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Polycyclic Aromatic Hydrocarbon in Sediments Taken from the Severn Estuary Drainage System

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Polynuclear aromatic hydrocarbons (PAH) are a class of organic compounds of particular interest because of their carcinogenic activity (HARTWELL 1951). They may be created by the pyrolysis of organic materials including fossil fuels (SHABAD 1975), or by the natural processes of certain species (BORNEFF et al. 1968). These compounds usually occur as complex mixtures covering a wide range of molecular weight and isomeric structure (GIGER & BLUMER 1974). Particular sources of PAH's in the environment are oils (LIJINSKY et al. 1963), tars (POPL et al. 1974, 1975) and coal (WOO et al. 1978).

Extraction of PAH's from environmental samples may be accomplished by Soxhlet extraction (JOHN & NICKLESS 1977) or steam distillation (COOKE et al. 1978) from solid samples, by ion-exchange chromatography (NAVRATIL et al. 1977) from water, and by glass-fibre filters (GIGER & SCHAFFNER 1978) from air.

A variety of analytical methods have been applied to the determination of PAH's. Amongst the most recent are gas-solid chromatography (JOHN & NICKLESS 1977), X-ray excited optical luminescence (WOO et al. 1978) and high performance liquid chromatography (WISE et al. 1977).

We have previously reported a method for the analysis of nine PAH's commonly present in environmental samples together with some typical results from a selected site (JOHN & NICKLESS 1977). We now report fully the results of our study of PAH's present in a tributary of the River Taff (Glamorgan, South Wales, U.K.) together with the results of a study of sediments taken from the estuary of the River Severn which receives the contents of this river together with the flow from several other rivers (Wye, Usk, Severn, Avon, Yeo, Parrett). Of these rivers the Taff, Usk, Wye, Severn, and Avon flow through known coalfields, (see Figure 1).

The Severn Estuary is situated between the south-western peninsula of England and the southern coast of Wales. It possesses a very large tidal range (about 40 feet). Several rivers flow into the Estuary carrying domestic and industrial effluent. Heavy industry (chemicals and steel) is located along both the north and south-eastern coastal regions. The river Taff flows due south across the South Wales coastal plain and drains a large area of the South Wales coalfield. Two of its major tributaries are the rivers

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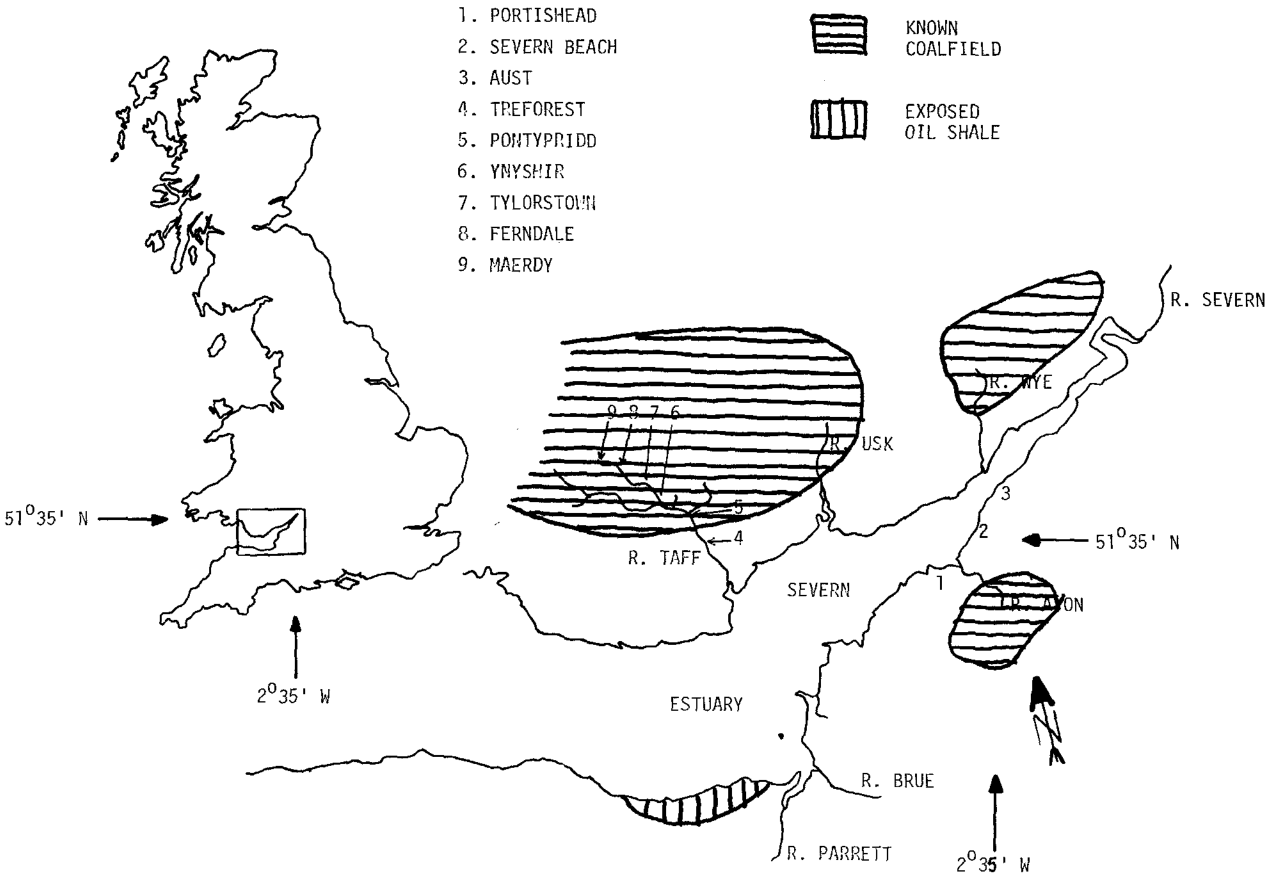
FIGURE 1. LOCATION OF SAMPLING SITES



