

This manuscript has been prepared for  
the International Association on  
Water Pollution Research and Control Conference  
and the contents are subject to change.

This copy is to provide information  
prior to publication.

PAH TRANSPORT BY URBAN RUNOFF  
FROM AN INDUSTRIAL CITY

by

J. Marsalek

Rivers Research Branch  
National Water Research Institute  
Canada Centre for Inland Waters  
Burlington, Ontario, L7R 4A6

November 1989  
NWRI Contribution #89-169

## ABSTRACT

Urban runoff from an industrial city was found to produce annual PAH loadings comparable to those from point sources. More than 95% of these loadings were transported by sediments in runoff. Variations of PAH levels in runoff were explained by variations of sediment concentrations in runoff and by variations in PAH levels in sediment. The annual load of PAHs in runoff from the study area was estimated at 75 kg per year and about one third of this quantity was contributed by atmospheric deposition. A great degree of similarity among PAH profiles in urban runoff, river sediment and caged mussels was found and confirmed the PAH pathways from urban anthropogenic sources via runoff to the receiving waters.

## RÉSUMÉ

On a trouvé que le ruissellement urbain d'une ville industrielle produisait des charges annuelles en HAP comparables à celles de sources ponctuelles. Plus de 95 % de ces charges étaient transportées par des sédiments dans le ruissellement. Les variations de concentration en HAP dans le ruissellement ont été expliquées par des variations de concentration de sédiments dans le ruissellement et par des variations de concentration de HAP dans les sédiments. On a estimé à 75 kg par an la charge annuelle des HAP dans le ruissellement de la zone étudiée. Environ un tiers de cette charge provenait du dépôt atmosphérique. On a trouvé beaucoup de ressemblance entre le profil des HAP présents dans le ruissellement urbain, les sédiments de la rivière et des moules en cage, ce qui confirme le trajet emprunté par les HAP, des sources anthropiques urbaines aux eaux réceptrices, en passant par le ruissellement.

## MANAGEMENT PERSPECTIVE

In preparation of remedial action plans for the areas of concern in the Great Lakes Basin, the magnitudes of pollutant contributions from various sources need to be assessed. In one of such areas, the St. Mary's River in Sault Ste. Marie, concerns were expressed about the levels of PAHs in river sediment and biota. Consequently, contributions of polycyclic aromatic hydrocarbons, (PAHs) from various point and nonpoint sources were assessed and urban runoff was found to contribute annual PAH loadings comparable to those from point sources. Such a finding confirms the importance of urban nonpoint sources in transport of pollutants of anthropogenic origin to the receiving waters and the need to consider both point as well as nonpoint pollution sources in environmental planning and protection.

## PERSPECTIVE-GESTION

Pour établir des plans d'assainissement pour les zones critiques du bassin des Grands Lacs, il est nécessaire d'évaluer dans quelle mesure les polluants des diverses sources contribuent au problème. Dans l'une de ces zones, la rivière St. Marys à Sault Ste. Marie, on s'inquiétait de la concentration des HAP dans les sédiments et le biotope de la rivière. Nous avons donc évalué les apports d'hydrocarbures aromatiques polycycliques (HAP) de diverses sources, ponctuelles et non ponctuelles, et nous avons trouvé que le ruissellement urbain produit des charges annuelles en HAP comparables à celles des sources ponctuelles. Ce résultat confirme le rôle important des sources urbaines non ponctuelles dans le transport des polluants des sources anthropiques aux eaux réceptrices, et il montre la nécessité de prendre en considération les sources de pollution ponctuelles et les sources non ponctuelles dans la planification et la protection environnementales.

# PAH TRANSPORT BY URBAN RUNOFF FROM AN INDUSTRIAL CITY

J. Marsalek

National Water Research Institute  
Burlington, Ontario, Canada

**ABSTRACT:** Urban sediments account for more than 95% of polycyclic aromatic hydrocarbons (PAHs) in urban runoff. Variations in sediment concentrations and in PAH levels in sediment cause even greater variations in PAH levels in urban runoff. Using the lognormal distribution, the annual PAH load in runoff from the study area was estimated at 75 kg yr<sup>-1</sup>.

