

Polyaromatic Hydrocarbons (PAHs) and Polychlorinated Biphenyls (PCBs) in Surface Sediments from the Inner Clyde Estuary, U.K.

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The Clyde Estuary and its tributaries have been an important reservoir for contaminated waste from a succession of industries located in the conurbation of Glasgow during the 19th and 20th centuries. Subsurface coal mining, shipbuilding, textile and paper as well as engineering industries have all had a significant environmental impact on sediments quality of the urban area of Glasgow (Edgar et al., 1999; Edgar et al., 2003; Hume, 1974). Although heavy industry on the banks of the River Clyde declined from 1950s-1970s and shipbuilding ended in 1971 Glasgow remains a thriving city with much of the infrastructure necessary to maintain a modern mixed economy such as power stations, oil refineries, landfill sites and sewage works located in close proximity to the main channel and tributaries. The aim of this study was to determine individual concentrations of three important groups of pollutants namely, parent polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organotins in surface sediments of the Inner Clyde Estuary.

Sediments were collected between October and February 2003 at 11 sites using a stainless steel Van Veen grab. An aliquot of each (~500 g) sediment was freeze-dried and sieved through a mesh aperture of 2 mm. Total organic carbon (TOC) content was determined using Elementar VarioMax C, N analyser after acidification with HCl (50 % v/v) to remove carbonate. The limits of quantification reported for a typical 300mg sample were 0.18%.

For PAH extraction, 0.5g sieved sediment was weighed into a amber bottle and 25 mL of 50/50 v/v HPLC grade acetonitrile and tetrahydrofuran (THF) was added. After brief swirling the contents were sonicated (Camlab, 300W) for 45 minutes at 50°C. The capped bottle was then stored (*ca.* 2 hours) in the dark before taking a 1 mL aliquot of the supernatant in a gas-tight glass syringe, attaching a 0.45 µm in-line syringe filter (Nylon 66), and injecting into a 5 µL sample loop on the HPLC (Waters 600E). A Hypersil®PAH column (100 mm x 4.6 mm i.d.) with guard was employed for PAH separation. Gradient elution at 1 mL/min was initiated with a 50/50 mix of gradient HPLC grade acetonitrile (Rathburn Ltd.) and HPLC grade water (Milli-Q)

maintained for 5 minutes. Thereafter, up to 27 minutes, the proportion of acetonitrile was linearly increased from 50% to 100%. From 27 minutes until the end of the run (40 mins.) elution with 100% acetonitrile was maintained. PAH detection was achieved with a programmable fluorescence detector (Waters 474). Quality control was accomplished by subjecting a low-level PAH reference material (LGC 6188 – River Sediment) to the above procedure. A total of four QC (LGC 6188) runs were conducted at intervals throughout the analysis of the samples. Limits of detection are presented in Table 2.

The method used to extract and determine PCB concentrations was based on that by Ayris *et al.*, (1997) and has been described by Vane *et al.*, (2007). Combined gas chromatography-mass spectrometry (GC-MS) was performed on a Fisons 8000 GC directly coupled to Fisons MD-800 single-quadrupole mass spectrometer operating in full scan mode (ionization energy 70 eV, mass range 39-600 amu). Sample application (1 µl) was by on-column injection, the GC was fitted with a fused silica ZB-5 column (60 m length x 0.32 mm i.d. x 0.25 µm film thickness). The GC oven was temperature-programmed from 100°C (1 min. isothermal) to 200°C (at 5°C / min.) to 280°C (at 2.4°C / min.) to 320°C (at 20°C / min.) and held isothermally at 320°C for 5 min and helium was used as carrier gas at 16 p.s.i. The limit of detection (LOD) based on the minimum concentrations that gave clearly defined peaks was between 0.1-0.20 µg/kg. Quality control was achieved by subjecting a PCB certified reference material (LGC 6113–Soil) to the above procedure and analysing it by the same method as for the samples.

Tributyltin, (TBT), was prepared for analysis using a method described by Łobiński *et al.*, 1992. Organotin compounds were analysed using a Fisons MD 800 mass spectrometer operated in full scan mode (m/z : 39-600), with electron impact and quadrupole analyser. On-column injection was onto a DB-1 column (60m length x 0.32 mm i.d. x 0.25 µm film thickness). Oven temperature programme: 60°C (1 min. isothermal) to 320°C (at 10°C / min.) and isothermal at 320°C for 30 minutes. Carrier gas: helium at 16 p.s.i. The limit of detection = 0.15 µg as Sn/g dry weight.