Rhondda Fach and Rhondda Fawr.

Oil bearing shales are exposed and form low cliffs on the southern coast of the estuary. Any PAH found in sediments in this region may thus be derived from a variety of sources.

Materials and Methods

Samples were collected using a metal scoop and placed in clean glass vessels sealed with aluminium foil. Storage was at $0^{o}C$ until use.

About 100-150 g of each sample was used for analysis. After mixing with excess sodium sulphate the sample was Soxhlet extracted with dichloromethane for 12 h. The extract was simplified by column chromatography on alumina followed by TLC on Kieselgel G Type 60 to give a suitable sample for injection onto the gas chromatograph. Full details of the extraction and clean-up procedure have appeared elsewhere (JOHN & NICKLESS 1977).

The gas chromatographic analysis was performed on a Pye Unicam Series 104 instrument fitted with a dual FID head. For gas-liquid chromatography a glass column (1 m x 4 mm i.d.) packed with 5% Dexsil 300 GC on 60/80 mesh Chromosorb W NAW was used with a nitrogen carrier gas flow rate of 40 mL min^{-1}. The inlet and detector temperature were both 330 ^{o}C. The temperature programme employed was 100 ^{o}C for 2 min, programme at 10 ^{o} min^{-1} to 340 ^{o}, then hold for 7 min.

Identification of compounds was by retention time and confirmation by co-injection. Previously, positive identification of the components of selected samples had been obtained from GC-MS studies (JOHN & NICKLESS 1977).

Quantitation was by measurement of peak height and comparison with standard calibration curves.

Results and Discussion

The levels, both for wet weight and dry weight of the nine PAH's studied in the samples, are given in Table 1. Samples 1, 2 and 3 were taken from the south bank of the estuary of the river Severn (see Figure 1). Samples 4 and 5 represent samples from the upper reaches of the River Taff and are included for comparison. Samples 6, 7, 8 and 9 were taken from sites along a 9 mile section of the Rhondda Fach; one of several tributories of the Taff.

All nine PAH's studied were present in all the samples studied though in the case of coronene only trace amounts (ca. <0.1 p.p.m.) were found in the samples from the main river (4,5) and the estuary (1,2,3). In general levels were higher for the tributary (Rhondda Fach) than the main river. Levels in the

TABLE 1

Concentration of PAH's in Sediments Expressed in ppm Dry Weight (Wet Weight Values are given in Parenthesis)

Sample site No.	Source	Anthracene[a]	Fluoranthene	Pyrene	2,3-Benzofluorene	Chrysene[b]	3,4-Benzpyrene[c]	1,2,3,4-Dibenzanthracene	Benzo(*ghi*)-perylene	Coronene
1	Portishead	0.1(0.1)	0.5(0.3)	0.3(0.2)	d	d	0.3(0.2)	0.2(0.2)	0.2(0.1)	✓
2	Severn Beach	0.3(0.2)	1.3(1.0)	0.8(0.6)	0.3(0.2)	2.3(1.6)	0.7(0.5)	0.6(0.4)	0.4(0.3)	✓
3	Aust	2.3(1.4)	5.2(3.2)	3.3(2.0)	1.2(0.7)	5.6(3.4)	2.7(1.7)	1.7(1.0)	1.5(0.9)	✓
4	Treforest	1.8(1.3)	1.6(1.1)	1.9(1.4)	0.6(0.4)	2.5(1.8)	5.0(3.6)	1.1(0.8)	1.3(0.9)	✓
5	Pontypridd	0.6(0.6)	0.6(0.5)	0.7(0.6)	0.2(0.2)	1.1(0.9)	2.7(2.4)	0.4(0.4)	0.6(0.5)	✓
6	Ynyshir	2.6(1.8)	2.2(1.6)	1.8(1.3)	0.9(0.6)	3.1(2.2)	2.4(1.7)	1.3(0.9)	1.3(0.9)	1.1(0.8)
7	Tylorstown	6.4(5.5)	3.8(3.3)	3.5(2.9)	1.2(1.0)	3.9(3.4)	2.9(2.5)	1.7(1.4)	1.3(1.1)	1.0(0.9)
8	Ferndale	4.6(4.2)	3.2(2.4)	3.0(2.7)	0.8(0.8)	3.4(3.1)	2.6(2.4)	1.1(1.0)	1.1(1.0)	0.6(0.5)
9	Maerdy	2.7(2.5)	1.7(1.6)	1.5(1.4)	0.4(0.4)	1.6(1.5)	1.1(1.0)	0.6(0.6)	0.4(0.4)	0.3(0.3)

