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Occurrence of polycyclic aromatic hydrocarbons below coal-tar-sealed parking lots and effects on stream benthic macroinvertebrate communities

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Abstract. Parking-lot pavement sealants recently have been recognized as a major source of polycyclic aromatic hydrocarbons (PAHs) in urban stream sediments in Austin, Texas. Laboratory and field studies have shown that PAHs in sediments can be toxic to aquatic organisms and can degrade aquatic communities. After identifying increases in concentrations of PAHs in sediments below seal-coated parking lots, we investigated whether the increases had significant effects on stream biota in 5 Austin streams. We sampled sediment chemistry and biological communities above and below the point at which stormwater runoff from the parking lots discharged into the streams, thus providing 5 upstream reference sites and 5 downstream treatment sites. Differences between upstream and downstream concentrations of total PAH ranged from 3.9 to 32 mg/kg. Analysis of the species occurrence data from pool and riffle habitats indicated a significant decrease in community health at the downstream sites, including decreases in richness, intolerant taxa, Diptera taxa, and density. In pool sediments, Chironomidae density was negatively correlated with PAH concentrations, whereas Oligochaeta density responded positively to PAH concentrations. In general, pool taxa responded more strongly than riffle taxa to PAHs, but riffle taxa responded more broadly than pool taxa. Increases in PAH sediment-toxicity units between upstream and downstream sites explained decreases in taxon richness and density in pools between upstream and downstream sites.

Key words: stream, PAH, coal-tar sealant, sediments, bioassessment, urbanization.

Localized high concentrations (hot spots) of polycyclic aromatic hydrocarbons (PAHs) were found through routine sediment sampling in small tributaries and streams in Austin, Texas. Sites where PAH levels exceeded the probable effect concentration (PEC; MacDonald et al. 2000) were identified in 13% of Austin-area streams, and some values of total PAH (TPAH) in sediment were >1000 mg/kg (City of Austin 2005). These results led the city of Austin to conduct several studies to identify the source(s) of the PAHs. Subsequent studies attributed these hot-spot concentrations to particulates eroded from parking-lot sealants (City of Austin 2005, Mahler et al. 2005).

Pavement sealants are surface finishes designed to provide a protective barrier against weather and chemicals for parking lots, driveways, and airport runways. The sealants are primarily of 2 types: emulsions containing up to 35% coal tar and emulsions containing up to 35% asphalt. Coal tar is formed during the coking of coal, primarily for the steel industry, and it is ≥50% PAH by mass. Asphalt is derived from the refinement of petroleum and is generally <1% PAH by mass. In the Austin area, as in the rest of USA east of the Rockies, coal-tar-based products historically have dominated the sealant market. Industry estimates that 225 million liters of coal-tar sealant are applied in Texas annually (Gemseal

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of Texas 2006). In Austin, an estimated 2.5 million liters of sealants are applied annually (City of Austin 2005). Manufacturer recommendations call for reapplication every 3 to 5 y because the sealants wear with traffic volume and time. As these materials wear off the surface of parking lots, abraded particulates are washed into adjacent surface waters via stormwater runoff. A recent study indicates that these sealants might contribute most of the PAH load in the Texas streams evaluated (Mahler et al. 2005).

PAHs have been studied extensively in the aquatic environment, and they cause a broad range of direct and indirect biological effects on aquatic invertebrates. These effects include inhibition of reproduction, delayed emergence, mortality, and sediment avoidance (Eisler 1987, Den Besten et al. 2003, Fleeger et al. 2003, USEPA 2003). PAH concentrations above the PEC are common in Austin-area streams, but little is known about the environmental effects of pavement sealants and the high PAH load they carry, particularly after they leave parking lots as particulates in stormwater runoff. Sediment-quality guidelines (SQGs) like the PEC are reliable predictors of toxicity in large data sets (MacDonald et al. 2000, Ingersoll et al. 2001), but toxicity can vary considerably depending on local conditions and the mixture of PAHs present (Catallo and Gambrell 1987, Paine et al. 1996, USEPA 2003).

Coal-tar sealant as a contaminant in aquatic systems is generally in a particulate form because of its abrasion from parking lots and its hydrophobicity, which causes it to adsorb quickly onto available sediment substrate (Burgess et al. 2003). The potential toxicity and bioavailability of this form of PAH are relatively unknown. However, one recent study showed that particulate coal-tar sealant altered the growth and development of the model amphibian species, *Xenopus laevis* (Bryer et al. 2006). The effects of PAHs on aquatic ecosystems have been evaluated in a number of field studies (Catallo and Gambrell 1987, Bennett and Cubbage 1992, Casper 1994, Maltby et al. 1995, Hinkle-Conn et al. 1998, Van Hattum et al. 1998), but coal-tar sealants as the PAH source and the phenomenon of in-stream PAH hot spots below parking lots have not been evaluated under field conditions.

We carried out a field study to evaluate the potential for parking-lot sealants to cause locally isolated PAH hot spots in Austin-area streams and to determine whether these hot spots have significant effects on stream biota. Coal-tar-sealed parking lots adjacent to streams were identified from field reconnaissance, and PAH concentrations were measured in stream sediment above and below the discharge points of these lots. PAH concentrations were greater in the downstream sample in most cases. In 5 streams where these PAH increases were pronounced, benthic macroinvertebrate communities were sampled as indicators of biological health, and upstream and downstream sites separated by a parking-lot discharge point were compared.

Methods

Site selection and study design

The studied streams were located in and around the city of Austin, Travis County, in central Texas, USA. Austin is in the transitional area between the Central Texas Plateau and Blackland Prairie ecoregions (Omernik 1987). It has a semiarid climate with an average annual precipitation of 810 mm, spread relatively evenly throughout the year. However, the climate is characterized by high-intensity, short-duration precipitation events and a high average rate of pan evaporation (1956 mm/y).

An upstream–downstream study design was chosen (Burton 2001) with matched pairs of upstream (reference) and downstream (treatment) sites within the same stream reach (Fig. 1). This design provides an extra degree of certainty that the variation present in the results is caused by the treatment and not by inter- or intrastream differences. The treatments were concentrations of PAHs in stream sediments immediately above and below parking lots that had been sealed with coal-tar sealant. The distance from the parking-lot discharge point to the downstream sampling site, type of discharge (pipe, grassy swale, rip-rap channel), age of sealant, and traffic use in the parking lots all were potentially important variables in explaining PAH concentration in stream sediments, but the number of sites and replication necessary to evaluate these variables were beyond the scope of this initial field study.

Seal-coated parking lots immediately adjacent to $\geq 2^{nd}$-order streams in urban Austin were identified based on observable wear patterns with high-resolution (pixel = 0.15 m) aerial photography in a geographic information system (GIS). Areas of coal-tar-sealed parking lots that receive consistent vehicle wear appear lighter in color than other parts of the parking lot, and light areas show where the sealant has worn off the pavement. The city of Austin has been screening PAH levels in stream sediments with enzyme-linked immunosorbent assay (ELISA) methods since 1997 and has identified a number of streams with PAH levels of concern. Seven of these streams had adjacent coal-tar-sealed parking lots that drained directly to the stream and appropriate sampling

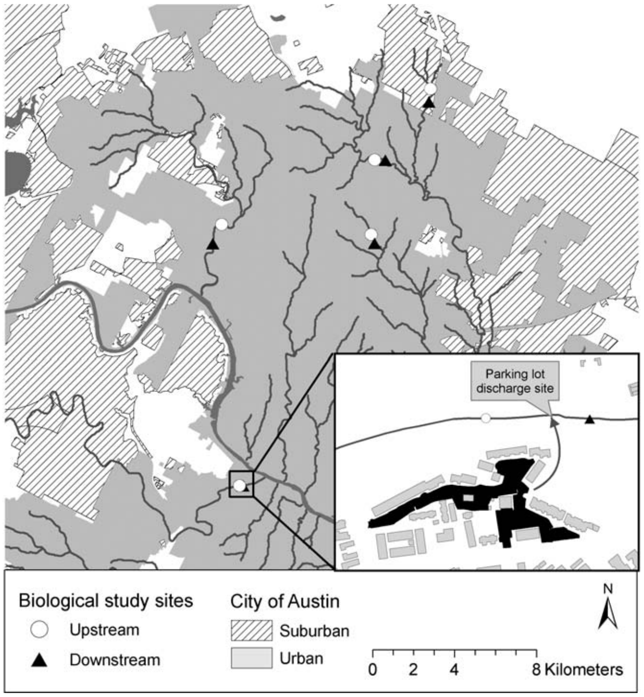

FIG. 1. Locations of study sites in tributary catchments in Austin, Texas, with inset example of upstream/downstream sites bracketing a parking-lot drainage point.

habitat upstream and downstream of that drainage and were selected for our study.

