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Coal-tar based pavement sealant toxicity to freshwater macroinvertebrates

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Coal-tar pavement sealants degrade stream invertebrate communities.

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ABSTRACT

Non-point-source pollution is a major source of ecological impairment in urban stream systems. Recent work suggests that coal-tar pavement sealants, used extensively to protect parking areas, may be contributing a large portion of the polycyclic aromatic hydrocarbon (PAH) loading seen in urban stream sediments. The hypothesis that dried coal-tar pavement sealant flake could alter the macroinvertebrate communities native to streams in Austin, TX was tested using a controlled outdoor laboratory type approach. The treatment groups were: control, low, medium, and high with total PAH concentrations (TPAH = sum of 16 EPA priority pollutant PAHs) of 0.1, 7.5, 18.4, & 300 mg/kg respectively. The low, medium, and high treatments were created via the addition of dried coal-tar pavement sealant to a sterile soil. At the start of the 24-day exposure, sediment from a minimally impacted local reference site containing a community of live sediment-dwelling benthic macroinvertebrates was added to each replicate. An exposure-dependent response was found for several stream health measures and for several individual taxa. There were community differences in abundance ($P = 0.0004$) and richness ($P < 0.0001$) between treatments in addition to specific taxa responses, displaying a clear negative relationship with the amount of coal-tar sealant flake. These results support the hypothesis that coal-tar pavement sealants contain bioavailable PAHs that may harm aquatic environments.

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1. Introduction

Recently, a link between coal-tar based pavement sealants and polycyclic aromatic hydrocarbons (PAHs) in sediment of urban water bodies has been recognized (Mahler et al., 2004, 2005; Scoggins et al., 2007; Van Metre et al., 2009). In a series of simulations, rainfall runoff has been shown to be able to transport PAHs, in particulate form, from the sealed pavement areas into the stormwater flow path. Parking lots sealed with coal-tar based sealants showed elevated levels of PAHs (particle runoff from sealed lots had PAH concentrations 65 times higher than in runoff from unsealed asphalt and cement parking lots), a result that was consistent regardless of parking lot usage. In many cases, small black particulates eroded from coal-tar sealed lots are visually apparent in the areas receiving runoff (Mahler et al., 2005, personal observation). Dust sweepings collected from parking lots across the U.S. Van Metre et al. (2009) demonstrated that coal-tar sealed parking lots had much higher concentrations of PAHs than unsealed parking lots. Additionally, the profile of individual PAHs in urban lake sediments where coal-tar sealant was used most closely resembled the coal-tar sealant dust that they sampled (Van Metre et al., 2009). Scoggins et al. (2007) found a pattern of elevated PAHs and degraded macroinvertebrate communities downstream of parking lots sealed with coal-tar sealant. Manufacturers of these pavement sealants recommend reapplication of the sealant every 2–3 years (Dubey, 1999) additionally supporting the observation that coal-tar based pavement sealant could be contributing to the PAHs accumulating in waterways.

Coal tar is a hazardous waste byproduct of the coking of coal and is a frequent waste product in steel and electricity industries (ASTDR, 1996). Currently, coal-tar byproduct is recycled into products that are presumably relatively inert, such as pavement sealants, thereby avoiding hazardous waste disposal issues described by the Resource Conservation and Recovery Act, RCRA, (40 CFR 261.31 and 40 CFR 261.32 in (ASTDR, 1996)). Coal-tar pavement sealers contain approximately 20–35% coal-tar by volume, depending on the brand and formulation (SealMaster, 2002). For example, a selection of ready-to-use coal-tar based pavement sealant products had a median total polycyclic aromatic

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hydrocarbon (TPAH; sum of 16 EPA priority pollutant PAHs) concentration of approximately 40,000 mg/kg (City of Austin online database http://www.ci.austin.tx.us/wrequery/query_form.cfm, accessed 11/12/08).

It is well established that PAHs can have detrimental effects on a variety of organisms. Environmental data exist demonstrating toxicity of PAHs to many freshwater organisms (e.g., algae (Shoney et al., 1988); bacteria (Catello and Gambrell, 1987); annelids (Weinstein, 2001); crustaceans (Boese et al., 1966); mollusks (Akcha et al., 1999); insects (Beasley and Kneale, 2002); fishes (Steward et al., 1991); amphibians (Sadinski et al., 1995); and see reviews in (Eisler, 1987; Peter, 2003)). As highly hydrophobic molecules, it has been proposed that PAHs in coal tar may not pose a problem to biota in receiving water bodies because they typically stay sorbed to clay (a major component of coal-tar based pavement sealants) or the sediment and organic components of the sediments (May et al., 1978; Klassen, 2001).

The objective of this project was to determine whether coal-tar pavement sealant products could alter aquatic macroinvertebrate abundance and richness patterns of communities common to streams in our study area (Austin, Texas, USA). We performed a controlled outdoor laboratory experiment to evaluate the effect of three concentrations of coal-tar pavement sealant on a macroinvertebrate community collected from a reference site.