[a] includes phenanthrene; [b] includes triphenylene; [c] includes perylene; [d] peaks obscurred by interfering compound,

✓ = trace

estuary samples were lower than either river. This may be attributed to dilution of the contaminated sediment with non-contaminated material on passage down the drainage system. The source of contamination would thus appear to be at the head of the river. Whether this contamination occurs by 'natural' leaching from coal-bearing strata or may be attributed to coal mining activity is not clear. However, the association of PAH's with coal dust in this estuary has been previously demonstrated (COOKE et al.). Thus whilst a certain base level of PAH's in sediment samples from this area is to be expected, it seems likely that mining activity will also be contributing to the levels found.

The differences between wet weight and dry weight values gave an indication of the nature of the sediment sample studied. For example a coarse sediment with a low water content (Maerdy) shows little difference between wet and dry values whereas a fine sediment with high moisture content (Aust) shows much larger differences. In addition differences may be larger than these illustrated as losses during the drying procedure will tend to reduce the dry weight values.

Although the sites 1, 2 and 3 are apparently similar in geographical location the levels of PAH's found at Aust (3) are significantly higher than those found at Portishead (1) and Severn Beach (2). Whilst variation of sample types i.e. variation of the ratio of carboniferous to siliceous material in the sample may account for this observation, it may also be significant that the Aust (3), sample was obtained from an area near to a major road bridge across the estuary. This bridge, which is about 1 mile in length, carries a high density of heavy industrial traffic and the levels of PAH's in the sediments near the bridge may well be enhanced by its' presence.

Within the group of compounds studied there appears to be little correlation of the relative concentration of the various components. 2,3-Benzofluorene, 1,2,3,4-dibenzoanthrocene and benzo(ghi)perylene are generally present at low concentrations. The isomeric pairs anthracene/phenanthrene and fluoranthene/pyrene tend to occur at higher concentrations. Although resolution of the anthracene/phenanthrene pair is not achieved by GLC the ratio of fluoranthene to pyrene may be obtained and appears to favour fluoranthene in most cases. The only significant exception occurs at site 4 where the concentration of pyrene appears to be higher than expected from this location. However, local industry, particularly the manufacture of carbon black, may well be an additional source of pyrene at this site. The levels of PAH's at site 5 are all lower than expected possibly reflecting the influx of a relatively uncontaminated side-stream near the sampling point.

The values given for chrysene include the contribution from triphenylene. Resolution of chrysene from triphenylene may be achieved via GSC on a 2% RbCl column should the relative levels of these two compounds be required. A further advantage of GSC is illustrated by the analysis of the Portishead samples. By GLC the peaks due to 2,3-benzofluorene and chrysene/triphenylene are obscurred by an interfering component. This problem is solved by GSC, however, as the interfering compound does not elute and thus levels of the two PAH's may be determined. Presumably it decomposes on, or is retained by, the salt column. The removal of phthalate esters from environmental extracts by salt columns has been previously observed in our laboratory (COOKE et al. in the press). Other classes of compounds including hydroxy-aromatic species are retained by a 2% RbCl column. The interfering component in the Portishead sample (site 1) is thus likely to be an organic species possessing one or more electronegative substituent groups.

Conclusions

The 9 PAH's studied are ubiquitous in the area considered. Levels of contamination appear to be highest in areas of recent coal mining activity. However, the contaminants are bound up in the sedimentary material of the drainage system. Translocation of the PAH's is thus slow and predictable and hence possible health hazards are much reduced.

Although the pyro-synthesis of PAH's upon combustion of fossil fuels such as coal is well known little attention has been paid to the "natural" occurrence of PAH's in the various types of coal and to the liberation of these compounds by erosion and, more importantly, by mining activity. In view of the declining importance of oil and the re-emergence of coal as a primary source of energy the contribution to environmental contamination by PAH's from this source merits further study.

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