The selected streams had catchments ranging from 5 to 310 km^2 and development levels from 4 to 48% impervious cover. Most of the development in the catchments was urban in nature, and no agricultural land uses were noted at the time of our study. In May 2004, pool sediment chemistry, habitat quality, and riffle and pool benthic macroinvertebrate communities were surveyed in sites upstream and downstream of all 7 parking-lot discharge sites.

Data collection

Habitat was assessed at each site using the US Environmental Protection Agency (EPA) Rapid Bioassessment Protocol (RBP) Habitat Quality Index (HQI; Barbour et al. 1999). This protocol is a visually based method that allows general comparison of habitat quality among stream reaches. Stream physicochemical variables were measured with a multiprobe (Hydrolab Quanta, Hach Company, Loveland, Colorado), and discharge was measured using a handheld Marsh–McBirney Flomate flow meter (Hach/Marsh–McBirney, Frederick, Maryland). Benthic macroinvertebrates were collected in both riffle and pool habitats. Riffle benthic communities were assessed using a modification of the EPA RBP (Barbour et al. 1999), in which a Surber sampler (0.093 m^2, mesh = 500 μm) was used instead of a kick-net at 3 discrete riffle locations. Detritus and associated biota collected in the Surber from the bottom, middle, and top of the riffle were placed in 1-L jars and preserved in the field with 90% ethanol. Sediment-dwelling benthic communities were assessed by collecting 3 discrete ½-L sediment composite grabs from the top 10 cm in representative areas in the study pools using a Teflon scoop. Sediment and associated biota were placed in 1-L jars and preserved in the field with 90% ethanol.

Sediment chemistry was evaluated in each pool by collecting a 1-L grab composite sample from depositional areas around the pool using a Teflon scoop. Samples were stored at 4°C, submitted to the testing laboratory within 5 d of collection, and analyzed by the laboratory within 15 d of collection. Sediments were analyzed for 16 parent PAHs using gas chromatographic/mass spectrophotometric (GC/MS) techniques according to EPA method 8270C (USEPA 1996). In addition to PAHs, several other variables were measured, including pesticides and polychlorinated biphenyls (PCBs) (EPA 8081A and 8082, respectively), total organic C (EPA 5310B, in which organic C was oxidized into CO_2 and H_2O and measured with an infrared analyzer), trace metals (EPA 6020), Hg (EPA 7471A), and total petroleum hydrocarbons (TNRCC 1005). All analyses were done by DHL Analytical in Round Rock, Texas, using standard laboratory methods (APHA 1995, USEPA 1996, TNRCC 2001).

Data analysis

Benthic macroinvertebrates were sorted from associated detritus in the laboratory according to EPA RBP laboratory methods (Barbour et al. 1999), with the exception that all organisms were sorted and no subsampling method was used. Insects were identified to the lowest practical taxonomic level, usually genus, by city of Austin staff using standard taxonomic keys (Berner and Pescador 1988, Pennak 1989, Epler 1996, Merritt and Cummins 1996, Westfall and May 1996, Wiggins 1996, Needham et al. 2000, Thorp and Covich 2001, Stewart and Stark 2002). Chironomidae and noninsect taxa were identified to genus by M. Winnell (Freshwater Benthic Services, Petoskey, Michigan).

Nine community attributes (metrics) were used to evaluate differences between upstream and downstream sites: density, taxon richness, Diptera richness, % dominant taxa, % Chironomidae density, number of noninsect taxa, the Hilsenhoff Biotic Index (HBI), % tolerant taxon density, and number of intolerant taxa. The metrics were selected a priori based on traditional categories of benthic macroinvertebrate community structure (taxonomic richness, composition, and tolerance; Resh and Jackson 1993, Merritt and Cummins 1996, Barbour et al. 1999, Karr and Chu 1999) and experience with these metrics in Austin-area streams. Abundances from the riffle and pool samples were converted to density measurements. Densities in riffles were expressed as ind./m^2; densities in pools were expressed as ind./L.

Within-habitat variability was not evaluated for this paper. Therefore, the 3 benthic-community replicate samples within each habitat in each stream were combined into single composite samples to allow a more robust statistical comparison among streams. The Wilcoxon matched-pairs test (Statistica, version 7, Statsoft, Tulsa, Oklahoma) was used to distinguish significant differences between upstream and downstream data sets for community metrics, taxon responses, and other environmental variables. Our data set was relatively small, so significance was interpreted using $\alpha = 0.1$ (Helsel and Hirsch 1995); p values from the analyses are reported to facilitate interpretation, and values <0.20 were considered to evaluate trends. Means and standard deviations were calculated and are presented for purposes of interpretation, but the Wilcoxon matched-pairs test is a nonparametric test of distribution, not means. The Spearman rank-order correlation coefficient (Statistica) was used to evaluate correlations between metrics.

SQGs were used to assess potential toxicity of PAHs in stream sediments and to compare levels of contamination among study sites. The PEC is the value above which adverse effects on sediment-dwelling organisms are likely to be observed; this value was developed from a consensus-based review of the literature (MacDonald et al. 2000). MacDonald et al. (2000) calculated TPAH as the sum of the concentrations of 13 parent (unsubstituted) PAH compounds, where ½ the value of the detection limit was used as the concentration for any nondetected compounds, and the PEC for TPAH was set at 22.8 mg/kg. In our study, TPAH was calculated as the sum of the concentrations of the 16 EPA priority pollutant PAHs (Table 1; USEPA 2002) plus 2-methyl naphthalene; nondetected values were not included in the sum. This method gives results that are comparable to, but slightly greater than, TPAH calculated by the method of MacDonald et al. (2000).

Equilibrium partitioning sediment benchmark toxicity units (ESTBU; DiToro and McGrath 2000, USEPA 2003) also were used to assess levels of contamination. This approach uses equilibrium partitioning theory to generate toxicity units (ESBTUs) for mixtures of PAHs in sediment and is applicable to a wide range of aquatic organisms. ESBTUs >1 suggest toxicity, whereas values <1 are acceptable for protection of benthic organisms. The EPA ESBTU method recommends summing the concentrations of 34 PAHs for this approach. However, our laboratory analysis was limited to the 16 EPA priority PAH pollutants. Therefore, a recommended adjustment factor was applied to compensate for this discrepancy (USEPA 2003), and the increase in ESTBUs from upstream to downstream was used to predict community changes at the downstream sites using linear regression with ln(x)-transformed data.

GIS was used to evaluate land use and impervious cover at the catchment and local scales for each of the study sites. Local scale refers to a buffer width of 300 m on each side of the stream centerline (600 m total). For the downstream sites, the length of the buffer was the stream distance from the downstream to the upstream site, which ranged from 175 to 1100 m. For the upstream sites, the maximum distance between sites (1100 m) was used as the standard buffer length. City of Austin landuse categories and methods for measuring impervious area were used to compare landuse variables among study sites.

Results

Sediment chemistry

TPAH concentrations were markedly higher at downstream than upstream sites in 5 of the 7 study streams (Table 1, Fig. 2). Downstream TPAH values were above the PEC of 22.8 mg/kg at 2 streams (Barton and Walnut); downstream TPAH values ranged from <1 to 10 mg/kg in the remaining streams (Fig. 2). Differences in PAH concentration and ESBTUs between upstream and downstream sites were minimal in 2 streams (Buttermilk and Manor). The remaining 5 streams were chosen for further evaluation.

