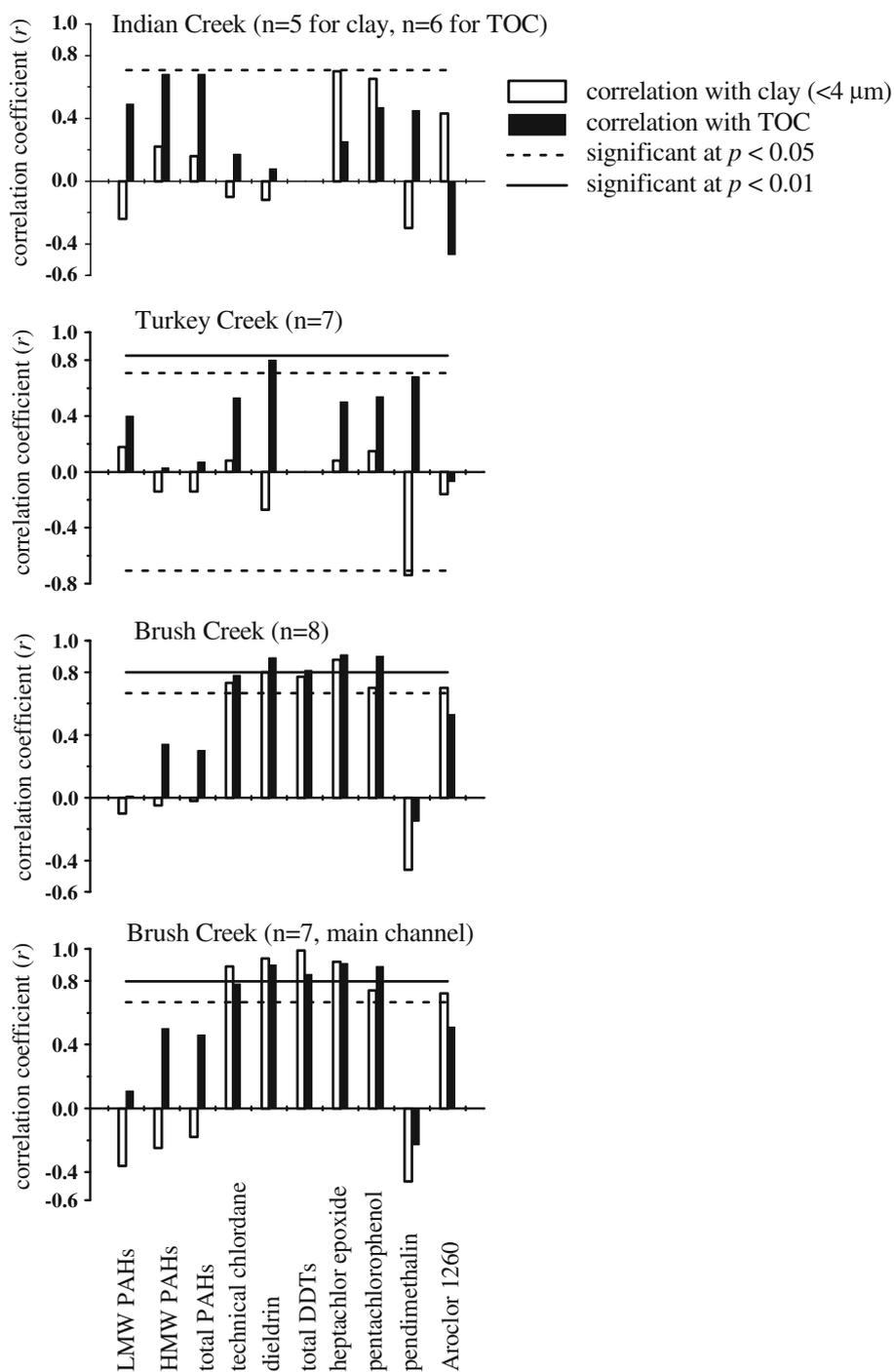
deposited PAHs through its transport pathways may also have altered the PAH assemblages to render unrecognizable the signature of a potential source of PAHs from local intense transportation activities.

