British Geological Survey

NATURAL ENVIRONMENT RESEARCH COUNCIL

Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments from the Irish Sea.

Continental Shelf and Margins Programme

Internal Report IR/02/29

BRITISH GEOLOGICAL SURVEY

INTERNAL REPORT IR/02/29

Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments from the Irish Sea.

I.Harrison

Key words

Report; key; words.

Bibliographical reference

HARRISON,I., 2002. Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Sediments form the Irish Sea. *British Geological Survey Internal Report*, IR/02/29. 32pp.

Keyworth, Nottingham British Geological Survey 2002

BRITISH GEOLOGICAL SURVEY

The full range of Survey publications is available from the BGS Sales Desks at Nottingham and Edinburgh; see contact details below or shop online at www.thebgs.co.uk

The London Information Office maintains a reference collection of BGS publications including maps for consultation.

The Survey publishes an annual catalogue of its maps and other publications; this catalogue is available from any of the BGS Sales Desks.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as its basic research projects. It also undertakes programmes of British technical aid in geology in developing countries as arranged by the Department for International Development and other agencies.

The British Geological Survey is a component body of the Natural Environment Research Council.

Keyworth, Nottingham NG12 5GG

☎ 0115-936 3241 Fax 0115-936 3488
e-mail: sales@bgs.ac.uk
www.bgs.ac.uk
Shop online at: www.thebgs.co.uk

Murchison House, West Mains Road, Edinburgh EH9 3LA

☎ 0131-667 1000 Fax 0131-668 2683
e-mail: scotsales@bgs.ac.uk

London Information Office at the Natural History Museum (Earth Galleries), Exhibition Road, South Kensington, London SW7 2DE

☎ 020-7589 4090 Fax 020-7584 8270
☎ 020-7942 5344/45 email: bgslondon@bgs.ac.uk

Forde House, Park Five Business Centre, Harrier Way, Sowton, Exeter, Devon EX2 7HU

☎ 01392-445271 Fax 01392-445371

Geological Survey of Northern Ireland, 20 College Gardens, Belfast BT9 6BS

☎ 028-9066 6595 Fax 028-9066 2835

Maclean Building, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB

☎ 01491-838800 Fax 01491-692345

Parent Body

Natural Environment Research Council, Polaris House, North Star Avenue, Swindon, Wiltshire SN2 1EU

☎ 01793-411500 Fax 01793-411501
www.nerc.ac.uk

Foreword

This report is the published product of a study by the British Geological Survey (BGS) on the polycyclic aromatic hydrocarbon (PAH) content of a variety of intertidal and offshore core sub-samples obtained from the Irish Sea.

Acknowledgements

The author would like to thank :

Dr DG Jones, Dr J Ridgway, Dr NJ Fortey, Dr SRN Chenery and Dr DJ Morgan for their assistance in acquiring the scanning fluorescence detector that made this investigation possible.

Miss CA Carlick for her assistance with the analyses.

Contents

Summary

The analysis of 26 marine sediment samples taken from the Irish Sea was accomplished using high performance liquid chromatography (HPLC) and fluorescence detection. The air-dried, powdered samples used were subsamples of cores obtained from offshore of the Cumbrian coast and from the intertidal zones of the Solway Firth. The analytical technique permitted the quantification of fifteen PAHs, *i.e.* all the commonly encountered suite of sixteen PAHs specified by the USEPA with the exception of one member that could not be detected because of its non-fluorescent nature. The method was found to be both sensitive and selective and the limit of detection ranged from 0.4 μg/kg for acenaphthene to 0.03 μg/kg for anthracene.

Using the chromatographic data the concentrations and distribution patterns of the PAHs in the sediments could be examined, permitting conclusions to be drawn on the likely sources of the PAH in the sediments. For the Solway Firth samples total PAH concentration was found to range from 12 μg/kg to 1512 μg/kg and for the Cumbrian offshore coastal samples the range was 274 μg/kg to 4856 μg/kg. Inspection of the literature disclosed that such ranges are fairly typical of marine sediment PAH concentration levels.

The PAH distribution patterns revealed that the relative proportions of PAH were similar in all the samples regardless of sampling location and total concentration. The pattern corresponded with one that is encountered globally and typifies PAH assemblages resulting from high temperature combustion of fossil fuels. Such PAH generation is referred to as being *pyrolitic* in origin, distinguishing it from the *petrogenic* PAHs that arise from fossil fuel spillages *etc*. Unlike petrogenic PAH that is dominated by low molecular weight PAHs, pyrolitic PAH is marked by a predominance of the high molecular weight PAHs fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, indeno(1,2,3-cd) pyrene and benzo(ghi)perylene, together with some prominence for the low molecular weight PAH phenanthrene, the most stable of the three-ringed members. It was observed for the offshore Cumbrian sediments that these nine pyrolitic PAHs were the dominant species, in all except one core taken close to Whitehaven and its harbour. It was concluded that the pyrolitic PAH output from local coal-burning industry was the main contributor to the relatively high levels of PAH in the offshore Cumbrian coastal samples. The typical pyrolitic PAH signature was modified by a small petrogenic input, assumed to have resulted from incomplete fuel combustion and/or leakage attending shipping activities in Whitehaven harbour.

For two offshore Cumbrian coastal cores where depth profiles were available the surficial sediment had the lowest total PAH concentration in both cases. Assuming that sediment from the surface is more recent than underlying sediment this may betoken the decline of coal-burning industry in the Cumbrian coastal region. However, because the surficial sediment is more oxic than deeper sediments, aerobic biodegradation of PAH, a more favourable process than anerobic biodegradation, may be responsible for the diminished surface concentrations. The only other core for which a depth profile was available was SF 00/7 (Figure 5) and this exhibited low total PAHs concentration down to 100 cms, but a comparatively high level of total PAHs concentration between 175-190 cms. Once more perhaps, this reflects the history of PAH deposition, *i.e.* the reduced use by modern shipping of the Solway Firth because of its comparative shallowness.

Unlike the offshore Cumbrian coastal sediments, the Solway Firth intertidal sediments displayed an appreciable presence of low molecular weight PAHs in addition to the nine pyrolitic members (Table 4). Naphthalene, acenaphthene and fluorene were frequently present in significant quantity. Their presence suggested a proportionally greater petrogenic contribution to the total PAHs than for the Cumbrian samples and this may stem from a locally flourishing leisure and tourist industry and the consequent likelihood of leakage and incomplete combustion of the fuel employed in boats.

Some correlation was found between the total organic matter content (TOC) and the total PAH concentration in all the sediments. Given the primarily pyrolitic nature of the PAHs from both regions, it was surmised that the PAH was probably bound to the soot particles, simultaneously generated during fossil fuel combustion, and that these formed a somewhat variable proportion of the total organic phase of the sediments leading to a loose though perceptible correlation. The TOC in the offshore Cumbrian sediments had a higher PAH loading than did the intertidal Solway Firth sediments. This implied larger concentrations of the soot combustion particles, containing PAH, associated with the TOC of the former, presumably, because the Cumbrian coastal region was more industrialised compared with the more rural Solway. Coal-burning industry then was held principally responsible for the greater PAH input to the offshore Cumbrian sediments.

The findings were supported by an alternative form of PAH pattern analysis that employed ratios for certain isomeric pairs of PAHs called molecular indices. The molecular indices revealed the same sort of conclusions that the ranking of abundance had produced, *i.e.* that the offshore Cumbrian sediments contained greater proportions of pyrolitic PAHs than did the intertidal Solway Firth sediments which in turn had increased contributions of petrogenic PAHs.

1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds that consist of two or more fused aromatic rings and occur in the environment as a result of numerous anthropogenic and biogenic inputs. Currently, it is held that the pyrolitic contribution, stemming in the main from the incomplete combustion and pyrolysis of fossil fuels is the principal source of environmental PAH in marine sediments (McCready *et al*., 2000). This pyrolitic contribution is augmented to some extent by PAHs originating from grass and forest fires and transported to the marine environment by æolian (atmospheric) and fluvial (riverine) processes. Sometimes, there is also a petrogenic input of PAH to marine sediments from crude oil, coal or various refinery products. This source can be either natural as for instance oil seepage from depth or more commonly it is anthropogenic and arises as a result of runoff, industrial and sewage discharges, shipping activities, spillage *etc*. A small component also derives from the diagenesis of natural precursors like terpenes, pigments and steroids.

PAHs are ubiquitous, even adulterating sediments from formerly pristine regions like the Beaufort and Barents Seas of the Arctic (Yunker *et al.*, 1996). They give cause for concern because certain of their number exhibit toxic, mutagenic and carcinogenic activity (Lehr & Jerina, 1977). In general, the low molecular weight two- and three-ringed PAHs have a significant acute toxicity, whereas the four- to six-ringed PAHs reveal the higher carcinogenicity. Although hundreds of PAHs exist in the environment, the US Environmental Protection Agency has listed sixteen as "Consent Decree" priority pollutants and it is these that are most frequently monitored for regulatory purposes. The distributions and ratios of some of these, (*e.g.* phenanthrene: anthracene and fluoranthene:pyrene), can provide information on the likely sources of anthropogenic PAH contamination (Readman *et al*., 2002).

Because PAHs are extremely non-polar, hydrophobic entities they tend to partition strongly into sediment organic matter leaving low concentrations of PAH in equilibrium with any surrounding aqueous phase. Often, PAH concentrations in the porewaters of sediment cores are very much lower than predicted by equilibrium partioning models (even by as much as 100 times) because of the presence of soot particles (Bucheli & Gustafsson, 2000). Generated concomitantly with PAHs during incomplete combustion processes, sediment soot particles increase the partition of PAH into the particulate phase. This impacts the bioavailability of PAHs as microrganisms can only degrade them as dissolved species. In the marine environment, the continuous settling of particulate matter, flocs and fæcal pellets favours the transport of PAHs to bottom sediments which then act as a long term reservoir (sink) for these hydrophobic contaminants (Tolosa *et al*., 1996).

As part of a larger study on sediments from the Irish Sea, this report details the speciation and determination of the PAH content of 26 samples of air-dried, powdered marine sediments. Thirteen of the samples were from cores taken in the intertidal zones of a variety of locations in the Solway Firth. The remaining thirteen were from cores obtained offshore of the Cumbrian coast, again from a variety of locations, mostly in the vicinity of Sellafield.

Following solvent extraction of the PAHs from the sediments, high performance liquid chromatography (HPLC) was used for their separation and fluorescence detection applied for their individual quantification. Fluorescence detection is a selective and sensitive means of determining PAHs, however, it will only allow 15 of the 16 PAHs specified in the USEPA methods to be quantified (Figure 1). This is because one of the 16 USEPA PAHs, *viz.* acenapthylene, is not a fluorescent compound. Nevertheless, sufficient data can be generated to

gain a meaningful assessment of the PAH content and distribution in the samples without necessarily having knowledge of the acenaphthylene concentrations.

It was possible using the chromatographic data to draw conclusions concerning the likely origins of the PAH in the sediments.

2 Materials and Methods

2.1 SAMPLES FOR ANALYSIS

The samples for analysis were 25 g. subsamples of core material that had been collected from either intertidal zones in the region of the Solway Firth, during Ocober 1999 and April 2000, or offshore of the Cumbrian coast in July 1999. Sampling locations appear in Figures 2 and 3. Locations for which PAH data were obtained are denoted by rectangular enclosures.

The subsamples, air-dried and powdered by agate ball-milling, were placed in sealed polythene bags and stored in the dark at room temperature prior to analysis. Storage in plastic bags is not normally deemed appropriate for samples that are to undergo any form of organic geochemical analysis because of the possibility of adulteration by organic chemicals emanating from the plastic, *e.g.* plasticizers (di-octyl phthalate *etc*.). However, because of the selectivity of the technique that was to be used for the PAH analysis this form of storage was considered tolerable, if not strictly ideal, insofar as plastic-derived adulterants would not be likely to interfere with the chromatography.

2.2 EXTRACTION OF PAHs FROM SAMPLES

In order for the samples to be in a form suitable for chromatographic analysis it was necessary to leach the PAHs into solution by means of solvent extraction. This was accomplished in the following manner :

For each sample, 5.00g was weighed into a pre-cleaned 25 mL amber bottle. To this was added 24 mL of HPLC grade acetonitrile, from a 25 mL measuring cylinder, and 1 mL of a solution containing 5 mg/L *p*-terphenyl in HPLC-grade acetonitrile, from a 1 mL gas-tight syringe. The latter was added to serve as an internal standard. The bottle was sealed with a screw-cap closure containing a PTFE-faced silicone rubber septum (PTFE face towards the bottle contents). After sealing the bottle was shaken vigorously to suspend the contents which were then sonicated in an ultrasonic bath (Camlab, 300W) for 45 minutes. During this period the bottle was occasionally inverted and shaken to continually resuspend the sample. The bottle was then stored in the dark for 12 hours with intermittent shaking, followed by a further 12 hours without shaking to permit the supernatant to clarify.

Quality control was achieved by subjecting a low-level PAH interlaboratory comparison material (LGC Contest 33.3c) to the above procedure and analysing it by the same method as for the samples.

2.3 PAH ANALYSIS

A small aliquot, *ca.* 50 µL, of the clarified supernatant was taken from each sample extract (including that for the QC) by an HPLC syringe and used to completely rinse and fill the 5 µL sample loop installed on the HPLC (Waters 600E). This was then connected into the flow of eluent (1mL/min) from the HPLC pump and swept through the chromatographic separation column (Hypersil®PAH 100 mm x 4.6 mm i.d.). Baseline separation of the 15 PAHs was

achieved within 40 mins by gradient programming the eluent *i.e.* increasing its eluotropic strength with time according to a defined programme. Thus, far-UV HPLC grade acetonitrile (Rathburn Ltd.) with a high eluotropic strength, and HPLC grade water (Milli-Q) with a low eluotropic strength were pumped as a 50/50 mix at the start of each chromatographic run. This condition was maintained for 5 minutes into the run. Thereafter, up to 27 minutes, the proportion of acetonitrile was continuously and steadily increased from 50% to 100%. From 27 minutes until the end of the run (40 mins.) elution with 100% acetonitrile was maintained.

As each individual PAH exited the column, with its own distinctive retention time, it was directed into the scanning fluorescence detector (Waters 474). The detector was programmed so that optimized excitation and emission wavelengths for each PAH were selected based on their retention times. The following programme was found to produce the most satisfactory chromatography :

Time from run start (mins)	Excitation (nm)	Emission (nm)
0.0 –10.0	275	325
10.0 – 14.2	253	333
14.2 – 16.2	253	373
16.2 – 21.5	240	425
21.5 – 35.2	254	395
35.2 – 40.0	302	506

Table 1 Wavelength Programming of the Fluorescence Detector

By reference to one of the chromatograms (Figure 1), generated for the 16 USEPA PAH standard that was used to calibrate the HPLC system, it can be seen how the programme relates to the elution order of the PAHs and their respective retention times.