Individual PAH compounds showed the same pattern as TPAH, with minimal variation. Concentrations of 6 of the 9 PAH constituents for which PECs have been proposed (including benzo[a]pyrene [B{a}P], possibly the most carcinogenic of the PAH parent compounds) were above the PEC at the downstream sites in Walnut and Barton (Table 1). Fluoranthene was generally the dominant PAH in all samples, followed by chrysene, pyrene, and benzo(b)-fluoranthene, all of which are relatively high-molecular-weight PAHs and are EPA priority pollutants (USEPA 2004). Each of these PAHs has distinct chemical and toxicological characteristics, but increases in TPAH were generally proportional to increases in PAH parent compounds. Therefore, TPAH values are

TABLE 1. Sixteen parent polycyclic aromatic hydrocarbon (PAH) concentrations and organic C in upstream (UpSt) and downstream (DnSt) pool sediments at 7 study streams in Austin, Texas, and the probable effect concentration (PEC) for 9 PAH compounds (MacDonald et al. 2000). Equilibrium partitioning sediment benchmark toxicity units (ESBTU) are toxicity units as calculated by the USEPA (2003) using the equilibrium partitioning approach. All concentrations are given in mg/kg dry mass except organic C (%) and represent composite samples taken from each site. Bold font indicates concentrations above the PEC. nd = not detected, – = PEC not available.

PAH parent compound	Barton		Bull		Little Walnut		Walnut		Wells Branch		Buttermilk		Manor		
	UpSt	DnSt	UpSt	DnSt	UpSt	DnSt	UpSt	DnSt	UpSt	DnSt	UpSt	DnSt	UpSt	DnSt	PEC
Acenapthene	nd	nd	nd	nd	nd	0.04	nd	0.04	nd	0.04	nd	nd	nd	nd	–
Acenapthylene	nd	0.06	nd	0.01	nd	0.02	0.02	0.04	nd	0.01	nd	0.01	nd	nd	–
Anthracene	nd	0.16	nd	0.05	0.03	0.13	0.04	0.16	nd	0.08	0.01	0.02	0.01	nd	0.85
Benzo(a)anthracene	nd	**1.54**	nd	0.43	0.12	0.69	0.26	**1.81**	nd	0.29	0.06	0.15	0.05	0.05	1.1
Benzo(a)pyrene	0.03	**2.46**	0.04	0.50	0.18	0.87	0.32	**2.52**	nd	0.32	0.08	0.20	0.08	0.07	1.5
Benzo(b)fluoranthene	0.06	4.03	0.05	0.64	0.22	1.09	0.39	4.38	0.03	0.35	0.10	0.28	0.11	0.09	–
Benzo(g,h,i)perylene	nd	2.37	nd	0.43	0.14	0.64	0.30	1.89	nd	0.26	0.07	0.19	0.08	0.06	–
Benzo(k)fluoranthene	nd	3.39	nd	0.48	0.16	0.69	0.32	2.74	nd	0.26	0.07	0.19	0.07	0.05	–
Chrysene	nd	**4.23**	nd	0.86	0.24	1.20	0.51	**3.78**	nd	0.42	0.12	0.33	0.11	0.09	1.3
Dibenz(a,h)anthracene	nd	0.69	nd	0.14	0.06	0.21	0.11	0.77	nd	0.09	0.04	0.07	0.05	0.04	–
Fluoranthene	0.02	**5.31**	0.02	1.36	0.35	1.75	0.58	**4.81**	0.01	0.62	0.15	0.35	0.11	0.09	2.2
Fluorene	nd	0.04	nd	0.01	0.01	0.05	nd	0.05	nd	0.04	nd	nd	nd	nd	0.54
Indeno(1,2,3-cd)pyrene	0.04	1.97	0.04	0.36	0.13	0.53	0.26	1.61	nd	0.22	0.07	0.17	0.08	0.07	–
Napthalene	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.01	nd	nd	nd	nd	0.56
Phenanthrene	nd	**1.46**	nd	0.42	0.16	0.85	0.20	**1.40**	nd	0.42	0.06	0.13	0.05	0.04	1.2
Pyrene	nd	**4.23**	0.024	1.09	0.24	1.38	0.59	**3.88**	nd	0.57	0.13	0.36	0.11	0.10	1.5
Total PAH	0.15	**32**	0.17	6.8	2.0	10	3.9	**30**	0.04	4.0	0.961	2.423	0.901	0.747	22.8
Organic C	1.53	4.70	1.99	0.61	0.41	1.16	2.19	1.43	0.72	0.66	0.3	0.43	0.65	0.42	–
ESBTU	0.01	0.843	0.01	1.416	0.626	1.117	0.223	2.583	0.006	0.787	0.40	0.70	0.17	0.22	–

used to represent PAH contamination throughout our study.

Other environmental variables at study sites

Water-quality variables, such as pH, specific conductance, and dissolved O_2 were relatively consistent within streams, and there were only minimal differences between upstream and downstream sites (Table 2). On average, conductivity was 17 μS/cm higher and temperature was 1.7°C lower at downstream sites than at upstream sites ($p = 0.04$, $p = 0.08$, respectively; Table 2). Sediment grain size was not measured in the pool sediment samples. However, from observations documented on field sheets, grain size was relatively uniform between upstream and downstream sites; some streams had predominantly fine sediments and others had predominantly gravel-size sediments. The EPA HQI ranged from 57 to 89% of reference values and was supportive of optimal or suboptimal biological-condition categories at all study sites. HQI values were, on average, 8% lower at downstream sites than at upstream sites (Table 2).

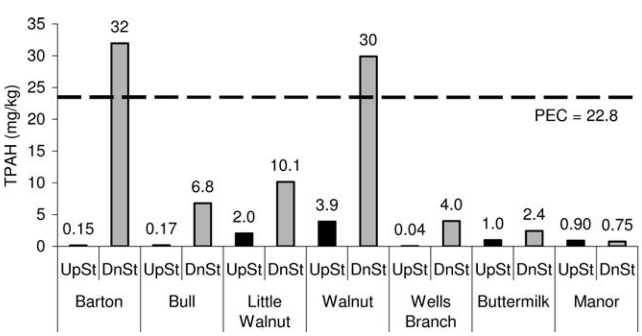

FIG. 2. TPAH concentration above (UpSt) and below (DnSt) coal-tar–sealed parking-lot discharge points at study streams. PEC = probable effect concentration.

Concentrations of trace metals, pesticides, and polychlorinated biphenyls (PCBs) generally were below values of concern (Table 2). Arsenic was elevated at the upstream (17 mg/kg) and downstream (28 mg/kg) sites at Wells Branch (above the threshold effect concentration [TEC] of 9.79 mg/kg, below the PEC of 33 mg/kg). Cu was between the TEC and the PEC at the upstream site at Barton (38 mg/kg). Pb was slightly higher, on average, at downstream sites ($p = 0.04$) but did not approach the TEC of 35.8 mg/kg at any site. Organochlorine pesticide concentrations were uniformly low at all sites (only 4 detected values, all below the TEC, distributed among 3 downstream sites and 1 upstream site).

Parks/open space was the predominant local-scale

TABLE 2. Values of environmental variables at upstream (UpSt) and downstream (DnSt) sites on 5 study streams in Austin, Texas, and mean (SD) values for upstream vs downstream pairs. Difference between upstream and downstream condition was assessed using the Wilcoxon matched-pairs test, and p values <0.10 were considered significant (bold). DDE = dichlorodiphenyldichloroethylene, DDD = dichlorodiphenyldichloroethane, HQI = Habitat Quality Index, nd = not detected, na = statistics not applicable.