Our deduction regarding PAH sources is further supported by the absence of correlation between PAHs and either the clay or the TOC content of the sediments. Since organic matter and fine-grained particles in sediment both have sorption affinity for nonionic organic compounds

(including PAHs) and tend to accumulate in the same locations (Burone et al. 2003; Lawrence et al. 2004), correlations between these organic contaminants and the two sorbents are expected. However, the weathered coal tar residues and traffic-related particles seem to have been the primary matrices that harbor PAHs for the receiving streams. The deposition of PAHs of such origins can deviate from the settling of bulky organic matter and fine particles, because the association of these pyrogenic PAHs

An: anthracene; Pn: phenanthrene; Fla: fluoranthene; Py: pyrene; IP: indeno[1,2,3-*cd*]pyrene;
B*ghi*: benzo[*g,h,i*]perylene; B*a*A: benzo[*a*]anthracene; Ch: chrysene;
B*b*F: benzo[*b*]fluoranthene; B*k*F: benzo[*k*]fluoranthene

Fig. 9 A comparison of the diagnostic isomer ratios for sedimentary PAHs derived in this study with the empirical ratio guidelines established for major emission sources

Table 2 A comparison of representative isomer ratios between sediment and coal tar

Isomer ratio	An/(An + Pn)	Fla/(Fla + Py)	IP/(IP + B*ghi*)	Fla/Py	IP/B*ghi*
This study	0.16 (±0.03)/9[a]	0.55 (±0.01)/14	0.55 (±0.01)/16	1.20 (±0.06)/14	1.23 (±0.03)/16
Coal tar (SRM 1597)	0.18[b]	0.58[b]	0.53[b]	1.31[c]	1.10[c]

An, anthracene; B*ghi*, benzo[*g,h,i*]perylene; Fla, fluoranthene; IP, indeno[1,2,3-*cd*]pyrene; Pn, phenanthrene; Py, pyrene

[a] Mean value (±standard deviation)/number of samples

[b] From Wise et al. (1988)

[c] From Marvin et al. (2000)

with combustion particles may limit the partitioning of PAHs into other organic or inorganic matter (McGroddy et al. 1996; Rockne et al. 2002). This mode of PAH affinity may also explain the observed low toxicity of the sediments, with $\Sigma ESBTU_{FCV,34}$ (Equilibrium Partitioning Sediment Benchmark Toxic Units for Final Chronic Values of 34 PAHs) exceeding 1.0 (Tao et al. 2010).

The above interpretation of PAH sources is at most a qualitative deduction as a result of direct and simplified comparison between the parent PAH data of surficial sediment from local streams and several empirical guidelines for major PAH emission sources. To gain more insight into regional PAH origins, additional studies should examine PAHs in aerosol, stormwater runoff, water columns, and

suspended sediment and should target additional PAHs, especially alkylated PAHs, some of which have been shown to be effective in fingerprinting specific PAH origins (Yunker et al. 2002).

PAHs: Environmental Implications

The difference in the occurrence and concentration of PAHs between the adjacent Tomahawk/Cedar creeks and Brush/Indian/Turkey creeks has three implications (Fig. 2). First, it qualitatively indicates that the current urbanization status of each watershed influences sedimentary PAH contamination of the receiving streams. Concentration and detection frequencies of PAHs increased in correspondence with increasing urbanization of the residential watersheds, which include the established residential Brush and Turkey Creek watersheds and the urbanizing Indian Creek watershed. Second, PAHs in the study streams were not likely introduced via atmospheric processes; instead, stormwater runoff seemed to be the primary transport mode for the PAHs. PAHs can enter surface waters from land sources through atmospheric dispersal or aerosol deposition (Gigliotti et al. 2005). However, the study area, located under the convergence of moist currents from the Gulf of Mexico, dry currents from the semiarid southwest, and cold polar continental currents, is subject to rapid changes of wind directions due to the lack of substantial natural physiographic obstructions (USACE 1979). No single wind direction is prevalent year-round. But within 30 km south or southwest of the urban core of the Kansas City area, Tomahawk and Cedar creeks both show distinct local variations in concentrations and detection frequencies of PAHs. Therefore, atmospheric transport is not likely a significant pathway for diffusing regional PAHs. The above observation can readily be explained if stormwater runoff is the dominant transport medium. Mahler et al. (2005) reported that runoff from sealed parking lots might account for the majority of stream PAH loads in their study urban watersheds. Zakaria et al. (2002), in their investigation of the distribution and sources of PAHs in riverine and coastal sediments in Southeast Asia, concluded that runoff from a heavy rainfall can result in the rapid transfer of land-based pollutants into aquatic environments. Thus, for the urban settings in the present study, it is reasonable to expect that stormwater runoff primarily transports various PAH contaminants from within each watershed into its receiving streams.