2. Methods

2.1. Experimental overview

Four treatments were used to assess the effect of coal-tar pavement sealant on stream macroinvertebrates: a control and three treatments that received differing levels of dried and scraped coal-tar pavement sealant (coal-tar sealant flake). In order to create an environmentally realistic coal-tar pavement sealant affected sediment, we first allowed all four treatments to equilibrate with a sterilized clean sediment for 24 days. At the end of this chemical equilibration period, reference sediment, containing a live native stream macroinvertebrate community, was added and all experimental units were set in a temperature controlling water bath. The experiment ended after 24 days of exposure, when the containers were sampled and the organisms sorted and preserved.

2.2. Dried coal-tar pavement sealant preparation

Five gallons of SealMaster 1080 (a commonly used brand in Austin, TX area) was purchased and stored in its original container at room temperature. The coal-tar sealant flake was prepared by thinly brushing the wet sealant onto clean glass, allowing it to cure for 72 h, scraping it off with a razor blade, and storing the flakes in certified clean glass containers at 4 °C until use. SealMaster is 20–24% coal tar by volume (SealMaster, 2002).

2.3. Treatments and replicates

There were four replicates in each treatment. Each replicate consisted of an opaque Sterlite brand 37-liter plastic storage container. With this study design, any PAHs that sorbed and/or desorbed from the plastic containers were standardized amongst all replicates since all containers were the same material. Lids were modified to allow light in and then fitted with plastic mesh screening to exclude colonizing insects. Clean sediment was collected from a reference pond in Austin, TX (no detectable PAHs or metals at or above threshold levels, City of Austin, unpublished data) and sieved through a 500 micron net and dried at 50 °C in an attempt to remove and kill all incidentally collected organisms and eggs.

At the beginning of the 24-day equilibration period, containers received 3 L of well water and 1.5 L of clean sediment according to the following preparation: the low treatment group received a mean of 0.4868 (S.D. ±0.0004) grams coal-tar sealant flake; the medium treatment received a mean of 1.0671 (S.D. ±0.0001) grams; and the high treatment received a mean of 10.6667 (S.D. ±0.001) grams. The control treatment did not have any sealant flake added. Throughout the 24-day equilibration period the containers were stirred with wooden paint stirrers every 3–5 days.

Following the 24-day equilibration period, 1.5 L of reference stream sediment with accompanying organisms and algae, 10 ml of *Lumbriculus variegatus*, and 18 L of well water were added to all treatments. All replicates were positioned outdoors in a flow-through aquaculture stream channel in a stratified random block design. The ultraviolet-b (UV-B) radiation for Seguin, TX, USA (35 km away) maximum peak averages were 0.0129 W/m^2/nm taken at $\lambda = 300$ nm for the month of July (data taken from USDA UV-B Monitoring and Research Program online database at http://uvb.nrel.colostate.edu, accessed 12/29/05). Once in position the containers were gently stirred with wooden stirrers in order to homogenize the innoculum and the equilibrated PAH-containing sediment evenly. All containers including the control replicates received similar treatment, *i.e.*, they experienced similar exposure to the plastic container and the wooden stirrer. Sediment samples were collected at the initiation and termination of the exposure period for the measurement of PAH concentration, using certified clean glass jars, and sent to DHL Analytical, Inc., Round Rock, TX, USA (Table 1).

PAH data are reported because of the known relationship between PAHs and coal tar. However, this study does not test the role of PAHs explicitly but rather to address the effect of coal-tar pavement sealant on stream communities, with the understanding that the sealant product is a complex mixture. We measured dissolved oxygen (DO), conductivity, temperature, and pH every 4 days, and performed 3 L partial water changes at the same frequency. Three liters was the maximum water volume that could be changed without disturbing the sediments. Aside from the water changes nothing was added to or removed from the containers until the end of the experiment.

2.4. Benthic community

We collected surface sediments from the top 10 cm or less from a stream pool in a reference section of Barton Creek in Hays County, Texas, USA that had minimal development and associated degradation (<2% impervious area in the watershed of the reference site). The innoculum was distributed in a stratified random fashion with respect to each treatment. Each replicate was thoroughly (though gently) homogenized to ensure that the innoculum was distributed evenly amongst the PAH-equilibrated sediment. The filamentous algae incidentally collected during the reference sediment collection was divided equally and dispersed among the replicates. Additionally, to ensure adequate organism numbers, each replicate received 10 ml of *L. variegatus*, purchased from Aquatic Foods, Fresno, CA, USA.

2.5. Benthic community processing

At the end of the 24-day exposure period, the experiment was concluded. A coarse visual inspection of the containers was made, noting chiefly the abundance of algae. The water was separated off and the sediment partitioned into three aliquots:1 L was placed in an equal amount of 95% ethanol for later invertebrate sorting and processing, 0.5 L was composited, by treatment, in a certified clean glass container and placed on ice for the laboratory analyses of final PAH concentration, and the remaining sediment was preserved with 10% buffered formalin for long term storage. Invertebrates were separated from the sediment using an elutriation method, in which sugar and water are mixed to create a dense liquid that buoys the invertebrates to the surface where they are separated from the sample (Anderson, 1959). The insects were identified to the lowest practical taxonomic level, usually genus, using standard taxonomic keys (Berner and Pescador, 1988; Epler, 1996; Merritt and Cummins, 1996; Needham et al., 2000; Pennak, 1989; Perez et al., 2004; Thorp and Covich, 2001; Westfall and May, 1996; Wiggins, 1996) by City of Austin staff. Chironomidae and non-insect taxa were identified to the generic level by Freshwater Benthic Services, Petoskey, Michigan, USA (M. Winnell).