	Barton		Bull		Little Walnut		Walnut		Wells		All		
Variable	UpSt	DnSt	UpSt	DnSt	UpSt	DnSt	UpSt	DnSt	UpSt	DnSt	UpSt	DnSt	p value
Physicochemical													
Dissolved O_2 (mg/L)	8.3	9.0	7.6	7.6	9.1	8.1	9.9	10.4	6.8	6.4	8.4 (1.2)	8.3 (1.5)	0.89
Conductivity (µS/cm)	622	644	623	635	719	729	593	635	726	723	657 (61)	673 (48)	**0.08**
Temperature (°C)	25.8	24.5	26.6	24.3	25.9	24.4	27.5	26.6	25.3	22.7	26.2 (0.9)	24.5 (1.4)	**0.04**
pH	7.55	7.34	7.99	7.91	7.32	7.57	7.87	7.69	7.55	7.58	7.66 (0.27)	7.62 (0.21)	0.68
HQI (%)	83	72	89	70	63	57	82	82	80	77	79 (10)	72 (10)	**0.08**
Contaminants													
Pb (mg/kg)	3.7	15.8	1.9	3.4	4.2	15.5	6.7	9.0	8.2	9.5	5.5 (2.6)	10.7 (5.2)	**0.04**
Cu (mg/kg)	38	6.32	4.77	1.9	2.38	4.21	5.66	4.02	8.01	7.48	11.8 (14.8)	4.8 (2.2)	0.22
Zn (mg/kg)	7.3	36.9	11.6	8.8	14.1	26.7	45.5	24.5	23.0	26.3	20.3 (15.2)	24.6 (10.1)	0.5
As (mg/kg)	3.85	1.4	1	1.44	3.34	1.84	7.03	3.65	17	28.4	6.4 (6.3)	7.3 (11.8)	0.68
4_4′-DDE (mg/kg)	nd	nd	nd	0.010	nd	0.008	0.022	nd	nd	nd	na	na	na
4_4′-DDD (mg/kg)	nd	nd	nd	nd	nd	nd	nd	0.012	nd	nd	na	na	na
Local-scale land use													
% single-family residential	22	0	14	22	69	42	4	5	38	0	29 (25)	14 (18)	0.22
% multifamily residential	6	29	6	10	0	29	25	47	9	25	9 (9)	28 (13)	**0.04**
% commercial	0	0	0	0	2	4	0	11	5	13	1 (2)	6 (6)	0.14
% office	19	0	9	10	0	1	5	0	1	5	7 (8)	3 (4)	0.68
% civic	0	0	0	0	8	0	13	1	4	5	5 (6)	1 (2)	0.46
% transportation	7	8	19	19	22	20	6	13	19	20	14 (8)	16 (5)	0.14
% parks/open space	45	63	53	39	0	3	47	23	24	31	34 (22)	32 (22)	0.89
% impervious area	24	23	21	27	32	41	30	45	30	41	28 (5)	36 (10)	**0.08**

TABLE 3. Mean (SD) values of 9 biological metrics and results (p value) of Wilcoxon matched-pairs test comparing upstream to downstream sites in pool and riffle habitats ($n = 5$). HBI = Hilsenhoff Biotic Index, n/a = metric that could not be calculated because of an insufficient number of organisms.

	Pool habitat			Riffle habitat		
Biological metric	Upstream	Downstream	p	Upstream	Downstream	p
Taxon richness	32.8 (13.7)	19.2 (8.2)	0.08	36.0 (11.1)	29.2 (7.2)	0.07
Density	232.7 (176.2)	116.4 (128.4)	0.22	4106 (1593)	2044 (1487)	0.08
% Chironomidae	77.9 (10.2)	66.8 (26.0)	0.22	19.0 (8.8)	21.7 (15.5)	0.68
Diptera richness	18.2 (7.5)	11.4 (5.7)	0.14	13.8 (5.8)	9.6 (3.8)	0.07
No. noninsect taxa	8.4 (3.4)	4.8 (1.3)	0.04	7.6 (1.8)	7.0 (2.8)	0.85
No. intolerant taxa	3.0 (2.1)	1.2 (1.6)	0.11	8.0 (4.4)	6.6 (2.8)	0.27
% tolerant taxa	12.5 (9.6)	12.1 (7.4)	0.89	0.0 (0.0)	0.0 (0.0)	n/a
HBI	6.8 (0.5)	7.0 (0.4)	0.22	5.5 (0.3)	5.6 (0.2)	0.50
% dominance	13.8 (4.8)	15.0 (6.2)	0.35	18.4 (3.3)	15.7 (3.9)	0.08

land use at both upstream and downstream sites (34% and 32%, respectively). Single-family residential landuse was more important at upstream than at downstream sites (29% vs 14%), whereas multifamily residential land use was more important at downstream than upstream sites (28% vs 9%). The percentages of the remaining landuse classes were either relatively similar between upstream and downstream sites or were small. Percent impervious area was slightly higher at the downstream sites than at the upstream sites (36% vs 28%).

Benthic macroinvertebrate community response

Four biological measures (2 with $p < 0.10$) indicated that the benthic macroinvertebrate community in pools was degraded at the downstream sites relative to the upstream sites (Table 3). Three of the measures (taxon richness, Diptera richness, and number of noninsect taxa) were strongly correlated ($r > 0.90$). Density also indicated significant degradation at the downstream sites when Wells Branch was excluded from the analysis ($p = 0.07$). This site had the lowest downstream TPAH concentration (4.00 mg/kg), and all of the biological measures indicated little or no biological change in its downstream biological community relative to its upstream community.

Three biological measures (all with $p < 0.10$) indicated that the benthic macroinvertebrate community in riffles was degraded at the downstream sites relative to the upstream sites (Table 3). Average densities were 2× higher at upstream than at downstream sites in both habitats (pools: ~200 vs ~100 ind./L, riffles: ~4000 vs ~2000 ind./m^2). A small, but significant decrease in % dominance was noted at the downstream sites relative to the upstream sites ($p = 0.08$). However, the decrease in % dominance was not considered degradation because this metric generally responds positively to environmental stress. Some of the biological metrics from the riffle community were correlated but not to the extent observed in the pool community ($r < 0.90$).

Benthic macroinvertebrate organismal response

Across the 5 study streams, 74 taxa were collected from riffles and 78 were collected from pools. Ten taxa in the pool community and 13 taxa in the riffle community showed an apparent treatment effect ($p \leq 0.20$; Table 4). In pools, individual taxon responses were noted primarily among the Chironomidae. Average Chironomidae densities were 270 ± 209 ind./L at upstream sites and 137 ± 171 ind./L at downstream sites. Densities of 3 genera (*Paratendipes, Cladotanytarsus*, and *Ablabesmyia*) were significantly lower at downstream than at upstream sites ($p < 0.10$), and densities of 4 other genera were apparently, but not significantly, lower at downstream sites ($p \leq 0.20$). Densities of *Stenelmis* beetles were significantly lower at downstream sites than at upstream sites, whereas the amphipod *Hyallela* and the snail *Physa* were apparently, but not significantly, lower at downstream sites ($p \leq 0.20$). These organisms were well represented in the 5 study streams and were present in at least 3, but usually 4 or 5 streams.

Individual taxon responses were more diverse in riffles than in pools. Thirteen taxa showed an apparent treatment effect ($p \leq 0.20$; Table 4), and densities of 6 of the 13 taxa were significantly lower in downstream sites than in upstream sites ($p < 0.10$). Across both habitat types, taxa with density decreases at downstream sites represented 6 orders of insects, including some typically sensitive groups (Zygoptera, Trichoptera, Ephemeroptera, Coleoptera), 6 Diptera (5 Chironomidae, 1 Empididae), and 1 snail (*Helisoma anceps*). The only taxon that appeared to have a positive

TABLE 4. Mean (+1 SD) densities of individual taxa that were significantly ($p \leq 0.10$, bold) or apparently ($p \leq 0.20$) responsive to polycyclic aromatic hydrocarbon (PAH) contamination from parking-lot runoff. Responsiveness was defined as a decrease in abundance between sites upstream and downstream of discharge points. No. sites = number of sites at which a taxon was found, No. streams = number of streams in which a taxon was found.

Order	Family	Genus	No. sites	No. streams	Upstream	Downstream	p
Pool habitat							
Diptera	Chironomidae	*Paratendipes*	8	5	47.6 (35.0)	14.0 (23.1)	**0.04**
Diptera	Chironomidae	*Cladotanytarsus*	6	4	6.0 (8.7)	2.8 (4.3)	**0.07**
Coleoptera	Elmidae	*Stenelmis*	5	4	2.3 (1.9)	0.3 (0.5)	**0.07**
Diptera	Chironomidae	*Ablabesmyia*	9	5	21.2 (17.5)	8.4 (6.5)	**0.08**
Diptera	Chironomidae	*Cryptochironomus*	8	5	17.0 (17.6)	8.2 (10.7)	0.11
Diptera	Chironomidae	*Dasyhelea*	3	3	3.7(4.6)	0.0 (0.0)	0.11
Amphipoda	Talitridae	*Hyallela*	5	3	14.0 (12.1)	4.7 (6.4)	0.11
Gastropoda	Physidae	*Physa (Physella)*	4	3	3.0 (1.7)	0.7 (1.2)	0.11
Diptera	Chironomidae	*Procladius*	8	4	22.8 (26.2)	2.8 (1.7)	0.11
Diptera	Chironomidae	*Nanocladius*	4	4	0.3 (0.5)	1.8 (1.7)	0.20
Riffle habitat							
Diptera	Chironomidae	*Tanytarsus*	8	5	3.0 (1.9)	1.2 (1.1)	**0.04**
Zygoptera	Calopterygidae	*Hetaerina*	6	4	6.5 (9.0)	1.3 (1.5)	**0.07**
Diptera	Chironomidae	*Meropelopia*	6	4	16.8 (21.1)	7.8 (10.4)	**0.07**
Trichoptera	Hydropsychidae	*Cheumatopsyche*	9	5	208.2 (192.2)	55.4 (57.8)	**0.08**
Diptera	Chironomidae	*Rheotanytarsus*	10	5	99.2 (34.0)	36.0 (41.8)	**0.08**
Coleoptera	Elmidae	*Stenelmis*	9	5	42.8 (32.3)	4.8 (4.7)	**0.08**
Gastropoda	Planorbidae	*Helisoma anceps*	6	4	6.8 (8.2)	5.0 (7.6)	0.11
Coleoptera	Elmidae	*Hexacylloepus ferrugineus*	3	3	8.7 (7.1)	0.0 (0.0)	0.11
Ephemeroptera	Baetidae	*Fallceon quilleri*	10	5	301.0 (160.3)	109.4 (51.7)	0.14
Coleoptera	Elmidae	*Microcylloepus pusillus*	8	4	30.8 (40.4)	7.5 (3.0)	0.14
Diptera	Chironomidae	*Pentaneura*	8	4	10.3 (1.7)	5.7 (5.3)	0.14
Diptera	Empidae	*Hemerodromia*	5	5	2.0 (2.8)	0.20	0.18
Coleoptera	Elmidae	*Macrelmis*	5	4	5.8 (5.1)	1.00	0.20