The following abbreviations are used on this chromatogram and throughout the report for the fifteen PAHs that were determined :

Ace.	Acenaphthene	Anth.	Anthracene	Chrys.	Chrysene
Fanth.	Fluoranthene	Fluor.	Fluorene	Phen.	Phenanthrene
Pyr.	Pyrene	Naph.	Naphthalene		
B(a)anth.	Benzo(a)anthracene	B(a)pyr.	Benzo(a)pyrene		
B(b)fanth.	Benzo(b)fluoranthene	B(k)fanth.	Benzo(k)fluoranthene		
B(ghi)per.	Benzo(ghi)perylene	DB(ah)anth.	Dibenzo(ah)anthracene		
I(123cd)pyr.	Indeno(1,2,3-cd)pyrene				

Table 2 Abbreviations for the 15 PAHs Determined in the Study.

Initially, the fifteen PAHs were quantified in relation to the internal standard (*p*-terphenyl). The peak area for this material should have varied little from chromatogram to chromatogram given that the same amount was added to each sample. However, it soon became apparent that for samples with high concentrations of PAH the internal standard peak was greater in area than anticipated. This indicated that the internal standard was being interfered with either by some fluorescent component of the sample (possibly a PAH) or by *p*-terphenyl that originated in the

sample. Fortunately, it was discovered that quantification on the basis of loop-filling, (*i.e.* reliance on injecting exactly the same volume of sample, or the standard PAHs solution, for each chromatogram), gave comparable uncertainties (RSD%) to quantification by an internal standard as shown in Table 3. Also presented in Table 3 are the limits of detection based on the minimum concentrations that gave clearly defined peaks, *i.e.* signal-to noise ratio ≈ 4.

Quality control performed with a low-level PAH interlaboratory comparison material (LGC Contest 33.3c) indicated that the HPLC fluorescence technique was yielding reliable data. Results obtained from the quality control material are shown in Table 5.

3 Results and Discussion

3.1 TOTAL PAH CONCENTRATIONS

The chromatographically determined values for the concentrations of the 15 PAHs together with the total organic carbon values (TOC %) appear in Table 3. Samples obtained from the Solway Firth region bear the prefix SF, whereas those from the Cumbrian coast are prefaced by 54/-04/. The PAH concentrations for each sample have been summed to give the total PAH for that sample. It should be borne in mind that this 'total', though useful for facilitating comparisons, is likely to underestimate the actual total concentration of PAH as it comprises only parental (*i.e.* non-alkylated) PAHs in the two- to seven-ringed range. Also the focus on these non-alkylated species can detract from the recognition of petrogenic PAH where lower molecular weight alkylated homologues and sulphur heterocyclics abound (Bouloubassi & Saliot, 1993). That said, most sediment PAH studies are based on the determination of a limited number of individual PAHs - typically between 9 and 28 (Readman *et al.*, 2002).

For the Solway Firth samples total PAH concentration ranges from 12 μg/kg to 1512 μg/kg and for the Cumbrian offshore coastal samples the range is 274 μg/kg to 4856 μg/kg. These ranges represent typical PAH marine sediment concentration levels, intermediate between the low levels observed in the relatively unpolluted sediments of the Barents Sea - 18 μg/kg to 500 μg/kg (Yunker *et al.*, 1996) and the highly contaminated sediments that commonly occur in proximity to urbanized areas, *e.g.* Boston Harbour, Massachusetts - 487 μg/kg to 718360 μg/kg (Shiaris & Jambard-Sweet, 1986).

There is some degree of correlation between the TOC and the total PAH concentration of the offshore Cumbrian coastal sediments. This is true also for the Solway Firth samples but to a slightly lesser extent as shown in Figure 4. Because PAHs are extremely hydrophobic they tend to sorb strongly to the organic content of a marine sediment rather than associate with the more hydrophilic mineral constituents. Moreover, when they originate, as most do, from pyrolitic sources, the high temperature combustion process leads to their invariably being bound to very fine "super-sorbent" soot particles. In such a form they can be transported great distances by the wind, hence their global ubiquity. The fine soot fraction has been found to comprise 2-30% of total organic carbon in coastal sediments (Bucheli & Gustaffson, 2000). The PAH then, in the samples analysed, was probably bound to soot particles that constituted a somewhat variable proportion of the total organic phase of the sediments leading to a somewhat loose though significant correlation.

Another feature of the correlation was that the organic matter (TOC) in the offshore Cumbrian sediments had a higher PAH loading than did the intertidal Solway Firth sediments. This implies larger concentrations of the soot combustion particles, containing bound PAH, associated with the organic matter content of the former. It seems likely that this is a consequence of greater industrialisation in the Cumbrian coastal region compared with the more rural aspect of the areas surrounding the Solway Firth. Coal burning industry would then be principally responsible for

the more substantial PAH input to the offshore Cumbrian sediments. These conclusions are of course based on the premise that the PAHs found in the sediments are primarily of a pyrolitic origin. That this was the case was demonstrated by examination of the distribution patterns of the PAHs in the sediments.

3.2 PAH DISTRIBUTION PATTERNS

Column charts that graphically display the concentrations and the distributions of the PAHs were constructed and appear in the Appendix. Inspection of these reveals that, in the main, the relative proportions of PAH are very similar in all the samples regardless of sampling location and total concentration. The pattern corresponds with one that is typical globally and epitomises PAH assemblages that result from high temperature combustion processes (McCready *et al*., 2000). It is characterised by an abundance of the high molecular weight PAHs, (*i.e.* the 4-, 5-, 6- and 7-ringed members), eight of which tend to predominate. They are fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(b)fluoranthene, indeno(1,2,3-cd) pyrene and benzo(ghi)perylene. Phenanthrene, the most thermodynamically stable of the 3-ringed PAHs, may be prominent also, although if it is present in large amounts, *i.e.* so that the phenanthrene:anthracene ratio is greater than 10, then this may be indicative of a petrogenic origin (Budzinski *et al*., 1997). The relative abundance of the PAHs in the sediments were ranked and tabulated (Table 4). The eight high molecular weight pyrolitic PAHs together with phenanthrene were ranked in order of their prevalence. It will be observed that for the offshore Cumbrian sediments there are few divergences from the nine pyrolitic PAHs being exclusively the predominant species, and these all occurred for only one core, *i.e.* 54/-0646A collected from location 646. It will be noted that this location is close to Whitehaven and its harbour. Although, now a small port with most of the large commercial shipping using Liverpool because of the shallowness of the Solway, the highest PAH levels in this study were nevertheless from this location (Table 3). It seems likely, therefore, that the local industrial pyrolitic PAH output would also be augmented by pyrolitic PAH from the engine exhausts of shipping. Fuel spills and unburnt fuel from engines may then account for the elevated naphthalene concentrations encountered and represent a petrogenic input.

It is interesting to note for locations 646 and 637, where depth profiles are available (Figure 5), that the surficial sediment has the lowest total PAH concentration in both cases. This may reflect the industrial decline of the Cumbrian coastal region, if it is assumed that sediment from the surface is historically more recent than sediment from depth and that sediment bioturbation rates are low (Latimer & Quinn, 1996). Alternatively, because the surface layer of sediment is more oxic than deeper sediments, aerobic biodegradation of PAH, which is widely acknowledged to be more favourable than its anerobic counterpart (Rockne & Strand, 1998; McNally *et al*., 1998; Coates *et al*., 1997) may have reduced the surficial PAH burden. The only other core for which a depth profile was available was SF 00/7 (Figure 5) and this exhibited low total PAHs concentration down to 100 cms, but a comparatively high level of total PAHs concentration between 175-190 cms. Again this might be a historical facet of PAH deposition and relate to the decline of shipping in the Solway Firth resulting from its limited accessibility to large modern merchant vessels.

In contrast to the largely pure pyrolitic PAHs contribution to the offshore Cumbrian coastal sediments, the Solway Firth intertidal sediments indicated the significant presence of low molecular weight PAHs in addition to the nine pyrolitic members (Table 4). Thus, appreciable amounts of naphthalene, acenaphthene and fluorene resulted in their being ranked as more abundant than indeno(1,2,3-cd)pyrene, which was usually the least abundant of the nine pyrolitic PAHs. Their presence was indicative of a proportionally greater petrogenic contribution to the total PAHs than for the Cumbrian samples. The Solway Firth and its environs support a thriving leisure and tourist industry and there is the possibility that petrogenic PAHs in the intertidal sediments stem from the leakage and incomplete combustion of the fuel employed in boats.

Another approach for the ascription of petrogenic/pyrolitic PAH origin is the use of molecular indices criteria based on isomeric ratios (Readman *et al*., 2002). The criteria arise from thermodynamic considerations of the behaviour of pairs of PAH isomers. For instance phenanthrene is more thermodynamically stable than its isomer anthracene. Accordingly, the phenanthrene: anthracene ratio is found to be temperature dependent. At low temperature, (*e.g.* the slow thermal maturation of organic matter in petroleum), the phen./anth. ratio is high (50 at 100°C) but at higher temperatures, (*e.g*. the combustion of fossil fuels), it is much lower (4 to 10). The criteria of phen./anth. >10 for petrogenic and <10 for pyrolitic inputs emerges. It must be borne in mind that this is not rigorous and borderline values need to be treated with caution. For example, phen./anth. ratios <15 usually relate to incomplete combustion of organic matter, yet the analysis of some petroleum products, can produce ratios as low as 4 to 10 for gas-oils and *ca.* 14 for crude oils before combustion (Budzinski *et al*., 1997). Similar logic may be applied to the fluor./pyr. ratio, where values >1 are classically related to pyrolitic origins, but again there are exceptions. A combination of these two ratios graphically provides more reliable estimate of PAH source (Baumard *et al.*, 1998). The ratio of another pair of isomers i.e. benz(a)anth./chrys. has also been used to provide the criteria: >0.9 (pyrolitic) and ≤ 0.4 (petrogenic) with the same caveat of caution, particularly in the intermediate zone (Gschwend & Hites, 1981).

Table 6 presents the molecular indices for the sediments. It will be observed that some of the phen/anth. ratios lie in the intermediate zone of >10 but <15, only one though is >15 and this occurs for the sediment from SF 00/7 where a petrogenic input has already been mooted. This view is reinforced by the fanth./pyr. ratio which is 7.10 for the same sample. Apart from one other sediment from SF 00/13 where this ratio is 5.83 the remainder all give values close to unity. If the benz(a)anth./chrys. ratio criteria are applied then a pyrolitic origin would have to be ascribed to all the sediments.

Plotting the phen./anth. ratio against the fanth./pyr. ratio gives the plot that appears in Figure 6. It can be seen from this that twelve of the total of fourteen offshore Cumbrian coastal sediments, that were analysed for PAH, plot within the pyrolitic quadrant of the graph with the remaining two being in close proximity to the borderlines of this quadrant. Only five Solway Firth intertidal sediment analyses plot in the pyrolitic quadrant, the remaining nine appear in the intermediate quadrants. No sample plotted in the petrogenic quadrant. Essentially the information provided by the graph supports the conclusions arrived at from consideration of the PAH distribution bar charts as expressed in Table 4.

References

Most of the references listed below are held in the Library of the British Geological Survey at Keyworth, Nottingham. Copies of the references may be purchased from the Library subject to the current copyright legislation.

BAUMARD, P, BUDZINSKI, H, MCHIN, Q, GARRIGUES, P, BURGEOT, T, and BELLOCQ, J. 1998. Origin and bioavailability of PAHs in the Mediterranean Sea from mussel and sediment records. *Estuarine, Coastal and Shelf Science*, Vol. 47, 77-90.

BOULOUBASSI, I, and SALIOT, A. 1993. Investigation of anthropogenic and natural organic inputs in estuarine sediments using hydrocarbon markers (NAH, LAB, PAH) . *Oceanologica Acta*, Vol. 16, 145-161.

BUCHELI , T D, and GUSTAFSSON, Ö. 2000. Quantification of the soot-water distribution coefficient of PAHs provides mechanistic basis for enhanced sorption observations. *Environmental Science and Technology*, Vol. 34 (24), 5144-5151.

BUDZINSKI, H, JONES, I, BELLOCQ, J, PIÉRARD, C, and GARRIGUES, P. 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the Gironde estuary. *Marine Chemistry*, Vol. 58, 85-97.

COATES, J D, WOODWARD, J, ALLEN, J, PHILP, P, and LOVLEY, D R. 1997. Anaerobic degradation of polycyclic aromatic hydrocarbons and alkanes in petroleum-contaminated marine harbor sediments. *Applied and Environmental Microbiology*, Vol. 63 (9), 3589-3593.

GSCHWEND, P M, and HITES, R A. 1981. Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern United States. *Geochimica et Cosmochimica Acta*, Vol. 45, 2359-2367.

LATIMER, J S, and QUINN, J G. 1996. Historical trends and current inputs of hydrophobic organic compounds in an urban estuary: The sedimentary record. *Environmental Science and Technology*, Vol. 30 (2), 623-633.

LEHR, R E, and JERINA, D M. 1977. Metabolic activations of polycyclic hydrocarbons: Structure-activity relationships. *Archives of Toxicology*, Vol. 39, 1-6.

MCCREADY, S, SLEE, D J, BIRCH, G F, and TAYLOR, S E. 2000. The distribution of polycyclic aromatic hydrocarbons in surficial sediments of Sydney Harbour, Australia. *Marine Pollution Bulletin*, Vol. 40 (11), 999-1006.

MCNALLY, D L, MIHELCIC, J R, and LUEKING, D R. 1998. Biodegradation of three- and four-ring polycyclic aromatic hydrocarbons under aerobic and denitrifying conditions. *Environmental Science and Technology*, Vol. 32 (17), 2633-2639.

READMAN, J W, FILLMANN, G, TOLOSA, I, BARTOCCI, J, VILLENEUVE, J-P, CATINNI, C, and MEE, L D. 2002. Petroleum and PAH contamination of the Black Sea. *Marine Pollution Bulletin*, Vol. 44 (1), 48-62.

ROCKNE, K J, and STRAND, S E. 1998. Biodegradation of bicyclic and polycyclic aromatic hydrocarbons in anaerobic enrichments. *Environmental Science and Technology*, Vol. 32 (24), 3962-3967.