Accordingly, the third implication is that PAHs likely deposited in the vicinity of their origins. This is consistent with the observation that the distribution pattern of PAHs along individual streams varied among Brush, Indian, and Turkey creeks and that there were no correlations between PAH concentrations and TOC or clay content. The spatial distribution of PAHs, unlike that of historical-use organochlorine

pesticides, may be more affected by localized discharges than fluvial transport processes or equilibrium partitioning between the aqueous and the sedimentary phases.

Neither discharges from the POTWs nor overflows from the CSS appeared to influence the spatial distribution of PAHs in the bed sediment (Tao 2005). POTWs and CSSs are recognized as sources of contaminants to surface waters (Tetra Tech EC, Inc. 2005; Fugate and Chant 2006). Lee et al. (2005) noted that discharges from POTWs along Indian, Tomahawk, Turkey, and Cedar creeks proved to be an important factor in the occurrence of many organic compounds and pharmaceutical compounds in the base-flow samples, while urban land uses resulted in the largest concentrations of PAHs and other organic compounds in bed sediments. Our data also showed that there was no distinct increase in the concentration or detection frequency of PAHs in sediment at the sites downstream of the POTW on Cedar or Turkey Creek. Along Indian Creek, sites downstream of the POTWs exhibited elevated concentrations of PAHs, but the corresponding stream reach also flows through an increasingly populous drainage area. Similarly, no elevation in PAH concentrations (dry weight or TOC-normalized data) was observed for the reach within Brush Creek that receives combined sewer overflows in comparison with other reaches of the same stream or the other streams. A caveat is that stormwater runoff contamination might have masked the impacts of both POTW and CSS sources in sediments. More in-depth studies are needed to assess the impact of these two potential sources of PAHs on sediment contamination.

Historical Pesticides: Inferred Origins

Pesticides can be transported over considerable distances via various routes and distribute remotely from the area of original application (Bidleman et al. 2002; Hageman et al. 2006). Noticeably, pesticides in the study streams likely originated from local sources, more specifically, from within their respective watersheds. Pesticide distribution was distinctly different across the streams despite the spatial proximity of the watersheds. Multiple historical pesticides—DDTs, chlordanes, and dieldrin—occurred in Turkey Creek, Brush Creek, or the downstream portion of Indian Creeks, but none of these compounds were detected in Cedar or Tomahawk creeks (Fig. 4). The presence of DDT isomers and their degradates distinguished the sites on Brush Creek, and the DDT compositions at these sites were similar. Furthermore, the concentrations of historical pesticides were generally higher at Brush Creek sites than those at Turkey and Indian Creek sites. These lines of evidence suggest a predominant, if not sole, localized watershed-based supply of pesticide-related compounds for the streams.