**KEYWORDS:** Atmospheric deposition of PAHs; loadings of PAHs; polycyclic aromatic hydrocarbons (PAHs); urban runoff; urban sediment.

## INTRODUCTION

Since 1973, the Great Lakes Water Quality Board has identified the areas of concern in the Great Lakes Basin where various water quality criteria or guidelines have been exceeded and remedial measures are needed to restore all beneficial water uses. In preparation of remedial action plans for these areas, the magnitudes of pollutant contributions from point as well as nonpoint sources need to be assessed. Preliminary load assessments were recently completed in three areas of concern for 16 critical pollutants (Marsalek and Ng, 1989). In one of these cases, the St. Marys River at Sault Ste. Marie (Ontario), the concerns about the polycyclic aromatic hydrocarbon (PAH) levels in the river sediment and biota indicated the need to improve the preliminary assessment and, consequently, a follow up study of PAHs in runoff from the adjacent urban area was conducted.

PAHs are widely distributed in the environment, because of their abundant anthropogenic and natural sources. The anthropogenic sources, which are predominant, include heating, power generation, industrial processes, incineration and open fire burning, and vehicular transportation (Seifert and Lahmann, 1980). Such sources are highly concentrated in urban areas where the emitted PAHs deposit on urban surfaces and are washed off by urban runoff during wet weather and transported into the receiving waters (Ellis et al., 1985; Hoffman et al., 1984; Yamane et al., 1989). Thus, urban runoff functions as an effective means of transport of PAHs from urban catchments into the receiving waters.

To complement the earlier studies of point sources of PAHs found in the St. Marys River, investigations of PAHs in urban runoff were conducted in three phases - an initial exploratory study of PAHs in runoff, a study of atmospheric PAH deposition in the study area and, finally, a study of PAHs in urban runoff and sediment. The principal results of all three phases are summarized in the paper that follows.

## STUDY AREA

The City of Sault Ste. Marie, located along the St. Marys River, is an industrial urban centre with population of 83,000 inhabitants. The main sources of pollution of the St. Marys River include municipal and industrial

effluents, and urban stormwater discharged from storm sewers. The principal industrial operations include a steel plant and a pulp and paper mill.

A comparative analysis of pollutant sources in the study area was conducted for 16 pollutants of concern and, for eight of them, urban runoff was the main or major source which significantly contributed to the total loads discharged to the river. These eight pollutants included cadmium, cobalt, copper, lead, nickel, hexachlorobenzene (HCB), PAHs, and polychlorinated biphenyls (PCBs). Considering the low magnitudes of their loads, the ambient water quality and the dilution of runoff in the river, the screening estimates of runoff loads of the above eight pollutants were found adequate and of minor concern for all pollutants except PAHs. For PAHs, it was desirable to improve the initial assessment of the load in runoff from the study area.

#### METHODS

The selection of the PAH substances studied was based on the toxicity of individual substances reported in the literature and on the available analytical support. Although some runoff and sediment samples were analyzed for up to 21 substances, only 14 substances were routinely studied and, consequently, the presentation and discussion of results is restricted to these 14 substances listed in Table 1.

Table 1. PAH Substances Studied

Substance	Adopted Abbreviation	Detection Limits		EPA Priority Pollutant
		Water (ug L <sup>-1</sup> )	Sediment (mg kg <sup>-1</sup> )	
2-Methylnaphthalene	2-MNA	0.050	0.05	
1-Methylnaphthalene	1-MNA	0.050	0.05	
2-Chloronaphthalene	2-CLN	0.050	0.05	x
Acenaphthylene	ANY	0.050	0.05	x
Acenaphthalene	ANE	0.050	0.05	x
Fluorene	F	0.050	0.05	x
Phenanthrene	PA	0.050	0.05	x
Fluoranthene	FL	0.050	0.05	x <sup>1</sup>
Pyrene	P	0.050	0.05	x
Benzo(b)fluoranthene	BbF	0.100	0.10	x <sup>1</sup>
Benzo(k)fluoranthene	BkF	0.100	0.10	x <sup>1</sup>
Benzo(a)pyrene	BaP	0.100	0.10	x <sup>1</sup>
Indeno(1,2,3-cd)pyrene	IP	0.100	0.10	x <sup>1</sup>
Benzo(ghi)perylene	BghiP	0.100	0.10	x <sup>1</sup>

