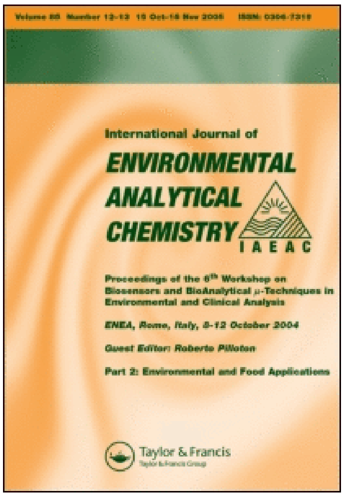

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Polyaromatic Hydrocarbon Distributions in Sediments of an Urban Catchment†

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The levels of six selected polyaromatic hydrocarbons (PAHs), anthracene, fluoranthrene, pyrene benzo(b)and(k)fluoranthenes, benza(a)pyrene and benzo(ghi)perylene, within the sediments of a 5.3 km^2 urban catchment in N.W. London have been investigated over a 12 month period. The variations in levels throughout the catchment are discussed in terms of the influence of established hydrocarbon-sediment associations on both the contributions of different source inputs and on the controlling effects of on-line sedimentation ponds and the terminal receiving basin. These factors cause local variations within the overall pattern which demonstrates an increase in sedimentary PAH concentrations downstream as the percentage urban surface area increases. The PAH distribution is essentially hydraulically controlled through discontinuous resuspension of the mobile surface sediment layer during turbulent storm flow conditions.

KEY WORDS: Polyaromatic hydrocarbons, surface sediments, urban catchment, storm runoff, storage ponds.

INTRODUCTION

Polyaromatic hydrocarbons (PAHs) are introduced into surface waters from a number of sources, including runoff and erosion,

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effluent discharges, atmospheric deposition and naturally occurring biological processes. Recent evidence[1] suggests that the majority of sedimentary PAHs originate from the deposition of atmospheric particulates derived from fossil fuel combustion, particularly coal, with an additional important input from used motor oil.[2] Analysis of urban runoff,[3,4] has shown that it provides an important transporting medium for PAHs to receiving waters and this is supported by sedimentary studies close to urban areas.[5] Contributions to PAH levels in road runoff are also provided from bituminous road surfaces,[6] car tyre wear[7] and deposited vehicle exhaust particulates.[8] In this paper the available evidence concerning the basis and importance of PAH—sediment interactions is assessed and used to interpret the significance of a range of sedimentary PAH concentrations found throughout an urban drainage basin in N.W. London. This catchment is dominated by stormwater inputs from both combined and separate sewer systems, with 60% of the storm flow coming from surface runoff.[9] Impervious area constitutes 25% of the catchment although there is a considerable change in the urban character through the drainage system from relatively rural headwater channel reaches to the heavily urbanised areas around the receiving basin of the Welsh Harp. The effectiveness of this basin as a sedimentary PAH sink as well as the efficiency of PAH removal by on-line sedimentation ponds is discussed.

EXPERIMENTAL

Sediment samples were collected from identified locations throughout the catchment of the Silk Stream in N.W. London (Figure 1) using a solvent washed stainless steel grab sampler. A number of surface samples were taken at each point and bulked prior to return to the laboratory.

The samples were oven dried at 50°C in glass containers for several days and a representative sub-sample was subjected to a modified version of the extraction and clean-up procedure of Giger and Schaffner.[10] Soxhlet extraction in dichloromethane, followed by rotary evaporation, preceded refluxing in glass distilled hexane. The latter process was utilised to remove extraneous material, without loss of PAHs, in order to reduce contamination of the Sephadex