Monitoring studies frequently report detection of organochlorine pesticides in sediment, aquatic biota, and surface waters in urban areas in the United States (Nowell et al. 1999, 2009). The actual sources of these pesticide residues are uncertain, because organochlorine insecticides had both urban and agricultural uses and many urban areas were formerly in agricultural land use before urban development (Nowell et al. 1999). Nevertheless, the selective confinement of the past-used organochlorine compounds and their degradates to Brush, Turkey, and Indian creeks might be exclusively attributed to their historical urban residential and commercial applications in these watersheds. This suggestion is supported by the correlation between the geographic distributions of several historical-use pesticides in the streams and urban development phases within individual watersheds (Fig. 10). The watershed development history summarized in Fig. 10 is based on documentation from multiple sources, including historical and recent aerial and orthoimages (AIMS), national land use and land cover data (USGS 1990; USEPA 1994), and county-level comprehensive plans for multiple years. Brush Creek watershed was completely developed before the 1960s, when the use of DDT peaked nationwide (Battelle 2000), and well before the legitimate cancellation of registration of DDT in the United States. Turkey Creek watershed lagged Brush Creek watershed in urbanization by one to two decades, and within its watershed the downstream portion had developed by the 1970s, followed by the development in the upper part of the watershed

before the early 1980s. Differential urban development also existed between the lower and the upper Indian Creek watershed and its overall urbanization pace was one to two decades later than Turkey Creek watershed. The urbanization of these watersheds (including their subwatersheds) coincided with the chronological bans on the usage of these chemicals in the United States, e.g., DDTs in 1972 and chlordane for aboveground uses in 1983 and, eventually, for subterranean termite control in 1988 (Battelle 2000). Not surprisingly, DDT was nearly confined to sites on Brush Creek, while chlordane and dieldrin had more extensive distribution; sediments from Brush Creek, of which the watershed was the earliest urbanized, were the most contaminated. The occurrences of organochlorine pesticides in these watersheds were likely associated with residential and commercial usage (e.g., housing structure protection, golf course maintenance, residential lawn and garden care) since no historical industrial sources of these compounds are known to have existed in the study area.

Since the occurrences of chlordane or DDTs covered both upstream and downstream sites along Brush or Turkey Creek, the sources of these pesticides and degradates were likely scattered over each watershed rather than being from point sources or from localized areas. Arguably, these pesticides could have been residues from the sediment deposited over past decades. However, portions of both Turkey and Brush creeks have been recently channelized and continue to be maintained. For instance, a few segments on the downstream reach of Brush Creek, where sites 21 and 22 are

Fig. 10 Occurrence of historical-use pesticides in association with watershed development history
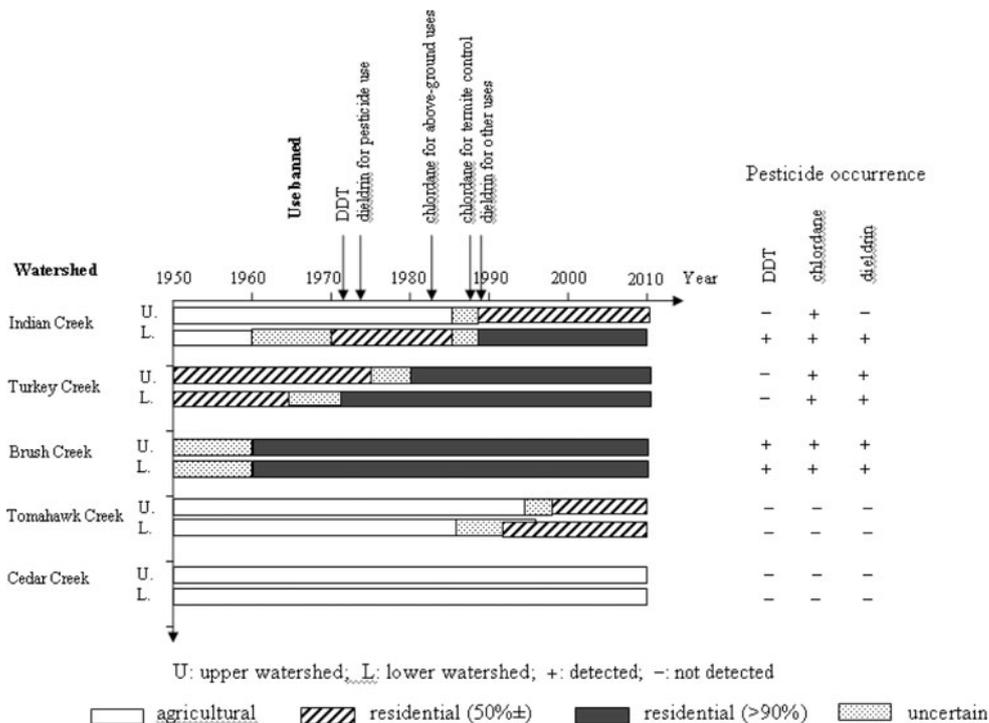
located (Fig. 1), are subject to annual dredging. The average sedimentation rate at the most downstream sampling site (site 19) is up to 15 cm/year by our direct measurement. As a result, the surficial sediment sampled in the creek was fresh sediment recently derived within the watershed, which suggests that there were continuous nonpoint sources of these historically used pesticides replenishing the local streams. The long-term weathering of the past pesticide residues was indicated by the ratios of trans-/cis-chlordane (<1) and sum DDE/sum DDTs (3–9), since technical chlordane used in the United States contained a racemic mixture of trans- and cis-chlordanes, and DDT slowly degrades to DDE through dehydrochlorinase in a microbial consortium from an aerobic pathway in the environment (Eitzer et al. 2001; Zook and Feng 2006).