response to the treatment effect was Oligochaeta, which had higher density in pool sediments at the downstream sites in 4 of the 5 study streams (Fig. 3). However, this response was not significant ($p = 0.42$). Wells Branch was the only study stream in which Oligochaeta density was higher at the upstream site than at the downstream site (21 and 6 ind./L, respectively). This stream had the lowest downstream PAH concentration.

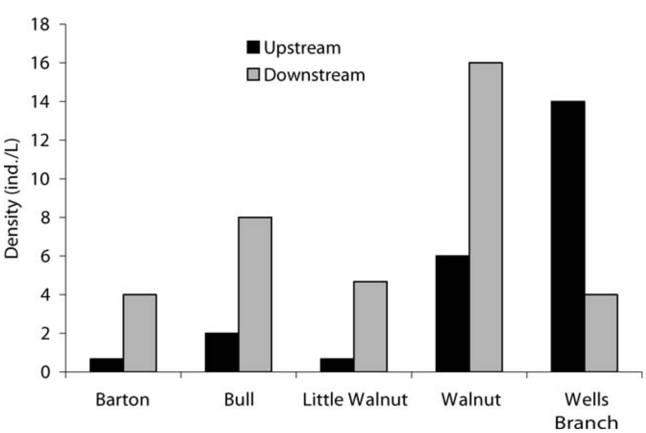

FIG. 3. Density of Oligochaeta in pool sediments at sites upstream and downstream of coal-tar–sealed parking-lot discharge points at study streams.

PAH toxicity units correspond to community changes

ESBTUs were calculated and compared to community changes from upstream to downstream sites to evaluate predicted toxicity of PAHs in pool sediments. Increases in ESBTU explained 76% of the taxon losses in pool communities at the 5 study streams ($R^2 = 0.76$, $p = 0.05$; Fig. 4A). Little Walnut was the only site at which taxon richness increased (1 taxon) from upstream to downstream. Increases in ESBTU also explained 72% of the reduction in density between upstream and downstream pools ($R^2 = 0.72$, $p = 0.07$; Fig. 4B). Wells Branch was the only study site at which density increased (+90 ind./L) from upstream to downstream.

Discussion

Sediment chemistry

PAH hot spots have been documented mostly below point-source discharges, where contaminated sediment from industrial wastes historically has been

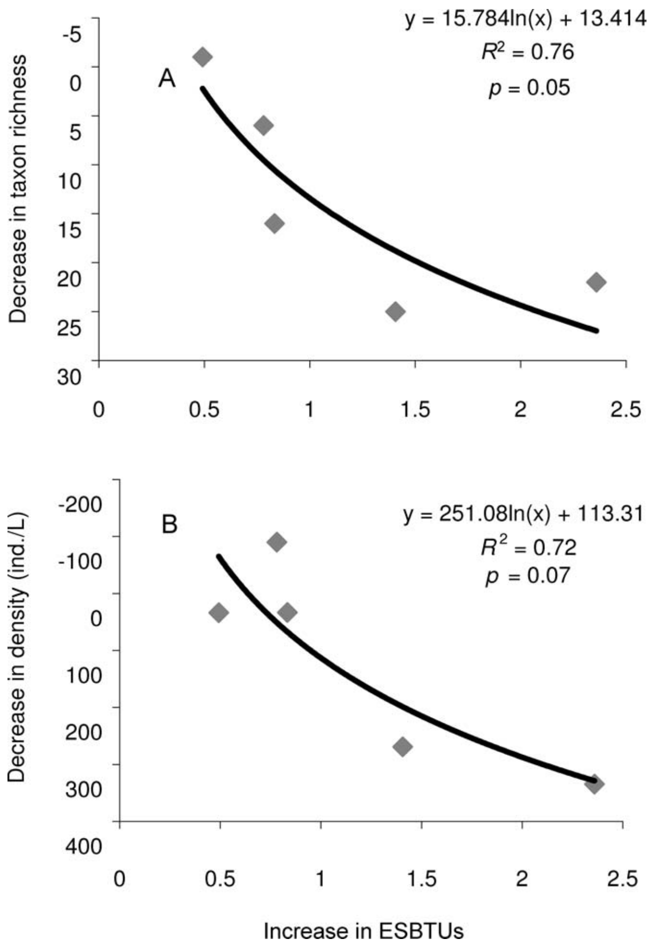

FIG. 4. Regression plot of the decrease in taxon richness (A) and density (B) between upstream and downstream sites within a stream as a function of the increase in polycyclic aromatic hydrocarbon (PAH) equilibrium partitioning sediment benchmark toxicity units (ESBTU) in pool sediments between upstream and downstream sites within a stream.

dumped into large receiving waters (Merrill and Wade 1985, Catallo and Gambrell 1987). However, some of the highest concentrations of PAHs found in the Austin area (1000–3500 mg/kg TPAH) cannot be explained by industrial wastes or by traditional urban runoff sources, such as tire wear, automotive fluid leakage, and atmospheric deposition (Steuer et al. 1997, Dickhut et al. 2000, Mahler et al. 2005, Neff et al. 2005). PAH concentrations in suspended sediment in runoff from coal-tar-sealed lots (mean = 3500 mg/kg TPAH) are 65× higher than concentrations in suspended sediment in runoff from unsealed lots (mean = 54 mg/kg TPAH), and total yields from sealed lots (average of coal-tar- and asphalt-sealed lots) are 50× higher than from unsealed lots (Mahler et al. 2005). PAHs from unsealed lots represent background automotive PAH sources, such as exhaust (atmospheric deposition), fluid leakage (used motor oil), and tire and brake wear (Mahler et al. 2005). In our study, TPAH was 4 to 216× higher at downstream sites than upstream sites and cannot be explained by the diffuse discharge from common urban runoff sources, such as roads and atmospheric deposition, in the small drainage area between the paired sites in each study stream. We propose that the primary source of the higher PAHs at the downstream sites was the sealed parking lots that drain to these streams.

Some investigators have successfully identified sources of PAHs in the environment using ratios of PAH constituents, or fingerprinting methods (Khalili et al. 1995, Dickhut et al. 2000, Yunker et al. 2002), whereas others have found these methods inconclusive or insufficient (Marvin et al. 2000, Bucheli et al. 2004, Zhang et al. 2005). We attempted to identify the sources of PAH in the sediments of our study streams using ratio methods, but we were unsuccessful and found no significant clustering of field data with known source data. A comprehensive analysis of a large suite of parent PAH compounds and alkyl homologues is often necessary for fingerprinting methods because certain forms of PAHs are more resistant to weathering than others (Burgess et al. 2003, Thorsen et al. 2004). Alternative, relatively complex sourcing methods that use multiple lines of evidence have been proposed to separate specific sources of pyrogenic PAHs in the urban environment (Brenner et al. 2002, Larsen and Baker 2003, Zhang et al. 2005). Our inability to associate PAH contamination in our study streams with coal-tar sealant might have been because we analyzed only the 16 EPA priority PAHs in field sediments or because extensive weathering and mixing with other materials occurs as the coal-tar sealant abrades and moves from parking lots to stream systems. Nevertheless, the location of these parking lots relative to the streams, the large increases in PAH concentrations below the lots, and absence of alternative high-PAH source material in the local catchment suggest that parking-lot sealants are the most probable source of the PAHs in the downstream sites.