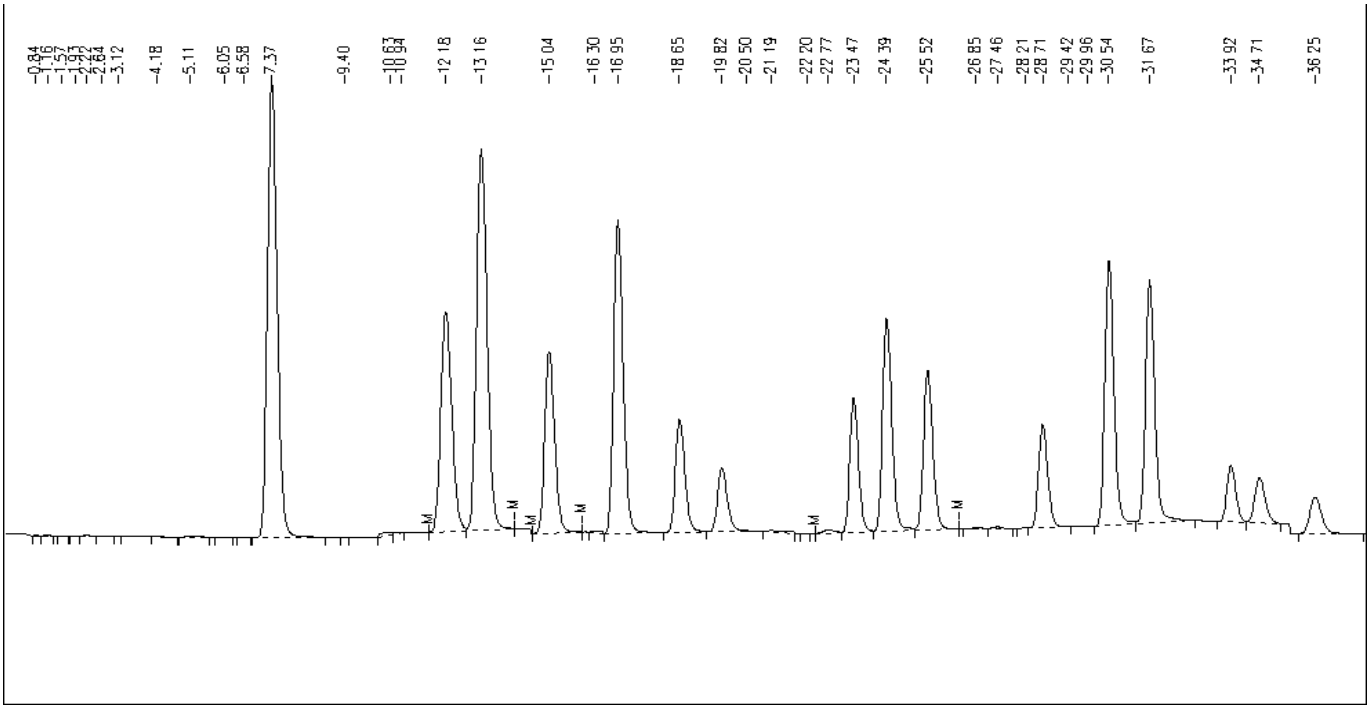
SHIARIS, M P, and JAMBARD-SWEET, D. 1986. Polycyclic aromatic hydrocarbons in surficial sediments of Boston Harbour, Massachusetts, USA. *Marine Pollution Bulletin*, Vol. 17 (10), 469-472.

TOLOSA, I, BAYONA, J M, and ALBAIGÉS, J. 1996. Aliphatic and polycyclic aromatic hydrocarbons and sulfur/oxygen derivatives in northwestern Mediterranean sediments: Spatial and temporal variability, fluxes, and budgets. *Environmental Science and Technology*, Vol. 30 (8), 2495-2503.

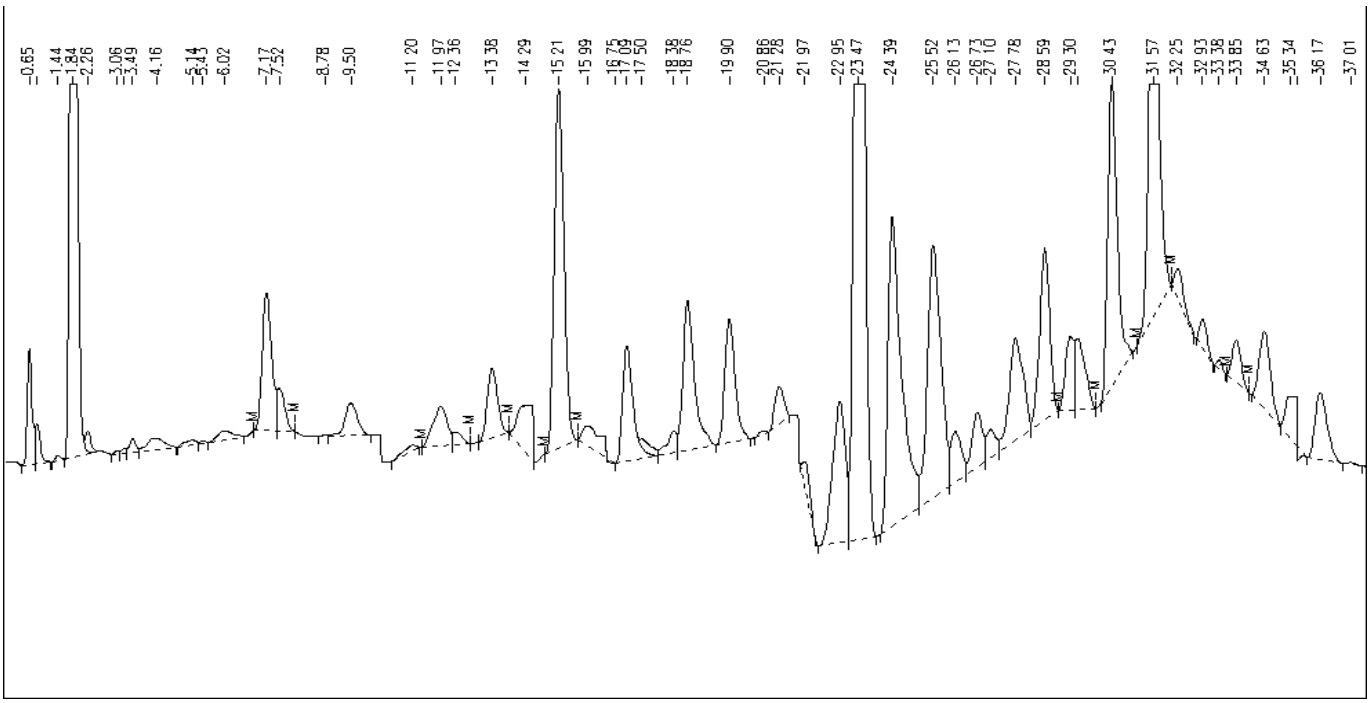
YUNKER, M B, SNOWDON , L R, MACDONALD , R W, SMITH, J N, FOWLER, M G, SKIBO, D N, MCLAUGHLIN, F A, DANYUSHEVSKAYA, A I, PETROVA, V I, and IVANOV, G I. 1996. Polycyclic aromatic hydrocarbon composition and potential sources for sediment samples from the Beaufort and Barents Seas. *Environmental Science and Technology*, Vol. 30 (4), 1310-1320.

FIGURES

PAH Standard Solution



1 2 3 4 5 6 7 IS 8 9 10 11 12 13 14 15



Sediment 54/-04/637A 0-8 cm

1 Naph. 3 Fluor. 5 Anth. 7 Pyr. IS Internal Std. 10 B(b)fanth. 12 B(a)pyr. 14 B(ghi)per.
2 Ace. 4 Phen. 6 Fanth. 8 B(a)anth. 9 Chrys. 11 B(k)fanth. 13 DB(ah)anth. 15 I(123cd)pyr.

Figure 1 PAH Chromatograms for a Calibration Standard and a Sediment.

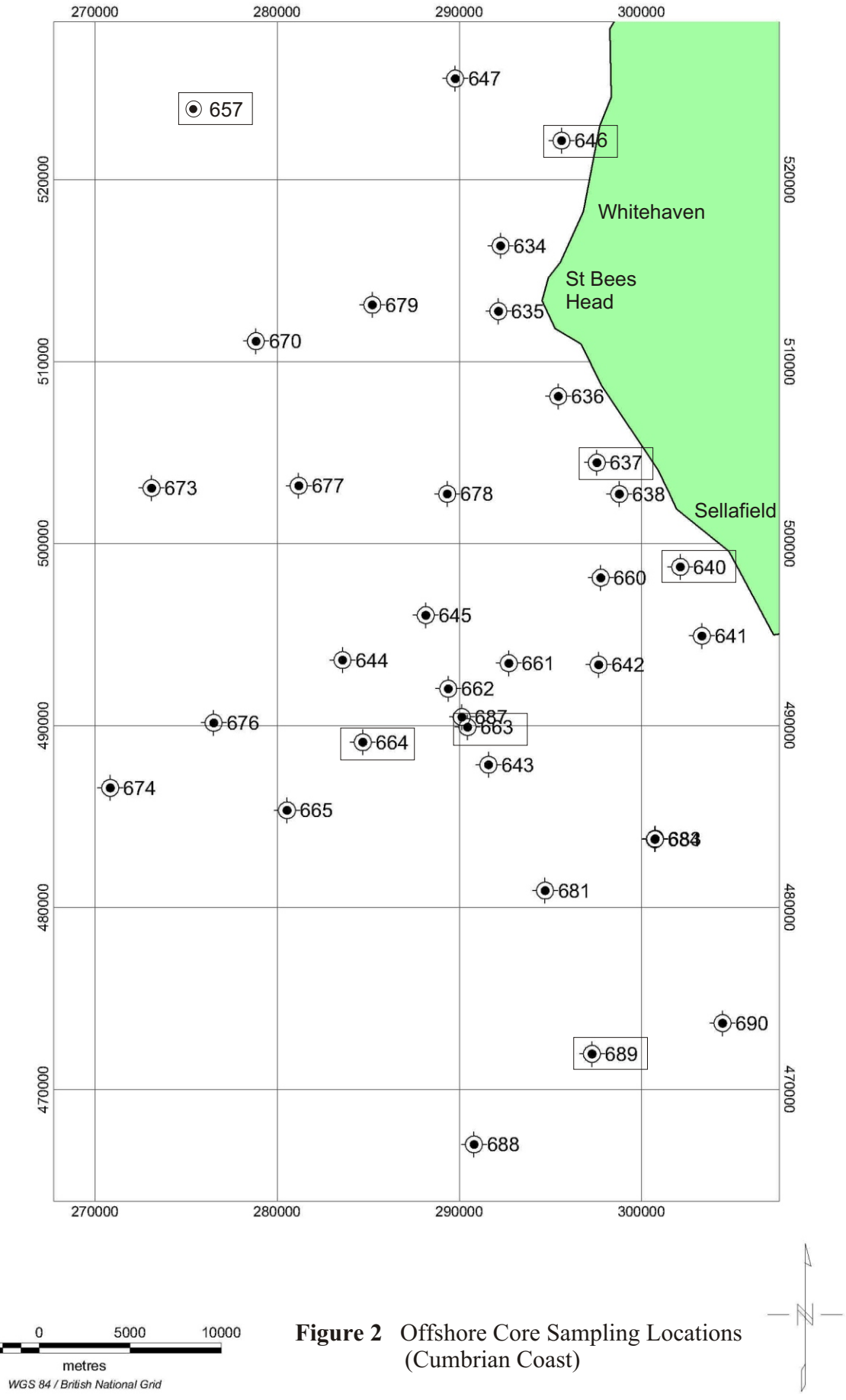


Figure 2 Offshore Core Sampling Locations (Cumbrian Coast)

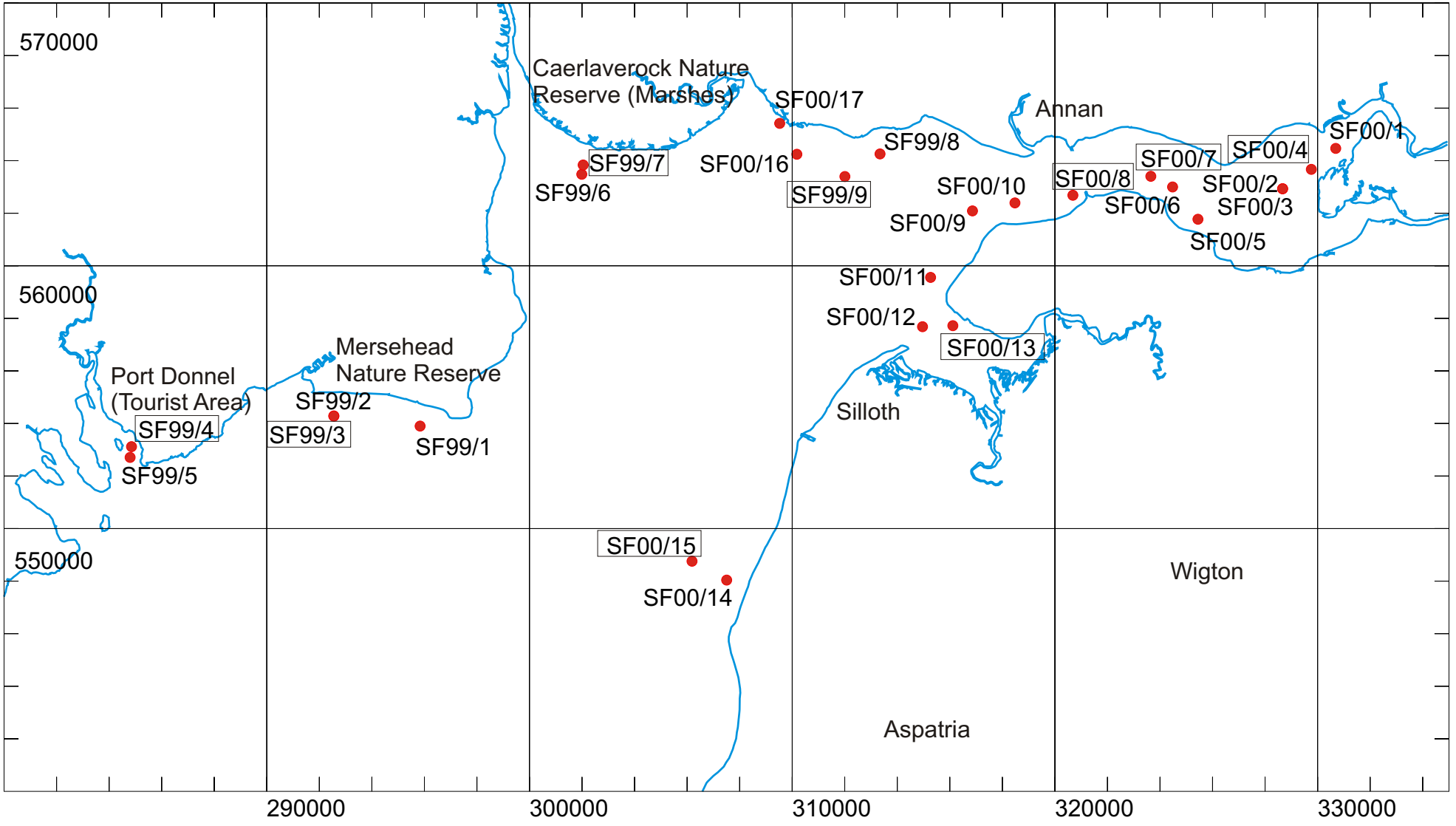
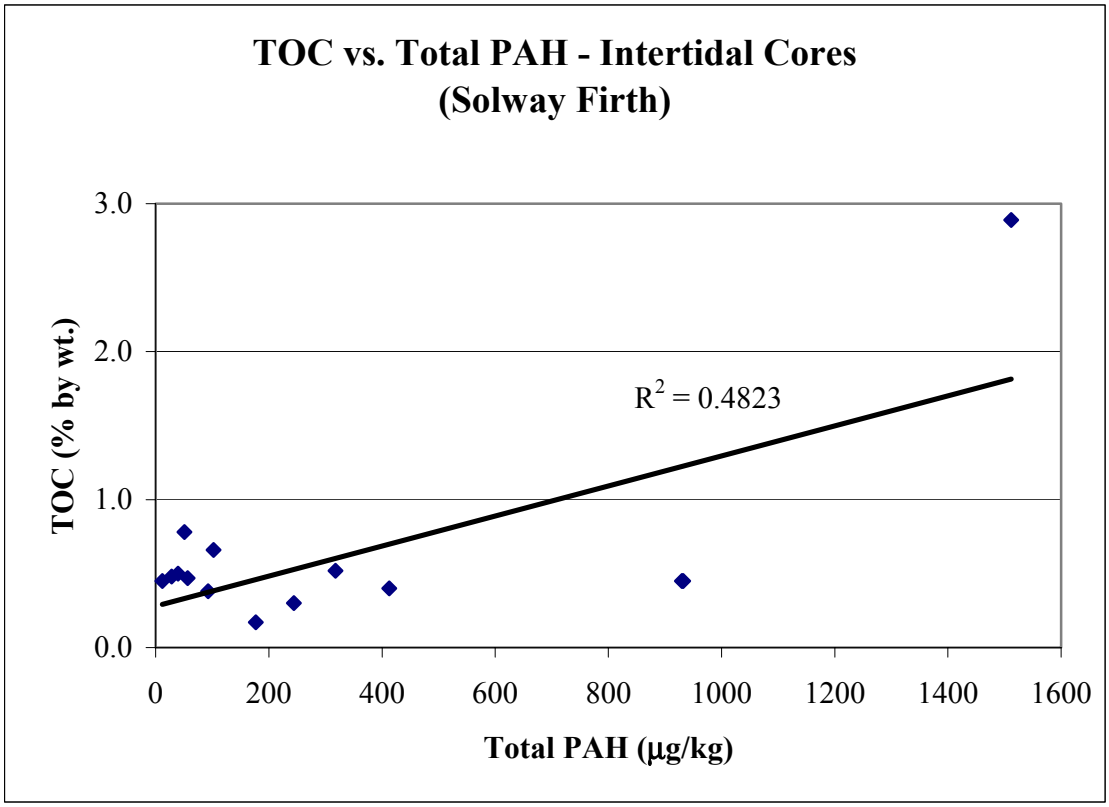