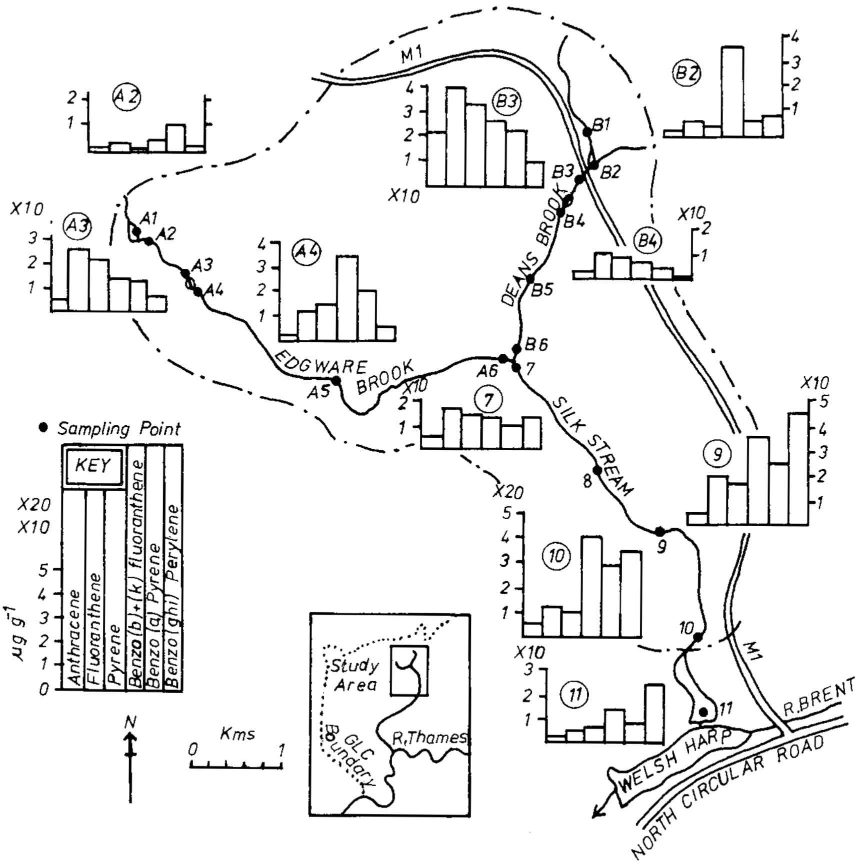

FIGURE 1 Sedimentary PAH distributions in the Silk Stream catchment.

LH20 and Silica Gel grade 40 (70–230 mesh ASTM) chromatography columns.

Specific analysis of the component hydrocarbons, both quantitative and qualitative, was performed on a Pye Unicam 204 Gas Chromatograph fitted with a flame ionisation detector and a 2.5 m × 2 mm glass column packed with 3% OV-1 on 100–120 mesh Diatomite CQ. Operating conditions were as follows:

Gas flows:	N_2, 60 cm^3 min^{-1}; H_2, 85 cm^3 min^{-1}; air, 300 cm^3 min^{-1}.
Temperatures:	Injector, 250°C; Detector, 300°C Oven, 160°C for 2 min. followed by temperature programming to 300°C at 8°C min^{-1}.

The identity of the PAHs was confirmed by additional analysis using a Hewlett-Packard Model 5995B GC/MS system fitted with a 25 m fused silica capillary column coated with crosslinked methyl silicone (0.2 mm i.d., 0.33 μm film thickness). Temperature programming from 120°C to 250°C at 10°C min^{-1} was employed.

RESULTS AND DISCUSSION

Hydrocarbon-sediment associations

It is now well recognised that hydrophobic hydrocarbon compounds are readily adsorbed by suspended materials in aquatic systems; the adsorption rate being determined by the extent to which the substance partitions to the solid medium. It is also recognised that stormwater runoff from urban surfaces can be associated with high levels of hydrocarbons. On a flow weighted basis, concentrations of hydrocarbons associated with stormwater suspended solids can be 1.7 to 6.2% of the total solids mass.[11] Total PAH levels of 60 μg l^{-1} have been recorded in road runoff[12] with concentrations as high as 18 mg l^{-1} having been recorded in stormwater runoff for the catchment under investigation.[4]

These results place storm runoff well within the grossly polluted classification given by Borneff.[13] The recent U.S. EPA National Urban Runoff Program documents individual PAH compounds ranging from 0.3 to 12 μg/l[14] with many occurring at concentrations well above the human carcinogen value. Herrmann[15] recorded average levels of 0.53 μg/g benzo(a)pyrene and 1.1 μg/g fluoranthene in street dusts and thus it is not surprising that sewered runoff from impermeable surfaces within urban catchments can yield such substantial concentrations of PAH to receiving waters.

The major proportion of the removed hydrocarbons are carried in association with the suspended solids. Zurcher *et al.*[16] have found flow weighted mean concentrations for hydrocarbons in motorway runoff of $4.6\,\mathrm{mg\,l^{-1}}$ of which $4.4\,\mathrm{mg\,l^{-1}}$ was associated with particulates. This is in agreement with a number of other studies which report that between 80 to 95% of all hydrocarbons in urban runoff are particulate associated and dominantly associated with the less than $63\,\mu$m size range. PAHs average about one third of this total hydrocarbon loading.[17,18]

A large number of studies have also clearly identified enhanced surficial hydrocarbon levels within sediments of urban receiving waters reflecting accumulating inputs from non-point runoff.[19–22]

Shelton and Hunter[23] reported total hydrocarbons for sediments in New Jersey rivers ranging from 0.12 to 38.3% on a dry weight basis. The lower end of the range represented uncontaminated rural waters but all the high values related to urbanised catchments.