<sup>1</sup>Included in the World Health Organization (WHO) group of six PAHs

Flow-proportional composite event samples of urban runoff were routinely collected at eight sites which were selected from the geographical distribution of primary PAH sources. Recognizing that PAH occur in urban runoff well below the acute toxicity levels and, consequently, that the main interest should focus on chronic effects and long-term loads, the use of event sampling was found highly advantageous. The flow-proportional event sampling is well suited for estimates of long-term loads, which can be estimated from the distribution of event loads, and leads to large savings on analytical costs.

PAH depositions were studied by surveying PAH accumulations in the urban snowpack. For this purpose, snow core samples were collected at 20 sampling

stations in a grid centred around the steel plant and the urban area. The samples were collected by means of a stainless steel core sampler (Boom and Marsalek, 1988). Sediments were routinely sampled at five sites and occasionally surveyed at eight additional sites. PAH analyses were performed on unprocessed samples as well as on various sediment fractions.

For extraction of water and sediment samples, the methylene chloride extraction method and ultrasonic extraction (the Soniffer method) were used, respectively. The dehydrated extracts were concentrated and further cleaned by gel permeation chromatography, in order to remove co-extracted interfering compounds. The final extract was analyzed for PAHs using one-column gas chromatography and a flame ionization detector (Water Quality Branch, 1981).

## RESULTS AND DISCUSSION

In the initial phase, runoff samples were collected at three sites with different land use - residential, industrial, and commercial, respectively. The main objective of this experimental design was to investigate the land use effects on PAH concentrations in runoff. Although in some cases the quality of runoff is related to land use, no such relationship was detected for PAHs in the study area. Similar findings were reported in the literature (Hoffman et al., 1984) and can be explained by the widespread presence of PAH sources, unrelated to urban land use categories, and by the transport of airborne PAHs across land use boundaries. To evaluate the significance of air transport of PAHs in the study area, their atmospheric deposition was studied by surveying PAH accumulations in the urban snowpack.

Accumulations of conservative chemicals in the snowpack can be used to evaluate atmospheric deposition of such chemicals. In the study area, PAH accumulations in the snowpack exhibited large variations described by unit loadings ranging from about  $100 \text{ ug m}^{-2}$  to  $1,600 \text{ ug m}^{-2}$ . The corresponding isoload contours were centred over the urban area, with the highest concentrations occurring just west of the steel plant. The displacement of contours in the westerly direction was explained by the easterly winds prevailing during the period of accumulation. From areal loadings, a city-wide mean deposition rate of the 14 PAHs studied was computed as  $25 \text{ ug m}^{-2} \text{ week}^{-1}$ . About two thirds of this rate were contributed by fluoranthene, phenanthrene, and pyrene (Boom and Marsalek, 1988).

Although the above deposition rates correspond to the winter period, high PAH depositions in industrial cities do not exhibit strong seasonal effects (Seifert and Lahmann, 1980) and, consequently, these rates may be extrapolated over the whole year, recognizing that the resulting estimate will be somewhat conservative. Such an extrapolation resulted in the estimate of the annual PAH deposition in the study area of about  $85 \text{ kg yr}^{-1}$ . A large part of this load (around 70%) will deposit on pervious urban surfaces and may become immobilized. Consequently, the deposited amount available for direct transport by urban runoff is probably just about  $25 \text{ kg yr}^{-1}$ .

In the next phase of the study, the PAH loads in urban runoff were estimated from characteristic PAH concentrations in runoff and runoff volumes. The characteristic PAH concentrations were established by sampling runoff and urban sediment at a number of sites.