The chromatographically determined concentrations of the 15 PAHs appear in Table 2. Total PAH concentrations in the samples were found to range between 630 µg/kg to 23711 µg/kg. This range broadly concurs with that from a recent study of UK estuarine PAH where sediments from the Clyde estuary ranged from 450 µg/kg to 41781 µg/kg for the summed concentrations of 22 PAHs and from 229 µg/kg to 28851 µg/kg for the 4-6 ring members (Rogers, 2002). It is also comparable with those of other estuaries whose environments are highly industrialised and where similar activities to those in the Clyde region occur, *e.g.* River Tyne (260 µg/kg to 43470 µg/kg); River Wear (205 µg/kg to 31715 µg/kg); River Tees (653 µg/kg to 26549 µg/kg) for the summed concentrations of 15 USEPA PAHs (Woodhead *et al.*, 1999).

There was some correlation ($r^2 = 0.56$) between the TOC and the total PAH concentration of the sediments as depicted in Figure 2. It was found that the organic matter content (TOC), and hence the total PAH concentration, roughly corresponded with sample type as shown in Table 2. It can be observed that the coarser sediments (sands and gravels) had the lowest TOCs (0.31% - 2.72%) and correspondingly the lowest PAH concentrations (630 µg/kg - 2615 µg/kg). All the sediments described as black muds had much higher TOCs (3.98% - 6.15%) and in turn a much higher range of total PAH (11701 µg/kg - 23711 µg/kg).

PAHs are of global ubiquity and reside in the environment mainly as a result of their production during fossil fuel combustion. This major pyrolytic contribution is characterized by the preponderance of eight high molecular weight PAHs (McCready et al., 2000):

Fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene and indeno[1,2,3-c,d] pyrene

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 tabulated such that the eight high molecular weight pyrolytic PAHs together with phenanthrene were ranked in order of their prevalence (Table 3). It can be noted that there are few divergences from the nine pyrolytic PAHs being exclusively the predominant species. The most significant of these divergences are for Stations 3 (Upper Harbour) and 8 (Yoker Burn). The Yoker Burn sample possessed appreciable amounts of naphthalene, acenaphthene, fluorene and anthracene such that these 2- and 3- ringed species were ranked as more abundant than benzo[g,h,i]perylene. Their presence was indicative of a proportionally greater petrogenic contribution to the total PAHs. Yoker Burn is in proximity to an oil refinery. It seems likely, therefore, that the local industrial pyrolytic PAH output may also be augmented by petrogenic PAH from possible fuel spills and leakages. For Upper Harbour the presence of low molecular weight PAHs, in addition to the nine pyrolytic members, probably stems from incomplete combustion of vehicle fuels, it being a general urban area close to the centre of Glasgow.

Another approach for the ascription of petrogenic/pyrolytic 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 pyrolytic 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 pyrolytic 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 (pyrolytic) and ≤ 0.4 (petrogenic) with the same caveat of caution, particularly in the intermediate zone (Gschwend and Hites, 1981). Yet another pair of isomers can be used in the form of the ratio of indeno(1,2,3-cd)pyrene to indeno(1,2,3-cd) pyrene plus benzo(ghi)perylene. The criteria that emerge are that if this ratio is <0.2 a petroleum source is indicated, 0.2 to 0.5 implies liquid fossil fuel (vehicle and crude oil) combustion, and ratios >0.5 betoken coal, grass or wood combustion (Yunker et al., 2002)

Table 7 presents the molecular indices for the sediments. It will be observed that all the phen./anth. ratios are <10; the two highest correspond to Dalmarnock Road Bridge (6.89) and Yoker Burn (5.96) where the possibility of a petrogenic input has already been discussed. This view is reinforced for the former by its fanth./pyr. ratio which is 0.84. If the benz(a)anth./chrys. ratio criteria are applied then a pyrolytic origin would have to be ascribed to all the sediments. All except three samples fall in the range 0.2 to 0.5 when the isomers indeno(1,2,3-cd)pyrene and benzo(ghi)perylene are considered, implying that the pyrolytic source for the region is primarily liquid fossil fuel combustion. The three samples falling outside the range are all >0.5 probably indicating a coal-burning contribution to their PAH distribution.

Plotting the phen./anth. ratio against the fanth./pyr. ratio gives the plot that appears in Figure 3. It can be seen from this that all but one of the sediments plot within the pyrolytic quadrant of the graph with the remaining one, Dalmarnock Road Bridge, being in close proximity to the borderlines of this quadrant. 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 6.