2.6. Chemical analyses

Composite samples were collected both at the start and the end of the exposure. Composites were made by taking a small amount of sediment from each of the four replicates in each treatment and placing the sediment into a certified clean glass jar. Samples were kept at 4 °C and transported to DHL Analytical, Inc. Quality assurance included split samples and standard laboratory quality control samples and all analyses were performed within 14 days. Although PAHs make up a considerable portion of the coal-tar pavement sealer mixture, we additionally tested for metals and total petroleum hydrocarbons. DHL Analytical laboratory performed the following analyses according to EPA standard methods: metals (SW 6020), Hg (SW7471), PAHs (SW8270C), total petroleum hydrocarbons (TX1005), percent moisture (D2216), and total organic carbon (SW9060).

Table 1
Representative water quality values for each treatment group. Water quality values come from routine sampling; values reported are means of the replicates ($n = 4$) from each treatment.

	Control	Low	Medium	High
Conductivity	467	439	442	445
Dissolved oxygen (mg/L)	5.5	6.5	5.6	5.3
pH	7.9	8.0	8.0	8.0
Temperature (°C)	23.3	23.4	23.4	23.4
Total organic carbon (wt%-dry)	2.59	2.29	3.23	2.91

2.7. Sediment-quality guidelines

Sediment-quality guidelines (SQGs) like the Probable Effect Concentration (PEC, MacDonald et al., 2000) and Equilibrium partitioning Sediment Benchmark Toxicity Units (∑ESBTU, USEPA, 2003) are reliable predictors of toxicity in large data sets (MacDonald et al., 2000; Ingersoll et al., 2001; USEPA, 2003), but toxicity can vary considerably depending on local conditions and the mixture and source of PAHs present (Catallo and Gambrell, 1987; Paine et al., 1996; USEPA, 2003). The PEC of 22.8 mg/kg of TPAH was used as a threshold value above which, biological effects are expected to occur. ∑ESBTUs were calculated following U.S. Environmental Protection Agency methods (USEPA, 2003) using the amended calculations for 16 individual PAHs. These toxicity units are used as endpoints, summing the toxicological contributions of mixtures of PAHs in sediments based on narcosis theory. Using this method, a sediment toxicity unit less than 1.0 should be protective of benthic organisms and values greater than 1.0 suggest that sensitive benthic organisms will be unacceptably affected. These toxicity units do not consider any antagonistic, additive or synergistic effects of other sediment contaminants in combination with PAHs or the potential for bioaccumulation and trophic transfer of PAHs. They are used in this study for comparative purposes and to evaluate relative toxicity of PAHs in the experimental treatments.

2.8. Statistical analyses

Homogeneity of variance was confirmed using Levene's test (Levene, 1960) and residuals from analysis of variance (ANOVA) showed that treatment data (number of organisms and number of taxa) did not violate the assumptions of normality (USEPA, 1998). When significant differences were found with ANOVA (Statsoft, 2007), Dunnett's two-tailed mean comparison test was used (Dunnett, 1955). The abundances among individual taxa were also compared using the Mann Whitney *U* test (StatSoft, 2007).

3. Results

Water quality parameters were uniform and constant within and between treatments during the 24-day exposure, with the exception of DO (Table 1). DO levels were higher in the low treatment group, with a mean of 6.5 mg/L vs. a range of 5.3–5.6 in the other treatments. The composite sample concentrations of PAHs ranged from 0.04 to 0.11 mg/kg in the control, 5.8–9.2 mg/kg in the low, 11–26 mg/kg in the medium, and 276–324 mg/kg in the high treatment groups. Table 2 identifies treatment mean TPAH concentration and the16 EPA priority pollutant PAH values (USEPA, 2002). Based on ESBTU's, the control and low treatments were not at risk from PAH narcosis, the medium exposure group was border line with a value of 1.0, and the highest exposure level should have experienced adverse effects due to PAH toxicity with an ESBTU of 16 (Table 2; USEPA, 2003).

Table 2
Contaminant concentrations are means from composite samples taken at the beginning and end of the exposure. All PAH values are given in mg/kg dry sediment. ∑ESBTU values show toxicity unit scores as summed across the entire exposure period.