Figure 3 Intertidal Core Sampling Locations (Solway Firth)



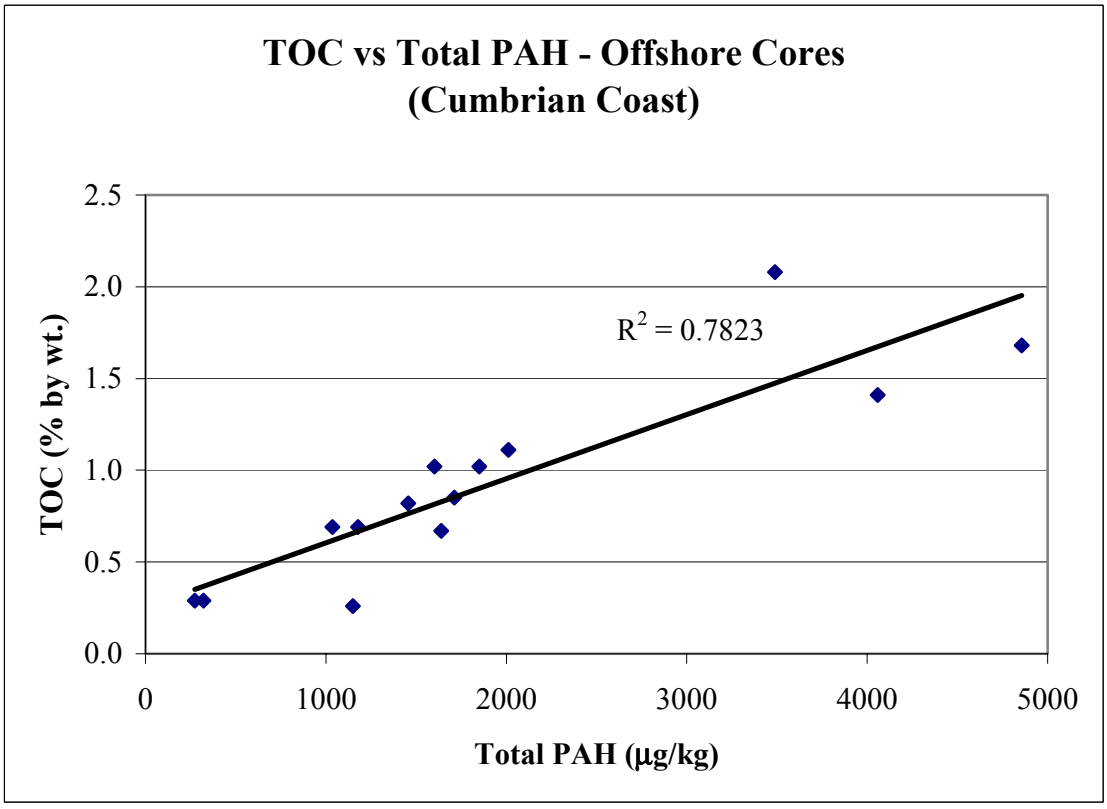


Figure 4 Correlation between Total PAH Concentration and TOC%

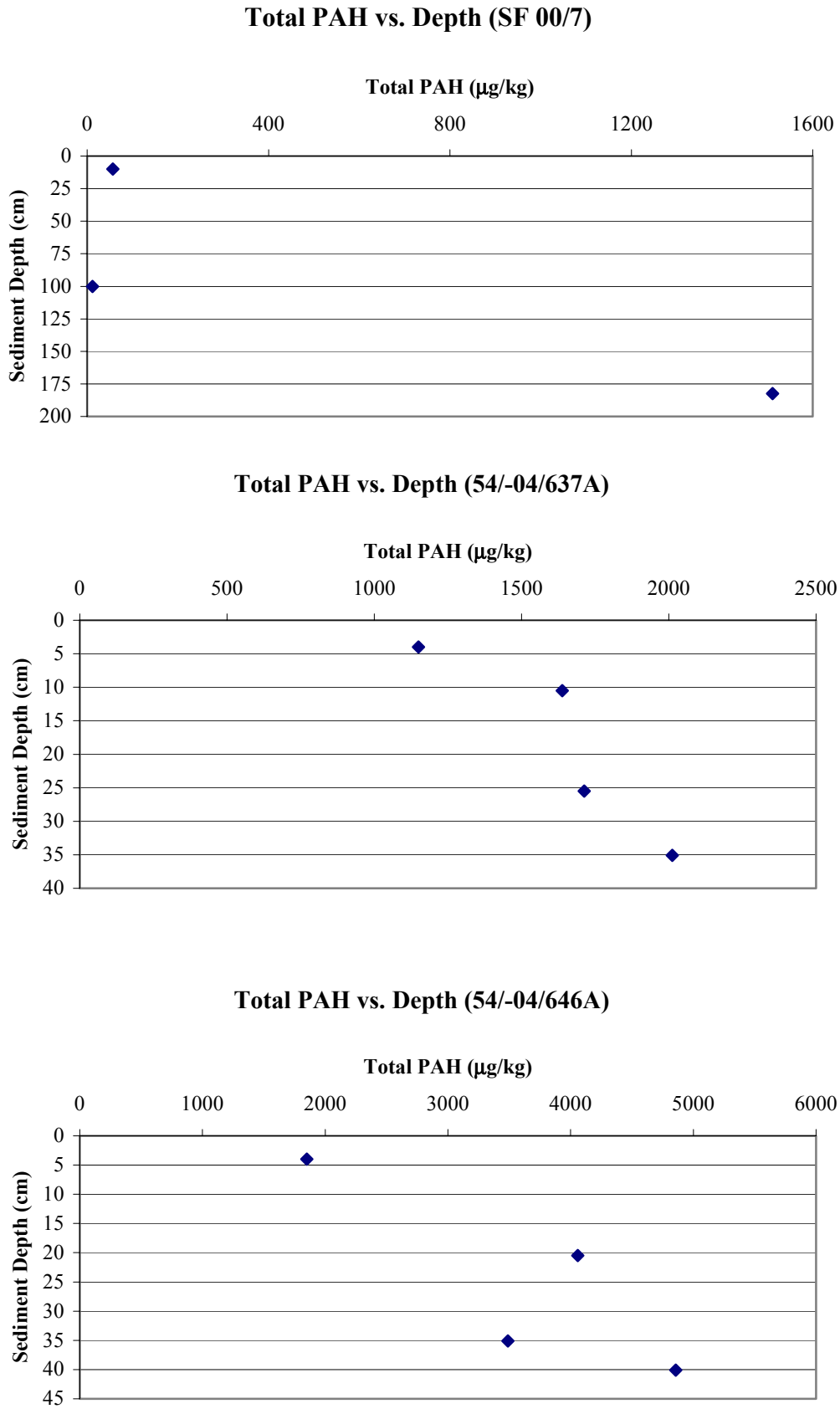


Figure 5 Total PAH Concentration Depth Profiles

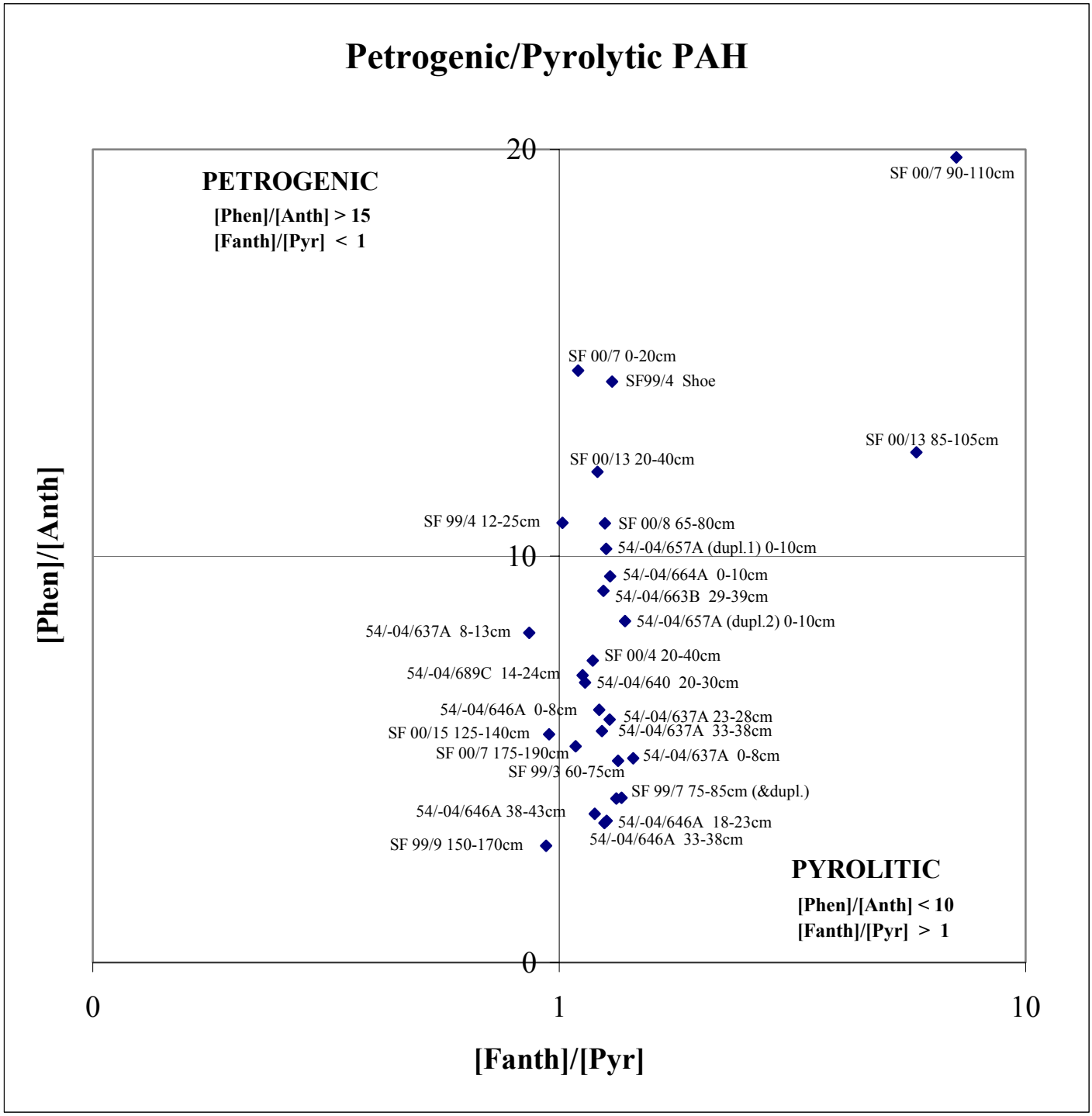
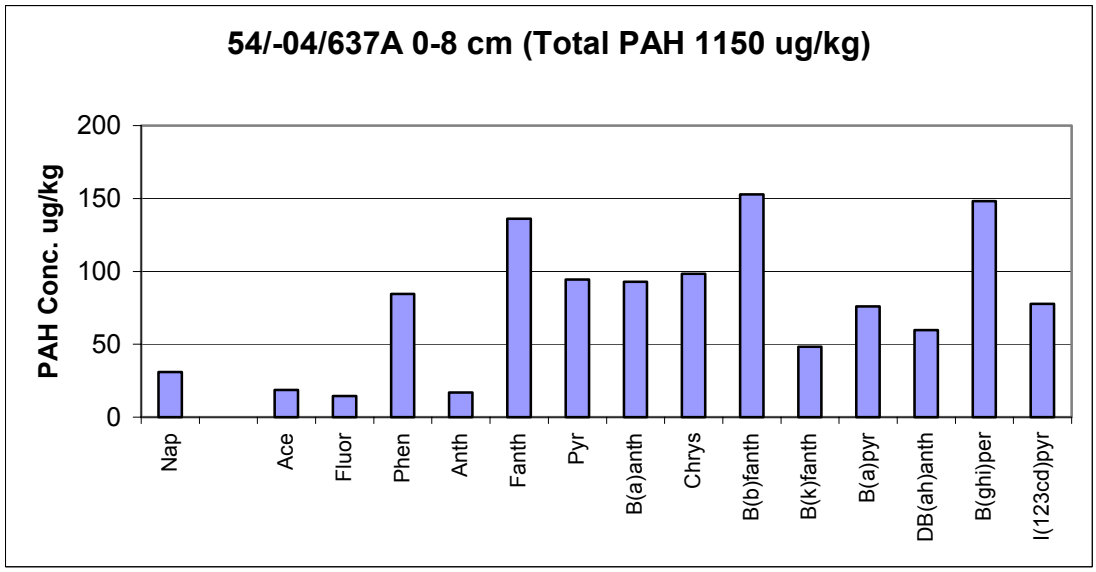
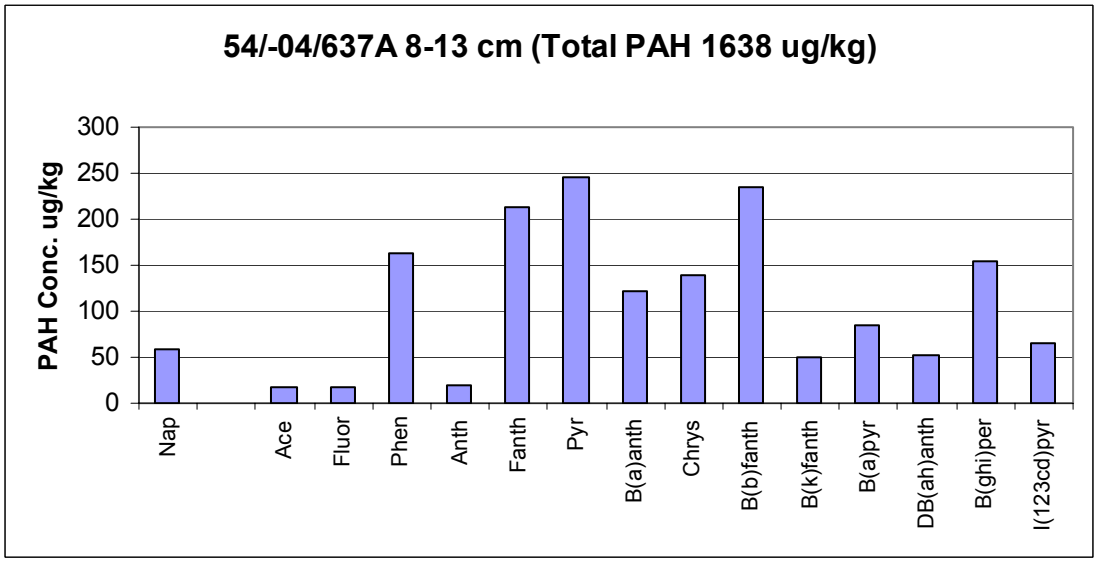


