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Pervious and Impervious Urban Stormwater Runoff in a Rapidly Urbanizing Region: Occurrence of Fluoranthene and Pyrene

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Abstract Stormwater runoff in a rapidly urbanizing region was analyzed for organic contamination to compare impervious and pervious surfaces. Total petroleum hydrocarbons (TPH) ranged between 5 and 277 mg/L, with impervious surfaces showing, on average, greater TPH concentrations. Pyrene and fluoranthene were identified in all impervious stormwater samples. Sediments from receiving waters also contained pyrene and fluoranthene. Runoff samples had concentrations in the range of 11–191 μg/L. Sediment samples ranged from 2.3×10^1–1.3×10^4 μg/kg. Results from this study are useful for identifying major urban contaminants and understanding the role of pervious surfaces in filtering urban contaminants.

Keywords Stormwater · PAHs · Urban · Pervious

The identification and quantification of organic compounds is necessary in order to understand the dynamics of urban stormwater runoff and the types of pollutant loadings that can occur. Oil and grease (O&G) detected in runoff samples have been previously characterized as compounds ranging from n-C_{10} to n-C_{40} (Bomboi and Hernandez 1991; Eganhouse et al. 1981). Most hydrocarbons detected in stormwater runoff are derived from petroleum products and are nonpolar. Pervious surfaces are recognized as potential best management practices (BMPs) for reducing urban stormwater pollutant loads, but very little research has documented this (Rushton 2001).

Polycyclic aromatic hydrocarbons (PAHs) are frequently detected in river water (Li et al. 2010), urban stormwater runoff (Mahler et al. 2005) and sediments (Li et al. 2010; Xu et al. 2007). The main contributors of PAHs in stormwater runoff from impervious surfaces are asphalt, road-wear particles, atmospheric dust, exhausts, and motor oils and greases (Bomboi and Hernandez 1991). There are 16 of these compounds on the USEPA list of priority pollutants. Several PAHs with four to six fused rings are known carcinogens and/or mutagens. Fluoranthene and pyrene are know to occur in asphalt, gasoline, motor oils, and are ubiquitous products of incomplete combustion and are probable human carcinogens. They have been detected repeatedly in urban runoff samples and aquatic sediments (Boxall and Maltby 1997; Murakami et al. 2004). In fact, Boxall and Maltby (1997) demonstrated that pyrene and fluoranthene account for the majority of toxicant effects of stream sediment extracts. This paper further documents the prevalence of these two PAHs. However, the main purpose of this work was to compare urban stormwater runoff from both pervious and impervious surfaces and document the value of pervious surfaces for reducing pollutant loads in urban environments.

Materials and Methods

Grab samples were taken from pooled runoff areas during rainfall events, acidified (when required by method) to a pH of less than two and stored at 4°C for a maximum of 28 days. Impervious sample sites included asphalt and concrete lots and pervious sites were grassy areas or

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drainage ditches. Two 1-L samples were taken at each site during a particular rainfall event. One sample was used to run COD and the other sample was stored for potential TPH analysis and gas chromatography–mass spectrometry (GC–MS). Sediment samples were collected from stream and river locations receiving runoff.

Chemical oxygen demand was assessed within 48 h after sample acidification using Standard Method 5220D (Standard Methods 1995). EPA Method 1664 (USEPA 1999) with solid phase extraction (SPE) was used to analyzed for O&G and TPH. A 47 mm Environmental Express StepSaver® glass with filtration manifold (Fisher Scientific, Fair Lawn, NJ) was used for analysis of oil and grease. C-18 bonded silica extraction disks (3 M Empore, St. Paul, MN) were conditioned with n-hexane to improve recoveries. Disks were then allowed to dry by vacuum for 2 min. Methanol was added and allowed to soak the disk for 1 min. Before the sample was added, DI water ($pH < 2$) was poured on top of the methanol. The sample (1-L) was added on top of the methanol/water mixture. Full vacuum was maintained for 5 min after the extraction was finished. For elution, n-Hexane was allowed to pass through the disk and soak the disk for 2 min. The hexane was collected in a pre-weighed flask after passing through a 5.5 g sodium sulfate cartridge (Environmental Express, Mount Pleasant, SC) and completely evaporated under negative pressure at a constant temperature of 84°C. The collection flask was cooled to room temperature in a desiccator and weighed on an analytical balance to determine O&G mass.