The absence of the historical pesticide-related compounds in Cedar and Tomahawk creeks, of which the watersheds still remain primarily to partially agricultural, might indicate the rare use of these pesticides for regional agricultural purposes, though it is possible that other factors (e.g., tilling and erosion) may have contributed to dissipating these pesticides (Eitzer et al. 2001). Mau (2002) also reported no detection of organochlorine insecticides in sediments collected from a lake within the Cedar Creek watershed.

Pesticides: Environmental Implications

The pesticide-related compounds evaluated included the class of organochlorine compounds, which tend to be the sole focus of a number of air, soil, sediment, and biota studies (e.g., Gillis et al. 1995; Aigner et al. 1998), and seven other classes (Table 1). Among these other classes, a few analytes (e.g., alachlor and 2,4-D) have been among the most commonly used conventional pesticides for various market sectors in the recent decade (Kiely et al. 2004); some compounds (e.g., atrazine, chlorpyrifos and metribuzin) have been frequently detected in surface waters in the Midwestern United States (Scribner et al. 2000); and organophosphate pesticides have been a primary focus of USEPA reregistration activities since the passage of the U.S. Food Quality Protection Act in 1996 (U.S. Public Law 104–170).

Pesticide occurrence in the local sediments is consistent with the study results of other geographic locations, environmental media, or periods within the past decades. Organochlorine compounds still remain a most persistent pesticide class in terms of occurrence and magnitude (Hageman et al. 2006). Several pesticides, which are commonly associated with regional agricultural practices (e.g., atrazine and alachlor; USDA), were not detected in the sediment samples. Organophosphate pesticides, though less persistent in the environment, were more commonly present at trace concentrations in the study streams. The ecological impact of organophosphate pesticides is not well known (USEPA 2006; Sparling and Fellers 2007). With increased use, these organophosphate compounds warrant further monitoring in environmental media.

Organochlorine pesticides from past applications can disperse into various environmental compartments (including atmosphere, soil, sediment, water, and biota) through various processes, e.g., volatilization, sequestration, precipitation, and absorption (Robertson and Alexander 1998; Bidleman et al. 2002; Evans et al. 2005; Yates 2006). Coupled with these migration processes, concentrations of pesticides in the environment can be reduced through various physical, chemical, and biological transformations (Evans et al. 2005). However, a primary route for historical-use pesticides to enter the study streams may have been through erosion of urban pervious surface (e.g., lawns and gardens at commercial or residential sites, golf courses, and park sports field), runoff washout, and stream flow transport. Direct application of organochlorine pesticides for a multitude of urban purposes in the past may have introduced these contaminants in soil in the watersheds. These compounds had gone through long-term weathering until soil erosion induced by various causes in urban settings (e.g., construction or increased runoff from the expansion of impervious surface) initiated the contaminant transport process. Subsequent storm water runoff and other urban drainages (e.g., lawn irrigation, pavement washing) may have mobilized contaminated substances into streams. These compounds might be further transported in various flow regimes and deposited at the bottom of streams. However, resuspension of the particles, as well as active bioturbation, can still influence the fate of these contaminants after their deposition (McGroddy et al. 1996).