The concentrations of individual congeners (ICES 7 group), summed tetra-, penta-, hexa-, heptachlorinated congeners and total PCBs as well as TOC data are presented in Table 4. The mean average total PCB content of the 11 stations was 46.9 µg/kg and all sampling sites showed some degree of PCB contamination. Total PCB concentration ranged from 5.2 µg/kg (station 3, Upper Harbour) to 129.9 µg/kg (station 6, Merklands) (Table 4). This range is consistent with findings of a recent study of the PCBs where sediments from the Clyde Estuary area were reported to have values of 0.5 µg/kg to 66 µg/kg for the summed concentrations of 22 chlorobiphenyl congeners with the exception of one contaminant hot spot in the vicinity of Battery Park (1,822 µg/kg) Greenock Clyde (Edgar et al., 1999; Edgar et al., 2003; Edgar et al., 2006). In this current work the sediment stations showing the highest concentrations of PCBs were numbers 4 (lower harbour) 99.96 µg/kg, 6 (Merklands) 129.89 µg/kg and 7 (King George V. Dock) 95 µg/kg located in close geographical proximity to the most urbanised and active zones of industrial activity in Glasgow (Fig. 1; Table 4) (Hume, 1974). In contrast the sediment stations in the vicinity of less historically urbanised or industrialised areas such as stations 1 (Cunningar) 15.48 µg/kg, 2 (Dalmarnock Rd. Rail Bridge) 31.35 µg/kg, 10 (Erskine) 13.25 µg/kg and 11 Milton 12.45 µg/kg had lower total PCB concentrations. This is supported by previous work in the Clyde by PCB concentrations of Otter (*Lutra lutra*) faeces collected from rural portions of the Upper River Clyde had nine times lower PCB concentrations than the more urbanised portions Lower River Clyde (Mason et al., 1992). Overall the mean PCB value of 46.9 µg/kg in this current work is somewhat lower than those reported for other U.K. Estuaries with comparable industrial histories such as the Mersey Estuary which has a mean PCB content of 123 µg/kg (Vane *et al.*, 2007). The relationship between higher PCB concentrations and a particular industrial location is however rather loose, for example Yoker Burn located near to an oil refinery gave a total PCB concentration of 19.35 µg/kg which is lower than the mean value determined for all the surface sediments.

The relative proportions of PCBs were broadly similar and independent of total concentration with the main components of the PCB mixtures being comprised of

tetra, penta and hexa-chlorinated homologues with lower percentages of tri and hepta-chlorinated PCB moieties (Table 4). Their distribution is partly indicative of the precursor industrial mixtures such as Arcolor 1254, which is comprised of tetra-, penta- and hexa-chlorinated biphenyls. No systematic change in PCB homologue percentages was observed from station 1 at Cunningar down stream to station 11 to Milton (Figure 1). The average homologue distribution for stations 1 to 11 are presented in Fig 4, in this respect the percentage of trichlorinated congeners (11 %) is higher than that previously reported for the Clyde Estuary by Edgar *et al.*, (1999). However the proportions of tetra, penta, hexa (24-31 %) in this current work are comparable with the tetra, penta, hexa chlorinated congeners (21-30%) previously reported. This similarity suggests that the sources of PCB contamination in the Clyde Estuary has remained unchanged over the past ten years.

Although PCB contamination of all of the Clyde Estuary sites was demonstrable, the risk to estuarine ecosystems and human health is more difficult to evaluate since the most immediate concerns are raised when residue levels in the food chain increase above concentrations harmful to human health. Numerical soil quality guidelines (SQG) for marine and fresh water ecosystems represent one method to assess sediment quality using criteria which evaluate whether a contaminant may cause adverse effects on sediment dwelling organisms (MacDonald *et al.*, 2000). Consensus based threshold effect concentrations (TEC) and probable effect concentrations (PEC) provide a means of classifying sediments as toxic or non-toxic, these have been reported for total PCB concentrations in freshwater sediments as 59.8 µg/kg and 676 µg/kg respectively (MacDonald *et al.*, 2000). On this basis, seven sites (1, 2, 3, 5, 8, 10, 11) fall below total PCB TEC where as three sediment stations namely Lower Harbour, Merklands and King George V. Dock (4, 6, 7) fell between TEC and PEC; overall the PCB concentrations encountered in the 11 surface sediments are probably not having an adverse effect on sediment-dwelling organisms.