Once the amount of oil and grease extracted was determined, the sample was redissolved in n-hexane and stirred. Silica gel was added to the solution to adsorb the polar oil and grease components. The amount of silica gel required for complete adsorption was calculated according to EPA Method 1664 (USEPA 1999). The remaining TPH component was separated from the silica gel matrix using gravity filtration with Whatman® 42 filter paper, pre-wetted with n-hexane. The n-hexane was evaporated from the flask as described above. Once evaporation was complete, the flask was cooled in a desiccator and weighed. Samples with measurable TPH values were resuspended in 5–10 mL of n-hexane.

Sediment samples were extracted by way of standard Soxhlet extraction using 5 g of sediment in Whatman cellulose extraction thimbles (22 mm × 80 mm—Sigma–Aldrich). Acetone and hexane (1:1) were used as the extracting solvents. Anhydrous sodium sulfate was also used to remove moisture. The samples were extracted for 16–24 h at 6 cycles per hour and concentrated down to 10 mL.

Runoff and sediment extracts were injected splitless into a Hewlett–Packard 6890 gas chromatograph (GC) equipped with an HP 5973 mass spectrometer (MS). The injector temperature was 280°C and the detector was set at 230°C. The helium flow was maintained at 0.8 mL/min. The HP-5MS capillary column (0.25 mm i.d., 0.25 μm film thickness) was programmed at 35°C and maintained for 2 min, increased by 10°C/min to 265°C and held for 10 min. The total run time was 35 min. Fluoranthene and pyrene standards were purchased from Sigma–Aldrich (St. Louis, MO).

Adsorption isotherm studies with the PAHs were batch experiments using 1.0 g of sediment which was allowed to equilibrate at 19°C for 48 h at 22 rpm on a mechanical shaker. The aqueous phase was extracted with hexane, filtered, and analyzed by GC–MS.

Results and Discussion

The role of COD analysis was as a screening tool to find runoff samples with high organic loadings for analysis with EPA Method 1664 and GC–MS. The COD results for the runoff samples ranged from the method detection limit (MDL) of 30 mg O_2/L up to 643 mg O_2/L. Although some samples seem exceedingly high (Table 1), it is important to mention that the samples were collected from pooled water (e.g., drainage ditches, parking lots), many with visible contamination. Since oxygen demanding substances in runoff are mostly organic, runoff sampling sites with elevated COD values (>35 mg O_2/L) were also analyzed for oil and grease and TPH. The average percent recovery and standard deviation for a TPH standard (hexadecane) was 92.6% ± 7.2%. This agrees well with literature values. Raisglid et al. (1994) had percent recoveries for hexadecane ranging from 88 to 104% with an average of 94% and a standard deviation of 5%. Schrynemeeckers et al. (1992) recovered 70–90% of fuel oil #2 standards with SPE.

Table 1 shows the results for O&G and TPH along with the corresponding COD values. Sample 1 and 2 refer to two distinct samples taken at the same site. Sample 1 was used for COD analysis and other water quality tests. Sample 2 was used for O&G and TPH measurements. Since they are distinct samples, no attempt was made to directly compare the two results. The concentrations of O&G in the runoff samples ranged from 6 to 840 mg/L. The concentrations of TPH found in the runoff samples ranged from 5 to 277 mg/L. The values for the percentage of the O&G that was TPH ranged from a few percent up into the ninety-percent range (Fig. 1). Each bar pair represents one sample. The samples are arranged in order of Table 1 starting from the top. The TPH amount is a portion of the total O&G reported. Examining Fig. 1 it can be seen that there is no visible trend. The amount of O&G present is clearly not a good predictor of the amount of TPH. Samples with high O&G numbers and low TPH values will contain large amounts of more polar stormwater constituents such as hydroxy acids. Oil and grease numbers

