Occurrence and phase distribution of polycyclic aromatic hydrocarbons in urban storm-water runoff

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Abstract
A total of 42 storm-water overland-flow samples were collected from four sampling sites (a highway off-ramp, a gas station, and a low- and high-traffic-volume parking lot). For each sample, the suspended-sediment and water phases were separated and analyzed for 16 polycyclic aromatic hydrocarbons (PAHs). The gas station site produced the highest total PAH loading (2.24 g/yr/m²), followed by the high-traffic-volume parking lot (5.56 X 10⁻² g/yr/m²), the highway off-ramp (5.20 X 10⁻² g/yr/m²), and the low-traffic-volume parking lot (3.23 X 10⁻² g/yr/m²). In several samples, one or more PAHs were detected in the aqueous phase at concentrations above its aqueous solubility. This result suggests the presence of colloidal-size particles capable of sorbing PAHs to an appreciable extent, or the presence of an oil-and-grease microemulsion. Based on rainfall and PAH data from seven discrete storm events, PAH concentrations were usually highest during the "first flush" of storm-water runoff and tapered off rapidly as time progressed. It is apparent from these analyses that storm-water runoff from parking lots, highways, and gas stations is a significant source of PAHs to the environment. Because some of the PAHs are carcinogens or suspected carcinogens, best management practices such as oil/grit separators should be implemented at "hot spots" in urban areas to mitigate potential PAH pollution.

Keywords: Polycyclic aromatic hydrocarbon; storm-water runoff; non-point source pollution; best management practice

Introduction
Storm-water runoff from urban areas is a potential non-point source of pollution to natural receiving waters. Polycyclic aromatic hydrocarbons (PAHs) are a class of anthropogenic organic compounds that have been detected in a variety of natural environments, including the sediment and biota of the Baltic Sea (Falandysz et al. 1996), sediments and waters of the Chesapeake and San Francisco Bays (Liu and Dickhut 1997; Maruya et al. 1996), and in urban, suburban, and rural terrestrial vegetation (Wagrowski and Hites 1997). Contamination of natural environmental systems by PAHs is cause for concern, as many of the high-molecular weight PAHs are known or suspected carcinogens and many of the low-molecular weights PAHs are acutely toxic to aquatic organisms (Smith et al. 1987).

We hypothesize that storm-water runoff from urban land may be an important non-point source of PAHs to the environment. The objectives of this study (Yu et al. 1997) were to quantify the concentration of PAHs in water and suspended sediment samples in storm-water runoff from four types of urban land: a highway off-ramp, a gas station, and a low- and high-traffic-volume parking lot, and relate these concentrations to measurable characteristics of the storm and land-use type.

Methods
Description of field sampling sites
All four sampling sites are located in Virginia, USA. The first sampling site is an exit ramp from Interstate Highway 264 onto alternate Route 460, near Bowers Hill in the town of Chesapeake. Storm-water runoff from this site came from part of the highway and the exit ramp, totaling an estimated area of 2,800 m². Runoff from the road and exit ramp is
collected in a 1-m wide concrete channel along the roadside. Runoff samples were collected upstream of a rectangular weir placed where the runoff entered a mitigated wetland. The average daily traffic rate is 7,500 and 22,000 vehicles per day for the exit ramp and highway, respectively. The second sampling site is a gasoline station located on Route 29 in Albemarle County. The drainage area is approximately 1,050 m². Runoff from the site is collected and combined with runoff from Route 29 and empties into an infiltration trench and a level spreader. The third site studied was a low-traffic volume parking lot located in the town of Brooke. The lot has an area of 14,600 m² and contains approximately 300 parking spaces. About 60% of the spaces are used during weekdays. Runoff is routed from several drop inlets around the parking lot into a drop inlet and pipe that empties into an artificial wetland. Samples were collected at the bottom of this drop inlet about 0.3 m into the exit pipe. The fourth sampling site was a high volume parking lot located at University Hall on the University of Virginia grounds. The lot is primarily used for commuter parking and is approximately 84% full during weekdays. The lot is also used for athletic event parking on evenings and weekends. There are three drainage areas within the parking area. Samples were collected only for the upper drainage area, which is approximately 17,000 m², contains about 530 parking spaces, and has a major and a minor bus stop. The area drains into one of four drop inlets which combine into a 0.67-m concrete pipe. A rectangular sharp-crested weir was constructed at the end of the pipe. After discharging from the weir, the runoff empties onto riprap and eventually joins runoff from another drainage area of the parking lot in a dry detention pond.