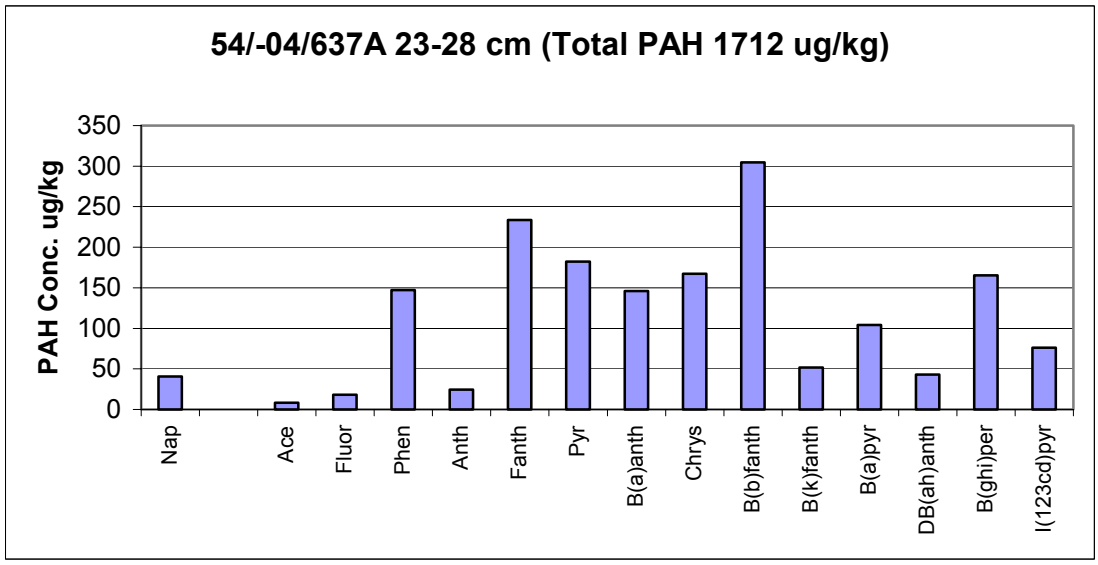
Figure 6 Isomeric Ratios Plot for Determination of PAH Origin

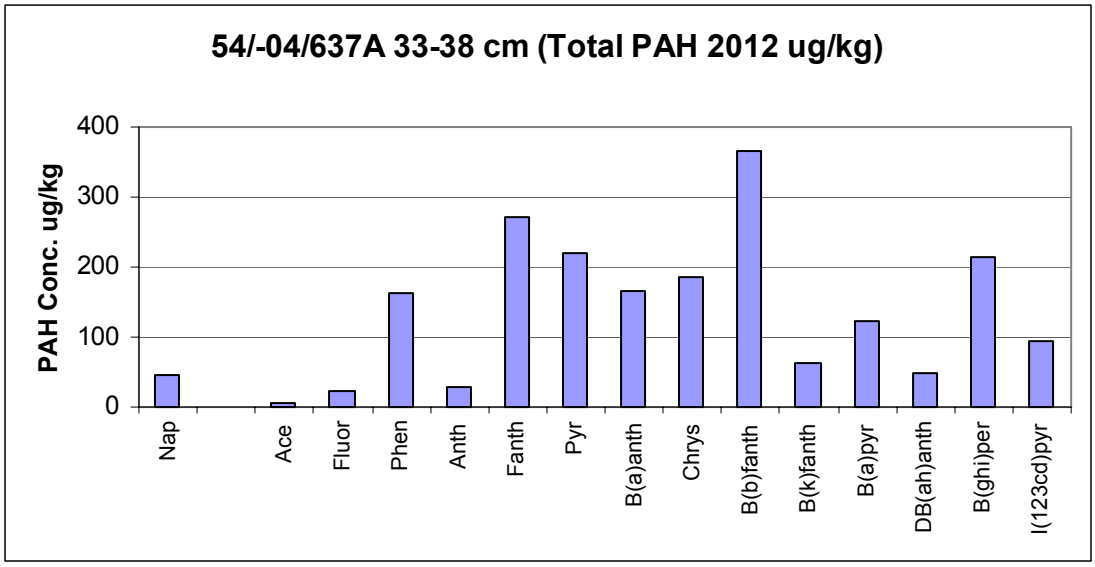
APPENDIX

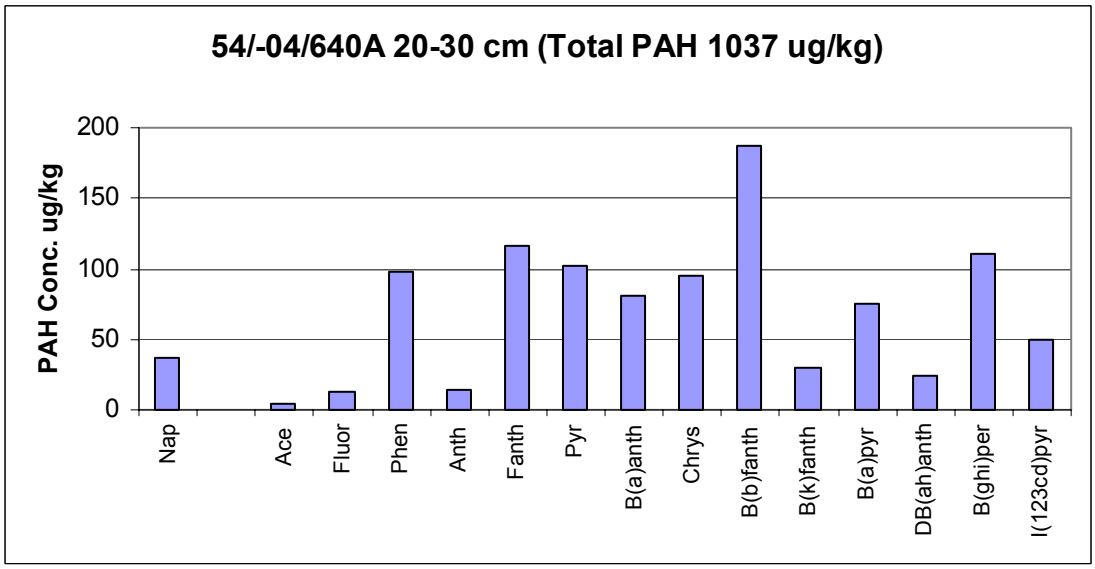
Bar Charts of PAH Distributions in Offshore and Intertidal Sediments
From the Irish Sea

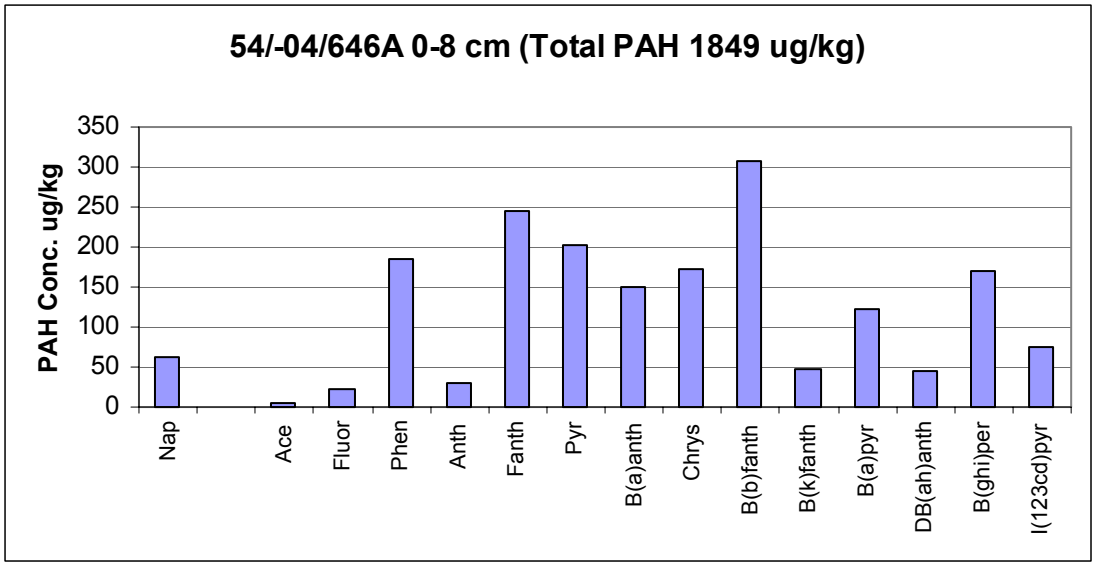

54/-04/637A 0-8 cm (Total PAH 1150 ug/kg)
PAH Conc. ug/kg
200
150
100
50
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

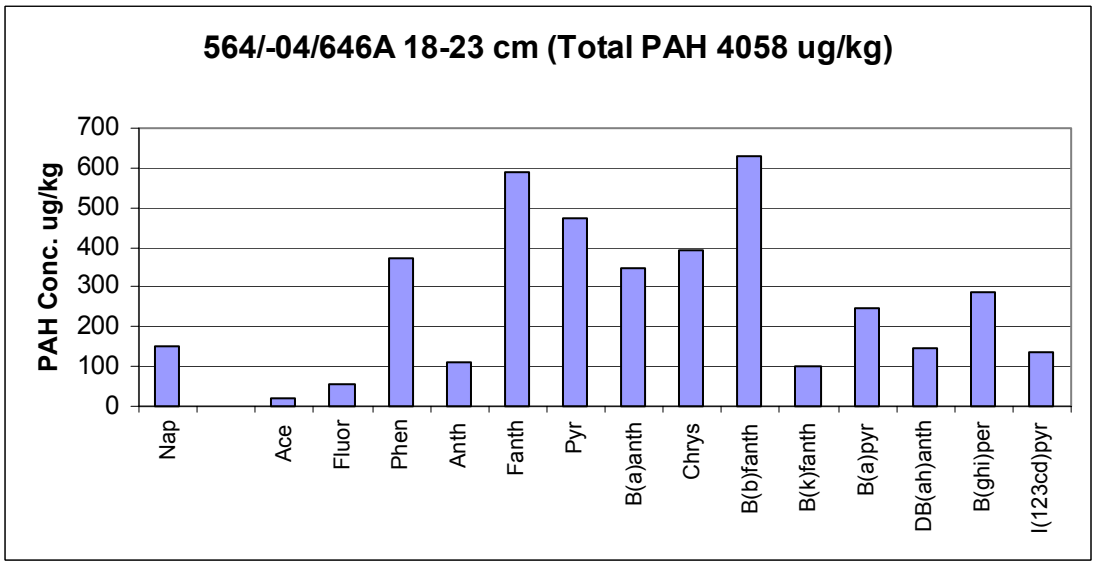

54/-04/637A 8-13 cm (Total PAH 1638 ug/kg)
PAH Conc. ug/kg
300
250
200
150
100
50
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

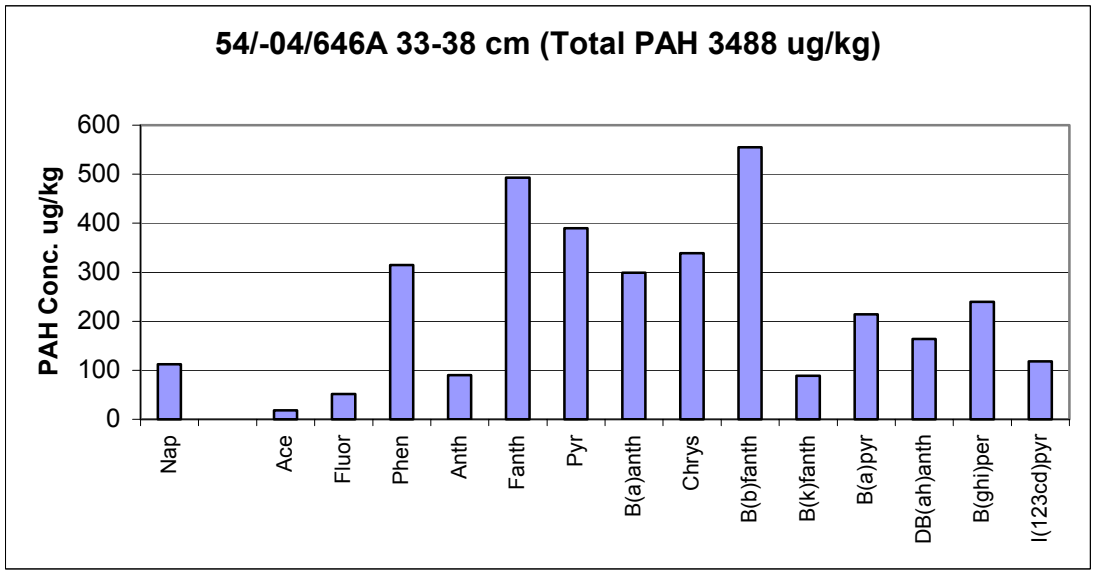

54/-04/637A 23-28 cm (Total PAH 1712 ug/kg)
PAH Conc. ug/kg
350
300
250
200
150
100
50
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