The observed increases in PAH concentration immediately below coal-tar-sealed parking-lot inflows should be useful for understanding downstream trends in PAH contamination because similar inflows could be present in a wide range of development conditions. Tributary hot spots are likely to be more common and to have much higher concentrations of PAHs than presently recognized PAH problem areas in large receiving waters throughout the USA because of the close proximity of high-concentration parking-lot sources to streams with small catchments that provide minimal dilution by clean sediments from erosion.

Benthic macroinvertebrate response

A significant treatment effect was found for ~½ of the biological metrics, including taxon richness (Table 3), and densities of 9 taxa (Table 4) in both pool and riffle habitats. Taxon richness was probably the most robust of the metrics used in our study. It often is used as a master variable for measuring community health because it has broad ecological implications (Resh and Jackson 1993, Rosenberg et al. 1997). Losses of sensitive or keystone species can have significant effects on ecosystem function and can lead to a wide range of indirect effects, such as trophic cascades, which can result in degradation of more-resistant species at lower trophic levels (Casper 1994, Fleeger et al. 2003).

Density generally is not used as a metric in bioassessments because of the high natural variability and patchiness of benthic macroinvertebrate communities (Allan 1995, Barbour et al. 1999, Karr and Chu 1999). However, density was used as a measure of community viability in our study because of the documented toxic potential of PAHs (Catallo and Gambrell 1987, Beasley and Kneale 2002, Den Besten et al. 2003, USEPA 2003). The lower macroinvertebrate densities in pools and riffles downstream of parking lots could indicate toxic PAH effects, such as mortality or reduced fecundity, at these sites. The significant downstream decrease in density in 2 types of habitat is striking when one considers the wide variation in TPAH concentrations at the study sites. Sediment TPAH was above the PEC at 2 sites (Barton and Walnut) and well below the PEC at 3 sites, but upstream-to-downstream effects were observed at 4 of the 5 sites. The relationship between PAH toxicity units and change in density in the pool habitat also was striking (Fig. 4B) because the increase in toxicity units corresponded with large decreases in density. Streams with <1.0 ESBTU had minimal density changes (losses of <50 ind./L of sediment), whereas the 2 streams with >1.0 ESBTU had large density losses from upstream to downstream (>250 ind./L). Our data set is very small, but our results suggest that the PAH hot spots in at least 2 of the study streams are having toxic effects on the benthic community in these sediments.

One potential response to perturbation is a relative increase in density or richness of more tolerant species as more sensitive species are extirpated. Several oligochaete species, particularly *Lumbriculus variegatus*, have the ability to biotransform and degrade PAHs, therefore they are potentially less toxic to the organism (Leppanen and Kukkonen 2000). In our study, the densities of oligochaetes increased at downstream sites in 4 of 5 streams. We also expected densities of Chironomidae to increase at downstream sites because many taxa in this family have high tolerances for poor environmental conditions (Merritt and Cummins 1996, Barbour et al. 1999). However, overall chironomid density and densities of at least 6 individual taxa decreased at downstream sites. Den Besten et al. (2003) also documented decreases in Chironomidae abundances in the Holland Deip as PAH concentration increased. Chironomidae bioaccumulate PAHs, and their exposure is heavily influenced by sediment quality and their feeding habits (Bott and Standley 2000). *Chironomus tentans* biotransforms fluoranthene, the most dominant PAH in our stream sediments, to a more toxic metabolite rather than a less toxic form (Schuler et al. 2004). The results of our study suggest that Chironomidae may be an important indicator of PAH effects in field sediment studies, and their tolerances should be investigated more closely.

The TPAH concentrations in our study streams were typical of the Austin area, where values range from low (<1 mg/kg) to relatively high (32 mg/kg). TPAH concentrations at sites below parking lots were higher than at sites above them in all study streams, but biological effects were not observed at the site with lowest TPAH concentration (Wells Branch, 4 mg/kg). The downstream Wells Branch site had the same parking-lot runoff effects, including hydrological pulses and any non-PAH chemical constituents associated with this land use, as the other study streams, strengthening the hypothesis that PAH toxicity was the variable most strongly influencing the biological degradation observed. This hypothesis is further supported by the clear relationship between biological degradation and levels of PAH toxicity at the downstream sites (Fig. 4A, B).

Other environmental variables

The study streams differed substantially with respect to environmental variables other than PAH level (e.g., catchment area and % impervious cover). The negative effect of PAH-contaminated parking-lot runoff was obvious despite the inherent variability of the streams. However, our conclusions are supported by correlations between biological degradation and PAHs in sediment rather than by manipulation of PAH levels; thus, potential confounding effects of other within-stream variables must be considered. Physicochemical variables (pH, dissolved O_2, temperature, and conductivity) varied very little among sites, but conductivity was slightly (17 μS/cm) higher and temperature was slightly (1.7°C) lower at the downstream sites than the upstream sites. The differences in both of these variables were small when compared to natural temporal variability or instrument precision. HQI was slightly lower at the downstream sites than the upstream sites, but the difference was very small considering expected precision of this qualitative method (Hannaford and Resh 1995). Moreover, the magnitude of biological degradation between upstream and downstream sites was not correlated with HQI, and all sites were within the suboptimal or optimal categories, suggesting they were capable of supporting an acceptable biological condition.

Measures of sediment quality other than PAHs did not indicate any values of concern or important upstream-to-downstream patterns. Pb concentrations was slightly higher at downstream than upstream sites, but all values were well below TEC. Increases in metal concentrations at downstream sites might have been related to runoff from parking lots (Maltby et al. 1995) but did not correspond to the increases in PAHs or to the biological degradation at the downstream study sites. Percent impervious area in riparian buffers was slightly higher at downstream than at upstream sites, and the fact that the study sites were selected on the basis of the presence of a parking lot adjacent to a stream biased the downstream sites toward higher impervious area. However, neither parking-lot area nor % impervious area explained biological degradation at the downstream sites. Considering the complex mix of urban stressors on the benthic communities in these streams, it is likely there were other variables that contributed to the degradation observed at our downstream sites. Nevertheless, ESBTUs explained the observed biological degradation better than any other measured variable. As is typical of the sediment chemistry of most urban streams in Austin and in the nation (Lopes and Furlong 2000), PAHs were the most common pollutant in the sediments in our study and were found at levels closest to acute toxicity criteria.

The authors of a number of pertinent studies have concluded that sediment-bound PAHs, particularly those from pyrogenic sources, might not be as bioavailable as would be predicted on the basis of concentrations derived with traditional laboratory extraction methods and national guidance associated with those concentrations (Paine et al. 1996, Volkering and Breure 2003, Thorsen et al. 2004, Jonker et al. 2005). However, growth and development of the model amphibian *Xenopus laevis* were negatively affected when larvae were exposed to coal-tar sealant at nominal concentrations similar to those in our study streams (Bryer et al. 2006). The significant negative response to the medium exposure (30 mg/kg TPAH) agrees with national guidance (PEC = 22.8 mg/kg TPAH), but the results from the low exposure (3 mg/kg TPAH) suggest that amphibians may experience chronic effects of exposure to PAH concentrations well below guidance values (Bryer et al. 2006). In our study, the site with the lowest toxicity (Wells Branch, 0.79 ESBTU) showed little to no apparent biological effect of PAHs, and this result supports the EPA's ESBTU as a measure of potential toxicity (Table 1). However, community changes were apparent at 4 of the 5 study streams despite the fact that only 2 of the streams had values above the PEC (Barton and Walnut). This result suggests that PEC guidance might not be sufficient to predict toxicity. Our experimental design precludes statistical verification of individual stream effects. However, our results and those of Bryer et al. (2006) suggest that sediment-bound PAHs, particularly those from coal-tar sources, are causing effects at, and possibly below, guidance values.