Tributyltin concentrations from 11 sample stations of the inner Clyde Estuary are presented in Table 5. Tributyltin concentrations ranged from 0.41-0.61 µg (as Sn)/g dry wt, however the TBT concentration presented here are 4 to 8 times higher than those reported for other major U.K. estuaries such as the Mersey (0.007-0.173 µg/g) and Thames (0.002-0.078 µg/g) but are lower than the TBT concentrations of up to 213 µg/g observed at Poole Harbour U.K. (Langston *et al.*, 2005; Langston *et al.*, 1987). One plausible explanation for the higher values reported in this work as compared to Thames and Mersey Estuaries could be due to the fact that sample stations 3 and 7 are in close proximity to Upper Harbour and King George V Dock which would have organotin contamination input from the marine paint applied to hulls of boats and shipping.

This survey of PAH, PCB and TBT concentrations in surface sediments of the Inner Clyde Estuary provide a baseline to underpin process driven research and monitoring in this heavily industrialised region of the U.K.

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Table 1. Quality Control Certified Reference Material (LGC 6188) PAH concentrations ($\mu\text{g/kg}$ dry wt) and Fluorescence Programming

PAH in CRM River Sediment for purposes of Quality Control (QC)															
Laboratory of the Government Chemist (LGC) , PAH Certified Reference Material LGC 6188 River Sediment															
	Naph	Acc	Fluor	Phen	Anth	Fanth	Pyr	B[a] A	Chrys	B[b]F	B[k]F	B[a]P	DBA	B[ghi]P	IP
LGC Assigned Value	220	70	120	1040	360	1790	1480	830	830	820	500	650	130	360	370
LGC Assigned Uncertainty	110	20	40	300	110	350	500	180	160	190	80	140	50	130	140
Permissible Max.	330	90	160	1340	470	2140	1980	1010	990	1010	580	790	180	490	510
Permissible Min.	110	50	80	740	250	1440	980	650	670	630	420	510	80	230	230
QC values obtained for LGC6188 extracted by the same method as used for the samples and run at intervals during the sample analyses :															
QC Run 1	203	62	84	978	279	2026	1547	753	845	789	570	513	144	253	289
QC Run 2	197	76	88	919	265	2084	1425	715	810	830	567	567	148	243	275
QC Run 3	206	75	95	911	268	2101	1349	705	807	813	562	582	156	259	271
QC Run 4	195	66	90	897	273	2084	1354	704	768	831	569	519	164	256	279
Wavelength Programming of the Waters 474 HPLC Programmable Fluorescence Detector															
Excitation Wavelength (nm)	275	275	275	253	240	240	240	254	254	254	254	254	254	254	302
Emission Wavelength (nm)	325	325	325	373	425	425	425	395	395	395	395	395	395	395	506
Average Retention Times (mins)	7.4	12.2	13.3	15.2	17.1	18.8	19.9	24.3	25.4	28.5	30.3	31.5	33.6	34.4	35.7

PAH Abbreviations : Naph: naphthalene Acc: acenaphthene Fluor: fluorene Phen: phenanthrene Anth: anthracene Fanth: fluoranthene Pyr: pyrene
 B[a]A: benz[a]anthracene Chrys: chrysene B[b]F: benzo[b]fluoranthene B[k]F: benzo[k]fluoranthene B[a]P: benz[a]pyrene
 DBA: dibenz[a,h]anthracene B[ghi]P: benzo[g,h,i]perylene IP: Indeno[1,2,3-c,d]pyrene

Table 2.Surface sediment PAH concentrations ($\mu\text{g}/\text{kg}$ dry wt) in Clyde Estuary