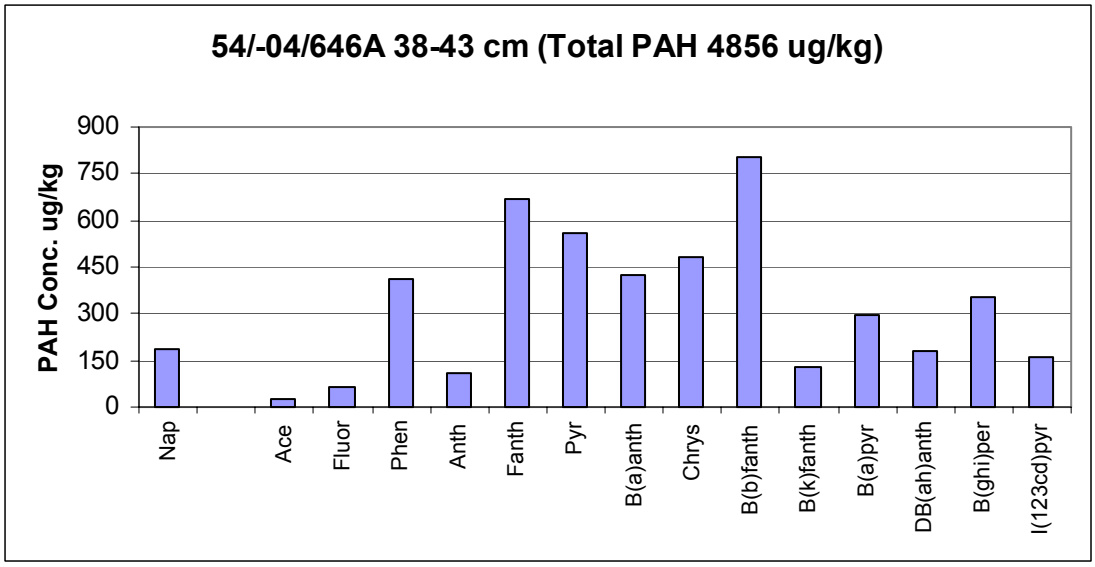

54/-04/637A 33-38 cm (Total PAH 2012 ug/kg)
PAH Conc. ug/kg
400
300
200
100
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

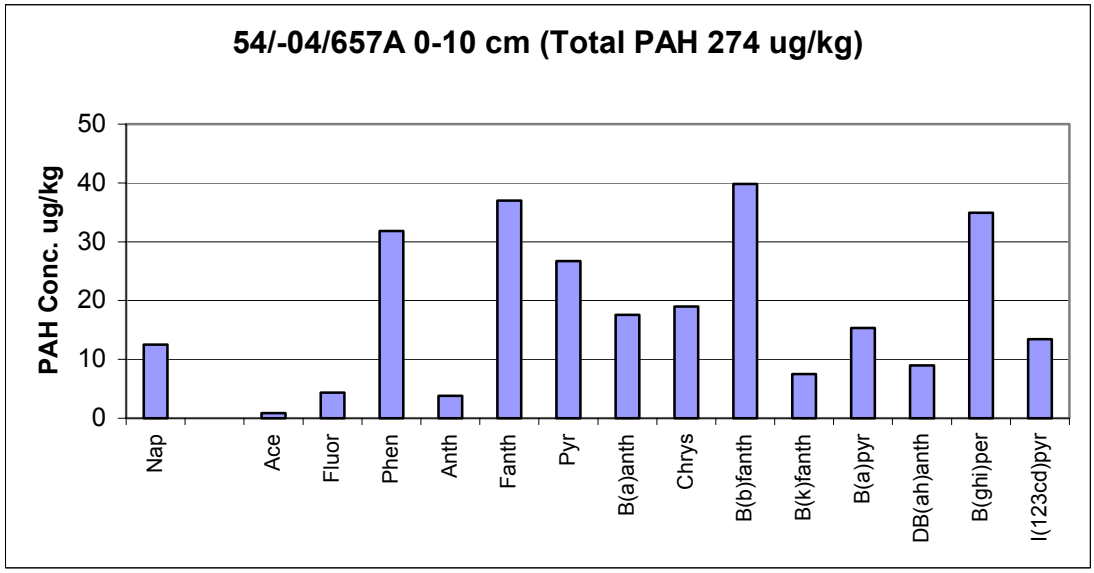

54/-04/640A 20-30 cm (Total PAH 1037 ug/kg)
PAH Conc. ug/kg
200
150
100
50
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

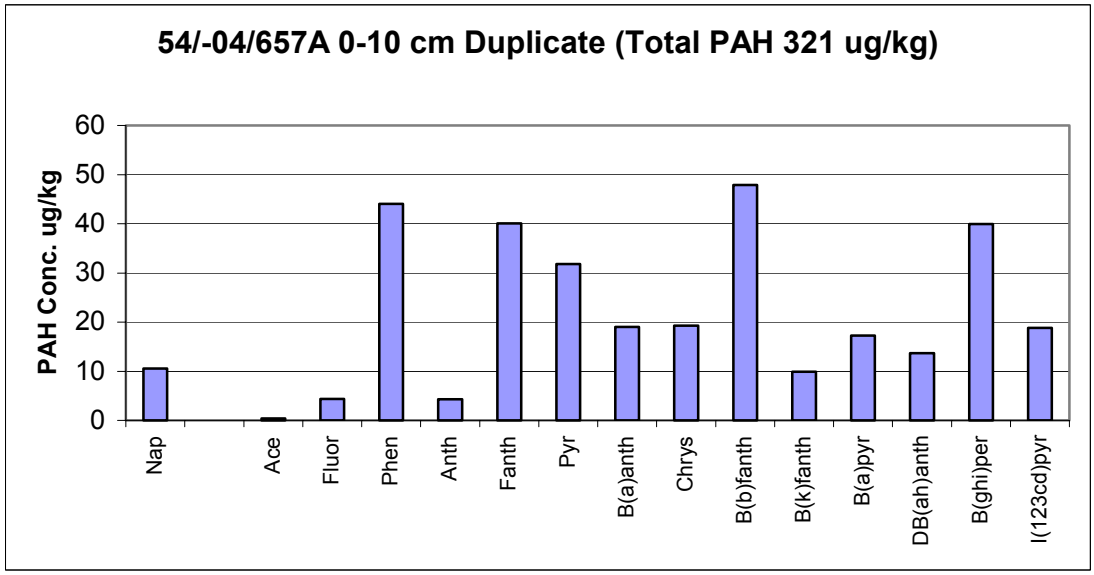

54/-04/646A 0-8 cm (Total PAH 1849 ug/kg)
PAH Conc. ug/kg
350
300
250
200
150
100
50
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

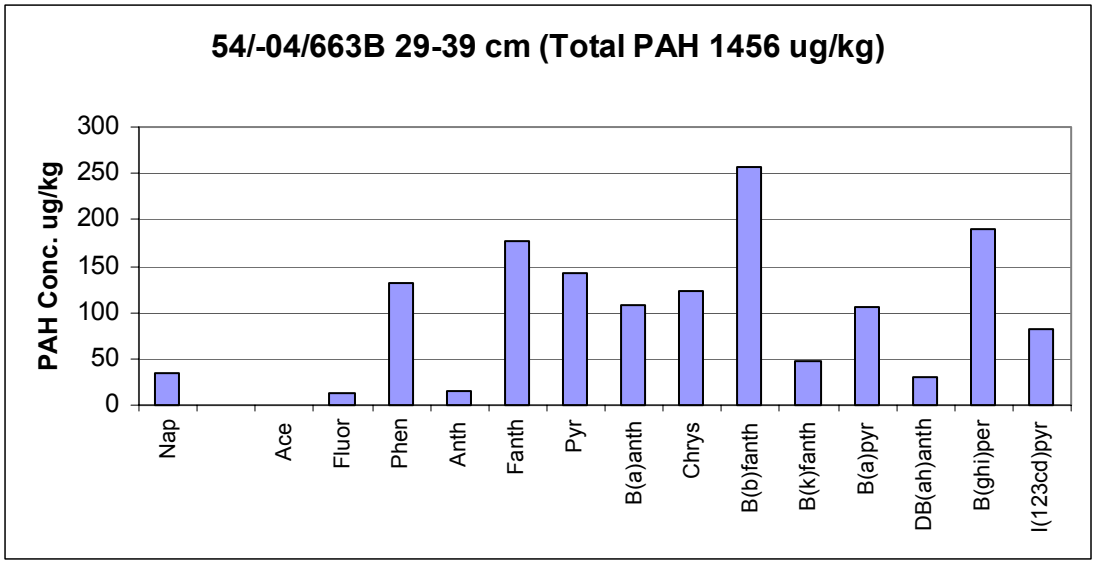

564/-04/646A 18-23 cm (Total PAH 4058 ug/kg)
PAH Conc. ug/kg
700
600
500
400
300
200
100
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

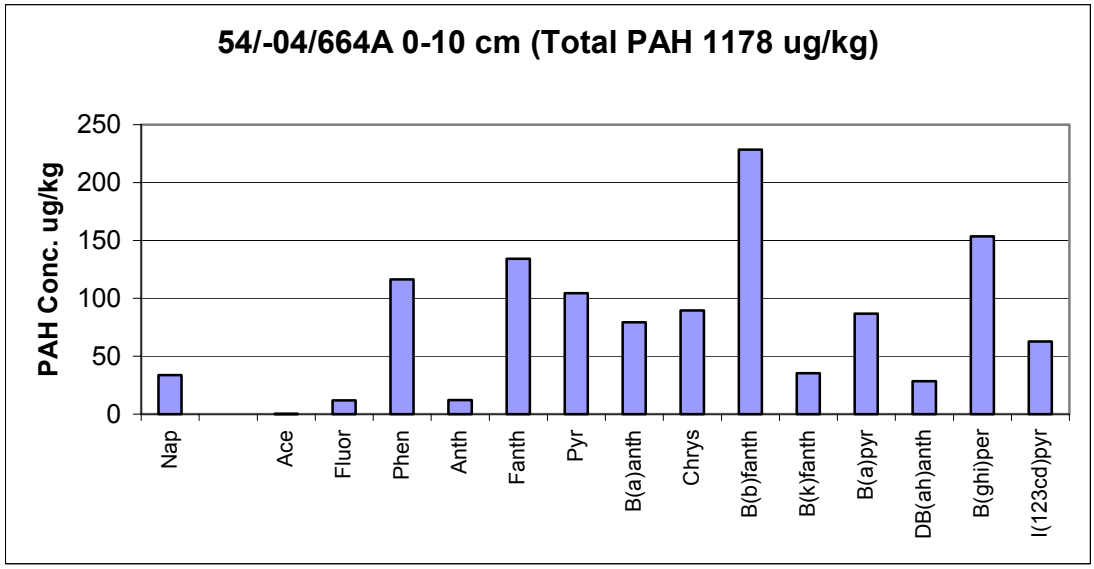

54/-04/646A 33-38 cm (Total PAH 3488 ug/kg)
PAH Conc. ug/kg
600
500
400
300
200
100
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

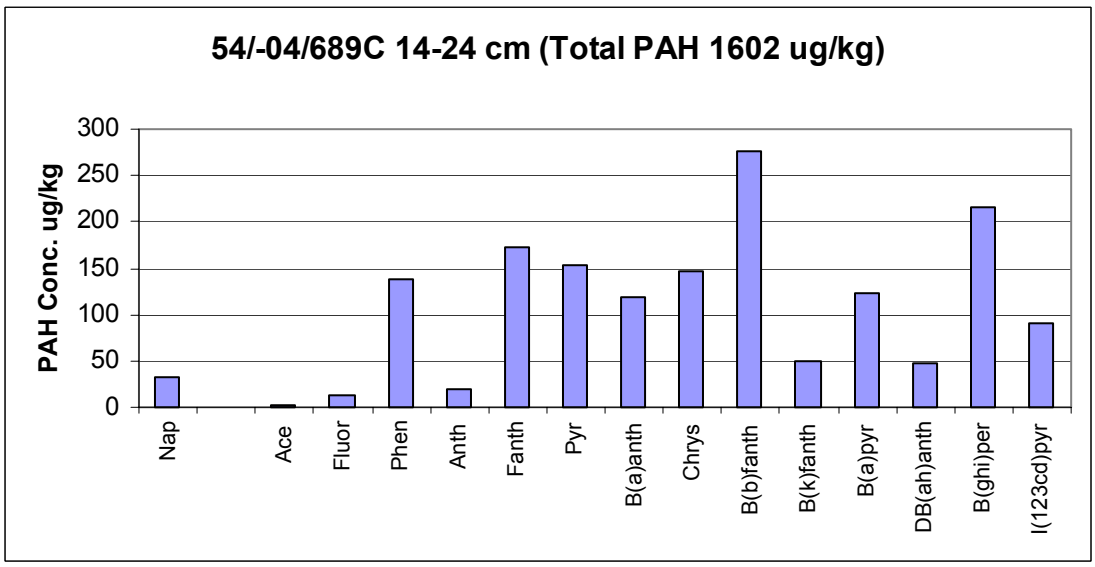

54/-04/646A 38-43 cm (Total PAH 4856 ug/kg)
PAH Conc. ug/kg
900
750
600
450
300
150
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

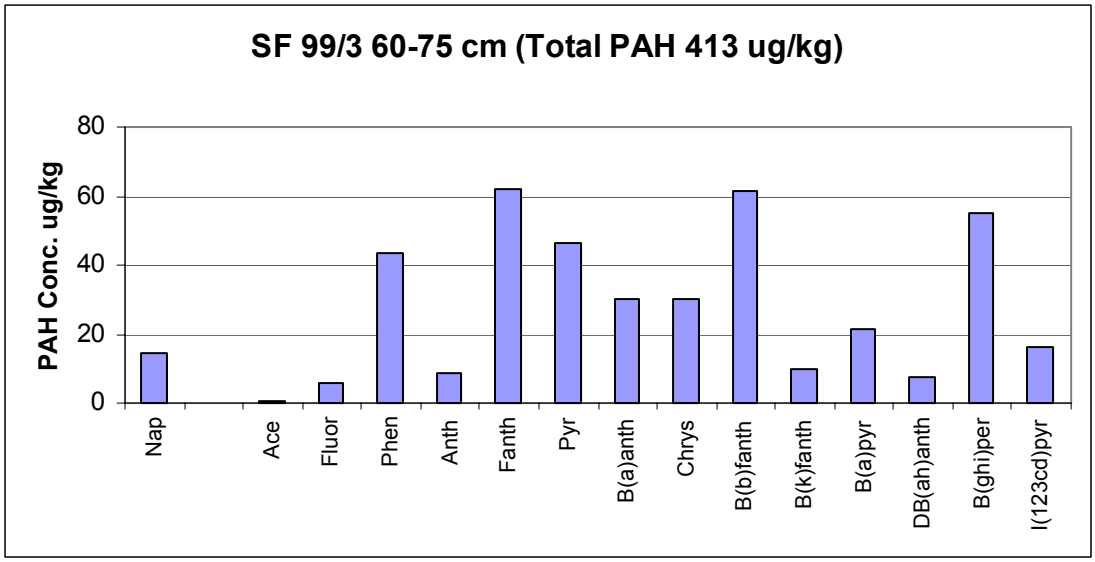

54/-04/657A 0-10 cm (Total PAH 274 ug/kg)
PAH Conc. ug/kg
50
40
30
20
10
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