We have shown that PAH concentrations in stream sediment downstream of coal-tar-sealed parking lots can be significantly above background concentrations and that those concentrations could be a primary factor in the biological degradation observed in the 5 study streams. Our results, when combined with those of other recent work on coal-tar sealants (Mahler et al. 2005, Bryer et al. 2006), provide a compelling link among PAH contamination in urban receiving water bodies, biological degradation, and parking-lot sealants.

Recommendations

Our study focused on the range of PAH values commonly detected in streams in the Austin area. We evaluated a newly identified source of PAHs, coal-tar-sealed parking lots (Mahler et al. 2005), and coal-tar sealants are used extensively in the USA. Verification studies are needed to evaluate the relationship between PAH hot spots and parking lots in urban streams in other parts of the country and to document the geographical scope and extent of the effects observed in our study. Van Metre and Mahler (2005) documented strong increases nationally in PAHs in urban lake cores over the past 20 y. It is logical to assume that recent suburban growth, with its parking-lot-intensive development, is contributing significantly to these trends. The city of Austin's practice of sampling sediment in small urban drainages and sequential upstream tracing of contaminant sources led to the documentation of remarkably high concentrations of PAHs and eventually resulted in the identification of coal-tar sealant as an important source of PAHs in the environment (City of Austin 2005). We recommend monitoring sediment and biological communities in tributaries to water bodies in which sediment PAH concentrations are increasing to identify PAH hot spots, compare hot spot concentrations with receiving-water concentrations, and evaluate potential biological degradation.

We attempted to explain the magnitude of PAH contamination at the downstream study sites with spatial data. Neither total area of sealed parking lot nor its proximity to sampling locations were significantly correlated with PAH concentrations in the sediments at the downstream sites. A complex mix of age of sealant applied, amount of traffic on lots, local rainfall patterns, flow paths, local stream hydrology, and sediment deposition patterns probably contributes to high variability in the movement of PAHs from parking lots to stream sediments. All of these factors are potential avenues of subsequent research. Our study focused on the biological responses to these PAH hot spots rather than on the specific physical and chemical processes that created them. Understanding the processes that create hot spots will require far more sites and replication of sites under different local conditions. Research on the fate of PAHs from sealant runoff may be particularly useful when designing specific best-management practices (BMPs) that could address this problem through remediation, structural and regulatory pollution controls, and catchment protection programs. The city of Austin has chosen to ban the use of coal-tar-based pavement sealants. This regulatory BMP is designed to stem a 40-y trend of increasing PAHs in its local receiving waters and to address high PAH concentrations identified in tributaries.

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Literature Cited

Allan, J. D. 1995. Stream ecology, structure and function of running waters. Kluwer Academic Publishers, Dordrecht, The Netherlands.

APHA (American Public Health Association). 1995. Standard methods for the examination of water and wastewater. 19th edition. American Public Health Association, American Water Works Association, and Water Environment Federation, Washington, DC.

Barbour, M. T., J. Gerritsen, B. D. Snyder, and J. B. Stribling. 1999. Rapid bioassessment protocols for use in streams and wadeable rivers: periphyton, benthic macroinvertebrates and fish. 2nd edition. EPA/841/B/98-010. Office of Water, US Environmental Protection Agency, Washington, DC.

Beasley, G., and P. Kneale. 2002. Reviewing the impact of metals and PAHs on macroinvertebrates in urban watercourses. Progress in Physical Geography 26:236–270.

Bennett, J., and J. Cubbage. 1992. Effects of PAHs in sediments from Lake Washington on freshwater bioassay organisms and benthic macroinvertebrates. Document 92-e01. Environmental Investigations and Laboratory Services Program, Toxics, Compliance and Groundwater Investigations Sections, Washington State Department of Ecology, Olympia, Washington. (Available from: Environmental Investigations and Laboratory Services Program, Toxics, Compliance and Groundwater Investigations Sections, Washington State Department of Ecology, Olympia, Washington 98504-7710 USA.)

Berner, L., and M. L. Pescador. 1988. The mayflies of Florida. Revised edition. University Presses of Florida, Gainesville, Florida.

Bott, T. L., and L. J. Standley. 2000. Transfer of benzo(a)pyrene and 2,2′,5,5′-tetrachlorobiphenyl from bacteria and algae to sediment-associated freshwater invertebrates. Environmental Science and Technology 34:4936–4942.

Brenner, R. C., V. S. Magar, J. A. Ickes, J. E. Abbott, S. A. Stout, E. A. Crecelius, and L. S. Bingler. 2002. Characterization and fate of PAH-contaminated sediments at the Wyckoff/Eagle Harbor Superfund Site. Environmental Science and Technology 36:2605–2613.

Bryer, P. J., J. N. Elliot, and E. J. Willingham. 2006. The effects of coal tar based pavement sealer on amphibian development and metamorphosis. Ecotoxicology 15: 241–247.

Bucheli, T. D., F. Blum, A. Desaules, and Ö. Gustafsson. Polycyclic aromatic hydrocarbons, black carbon, and molecular markers in soils of Switzerland. Chemosphere 56:1061–1076.

Burgess, R. M., M. J. Ahrens, and C. W. Hickey. 2003. Geochemistry of PAHs in aquatic environments: source, persistence and distribution. Pages 35–45 *in* P. E. T. Douben (editor). PAHs: an ecotoxicological perspective. John Wiley and Sons, West Sussex, UK.

Burton, G. A. 2001. Stormwater effects handbook: a toolbox for watershed managers, scientists, and engineers. Lewis Publishers, CRC Press, New York.

Casper, A. F. 1994. Population and community effects of sediment contamination from residential urban runoff on benthic macroinvertebrate biomass and abundance. Bulletin of Environmental Contamination and Toxicology 53:796–799.

Catallo, J. W., and R. P. Gambrell. 1987. The effects of high levels of polycyclic aromatic hydrocarbons on sediment physicochemical properties and benthic organisms in a polluted stream. Chemosphere 16:1053–1063.

City of Austin. 2005. PAHs in Austin, Texas. Draft technical report. City of Austin, Austin, Texas. (Available from: http://www.ci.austin.tx.us/watershed/downloads/coaltar_draft_pah_study.pdf)

DEN BESTEN, P. J., D. TEN HULSCHER, AND B. VAN HATTUM. 2003. Bioavailability, uptake and effects of PAHs in aquatic invertebrates in field studies. Pages 127–146 *in* P. E. T. Douben (editor). PAHs: an ecotoxicological perspective. John Wiley and Sons, West Sussex, UK.

DICKHUT, R. M., E. A. CUNUEL, K. E. GUSTAFSON, K. LIU, K. M. ARZAYUS, S. E. WALKER, G. EDGECOMBE, M. O. GAYLOR, AND E. H. MACDONALD. 2000. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay region. Environmental Science and Technology 43:4635–4640.

DITORO, D. M., AND J. A. MCGRATH. 2000. Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. II. Mixtures and sediments. Environmental Toxicology and Chemistry 19:1983–1991.

EISLER, R. 1987. Polycyclic aromatic hydrocarbon hazards to fish, wildlife and invertebrates: a synoptic review. Biological Report 85(1.11). Contaminant hazard reviews. US Fish and Wildlife Service, Laurel, Maryland. (Available from: http://www.pwrc.usgs.gov/infobase/eisler/CHR_11_PAHs.pdf)

EPLER, J. H. 1996. Identification manual for the water beetles of Florida. Florida Department of Environmental Protection, Tallahassee, Florida. (Available from: ftp://ftp.dep.state.fl.us/pub/labs/biology/biokeys/beetles.pdf)

FLEEGER, J. W., K. R. CARMAN, AND R. M. NISBET. 2003. Indirect effects of contaminants in aquatic ecosystems. Science of the Total Environment 317:207–233.

GEMSEAL OF TEXAS. 2006. Petition for the review of City of Austin Ordinance No. 20051117–070. Texas Commission on Environmental Quality Docket no. 2006–0056-MIS. Gemseal of Texas, Austin, Texas. (Available from: http://www7.tceq.state.tx.us/uploads/eagendas/Agendas/6-27-2007/GEM/gem1.pdf)

HANNAFORD, M. J., AND V. H. RESH. 1995. Variability in macroinvertebrate rapid bioassessment surveys and habitat assessments in a northern California stream. Journal of the North American Benthological Society 14:430–439.

HELSEL, D. R., AND R. M. HIRSCH. 1995. Statistical methods in water resources. Elsevier, Amsterdam, The Netherlands.