Analyses of unfiltered runoff samples confirmed that PAHs are predominantly transported by the residue in samples. Sample filtration, using glass fiber filters with pore openings of  $0.45 \text{ um}$ , removed more than 95% of PAHs from unfiltered samples and reduced PAH readings to the values in the proximity of the detection limits. Because PAHs in runoff samples are transported by



residue, linear correlations between PAH levels and three measurements of residue in runoff samples were examined. While for some sites and commonly occurring PAH substances the correlation coefficients were as high as 0.8, for the whole set of samples only very low values of correlation coefficients were found (about 0.3). This lack of correlation seem to follow from the diverse nature of residue in runoff samples and the widely varying levels of PAHs in residue. At individual sites, more homogeneity in residue composition was expected and better correlations between PAHs and residue levels in runoff samples were found.

The PAH levels found in runoff were not related to land use or the distance from the steel plant. This last finding indicates that the atmospheric deposition of PAHs, originating to a large extent from the steel plant emissions, can be overshadowed by releases from strong local sources, including automobile exhaust emissions, heating emissions, used crankcase oil, and pavement attrition. Because of lack of physically-based explanations for PAH variations in runoff, a probabilistic approach to evaluation of loadings was adopted. After observing that there were no statistically significant differences among the data sets from the individual areas sampled, the data from all sites were aggregated and subject to statistical analysis.

Probabilistic distributions of PAH concentrations are plotted in Fig.1 for the 14 PAHs studied, six PAHs in the WHO group, and BaP. The data in Fig.1 indicate that the concentration distributions can be approximated by the lognormal distribution, for which the 95% confidence levels were also plotted. Because of high variance of PAH data, it is unlikely that the width of these bands could be reduced by extended sampling. These levels of uncertainty in PAH levels and loads may have to be accepted in the planning analysis dealing with comparison of sources and targeting sources for pollution control. Using the plots in Fig.1 and the annual volume of urban runoff from the study area (Marsalek and Ng, 1989), the city-wide PAH loads were estimated at 75kg of the 14 PAHs studied, 55 kg of the six WHO PAHs, and 7 kg of BaP. If the atmospheric deposition rates, observed in the snowpack survey, are prorated for the impervious areas contributing runoff, they account for about one third of the load carried by urban runoff.