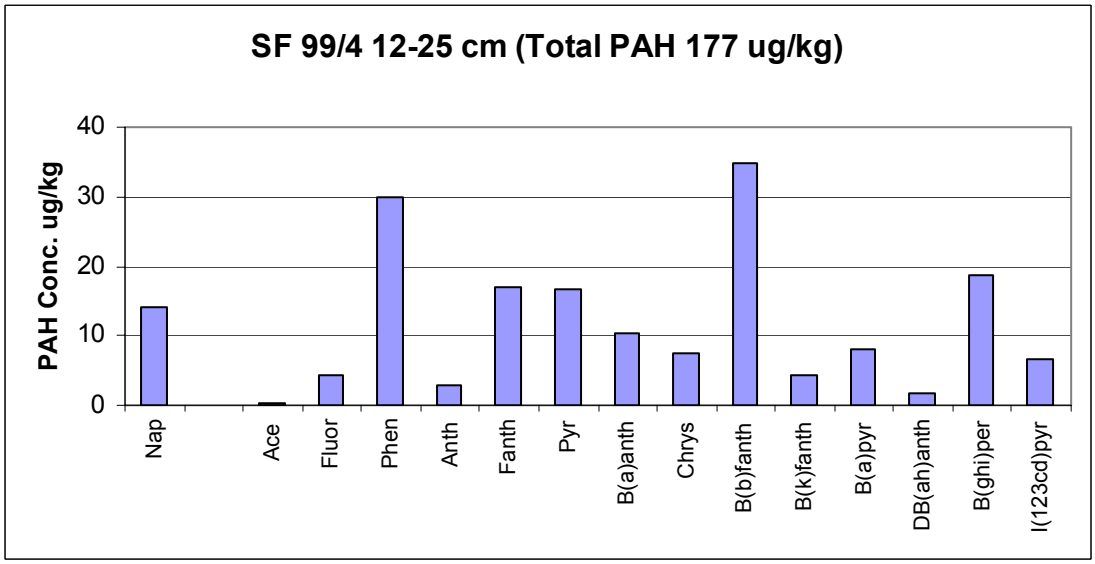

54/-04/657A 0-10 cm Duplicate (Total PAH 321 ug/kg)
PAH Conc. ug/kg
60
50
40
30
20
10
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

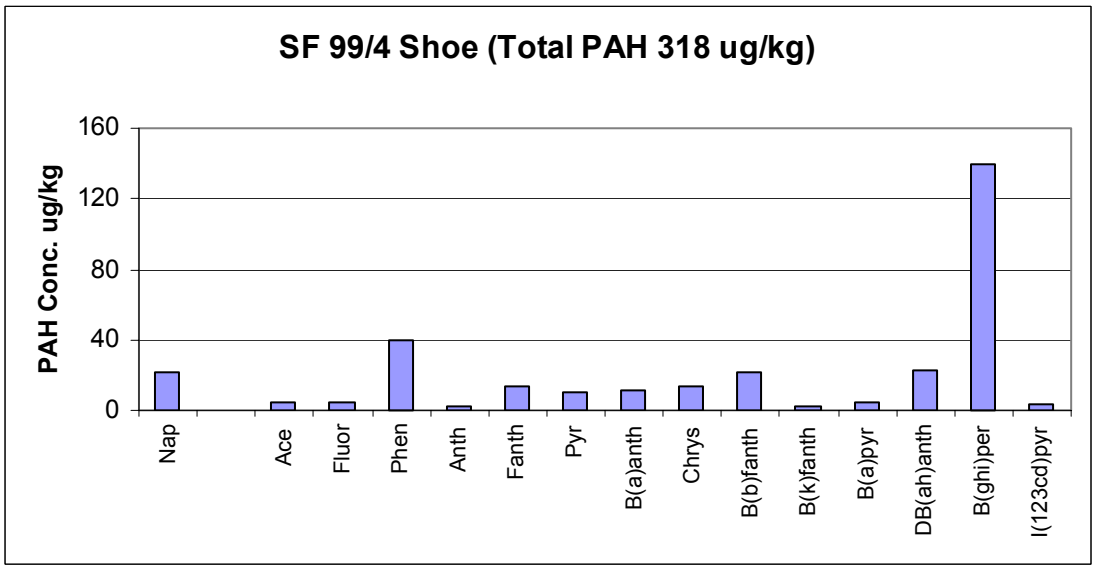

54/-04/663B 29-39 cm (Total PAH 1456 ug/kg)
PAH Conc. ug/kg
300
250
200
150
100
50
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

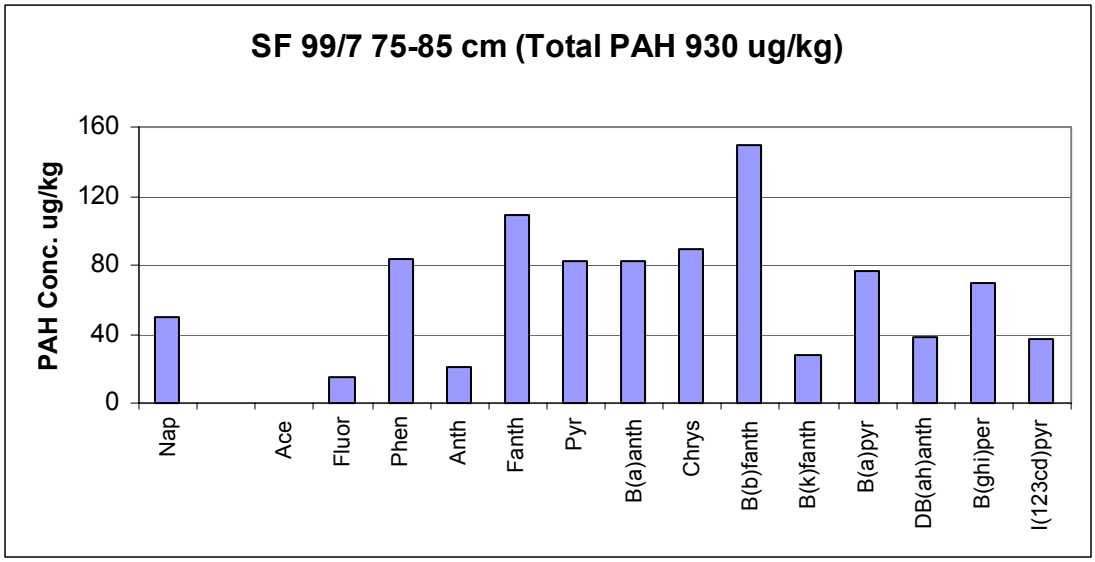

54/-04/664A 0-10 cm (Total PAH 1178 ug/kg)
PAH Conc. ug/kg
250
200
150
100
50
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

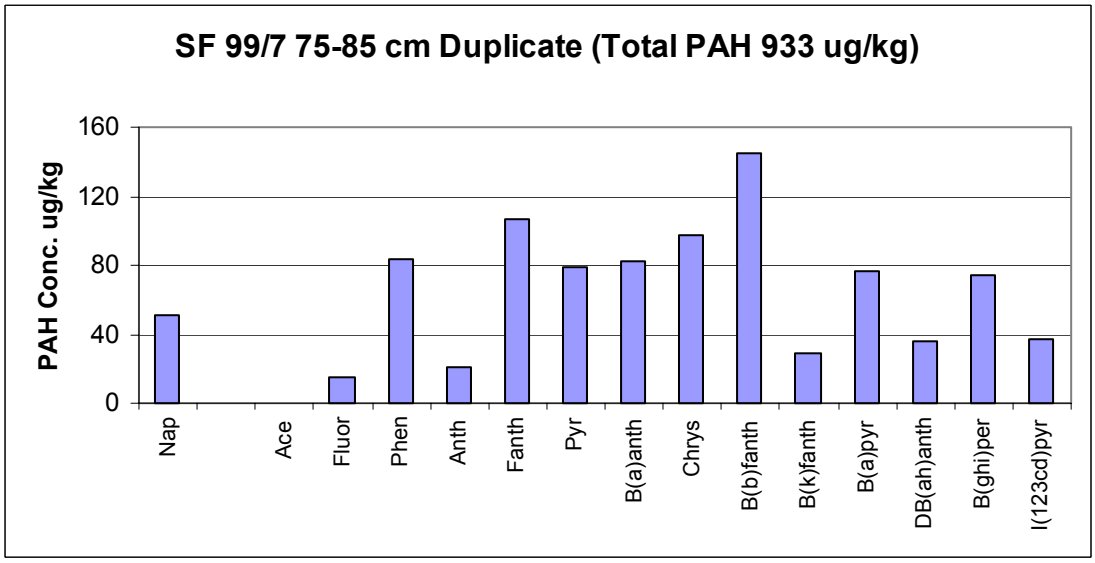

54/-04/689C 14-24 cm (Total PAH 1602 ug/kg)
PAH Conc. ug/kg
300
250
200
150
100
50
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

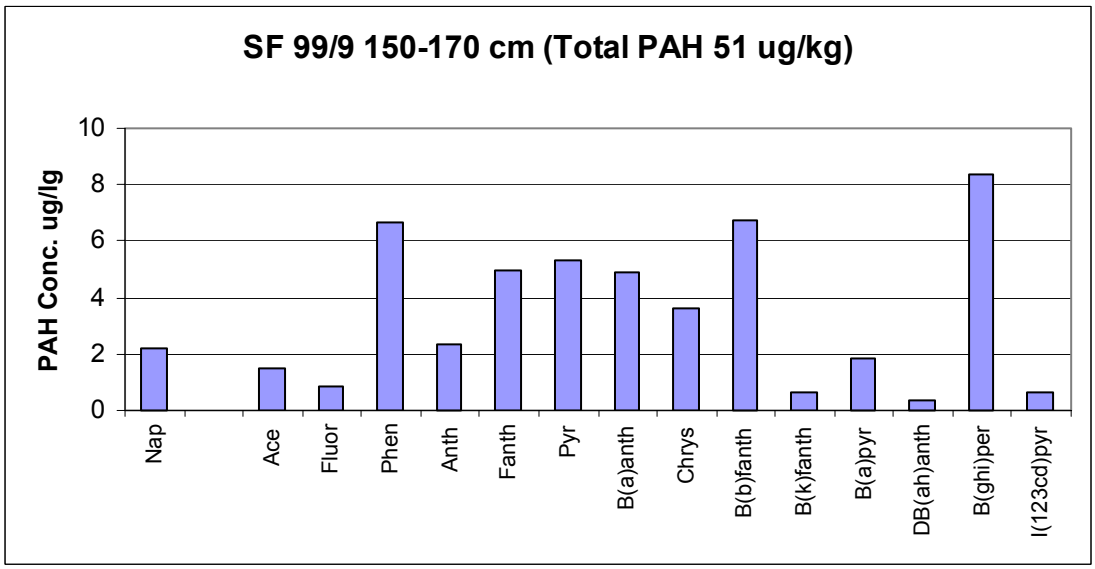

SF 99/3 60-75 cm (Total PAH 413 ug/kg)
PAH Conc. ug/kg
0
20
40
60
80
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

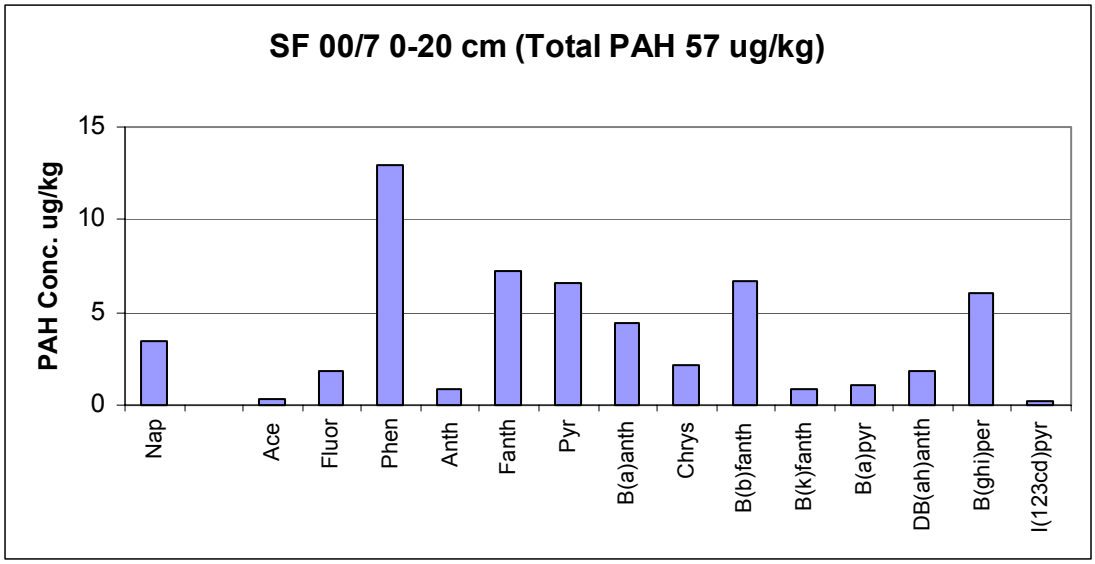

SF 99/4 12-25 cm (Total PAH 177 ug/kg)
PAH Conc. ug/kg
0
10
20
30
40
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

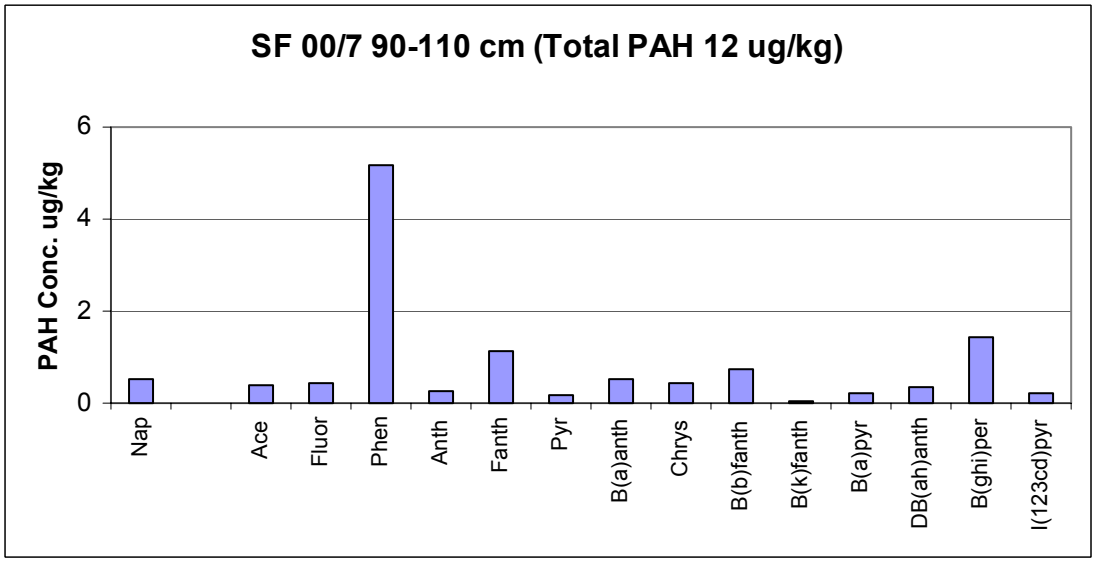

SF 99/4 Shoe (Total PAH 318 ug/kg)
PAH Conc. ug/kg
0
40
80
120
160
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