Table 1 Oil and grease and total petroleum hydrocarbons in runoff

Sample 1[a]	Sample 2[a]		GPS Location[b]
COD (mg O_2/L)	O&G (mg/L)	TPH (mg/L)	
Impervious surfaces			
197	405	49	50′ 43.8″N 21′ 50.4″W
47	54	22	50′ 43.8″N 21′ 50.4″W
427	538	277	50′ 53.7″N 22′ 26.1″W
298	13	12	50′ 3.5″N 22′ 28.2″W
643	840	27	51′ 17.3″N 22′ 1.5″W
147	309	119	49′ 54.3″N 22′ 36.5″W
89	20	17	50′ 3.5″N 22′ 28.2″W
205	27	22	50′ 57.9″N 21′ 31.6″W
143	45	18	49′ 55.3″N 22′ 30.1″W
133	27	17	50′ 42.8″N 21′ 54.7″W
367	93	50	50′ 53.7″N 22′ 26.1″W
87	38	11	50′ 3.5″N 22′ 28.2″W
Pervious surfaces			
143	6	5	50′ 4.7″N 22′ 37.1″W
205	61	0	49′ 56.1″N 22′ 25.3″W
180	31	0	50′ 50.9″N 22′ 22.1″W
89	70	31	50′ 53.9″N 22′ 26.8″W
39	56	30	49′ 56.1″N 22′ 25.3″W
137	18	17	51′ 6.2″N 22′ 46.3″W
120	13	0	50′ 53.9″N 22′ 26.8″W

[a] Samples 1 and 2 refer to two distinct samples taken at the same sampling site. Sample 1 was used for COD (chemical oxygen demand) and other water quality measurements and sample 2 was for O&G (oil and grease) and TPH (total petroleum hydrocarbons)

[b] All GPS locations are 35°N 86°W with elevations between 604 and 635 ft

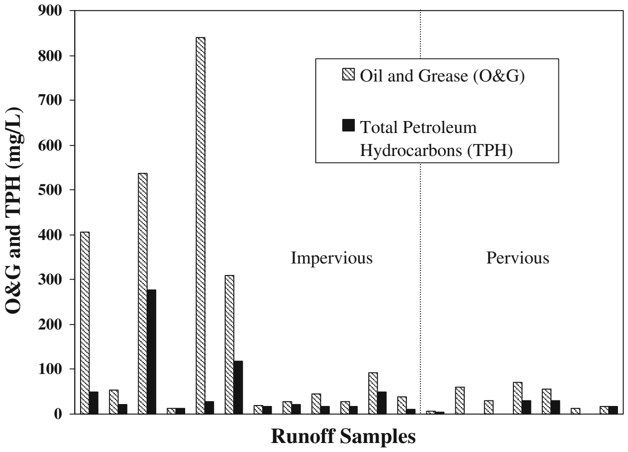

Fig. 1 Oil and grease (O&G) and total petroleum hydrocarbons (TPH) in runoff samples from both pervious and impervious surfaces

greater than corresponding COD values are difficult to explain and can in most cases be attributed to salt carry over from the drying step. However, TPH numbers would not be affected by this due to the subsequent separation step.

Many prior studies on O&G in urban runoff yielded values less than 25 mg/L (Eganhouse et al. 1981; Lopes et al. 2000). Considering the numbers recorded here, there may be cause for concern when one considers the potential for oxygen depletion after these organics enter surface and ground waters. In fact, these waters feed springs with known occurrences of oxygen depletion (James et al. 2006).