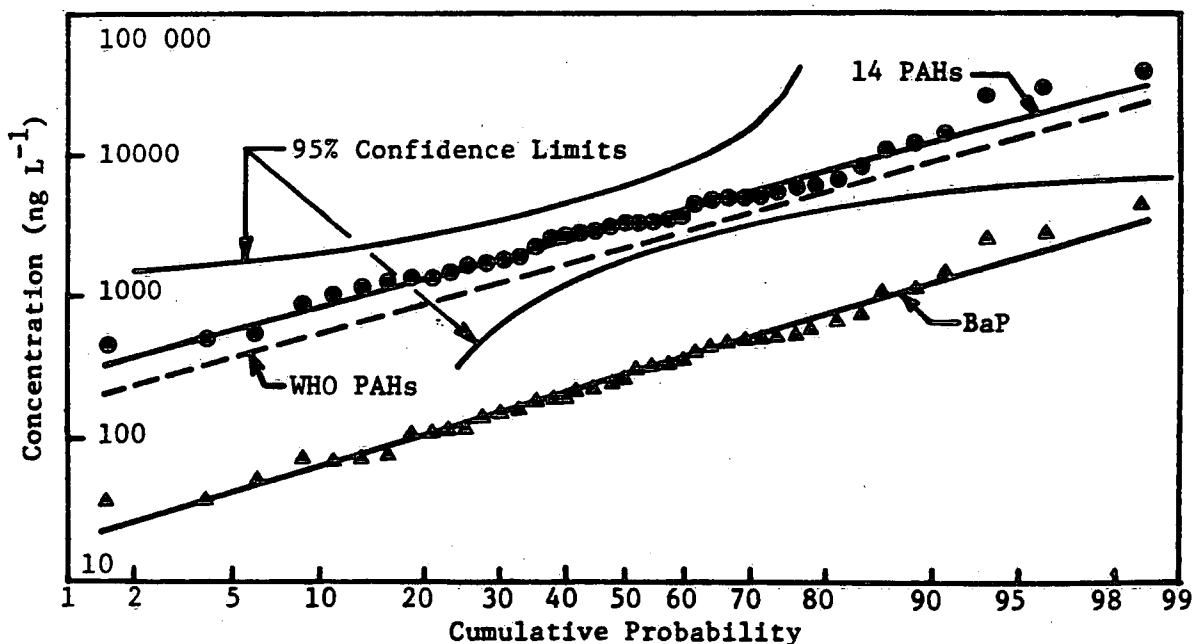


Fig.1. Probability Distributions of PAHs Studied

Recognizing that most of PAH loads in unfiltered runoff samples are transported by sediments, it was of interest to study PAHs in urban sediments by investigating spatial distributions of PAHs in urban sediments in relation to sources, the PAH profiles in urban sediment from various locations (and presumably sources), time variations in PAH concentrations in sediment, and variations of PAH concentrations with particle sizes.

In contrast to distributions of such conventional pollutants as metals, spatial distributions of PAHs in sediments showed great variations. For combined sets of concentrations of four common metals (copper, iron, lead, and zinc) in sediments from several sites in the study area, the coefficient of variation varied from 0.2 to 0.6. In the case of PAHs, however, the variations among various sites reached almost two orders of magnitude. Such great variations have to be caused by strong local sources including pavement attrition, tar-based pavement sealants, used crankcase oil, and depositions from car exhausts, industrial sources, and heating. Some of the highest concentrations were found in relatively clean residential areas with expected low imports of PAHs from outside sources. Consequently, constant potency factors, which are useful for the modelling of metals, may not be very helpful in the modelling of PAHs.

Variations in PAH levels in sediment at a site were also of interest. At two locations, sediments were collected on several different occasions and time history of PAH concentrations compared. Appreciable variations were noticed. At the first location, the sums of 14 PAHs in street sediment samples varied from 1.5 to 105 mg/kg. At the second location, sediment samples were collected from the bottom of an urban creek. In this case, the total PAHs varied from 0.2 to 3 mg/kg. PAH levels in street sediment varied greatly and this contributed to variations in PAH levels in runoff samples.

Finally, some sediment samples were divided into three fractions according to the particle sizes and the individual fractions were analyzed for PAHs. The fractions studied were characterized by  $D \leq 45 \mu\text{m}$ ,  $45 \leq D \leq 250 \mu\text{m}$ , and  $250 \leq D \leq 1,000 \mu\text{m}$ . If the forces binding PAH to the sediment were those of adsorption, skewed distribution of PAH concentrations in these fractions would be expected. This has not been observed, as the distributions of PAH in these three fractions were rather uniform. It would appear that there are other mechanisms involved, probably the attachment of PAHs to the sediment by oily films originating from traffic. The only site where skewed distributions favouring smaller fractions were observed was the bed of a creek flowing through the city and receiving stormwater discharges during wet weather. It could be expected that PAHs attached loosely to the sediment by oily films would be removed during extended transport.

Typical PAH profiles in samples of snow, unfiltered runoff, urban sediment, the river-bottom sediment, and caged mussels from the study area are shown in Fig.2. Most of these profiles are fairly similar and this similarity follows from the predominance of three most ubiquitous substances - fluoranthene, phenanthrene and pyrene. The predominance of these substances is widely recognized and detracts from the usefulness of PAH profiles in source tracking. Nevertheless, the profiles indicate PAH pathways comprising atmospheric deposition, surface runoff, and river sediment and biota, recognizing that the river sediment and biota profiles result from all PAH inputs, including those from point sources.