Field sample collection
Automated samplers (Sigma 900MAX) were used to collect storm-water runoff samples from the highway site and the Brooke parking lot site at designated sampling intervals. The automated samplers are equipped with Teflon tubing and 350-mL glass sample bottles. The automated samplers also record rain and flow data at 1-min intervals beginning with the start of rainfall. Storm events on September 9, 1996 and September 28, 1996 were sampled at the highway site and storm events on November 11, 1996 and November 26, 1996 were sampled at the Brooke parking lot site. Grab samples were collected in 1-L amber glass bottles at the gasoline station site and the University Hall parking lot. A storm event on November 16, 1996 was sampled at the gasoline station site and storm events on October 18, 1996 and January 24, 1997 were sampled for the University Hall parking lot site. Rain and flow data at the University Hall parking lot were collected manually every 15 min using a rain gauge and weir. No rain or flow data were collected at the gasoline station. Samples were only collected during the “first flush” of the storm event, as previous research has suggested that the highest concentrations of PAHs are present in this runoff (Hoffman et al. 1984). A minimum of 72 hr of dry conditions was required prior to collecting runoff samples for a given storm event.

Trip blanks (sample bottles filled with deionized, organic-free water) were carried to each field site being sampled. The trip blanks were returned to the laboratory for analysis for PAHs to insure that the sample bottles or sample handling did not contaminate the sample with PAHs. For all the reported sampling events, the trip blanks did not have detectable levels of PAHs. Based on preliminary laboratory experiments, it was determined that loss of PAHs from sample bottles in the automated sampler by volatilization were less than 6% over a 24-hr period and hence assumed insignificant.

Sample analyses
Concentrations of PAHs associated with the aqueous phase and suspended-solid phase for each sample were quantified in the laboratory. The target analytes were naphthalene, ace-
naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benz[b]fluoranthene, benz[k]fluoranthene, benz[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, and benzo[g,h,i]perylene.

Each sample in its entirety was passed through a 0.45 µm glass-fiber filter of known mass. To insure that no suspended solids remained in the sample bottles, the 1 L and 350 mL sample bottles were then rinsed with 30 or 15 mL (respectively) of deionized, organic-free water and this rinse water was again filtered. The filters were air-dried at 20°C for 4 hr, then placed in a desiccator and dried to a constant weight to determine the suspended solids concentration of the sample. The desiccator drying time was less than 1 hr for all samples. The filters were then extracted with 5 mL of methylene chloride at 45°C for 24 hr. The sample was filtered and the filter and sample vial were rinsed twice with 5 mL of methylene chloride. The filtrate was then concentrated prior to gas chromatographic analysis.

Aqueous samples that were passed through the filter were analyzed by Standard Method 6640 (Eaton et al., 1995). This method employs a methylene chloride extraction, concentration, and clean-up of the extract using silica gel. The extract is analyzed by gas chromatography with a flame-ionization detector. For some field samples, an emulsion formed in the separatory funnel. In most cases, the emulsion dissipated or concentrated at the methylene chloride/water interface. If the emulsion did not dissipate or concentrate at the liquid–liquid interface, the methylene chloride and the emulsion were separated by centrifugation at 1,600g for 2 min. The concentration procedure described in Standard Method 6640 was used for both the water and suspended solid extracts.