PAHs	Pre	Post	Pre	Post	Pre	Post	Pre	Post
Acenapthene	ND	ND	0.0	0.1	0.1	0.1	3.3	2.8
Acenapthylene	ND	ND	ND	ND	ND	1.0	0.1	0.1
Anthracene	ND	ND	0.3	0.34	0.5	1.0	13.9	14.2
Benzo(a)anthracene	ND	ND	0.4	0.6	0.7	1.5	20.1	18.2
Benzo(a)pyrene	ND	ND	0.4	0.7	0.7	1.7	20.0	18.8
Benzo(b)fluoranthene	ND	ND	0.7	1.1	1.1	1.5	19.2	32.0
Benzo(g,h,i)perylene	ND	ND	0.3	0.5	0.6	1.1	19.4	16.0
Benzo(k)Fluoranthene	ND	ND	ND	ND	ND	1.0	12.5	ND
Chrysene	ND	ND	0.4	0.7	0.7	1.6	21	18.8
Dibenz(a,h)anthracene	ND	ND	0.1	0.2	0.2	0.4	6.2	4.4
Flouranthene	0.1	0.0	1.0	1.7	1.8	4.9	60.8	49.5
Flourene	ND	ND	0.1	0.1	0.2	0.2	4.8	4.2
Indeno(1,2,3,-cd)pyrene	0.0	ND	0.3	0.4	0.5	0.9	15.2	11.2
Napthelene	ND	ND	ND	ND	ND	1	0.5	0.5
Phenanthrene	ND	ND	0.9	1.3	2.0	3.6	54.6	45.6
Pyrene	ND	ND	1.0	1.5	2.1	4.1	52.2	39.7
TPAH	**0.1**	**0.0**	**5.8**	**9.2**	**11.4**	**25.6**	**323.8**	**276.0**
∑ESBTU	**0.003**		**0.4**		**1.0**		**16**	

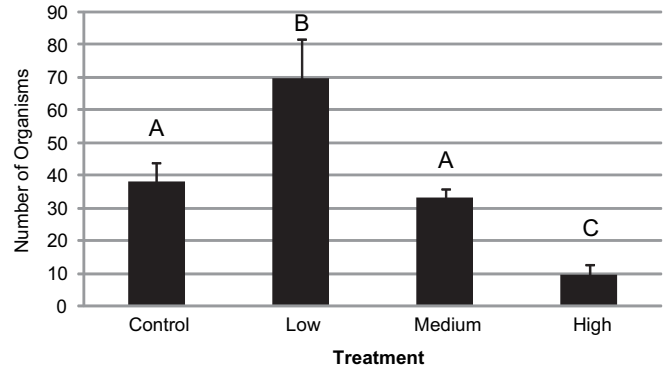

Fig. 1. Abundance patterns. Bars represent means (±SE). Letters represent results of Dunnett's multiple comparisons; different letters indicate significant ($P < 0.05$) differences between treatments.

The number of organisms among the treatment groups were different following the 24-day exposure period (d.f. = 3, $F = 13.38$, $p = 0.0004$) (Fig. 1). The low treatment (mean ± SE: 78 ± 12 organisms) had higher abundances than the control (mean ± SE: 43 ± 5.5) while the high treatment had lower abundance (mean ± SE: 14 ± 3.5) than the control. The medium treatment (mean ± SE: 38 ± 2.5) was not different from the control.

Similarly, the number of taxa present at the end of the exposure period was different among the treatment groups (d.f. = 3, $F = 27.8$, $p < 0.0001$) (Fig. 2). Comparison of means indicated an elevated number of taxa in the low treatment (mean ± SE: 17 ± 1.5) and a lower number of taxa in the high treatment (mean ± SE: 5 ± 0.6), relative to control (mean ± SE: 9 ± 0.8). The number of taxa in the medium treatment (mean ± SE: 12 ± 0.7) was not different from the control.

Not all organisms responded similarly to the treatments as differences between individual taxa were observed post-exposure (Fig. 3). Seven taxa had 10 or more individuals and were included in the pattern analysis, the remainder, being classified as rare, were excluded (Table 3). Four taxa decreased in abundance in the high treatment relative to the control, including two Chironomidae (*Clinotypus* and *Procladius*), an amphipod (*Hyallela*) and a megalopteran (*Sialis*). The three whose feeding habits are predatory (*Clinotanypus, Procladius* and *Sialis*) appeared to be affected by direct mortality in a consistent exposure-response manner, with decreasing abundances in the higher concentration treatments. *Procladius* had significant decreases, relative to the control in the medium treatment. Two taxa expressed a significant increase in

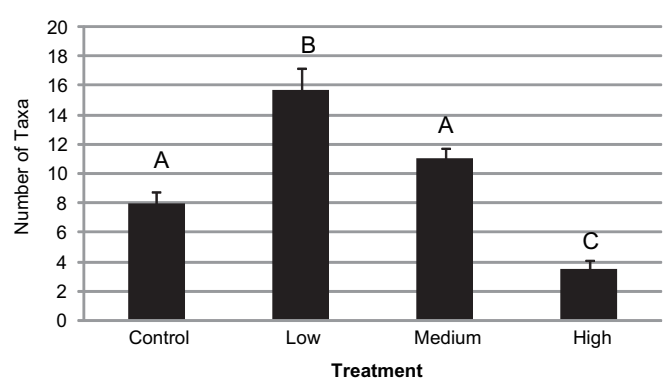

Fig. 2. Species richness. Bars represent means (±SE). Letters represent results of Dunnett's multiple comparisons; different letters indicate significant ($P < 0.05$) differences between treatments.