Given the large dilution capacity available in most modern urban receiving waters it is not surprising that the high concentrations which have been recorded in sewered runoff are substantially reduced within the receiving stream. Unfortunately there is a marked lack of information and knowledge concerning the interactions of organic compounds at residue levels with suspended solids and sediments. However, Lambert[24] has demonstrated the overwhelming importance of the organic carbon fraction in the sorption of neutral organic compounds. He derived a normalised partition coefficient: $K_{oc}=K_p/f_{oc}$, where K_p represents a linear partition coefficient and f_{oc} is the fractional organic carbon sorbent content. The partition coefficient was shown to remain virtually constant for any particular compound. The very high correlations found by Lambert would further suggest that factors other than organic matter may be of minimal importance in sorption reactions. Although this early work was concerned with soil/pesticide systems, the sorbent evaluation studies of Herrmann[15] and Weber *et al.*[25] have demonstrated the findings are equally applicable to urban aquatic sediments. Indeed the latter work indicated that even trace amounts of organic material can overshadow the effects of even large differences in surface area. Gjessing *et al.*[26] have shown that a highly organic soil (96% ignition loss) is 20 times more effective at retaining PAHs than in inorganic soil composed of 98% sand. Sorption to organically rich solids such as typically occur in urban rivers can therefore be visualised as an efficient and rapid phase partitioning reaction between the aqueous and associated non-polar phases.

Whilst it is feasible to accept the high hydrocarbon uptake potential of suspended particulate in urban receiving waters, once the adsorption sites become saturated it is probable that oil and grease residues are held only weakly within the sediment matrix. It is likely that they reside in the sediment by virtue of adhesive properties resulting from preferential wetting of the sediment by the oil. Field sampling of benthal sludges in urban rivers causes considerable *in-situ* disturbance which is normally accompanied by black odorous oil slicks representing release of oils from anaerobic or reducing sediment, but oil which is not directly in contact with sediment particle surfaces.[27] Absorption of oily residues may occur into open pore spaces of large particulates as well as absorption into the inter particulate spaces of aggregated particles. The latter sediment textures are especially characteristic of suspended sediments in urban runoff and are believed to be reactant products of organic flocculation.[28] Local disturbance and hydraulic storm resuspension of the oily, organic benthal sludges provides a continual hydrocarbon reservoir or innoculum. The entrainment and mobilisation of the contaminated particulate serves to enrich downstream surface sediment facies.

The microbial degradation of sediment hydrocarbons under enriched conditions is regarded as being extremely slow, although it is known that bacteria oxidise PAH to cis-diols while at least one fungus species, as well as mammalian enzymes, oxidise PAH to carcinogenic trans-diols.[29] Meinschein[30] has argued that aromatic hydrocarbons are found only in trace quantities in biological lipids and when found in recent benthal deposits usually only occur within basal anoxic sediment layers and are normally non-alkyl substituted PAHs. Hites[31] confirms that no biosynthesis of PAH compounds takes place in benthal sediments and that urban combustion products, followed by sedimentary deposition and subsequent microbial modification, accounts for the presence of alkylated PAH derivatives in aquatic sediments.

PAH sediment distributions

There is a general increase in the maximum recorded hydrocarbon sediment levels downstream through the catchment as can be clearly seen from Figure 1 which shows the incidence and distribution of six selected PAHs at 10 of the sampling sites. This pattern correlates with the increasing degree of urbanisation and percentage impervious surface area which occurs progressively downstream. The enhancement between the rural headstream sites (A1/A2 and B1/B2) and the southerly urban channel sites (10/11) is generally of the order of 10^2 to 10^3, although in the case of benzo(ghi)perylene an increase of the order of 10^4 is observed.