The detection limit for each PAH in water was determined to be 2 µg/L. The gas chromatograph was calibrated with both internal and external standards. The external standards used were 1,4-dichlorobenzene-d4, naphthalene-d8, acenaphthene-d10, and chrysene-d12. A subset of the samples (including a sample with PAH concentrations above the reported solubility limit) was also analyzed by gas chromatography/mass spectrometry by the National Laboratory of the U.S. Geological Survey (USGS). The reported PAH concentrations were in excellent agreement with the results from the University of Virginia laboratory, validating the laboratory procedures and providing positive confirmation of the identity of the PAHs in the storm-water runoff samples. Total PAH concentrations reported in this paper are the sum of all individual target analytes in both the aqueous (filtered) sample and suspended solid fraction. The oil and grease concentration was determined by Aqua Air Laboratories (Charlottesville, VA) for samples collected at the University Hall parking lot on January 24, 1997 and from the gasoline station on November 8, 1996.

Results and Discussion

Individual PAHs

Individual PAHs were detected 292 times in either the aqueous or solid phase in storm-water runoff samples from all the field sampling sites. Of 42 samples tested, acenaphthene (32 detections) and naphthalene (30 detections) were found most frequently. Indeno[1,2,3-cd]pyrene (6 detections), dibenzo[a,h]anthracene (9 detections) and benzo[g,h,i]perylene (9 detections) were found least frequently. For a given PAH, the ratio of its concentration on the suspended solids to its concentration in the aqueous phase was not consistent from sample to sample. For example, in some cases, a given PAH was detected in the aqueous phase, but not detected in the solid phase. In other cases, the PAH was detected in the solid phase in a runoff sample, but not in the aqueous phase. For many cases, however, if a PAH was detected in one phase, it was also detected in the other phase. The relatively poor correlation between solid- and aqueous-phase PAH concentrations likely is attributable to the heterogeneity of suspended sediment samples from site to site and/or nonequilibrium between the aqueous- and solid-phase PAH concentrations. These results suggest the
importance of quantifying the total PAH concentration in a storm-water runoff sample. The
analysis of only one phase may produce poor estimates of PAH loadings from urban storm-
water runoff.

There were 42 detections of PAHs in the aqueous phase at concentrations above the sol-
ubility limit of the PAH. However, there was no identifiable problem with regard to the
quality control and quality assurance protocol for any of these samples. Furthermore, one
of these samples fell in the subset of samples that were also analyzed by the USGS National
Laboratory. For this sample, collected on November 20, 1997 from the University Hall
parking lot site, the measured phenanthrene concentration was 1,420 µg/L, which is higher
than its aqueous solubility (1,200 µg/L). This result was confirmed by the USGS laborato-
ry, which quantified a phenanthrene concentration of 1,454 µg/L.

Several factors may have contributed to the above-solubility concentrations. First, there
may have been particulate, colloidal-size particles smaller than 0.45 µm in diameter that
passed through the filter used to separate aqueous and suspended solid phases. Colloidal
particles can sorb nonionic organic pollutants and enhance their apparent solubility in
water and facilitate pollutant transport in environmental systems (Choi and Corapcioglu
1997; Grolimund et al. 1996; Roy and Dzombak 1997). Second, oil and grease present in
the aqueous phase may have enhanced the PAH solubility. The oil and grease, if immiscible
with water, can form a separate, nonpolar phase capable of effectively solubilizing PAHs.
Two samples collected during this study were analyzed for oil and grease. The oil and
grease concentrations were 30 and 17 mg/L. Given the relatively high values, it is likely
that the oil and grease present in the sample affected the apparent solubility. If surface-
active agents (surfactants) are present in the runoff, they can facilitate the formation of oil
and grease microemulsions. These microemulsions can significantly increase the solubility
of PAHs (Soma and Papadopoulos 1997). By themselves, surfactants can form micelles
and enhance the apparent solubility of organic pollutants (Kile and Chiou 1989). Surfactants are components of many commercial gasoline formulations. Some components
of commercial gasoline formulations, such as MTBE or ethanol, are miscible with water.
However, these cosolvents can also increase the apparent solubility of organic pollutants in
water. For example, previous research has shown that the solubility of naphthalene in water
can be significantly increased by cosolvents such as methanol and ethanol (Li et al. 1996).
Although the precise mechanism causing the high pollutant concentrations is not known,
the observations presented here indicate that the operationally defined “aqueous phase” of
storm-water runoff from urban land can contain PAH loadings in excess of reported values
of aqueous solubility.