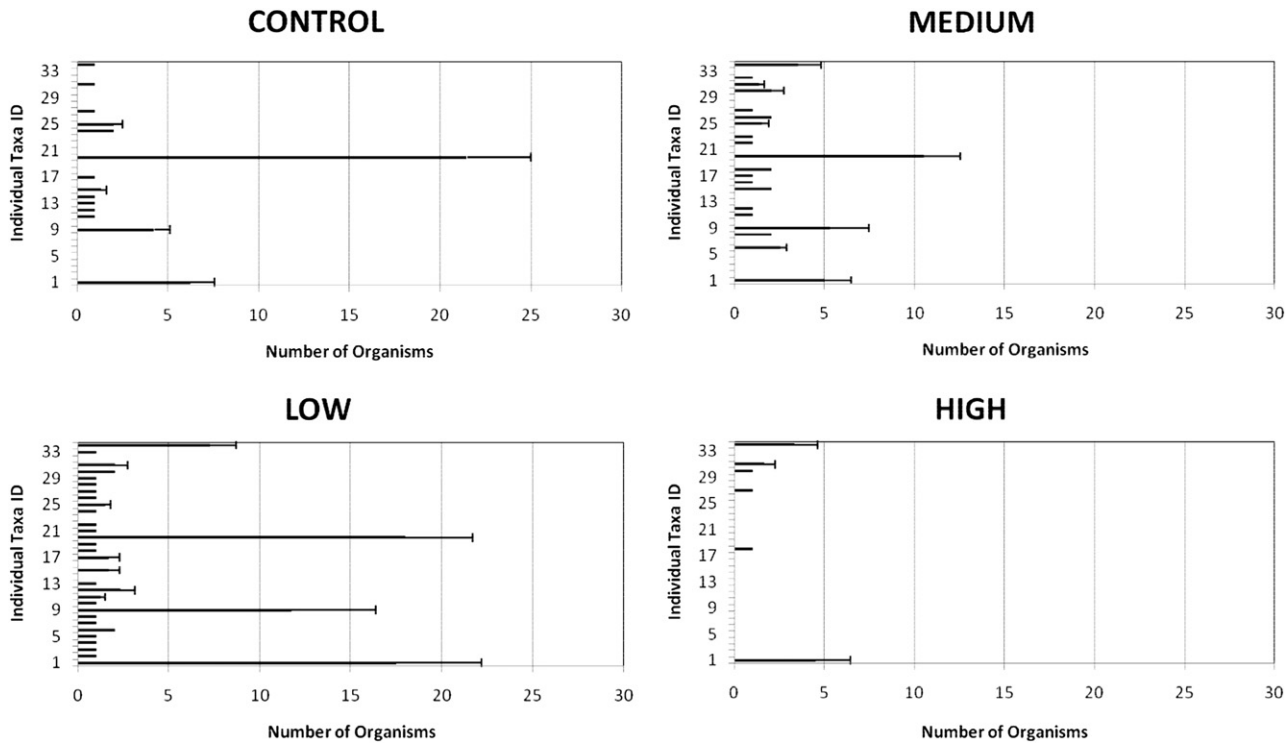

Fig. 3. Abundance patterns by taxa. Bars represent replicate means (±SE), $n = 4$. Individual taxa identification numbers are listed in Appendix 1.

abundances in the low treatment, the *Lumbriculus* earthworms and *Sphaerium* fingernail clams. *Sphaerium* also showed increases, relative to the control, in the medium treatment, going from a mean of 3 to mean of 14. *Helisoma anceps*, a grazing mollusk, expressed no significant response to any of the treatments relative to the control and may have actually increased in abundance, from a mean of 3 in the control to a mean of 5 in the high treatment.

4. Discussion

Using a controlled test environment we found that coal-tar pavement sealant significantly altered multiple endpoints in the benthic community used to assess the potential of this source of PAHs to degrade aquatic ecosystems. At the highest exposure level, a clear decrease in community health in terms of both abundance and diversity was observed. The taxa that declined in abundance tended to be predatory insects, though the amphipod (Crustacean) *Hyalella* decreased in abundance as well. One aspect of the taxa losses that occurred between the control and the high treatment was that of the large number of rarer taxa, those that could not be included in individual taxa analysis, very few appeared in the high treatment group which was generally made up of tolerant worms and bivalves (*Lumbriculus*, *Helisoma*, *Sphaerium*). This agrees with a large body of work showing that even among relatively tolerant sediment-dwelling benthic communities, some aquatic taxa are more sensitive to the toxic effects of PAHs in sediment while others are more tolerant and/or resistant (Bott and Standley, 2000; Catallo and Gambrell, 1987; Eisler, 1987; Leppanen and Kukkonen, 2000; Schuler et al., 2004; Van Hattum et al., 1998). For example, although the Chironomidae family of benthic insects has a wide range of

Table 3
Response of individual taxa to treatments, expressed as the summed total number of individuals. Taxa that were represented by more than ten individuals where assigned to one of the possible population level responses to a contaminant – decreased abundance, increased abundance, or no change. Of the 41 taxa identified in the study only 7 contained sufficient numbers to be included here. Values in parentheses are *p*-values from Mann Whitney *U* tests, evaluating difference relative to the control.