The proposed mode of contaminant transport via stormwater runoff is supported by the linear positive correlations between the concentrations of various historical-use pesticides and the percentages of both clay and TOC for Brush Creek sediment. This type of association is diagnostic of equilibrium partitioning as a predominant sorption process for nonionic organic compounds between aqueous and sedimentary phases (USEPA 2002). The fate of these compounds may be controlled by the transport of the two sorbents in that historical pesticides were enriched at the depositional zones via the accumulation of organic carbon and settling of clay particles. Note that nonionic PAHs of combustion-derived origin do not follow the above deposition pattern, likely due to the sorption phase of PAHs as discussed in Origins of PAHs.

The lack of correlation between historical pesticides and TOC or clay content for sites on Turkey Creek and Indian Creek does not preclude the proposed pesticide-transport mode for Brush Creek watershed being applicable to the other two watersheds. Instead, it may indicate the essential variation in the past application of these pesticides within

each watershed. According to the development history of these watersheds (Fig. 10), the distribution of pesticides from past urban uses might have dominated the middle to lower portions of the two watersheds. Degraded pesticides from past agricultural practices were likely limited to the upper watershed, though subsequent land use transformation to urban residential and commercial uses could have mobilized these compounds and supplied urban pesticides to the environment. No historical record was available describing the difference in the original usage of pesticides associated with urban and agricultural practices at a regional level. But studies of other geographic areas have demonstrated that the concentrations and composition profiles of pesticides in various environmental media are a function of land uses in terms of pesticide selection, application rate, and degradation process (Lewis et al. 1999; Van Metre and Mahler 2005). To extend this notion to the study watersheds, the correlations between pesticides and both TOC and clay in the stream sediments might have been affected by the geographically heterogeneous distribution of contaminants incurred from unsynchronized urban development within the Turkey Creek or Indian Creek watershed and, also, by the urbanization occurring during the decades over which multiple organochlorine pesticides were banned.

Conclusions

Sediment from the study residential streams contained concentrations of PAHs comparable to those subject to industrial impacts and multiple historical-use organochlorine pesticides and their degradates. Both the concentration and the frequency of detection of PAHs increased with the increasing urbanization of the watersheds. The compositional profiles of PAHs were similar among the samples collected from different streams. This indicates that a probably similar combination of nonpoint sources, including coal tar materials and traffic-related particles, contributed PAHs in the streams, although this needs to be evaluated further by examining additional parent PAHs and alkylated PAHs or PAHs in other environmental media (e.g., aerosol and water column). The occurrence of organochlorine pesticide-related compounds was confined to sites with drainage areas affected by past urban activities. These organochlorine compounds likely originated from past residential or commercial applications, instead of industrial or agricultural sources. The disparities in the spatial distribution and in the correlation with TOC and fines between PAHs and pesticides suggest that the two contaminant groups entered and deposited in the streams through different pathways. Deposition of PAHs did not seem to be controlled by fluvial transport processes, equilibrium partitioning, or locations of the POTWs and CSS. Rather, the

distribution of PAHs appeared to be influenced by nonpoint sources adjacent to each sampling site along the stream courses, primarily via stormwater runoff. Historical-use organochlorine pesticides may have entered the streams via a route starting with the erosion of pervious surfaces in the watershed, runoff washout, and stream flow transport. These contaminants, bearing long-term weathering imprints, may have been enriched where organic carbon concentrated and fine grain particles settled. Further study is needed to refine the transport mode of PAHs or pesticides from sources to the streambed and to determine the influence of environmental changes on the fate of these compounds. The study results provide a frame of reference for comparison against assessment on the impact of nonpoint source contaminants in other residential watersheds, as well as for future evaluation of the environmental impact resulting from continuous urbanization of the metropolitan Kansas City area. The conclusions drawn on these residential watersheds can help to formulate a strategy (e.g., on-site treatment of stormwater runoff, restoration of riparian buffer) to prevent or mitigate nonpoint source pollution in urban water bodies.

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