HINKLE-CONN, C., J. W. FLEEGER, K. R. CARMAN, AND J. C. GREGG. 1998. Effects of sediment-bound polycyclic aromatic hydrocarbons on feeding behavior in juvenile spot (*Leiostomus xanthurus*: Pisces). Journal of Experimental Marine Biology and Ecology 227:113–132.

INGERSOLL, C. G., D. D. MACDONALD, N. WANG, J. L. CRANE, L. J. FIELD, P. S. HAVERLAND, N. E. KEMBLE, R. A. LINDSKOOG, C. SEVERN, AND D. E. SMORONG. 2001. Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines. Archives of Environmental Contamination and Toxicology 41:8–21.

JONKER, M. T. O., S. B. HAWTHORNE, AND A. A. KOELMANS. 2005. Extremely slowly desorbing polycyclic aromatic hydrocarbons from soot and soot-like materials: evidence by supercritical fluid extraction. Environmental Science and Technology 39:7889–7895.

KARR, J. R., AND E. W. CHU. 1999. Restoring life in running waters: better biological monitoring. Island Press, Washington, DC.

KHALILI, N. R., P. A. SCHEFF, AND T. M. HOLSEN. 1995. PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels, and wood combustion emissions. Atmospheric Environment 29:533–542.

LARSEN, R. K., AND J. E. BAKER. 2003. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. Environmental Science and Technology 37:1873–1881.

LEPPANEN, M. T., AND J. V. K. KUKKONEN. 2000. Effect of sediment–chemical contact time on availability of sediment-associated pyrene and benzo(a)pyrene to oligochaete worms and semi-permeable membrane devices. Aquatic Toxicology 49:227–241.

LOPES, T. J., AND E. T. FURLONG. 2000. Occurrence and potential adverse effects of semivolatile organic compounds in streambed sediment, United States, 1992–1995. Environmental Toxicology and Chemistry 20:727–737.

MACDONALD, D. D., C. G. INGERSOLL, AND T. A. BERGER. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives of Environmental Contamination and Toxicology 39:20–31.

MAHLER, B. J., P. C. VAN METRE, T. J. BASHARA, J. T. WILSON, AND D. A. JOHNS. 2005. Parking lot sealcoat: an unrecognized source of urban polycyclic aromatic hydrocarbons. Environmental Science and Technology 39:5560–5566.

MALTBY, L., D. M. FORROW, A. B. A. BOXALL, P. CALOW, AND C. I. BETTON. 1995. The effects of motorway runoff on freshwater ecosystems: 1. Field study. Environmental Toxicology and Chemistry 14:1079–1092.

MARVIN, C. H., B. E. MCCARRY, J. VILLELA, L. M. ALLAN, AND D. W. BRYANT. 2000. Chemical and biological profiles of sediments as indicators of sources of genotoxic contamination in Hamilton Harbor. Part I: analysis of polycyclic aromatic hydrocarbons and thia-arene compounds. Chemosphere 41:979–988.

MERRILL, E. G., AND T. L. WADE. 1985. Carbonized coal products as a source of aromatic hydrocarbons to sediments from a highly industrialized estuary. Environmental Science and Technology 19:597–603.

MERRITT, R. W., AND K. W. CUMMINS (EDITORS). 1996. An introduction to the aquatic insects of North America. 3rd edition. Kendall/Hunt Publishing, Dubuque, Iowa.

NEEDHAM, J. G., M. J. WESTFALL, AND M. L. MAY. 2000. Dragonflies of North America. Revised edition. Scientific Publishers, Gainesville, Florida.

NEFF, J. M., S. A. STOUT, AND D. G. GUNSTER. 2005. Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: identifying sources and ecological hazard. Integrated Environmental Assessment and Management 1:22–33.

OMERNIK, J. M. 1987. Ecoregions of the conterminous United States. Supplement to the Annals of the Association of American Geographers 77:118–125.

PAINE, M. D., P. M. CHAPMAN, P. J. ALLARD, M. H. MURDOCK, AND D. MINIFIE. 1996. Limited bioavailability of sediment PAH near an aluminum smelter: contamination does not equal effects. Environmental Toxicology and Chemistry 15:2003–2018.

Pennak, R. W. 1989. Freshwater invertebrates of the United States: Protozoa to Mollusca. John Wiley and Sons, New York.

Resh, V. H., and J. K. Jackson. 1993. Rapid assessment approaches to biomonitoring using benthic macroinvertebrates. Pages 195–233 *in* D. M. Rosenberg and V. H. Resh (editors). Freshwater biomonitoring and benthic macroinvertebrates. Chapman and Hall, New York.

Rosenberg, D. M., T. B. Reynoldson, K. E. Day, and V. H. Resh. 1997. The role of abiotic factors in structuring benthic invertebrate communities in freshwater ecosystems. Pages 135–155 *in* C. G. Ingersoll, T. Dillon, and G. R. Biddinger (editors). Ecological risk assessment of contaminated sediments. SETAC Press, Pensacola, Florida.

Schuler, L. J., P. F. Landrum, and M. J. Lydy. 2004. Time-dependent toxicity of fluoranthene to freshwater invertebrates and the role of biotransformation on lethal body residues. Environmental Science and Technology 38: 6247–6255.

Steuer, J., W. Selbig, N. Hornewer, and J. Prey. 1997. Sources of contamination in an urban basin in Marquette, Michigan, and an analysis of concentrations, loads and data quality. Water-Resources Investigations Report 97–4242. US Geological Survey, Middleton, Wisconsin.

Stewart, K. W., and B. P. Stark. 2002. Nymphs of North American Stonefly Genera. 2nd edition. The Caddis Press, Columbus, Ohio.

Thorp, J. H., and A. P. Covich (editors). 2001. Ecology and classification of North American freshwater invertebrates. 2nd edition. Academic Press, San Diego, California.

Thorsen, W. A., W. G. Cope, and D. Shea. 2004. Bioavailability of PAHs: effects of soot carbon and PAH source. Environmental Science and Technology 38:2029–2037.

TNRCC (Texas Natural Resource Conservation Commission). 2001. Total petroleum hydrocarbons. TNRCC Method 1005, Revision 03. Texas Natural Resource Conservation Commission, Austin, Texas. (Available from: http://www.tceq.state.tx.us/assets/public/compliance/compliance_support/qa/1005_final.pdf)

USEPA (US Environmental Protection Agency). 1996. Test methods for evaluating solid waste, physical/chemical methods. EPA/SW-846. Office of Solid Waste, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2002. Priority pollutants in the water quality standards database. (Available from: http://oaspub.epa.gov/wqsdatabase/wqsi_epa_criteria.rep_parameter; PAH constituents most recent EPA-promulgated update, 2 December 2002.)

USEPA (US Environmental Protection Agency). 2003. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures. EPA/600/R-02/013. Office of Research and Development, US Environmental Protection Agency, Washington, DC.

USEPA (US Environmental Protection Agency). 2004. National recommended water quality criteria: 2004. Office of Water, US Environmental Protection Agency, Washington, DC. (Available from: http://www.epa.gov/waterscience/criteria/nrwqc-2004.pdf)

Van Hattum, B., M. J. Curto Pons, and J. F. Cid Montanes. 1998. Polycyclic aromatic hydrocarbons in freshwater isopods and field-partitioning between abiotic phases. Archives of Environmental Contamination and Toxicology 35:257–267.

Van Metre, P. C., and B. J. Mahler. 2005. Trends in hydrophobic organic contaminants in urban and reference lake sediments across the United States, 1970–2001. Environmental Science and Technology 39:5560–5566.

Volkering, F., and A. M. Breure. 2003. Biodegradation and general aspects of bioavailability. Pages 81–96 *in* P. E. T. Douben (editor). PAHs: an ecotoxicological perspective. John Wiley and Sons, West Sussex, UK.

Westfall, M. J., and M. L. May. 1996. Damselflies of North America. Scientifica Publishers, Gainesville, Florida.

Wiggins, G. B. 1996. Larvae of the North American Caddisfly Genera (Trichoptera). 2nd edition. University of Toronto Press, Toronto, Canada.

Yunker, M. B., R. W. MacDonald, R. Vingarzan, R. H. Mitchell, D. Goyette, and S. Sylvestre. 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry 33:489–515.

Zhang, X. L., S. Tao, W. X. Liu, Y. Yang, Q. Zuo, and S. Z. Liu. 2005. Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. Environmental Science and Technology 39:9109–9114.

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