	Control	Low	Medium	High	Habitat	Feeding	Taxon	
Decreased abundance in the high treatment								
Clinotanypus sp.	4	5	2	0 (0.05)	Burrow	Predator	Arthropoda	Insecta
Hyallela sp.	17	47	21	0 (0.01)	Benthic	Detritivore	Arthropoda	Amphipoda
Procladius sp.	86	72	42 (0.04)	0 (0.01)	Sprawler	Predator	Arthropoda	Insecta
Sialis sp.	6	6	3	0 (0.05)	Burrow	Predator	Arthropoda	Insecta
Increased abundance in the low treatment								
Lumbriculus	25	70 (0.04)	20	18	Sediment	Deposit	Annelida	Oligocheata
Sphaerium sp.	3	29 (0.02)	14 (0.04)	10	Sediment	Filterer	Mollusca	Bivalvia
No change in abundance								
Helisoma anceps	3	4	4	5	benthic	grazer	mollusca	gastropod
Taxa too rare to test								
Ablabesmyia, Argia, Aulodrilus, Berosus, Bezzia, Branchiura sowerbyi, Cernotina, Cryptotendipes, Dero, Dubiraphia, Epitheca princeps, Fallceon quilleri, Fittkaumyia, Gomphus, Helobdella, Hexagenia, Hirudinea, *Hydracarina, Larsia, Lauterborniella, Lebertia, Ophidonais, Physa, Planorbella, Polypedium, Probezzia, Pseudochironomus*, Sphaeriinae, *Tanytarsus*, Tubificidae								

environmental tolerances, only one individual (*Lauterborniella*) was present in the post-exposure high treatment, among all four replicates, compared to a mean of 23 individuals in the control, 22 in the low treatment and 13 in the medium treatment, confirming other studies findings that this group was particularly sensitive to PAH effects (Den Beston et al., 2003; Scoggins et al., 2007; Schuler et al., 2004).

At the lowest exposure level, the data did not follow a predictable dose–response pattern as there were significant increases in number of taxa and in abundance in the low exposure treatment compared to the control. Two individual taxa, *Lumbriculus* and *Sphaerium*, had significantly higher abundances in the low treatment than in the control. The low treatment replicates had the highest amount of algae (personal observation) and higher mean DO among the four treatments, probably due to the algae cover. This apparent biotic stimulation effect in the low treatment may be a spurious artifact of the experimental set-up, independent of the intended chemical stressor, but warrants attention considering the low variation and consistency among treatments. One potential explanation for this pattern could be the metabolism of PAHs by the microbial community, which, in turn, could have supported an increased freshwater microbial energy loop, resulting in greater macroinvertebrate biomass. The distinction between toxic vs. nutritive in microbial communities is important because although PAHs are known to inhibit microbial communities (Su and Yang, 2009), many soil remediation strategies rely on microbial degradation in which PAHs function as a microbial carbon source (Leahy and Colwell, 1990).

The decreases in abundance and richness in the high treatment are not unexpected as these PAH levels are well above guidance thresholds (MacDonald et al., 2000; USEPA, 2003). However, little work has been completed that directly evaluates exposures from coal-tar based sealants in freshwater sediments. Using coal-tar pavement sealer flake, similar to this study, Bryer et al. (2006) showed that TPAH concentrations of 3 mg/L could cause transient delays in growth and development in *Xenopus laevis*. At the 30 mg/L concentration there were significant changes in development and failure to metamorphose relative to the control individuals. The highest dose group, 300 mg/L, showed 100% mortality within the first 6 days of the experiment. Again, the Bryer et al. (2006) results are not unexpected given the PAH concentrations used; however, the clear effects on this model amphibian support the hypothesis that bioavailable PAHs can occur in coal-tar sealants.

Scoggins et al. (2007) sampled five streams in urban Austin, TX with direct runoff from coal-tar sealed parking lots. A comparison of upstream to downstream sediment chemistry and macroinvertebrate communities showed significant increases in TPAH concentrations in sediments correlated to decreases in abundance and richness in the downstream riffle and pool communities that received the runoff. The Scoggins et al. (2007) field study showed that PAH "hotspots" in streams could be linked to coal-tar sealed parking lot runoff and that benthic communities in the study streams were likely degraded by the runoff coming from these lots.

Results presented in this work generally agree with the Probable Effects Concentration (PEC, MacDonald et al., 2000) and $\sum$ESBTU (USEPA, 2003) guidance values for PAHs in sediments. The low and medium treatments were at or below the PEC of 22.8 mg/kg TPAH and the $\sum$ESBTU threshold 1.0. Neither of these treatments (Low, Medium) showed significant degradation of community health, with one exception. One midge taxon, *Procladius* sp., showed a significant decrease in abundance in the medium treatment group, with a mean TPAH concentration of 18.4 mg/kg. This value, just below the PEC of 22.8, resulted in an $\sum$ESBTU of 1.0, the threshold where losses of sensitive taxa are predicted to occur. It would appear that these guidance values are fairly protective of benthic communities in the particular experimental set-up we used and that the coal-tar sealant source of PAHs is equally as bioavailable as the composite sources used in developing the PEC and $\sum$ESBTU guidance values.