Figure 1 shows the important control that natural and artificial on-line ponds have on the PAH concentrations within the urban river sediments. Comparison of data for sampling points A3 and A4 on the Edgware Brook and between B3 and B4 on the Deans Brook demonstrates that three to twenty fold reductions in PAH levels are achieved by the presence of relatively large enclosed water bodies which permit the sedimentation of PAH associated particulates. The efficiency of the final receiving basin of the catchment in removing sedimentary PAHs is illustrated by the substantial decrease in levels between sites 10 and 11. Whipple and Hunter[32] have suggested, from simulated detention basin studies, that the close association of hydrocarbons with suspended solids can lead to a 61 to 73% removal efficiency over a 36 hour sedimentation period. However, their work was conducted in still water and with homogeneous particle sizes and types and the results cannot be satisfactorily translated into realistic settleability characteristics for normal urban runoff conditions. It is quite obvious that these in-channel ponds act only as temporary sediment/pollutant storage basins and that there is an overall movement of PAHs downwards through the catchment. The hydraulic turbulence generated during storm events is sufficient to resuspend and mobilise the detained bed sediments and transport them as an entrained sediment wave further downstream. The sediment associated PAHs therefore move in discontinuous waves, accumulating locally as lag deposits within the ponds and receiving basins. These act essentially as detention rather than retention basins and their long term trap efficiency can be considered to be relatively minimal.

The effects of source sediment mixing on the distribution of PAH levels can be determined by examination of combined flows occurring at junction points in the drainage system. Thus, the maximum sedimentary concentrations of $18.3\,\mu g\,g^{-1}$ and $7.4\,\mu g\,g^{-1}$ for benzo(a)pyrene at the tributary sites A6 and B6 respectively, are adjusted to 11.3 $\mu g\,g^{-1}$ at sampling site 7 on the trunk stream. This effect is observed for all measured PAHs. The impact of specific point discharges on PAH sediment levels in the receiving stream is further illustrated by the high values recorded at site A6 which is immediately downstream of a combined sewer overflow. This site recorded maximum concentrations of 21.4 $\mu g\,g^{-1}$, 20.9 $\mu g\,g^{-1}$ and 10.5 $\mu g\,g^{-1}$ of fluoranthene, pyrene and benzo(ghi)perylene respectively as well as at the high level of the carcinogenic benzo(a)pyrene noted above. These combined sewer overflow inputs, together with those from separate sewer systems continue between sampling sites 8 and 10 and are responsible for the rapid build-up in all the PAH levels which are observed in these highly urbanised channel sections. The extremely high individual PAH levels at site 10 (Figure 1) greatly exceed those found in surface lake sediments[26,33,34] and are comparable with those that have been measured in sediments of an effluent channel from an industrial coking plant.[35]

The deleterious effects of highway runoff on receiving stream PAH sediment levels can be observed by inspection of the data presented for site B3 (Figure 1). The sampling site is immediately below the outfall of stormwater discharging from the M1 Motorway and associated with consistently high PAH sediment concentrations. The highway runoff monitored at this site[4] possesses total PAH levels of 5.83 $mg\,l^{-1}$, and given the established affinity (79 to 93%) of high molecular weight PAHs for particular matter,[3] it is not surprising that correspondingly high sediment concentrations are found at this point.

Consideration of the minimum individual PAH levels throughout the catchment shows that although there is a progressive increase downstream, it is not as exaggerated as is the case for the maximum values. However, the fact that an increase of nearly an order of magnitude does occur, indicates that there is an undoubted long term, chronic impact resulting from urbanisation. The discrepancy between the maximum and minimum concentrations is greatest at the urbanised downstream sites and is usually negligible at the rural headwater sites. This implies that there is a constant input maintaining a "background" level. These levels are of similar magnitude to those found by Herrmann[15] for fluoranthene and benzo(a)pyrene in the suspended sediment and bedload of a stream receiving storm runoff from combined sewer overflows. However, in the present study, the effect of combined sewer overflows is to cause the greatest variation in maximum and minimum PAH levels at a particular site. Thus a temporal variation occurs in sediment concentrations which is highly dependent on the input source with the minimum levels being equivalent to those observed in the rural headwaters. The flux in PAH levels can be observed throughout the drainage system with "dilution" effects occurring between sampling sites where there are no direct inputs.

CONCLUSION

PAH levels in urban channel sediments can be extremely high and provide a readily available and easily mobilised reservoir of organic micropollutants to the overlying water column during storm surges. PAH incidence is highly source specific with discharges from highway runoff and combined sewer overflows being prime offenders. PAH are readily adsorbed on to the organically enriched suspended sediment and temporarily accumulate within on-line detention ponds. The removal efficiency of such ponds is found to be between 65 and 95% for the six particulate associated PAHs monitored in this study.

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