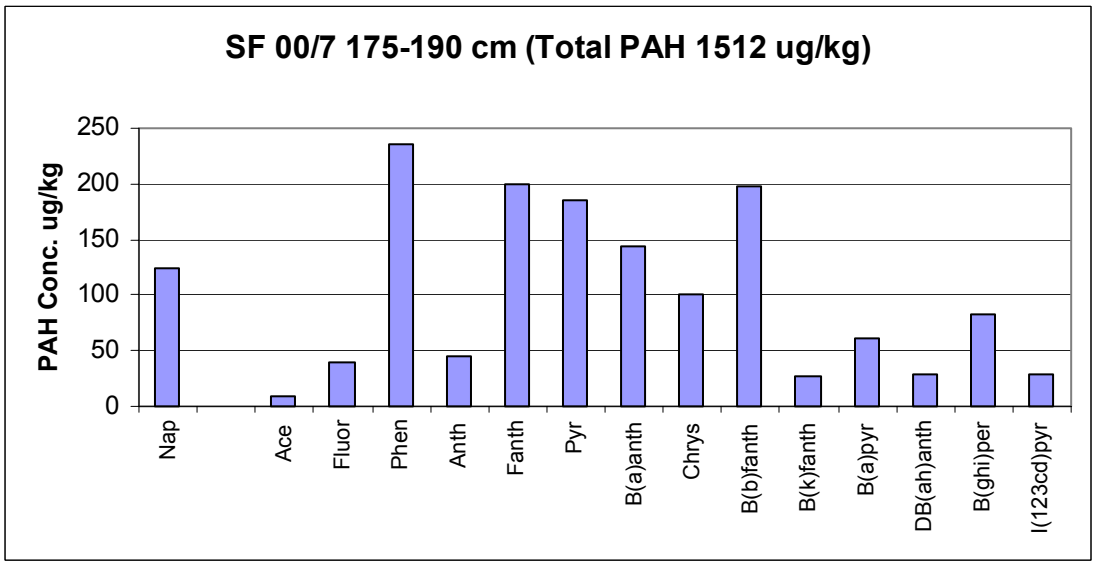

SF 99/7 75-85 cm (Total PAH 930 ug/kg)
PAH Conc. ug/kg
160
120
80
40
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

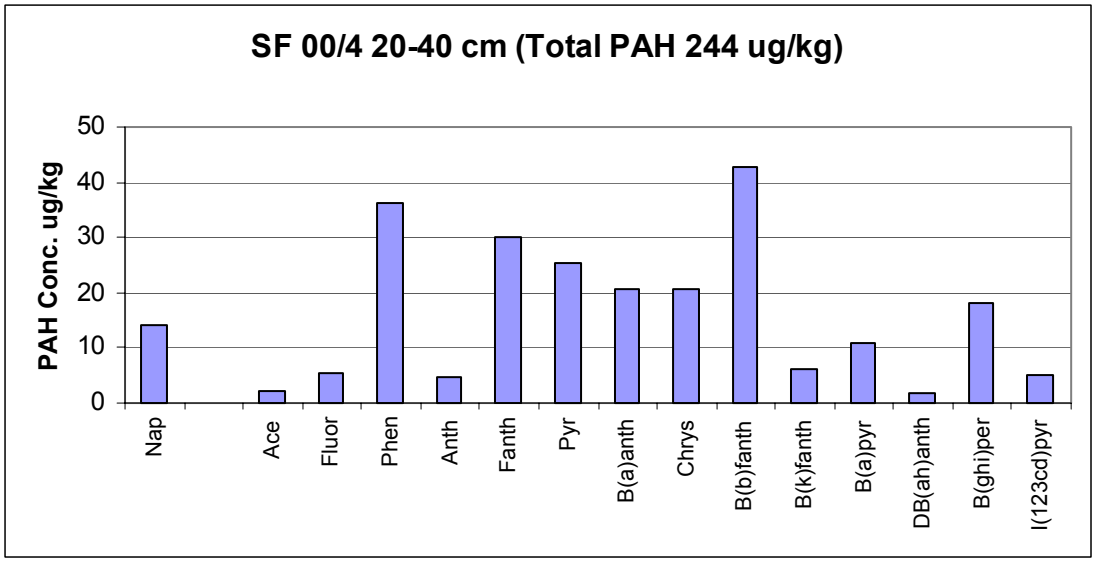

SF 99/7 75-85 cm Duplicate (Total PAH 933 ug/kg)
PAH Conc. ug/kg
160
120
80
40
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

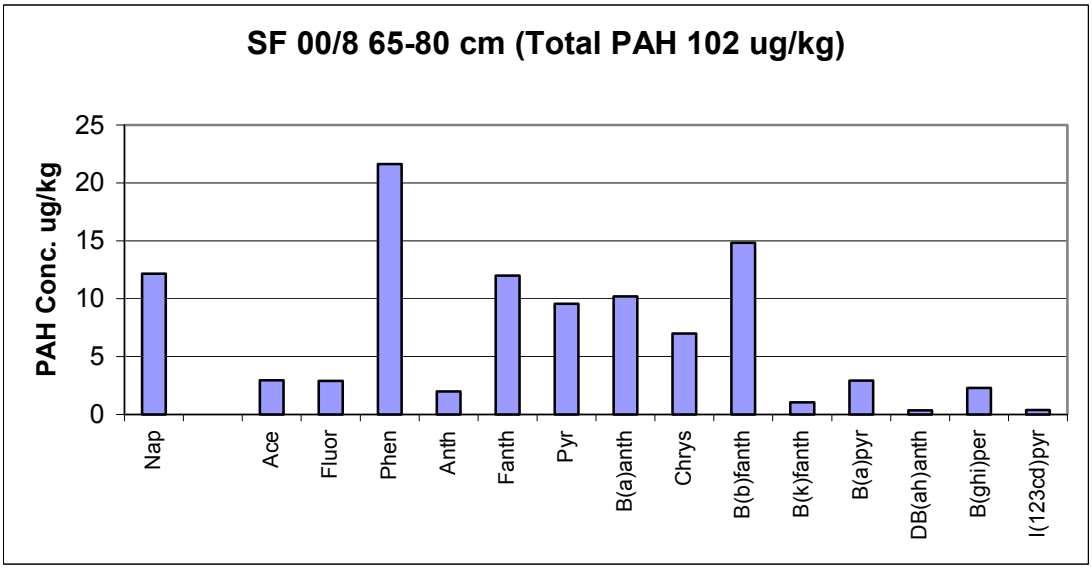

SF 99/9 150-170 cm (Total PAH 51 ug/kg)
PAH Conc. ug/lg
10
8
6
4
2
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

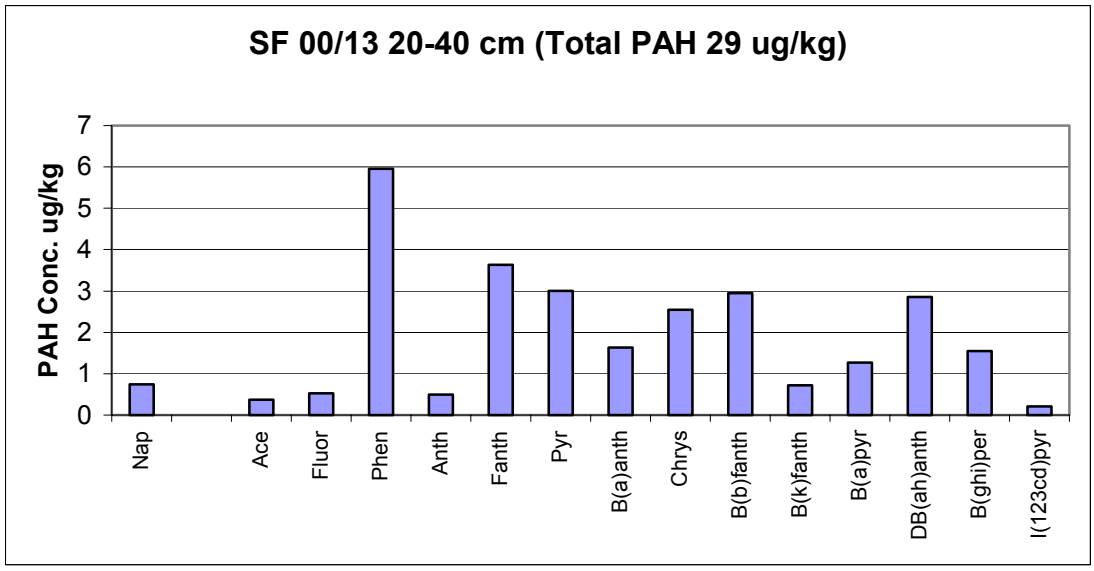

SF 00/7 0-20 cm (Total PAH 57 ug/kg)
PAH Conc. ug/kg
15
10
5
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

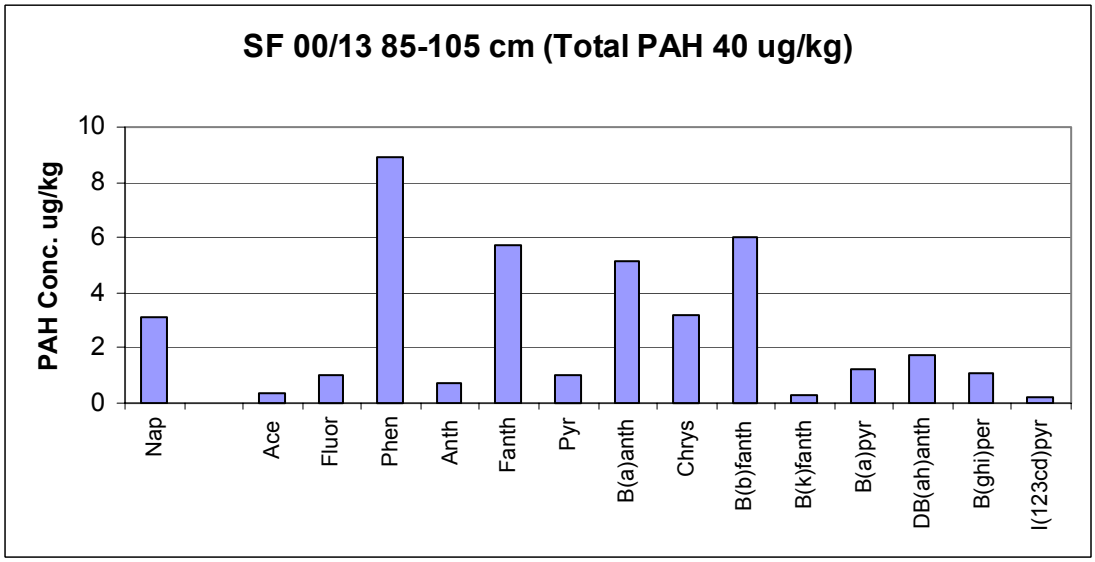

SF 00/7 90-110 cm (Total PAH 12 ug/kg)
PAH Conc. ug/kg
6
4
2
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr

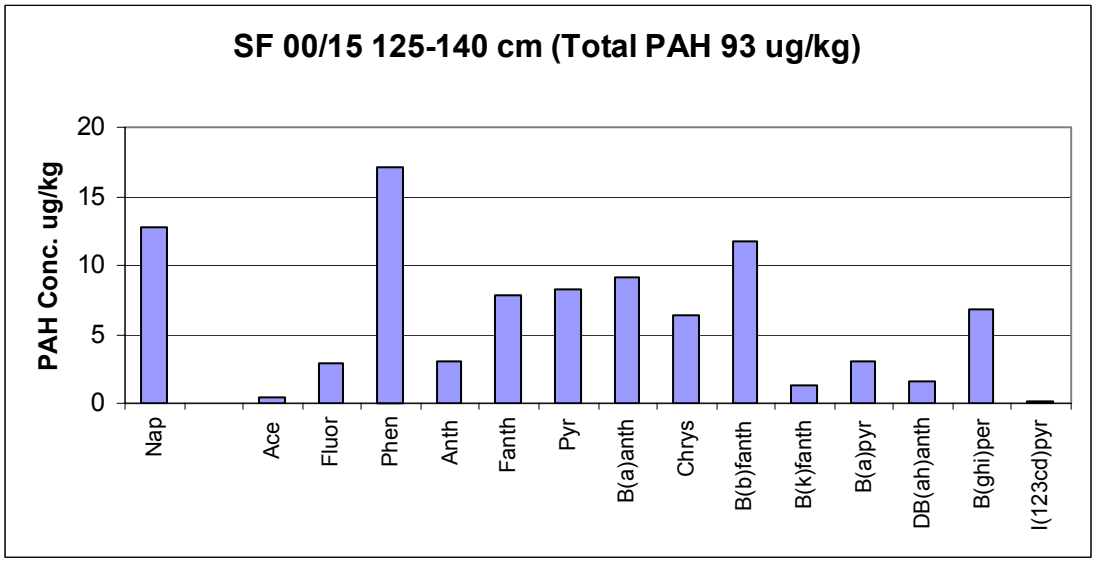

SF 00/7 175-190 cm (Total PAH 1512 ug/kg)
PAH Conc. ug/kg
250
200
150
100
50
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr


SF 00/4 20-40 cm (Total PAH 244 ug/kg)
PAH Conc. ug/kg
50
40
30
20
10
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr


SF 00/8 65-80 cm (Total PAH 102 ug/kg)
PAH Conc. ug/kg
25
20
15
10
5
0
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr


SF 00/13 20-40 cm (Total PAH 29 ug/kg)
PAH Conc. ug/kg
0
1
2
3
4
5
6
7
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr


SF 00/13 85-105 cm (Total PAH 40 ug/kg)
PAH Conc. ug/kg
0
2
4
6
8
10
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr


SF 00/15 125-140 cm (Total PAH 93 ug/kg)
PAH Conc. ug/kg
0
5
10
15
20
Nap
Ace
Fluor
Phen
Anth
Fanth
Pyr
B(a)anth
Chrys
B(b)fanth
B(k)fanth
B(a)pyr
DB(ah)anth
B(ghi)per
I(123cd)pyr