Runoff collected directly from impervious surfaces generally had the highest levels of O&G and TPH (Table 1; Fig. 1). The average concentration of O&G collected directly from impervious surfaces was 250 mg/L, and the average concentration of TPH was 62.6 mg/L. The average concentration of O&G collected from pervious surfaces was 36.3 mg/L, and the average concentration of TPH was 12.0 mg/L. This suggests that the O&G and TPH components in the runoff are more concentrated during the first flush of the impervious surfaces. Runoff entering the drainage ditches (pervious surfaces) is diluted by the receiving waters and will lose some of its organic constituents through interactions with soil and clay particles. These results lend credence to the idea that the use of pervious pavement materials and catch basins will enhance the filtering and cleansing of runoff waters, and also reduce their total volumes.

GC–MS analysis of stormwater runoff from impervious surfaces revealed the ubiquitous nature of fluoranthene and pyrene. All samples analyzed contained these two PAHs.

The concentrations of these contaminants in runoff ranged between 11 and 191 µg/L for fluoranthene, and between 33 and 140 µg/L for pyrene. In all cases the concentration of fluoranthene was greater than pyrene. These concentrations can be considered toxic based on LC50 values (Boxall and Maltby 1997), but dilution by receiving waters may eliminate this effect. Pervious surfaces showed only sporadic detection at very low concentrations for these two PAHs.

Sediment and water samples were collected from rivers and creeks receiving the impervious runoff and analyzed by GC–MS. Fluoranthene and pyrene would be expected to collect in the sediments due to their high distribution coefficients (log K_{oc}). This may explain the absence of fluoranthene and pyrene in runoff from pervious surfaces and the absence of any detectable levels in the receiving waters. Adsorption isotherm studies on the sediments (6.7% organic carbon) yielded log K_{oc} values of 4.93 and 4.98 for fluoranthene and pyrene respectively. These values agree well with the literature (Olmstead and LeBlanc 2005; Chiou et al. 1998). Once again, every sediment sample contained fluoranthene and pyrene. Sediment samples ranged from 23–1.3 × 10^4 µg/kg for fluoranthene, and between 44–1.1 × 10^4 µg/kg for pyrene. Although other PAHs were identified (e.g., phenanthrene, benzo [k] fluoranthene, triphenylene) fluoranthene and pyrene were found at much higher concentrations and they were the only ones found in all sediment samples analyzed. These levels are comparable to those found by Boxall and Maltby (1997). Although extracts could be potentially toxic, much of the sediment bound PAHs may not be bioavailable.

One can look at the ratio of fluoranthene to pyrene as an indication of the origin of the PAHs (Li et al. 2010). Pyrene concentrations are greater than fluoranthene concentrations in fossil fuels but tend to be reversed for combustion products. Figure 2 shows our results. Sampling site 1 is a composite of impervious stormwater runoff; all other sites represent sediment samples. In all cases except two, the fluoranthene to pyrene ratio is greater than one. This implies that the origin is from pyrolytic contamination rather than petroleum pollution. However, the ratios are very close to one and leaching of asphalt road surfaces may still be a major contributor (Mahler et al. 2005).

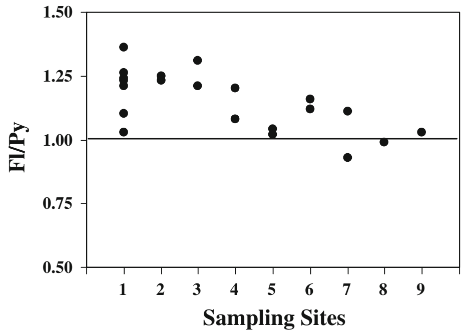

Fig. 2 Ratios of fluoranthene/pyrene (Fl/Py) in sediment and runoff samples

Overall, this study demonstrated that fluoranthene and pyrene were ubiquitous in impervious stormwater runoff and receiving sediments and probably originated mainly from combustion processes and road wear. Pervious surfaces served to reduce the pollutant loadings by adsorbing organics and filtering them out. However, due to their large distribution coefficients, fluoranthene and pyrene were shown to collect in the sediments at levels that may cause toxicity. This could have long term consequences on aquatic systems since these two PAHs account for the majority of toxicant effects of stream sediment extracts (Boxall and Maltby 1997).

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