## CONCLUSIONS

Widely-varying significant levels of PAHs were found in runoff from an industrial urban area. PAH loads in runoff were conveyed mostly by the sediment and did not depend on land use. Much of the variation in PAH event

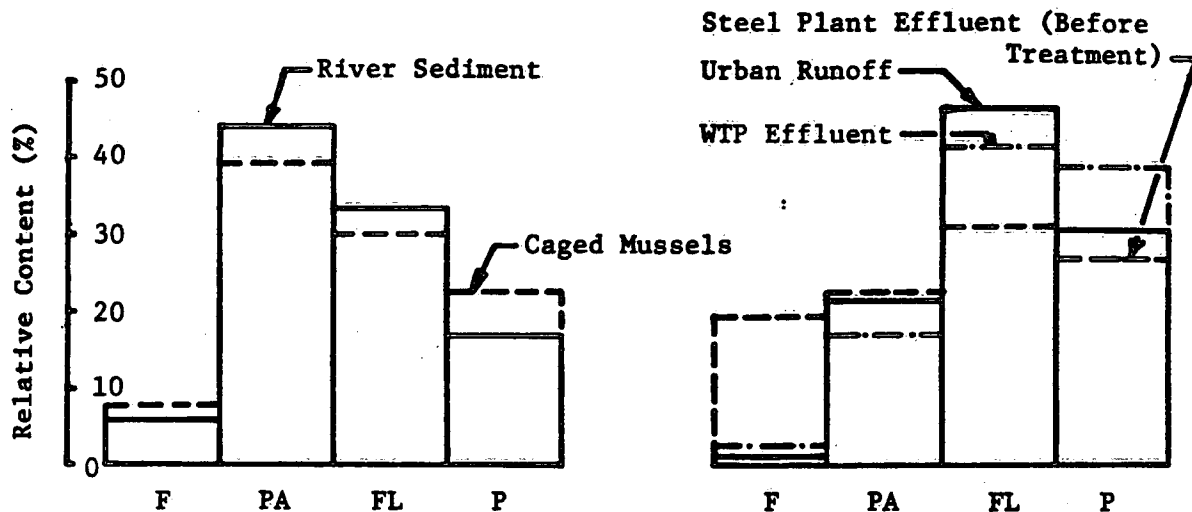


Fig.2. PAH Profiles in Various Media

loads was explained by variations in PAH levels in sediment at sampling sites and among the sites. The distribution of PAH concentrations in runoff was approximated by a lognormal distribution which was used to estimate the annual PAH loads in runoff at about  $75 \text{ kg yr}^{-1}$ , with about one third of this load originating from atmospheric deposition. Urban runoff was found to be an effective means of transport of PAHs from anthropogenic sources.

#### REFERENCES

- Boom, A. and J. Marsalek. 1988. Accumulation of Polycyclic Aromatic Hydrocarbons (PAHs) in an Urban Snowpack. *The Sci. of Tot. Env.*, 74: 133-148.
- Elis J.B., Revitt, M. and A. Gavens. 1985. Polyaromatic Hydrocarbon Distributions in Sediments of an Urban Catchment. *Intern. J. Environ. Anal. Chem.*, 21: 161-170.
- Hoffman, E.J., Mills, G.L., Latimer, J.S. and J.G. Quinn. 1984. Urban Runoff as a Source of Polycyclic Aromatics to Coastal Waters. *Environ. Sci. Technol.*, 18: 580-587.
- Marsalek, J. and H.Y.F. Ng. 1989. Evaluation of Pollution Loadings from Urban Nonpoint Sources: Methodology and Applications. *J. Great Lakes Res.*, 15(3): 444-451.
- Seifert, B. and E. Lahmann. 1980. Luftstaub-Untersuchungen mit der Hochleistungs-Fluoreszenz-Chromatographie. In: *Luftverunreinigung Durch Polycyclische Aromatische Kohlenwasserstoffe*. V.D.I. Berichte No.358, Duesseldorf, 127-131.
- Water Quality Branch. 1981. *Analytical Methods Manual*. Environment Canada, Ottawa, Ontario.
- Yamane, A., Nagashima, I., Okubo, T., Okada, M. and A. Murakami. 1989. Storm Water Runoff Hydrocarbons in the Tama River Basin in Tokyo and Their Fate in the River. Proc. 2nd Wageningen Conference on Urban Storm Water Quality and Ecological Effects Upon Receiving Waters, Wageningen, Sep.20-22, 1989.