![Figure 1](https://iwaponline.com/wst/article-pdf/42/3-4/383/428389/383.pdf)

Figure 1. Total polycyclic aromatic hydrocarbon (PAH) concentration and total rain as a function of sample
collection time for the University Hall parking lot site on January 24, 1997
Total PAH concentrations
Total PAH concentrations are defined here as the sum of the masses of all detected PAHs per unit volume of sample and include PAHs in both the aqueous and suspended solid phases. Total PAH concentrations from discrete storm-water runoff samples ranged from non-detectable to 3,500 µg/L with a mean of 44.5 µg/L. Figure 1 presents data collected from a typical storm event sampled as part of this investigation. As evident from the results in Figure 1, total PAH concentrations were highest during the early part of the storm event and decreased over time. During the early precipitation and runoff generation, the largest amounts of PAHs are transported from the field site. As such, it may be possible to only treat storm-water runoff generated in the early part of a storm event and allow later flows to bypass treatment.

The Simple Method was used to quantify PAH loadings from each of the field sites. The Simple Method employs the following relation (Northern Virginia Planning District Commission, 1992):

\[ L = P \times P_j \times R_v \times C \times A \times 0.227 \]

Where:
- \( L \) = total pollutant load, lbs
- \( P \) = total rainfall depth (inches) over time interval
- \( P_j \) = factor that corrects \( P \) for storms that produce no runoff (0.9 for this study)
- \( R_v \) = runoff coefficient
- \( C \) = flow-weighted mean concentration of pollutant (mg/L)
- \( A \) = area (acres)

Average rainfall data were collected for each field site from the Virginia State Climatology Office. Flow-weighted PAH concentrations were determined from the field data. These data were averaged for each site to give the mean flow-weighted total PAH concentrations. Because flow data was not collected for the gas station site, the average of two total PAH concentrations was used. Runoff coefficients were taken from the Northern Virginia BMP Handbook (1992). Values of 0.85, 0.90, 0.90, and 0.95 were used for the highway, the Brooke parking lot, the University Hall parking lot, and the gasoline station, respectively.

Results of these analyses show that the highest PAH loading originated from the gasoline station site (2.24 g/yr/m²). Loadings from the remaining three sites are as follows: University Hall parking lot site (5.56 ×10⁻² g/yr/m²), the highway exit-ramp site (5.2 ×10⁻² g/yr/m²), and the Brooke parking lot site (3.23 ×10⁻² g/yr/m²). These values are only approximate, as they rely on several assumptions. First, our PAH data was collected during the first flush of the storm event. It is unlikely that the relatively high PAH concentrations measured during this first flush are representative of PAH concentrations in runoff at later times. Second, the values from the gasoline station do not necessarily represent flow-weighted mean concentrations, as no flow data were collected during this sampling event. Nevertheless, it is apparent that PAHs are routinely present in significant quantities in storm-water runoff from urban land uses. Best management practices such as oil/grit separators should be implemented at “hot spots” to mitigate potential PAH pollution.

Conclusions
PAHs were routinely detected in storm-water runoff from a highway exit ramp, two parking lots, and a gasoline station in Virginia, USA. The most frequently detected PAH was naphthalene, followed by acenaphthene. There was poor correlation between the apparent aqueous phase concentrations of PAHs and the concentration of PAHs sorbed to suspended solids in the runoff. In a number of samples, PAHs were detected at apparent aqueous con-
centrations greater than solubility, and this observation is likely explained by solubility enhancing agents (e.g., surfactants, colloidal particles) present in the aqueous phase after filtration with a 0.45 µm filter. Total PAH concentrations were highest during the early periods of precipitation and runoff (e.g. during the first flush) and typically decreased at later times. Calculated PAH loadings from each site showed that the gas station produced the highest total PAH loading (2.24 g/yr/m²), followed by the high-traffic-volume parking lot (5.56 X 10⁻² g/yr/m²), the highway exit-ramp (5.2 X 10⁻² g/yr/m²), and the low-traffic-volume parking lot (3.23 X 10⁻² g/yr/m²).

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References