The concentrations of PAHs used in the current study are relevant to concentrations found in urban streams. Thirteen percent of the streams in Austin, TX have PAH concentrations above the PEC and on multiple occasions PAH concentrations have ranged between 150 and 3500 mg/kg (unpublished data, City of Austin, TX). Due to the nature of streams and runoff patterns the concentrations of PAHs in stream sediments are likely to shift and change with weather events. Mahler et al. (2005) collected runoff particles from parking lots and found the PAH concentrations ranged from 1000 to 10,000 mg/kg (10 summed PAHs) and actual coal-tar sealed parking lot scrapings ranged from roughly 10,000–100,000 mg/kg. Clearly there is the potential for localized collections of sediment that could contain high levels of PAHs and produce concentrations similar to those used in the current study.

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Appendix 1

1 Lumbriculus
2 Dero
3 Aulodrilus
4 Branchiura sowerbyi
5 Unid. genus
6 Helobdella
7 Lebertia
8 Unid. genus
9 Hyalella
10 Dubiraphia
11 Berosus
12 Bezzia/Palpomyia
13 Probezzia
14 Ablabesmyia
15 Clinotanypus
16 Cryptotendipes
17 Fittkaumyia
18 Lauterborniella
19 Polypedilum
20 Procladius
21 Pseudochironomus
22 Tanytarsus
23 Fallceon quilleri
24 Hexegenia
25 Sialis
26 Argia
27 Epitheca princeps
28 Gomphus
29 Cernotina
30 Physa

31 Helisoma anceps
32 Planorbella
33 Sphaeriinae
34 Sphaerium

References

Akcha, F., Burgeot, T., Venier, P., Narbonne, J.F., 1999. Relationship between kinetics of benzo(a)pyrene bioaccumulation and DNA binding in the mussel *Mytilus galloprovincialis*. Bulletin of Environmental Contamination and Toxicology 62, 455–462.

Anderson, R.0, 1959. A modified flotation technique for sorting bottom fauna samples. Limnology and Oceanography 4, 223–225.

Agency for Toxic Substance and Disease Registry (ATSDR), 1996. Toxicological Profile for Creosote. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA.

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

Berner, L., Pescador, M.L., 1988. The Mayflies of Florida, revised ed. University Presses of Florida, Tallahassee/Gainesville, FL, USA.

den Beston, P.J., ten Hulscher, D., Van Hattum, B., 2003. Bioavailability, uptake and effects of PAHs in aquatic invertebrates in field studies (Chapter 8). In: Douben, P.E.T. (Ed.), PAHs: An Ecotoxicological Perspective. Wiley and Sons Ltd., West Sussex, England.

Boese, B.L., Lamberson, J.O., Swartz, R.C., Ozretich, R.J., 1966. Photoinduced toxicity of fluoranthene to seven marine benthic crustaceans. Archives of Environmental Contamination and Toxicology 32, 389–393.

Bott, T.L., Standley, L.J., 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.

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

Catallo, J.W., Gambrell, R.P., 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.

Dubey, G., 1999. Selling Sealcoating. Pavement March/April, 42.

Dunnett, C.W., 1955. A multiple comparisons procedure for comparing several treatments with a control. Journal of the American Statistical Association 50, 1096–1121.

Eisler, R., 1987. Polycyclic Aromatic Hydrocarbon Hazards to Fish, Wildlife, and Invertebrates: a Synoptic View. USDI Fish & Wildlife Service, Biological report 85 (1.11). Contaminant Hazard Reviews, Report No. 11.

Epler, J.H., 1996. Identification Manual for the Water Beetles of Florida. Florida Department of Environmental Protection. Florida, USA, Tallahassee.

Ingersoll, C.G., Macdonald, D.D., Wang, N., Crane, J.L., Field, L.J., Haverland, P.S., Kemble, N.E., Lindskoog, R.A., Severn, C., Smorong, D.E., 2001. Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines. Archives of Environmental Contamination and Toxicology 41, 8–21.

Klassen, C.D., 2001. Casarett and Doull's Toxicology: The Basic Science of Poisons, sixth ed. McGraw Hill, New York, NY, USA.

Leahy, J.G., Colwell, R.R., 1990. Microbial degradation of hydrocarbons in the environment. Microbiology and Molecular Biology Reviews 54, 305–315.

Leppanen, M.T., Kukkonen, J.V.K., 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.

Levene, H., 1960. Robust tests for the equality of variance. In: Olkin, I. (Ed.), Contributions to Probability and Statistics. Stanford University Press, Palo Alto, CA, pp. 278–292.

MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives of Environmental Toxicology and Chemistry 39, 20–31.

Mahler, B.J., Van Metre, P.C., Wilson, J.T., 2004. Concentrations of Polycyclic Aromatic Hydrocarbons (PAHs) and Major and Trace Elements in Simulated Rainfall Runoff from Parking Lots, Austin, TX, 2003. U.S. Geological Survey Open-File Report 2004-1208. U.S. Geological Survey, Denver, CO USA. http://water.usgs.gov/pub/of/2004/1208/pdf/ofr2004-1208.pdf (accessed July 2005).

Mahler, B.J., Van Metre, P.C., Bashara, T.J., Wilson, J.T., Johns, D.A., 2005. Parking lot sealcoat: an unrecognized source of urban polycyclic aromatic hydrocarbons. Environmental Science and Technology 39, 5560–5566.

May, W.E., Wasik, S.P., Freeman, D.H., 1978. Determination of the solubility behavior of some polycyclic aromatic hydrocarbons in water. Analytical Chemistry 50, 997–1001.

Merritt, R.W., Cummins, K.W., 1996. An Introduction to the Aquatic Insects of North America. Kendall/Hunt Publishing Co., Dubuque, Iowa, USA.

Needham, J.G., Westfall Jr., M.J., May, M.L., 2000. Dragonflies of North America, revised ed.. Scientific Publishers, Inc., Gainesville, Florida, USA.

Paine, M.D., Chapman, P.M., Allard, P.J., Murdock, M.H., Minifie, D., 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 & Sons, Inc, NY, NY, USA.

Perez, K.E., Clark, S.A., Lydeard, C., 2004. Freshwater Gastropod Identification Workshop: a Primer to Freshwater Gastropod Identification (from the work of Jack Burch, University of Michigan). University of Alabama, Tuscaloosa, AL, USA.

Peter, D.E.T., 2003. PAHs: an Ecotoxicological Perspective. John Wiley & Sons.

Sadinski, W.J., Levay, G., Wilson, M.C., Hoffman, J.R., Bodell, W.J., Anderson, S.L., 1995. Relationships around DNA adducts, micronuclei, and fitness parameters in *Xenopus laevis* exposed to benzo[a]pyrene. Aquatic Toxicology 32, 333–352.

Schoeny, R., Cody, T., Warshawsky, D., Radike, M., 1988. Metabolism of mutagenic polycyclic aromatic hydrocarbons by photosynthetic algal species. Mutation Research 197, 289–302.

Schuler, L.J., Landrum, P.F., Lydy, M.J., 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.

Scoggins, M., McClintock, N.L., Gosselink, L., Bryer, P.J., 2007. Occurrence of polycyclic aromatic hydrocarbons below coal-tar-sealed parking lots and effects on stream benthic macroinvertebrate communities. Journal of the North American Benthological Society 26, 694–707.

SealMaster Industries, Inc., 2002. Material Safety Data Sheet for SealMaster Coal Tar Ready-Mix, S1080. SealMaster Industries, Inc., Sandusky, Ohio. Prepared February 21, 2002.

StatSoft, Inc., 2007. STATISTICA (Data Analysis Software System). StatSoft, Inc. Version 8.0. www.statsoft.com.

Steward, A.R., Kanaswami, C., Chidambaram, S., Ziper, C., Ruthowski, J.P., Sikka, H.C., 1991. Disposition and metabolic fate of benzo(a)pyrene in the common carp. Aquatic Toxicology 20, 205–218.

Su, Y.H., Yang, X.Y., 2009. Interactions between selected PAHs and the microbial community in rhizosphere of a paddy soil. Science of the Total Environment 407, 1027–1034.

Thorp, J.H., Covich, A.P., 2001. Ecology and Classification of North American Freshwater Invertebrates, second ed. Academic Press, Inc, San Diego, CA, USA.

USEPA (United States Environmental Protection Agency), 1998. Guidance for Data Quality Assessment: Practical Methods for Data Analysis. EPA. QA/G-9. EPA/600/R-96/084.

USEPA (United States Environmental Protection Agency), 2002. Priority Pollutants in the Water Quality Standards Database, http://oaspub.epa.gov/wqsdatabase/wqsi_epa_criteria.rep_parameter. PAH constituents most recent EPA-promulgated update, December 2, 2002.

USEPA (United States 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, Washington, DC, USA.

Van Hattum, B., Curto Pons, M.J., Cid Montanes, J.F., 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., Mahler, B.J., Wilson, J.T., 2009. PAHs underfoot: contaminated dust from coal-tar sealcoated pavement is widespread in the United States. Environmental Science and Technology 43, 20–25.

Weinstein, J.E., 2001. Characterization of the acute toxicity of photoactivated fluoranthene to glochidia of the freshwater mussel, *Utterbackia imbecillis*. Environmental Toxicology and Chemistry 20, 412–419.

Westfall Jr., M.J., May, M.L., 1996. Dragonflies of North America. Scientific Publishers, Inc., Gainesville, Florida, USA.

Wiggins, G.B., 1996. Larvae of the North American Caddisfly Genera (Trichoptera), second ed. University of Toronto Press Inc, Toronto, Canada.