Station	Locality (Sample Type)	Naph	Ace	Fluor	Phen	Anth	Fanth	Pyr	B[a]A	Chrys	B[b]F	B[k]F	B[a]P	DBA	B[ghi]P	IP	Total	TOC	
																			%
1	Cunningar (Mud)	76	73	81	485	115	730	551	342	306	563	122	335	107	505	237	4627	3.25	
2	Dalmarnock Rail Bridge (Slime)	14	58	16	229	75	1272	1023	757	815	907	367	1011	249	880	784	8456	0.84	
3	Upper Harbour (Sand & Gravel with some mud)	54	54	67	230	81	342	286	146	108	185	22	129	37	147	59	1948	0.82	
4	Lower Harbour (Black mud)	226	186	247	1025	282	2418	1881	1365	1089	1850	455	1387	458	1973	832	15675	6.15	
5	Princes Dock (Black mud)	137	204	256	936	348	2768	2301	1442	1130	2114	418	1355	507	1827	777	16520	4.95	
6	Merklands (Black Mud)	372	325	417	1383	548	4033	3337	1952	2061	2748	578	2070	308	2398	1180	23711	3.98	
7	K. George V Dock (Black mud)	219	151	209	940	315	2518	2121	1069	923	1964	423	1645	447	1141	863	14949	4.43	
8	Yoker Burn (Gravelly sand)	188	106	98	385	65	373	374	224	165	239	30	206	43	54	66	2615	1.51	
9	Duntocher Burn (Black mud)	202	208	254	801	305	2050	1886	1079	845	1368	384	1041	220	436	622	11701	4.42	
10	Erskine (Gravelly sand)	36	26	34	167	38	253	241	182	132	283	39	168	27	147	72	1843	2.72	
11	Milton (Slightly gravelly sand)	7	6	8	48	15	79	95	61	43	88	14	47	14	69	37	630	0.31	
	Limit of Detection	0.3	0.2	0.1	0.2	0.1	0.6	0.7	0.3	0.2	0.3	0.2	0.3	0.6	0.5	0.4			
	RSD % (Loop Filling)	2.7	2.3	1.5	3.8	1.9	2.9	10.7	3.5	1.9	2.3	2.9	2.7	5.3	3.7	4.4			

Table 3.Relative PAH abundances and total concentrations ($\mu\text{g}/\text{kg}$ dry wt) in Clyde Estuary samples

Station	Locality	Relative Abundance													Isomeric Ratios					
		Naph	Ace	Fluor	Phen	Anth	Fanth	Pyr	B[a]A	Chrys	B[b]F	B[k]F	B[a]P	DBA	B[ghi]P	IP	Phen/ Anth	Fanth/ Pyr	B[a]A/ Chrys	IP/ (IP+B[ghi]P)
1	Cunningar				5	1	3	6	8	2		7			4	9	4.21	1.32	0.93	0.32
2	Dalmarnock Rail Bridge				11	1	2	8	6	4	9	3	10		5	7	3.05	1.05	1.00	0.38
3	Upper Harbour		10		3	1	2	6	8	4		7		5	11	2.84	1.19	1.30	0.29	
4	Lower Harbour				8	1	3	6	7	4		5		2	9	3.63	1.29	1.36	0.30	
5	Princes Dock				8	1	2	5	7	3		6		4	9	2.69	1.20	1.25	0.30	
6	Merklands				8	1	2	7	6	3		5		4	9	2.53	1.21	0.95	0.33	
7	King George V Dock				7	1	2	6	8	3		4		5	9	2.99	1.19	1.16	0.43	
8	Yoker Burn			7	1	3	2	5	8	4		6		13	11	5.96	1.00	1.36	0.55	
9	Duntocher Burn		9	10	7	1	2	4	6	3		5		9	8	2.63	1.09	1.28	0.59	
10	Erskine				6	2	3	4	8	1		5		7	9	4.34	1.05	1.38	0.33	
11	Milton				6	3	1	5	8	2		7		4	9	3.18	1.55	1.33	0.35	

Table 4. PCB concentrations ($\mu\text{g}/\text{kg}$ dry wt) of surface sediments in the Clyde Estuary and Certified Reference Material (LGC 6113).

Station	Sample	TOC %	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	Total of 7 PCBs	Tri- Cl	Tetra- Cl	Penta- Cl	Hexa- Cl	Hept- a-Cl	Total
1	Cunningar	3.25	0.79	n.d.	0.61	1.32	0.65	0.08	2.73	6.19	2.98	0.71	4.76	2.84	4.19	15.5
2	Dalmarnock Bridge	0.84	0.46	7.24	n.d.	1.35	0.40	0.36	0.74	10.55	0.88	7.62	10.60	11.03	1.22	31.4
3	Upper Harbour	0.82	n.d.	n.d.	0.13	0.42	0.25	0.24	0.15	1.20	0.53	2.16	0.57	1.98	0.00	5.2
4	Lower Harbour	6.15	2.00	24.55	14.44	26.41	n.d.	n.d.	n.d.	67.40	2.62	25.32	41.34	15.41	15.28	100.0
5	Princes Dock	4.95	2.30	9.18	3.14	2.93	n.d.	n.d.	n.d.	17.56	3.70	14.28	7.66	17.24	4.79	47.7
6	Merklands	3.98	4.68	21.18	12.80	11.01	9.77	9.61	7.76	76.80	24.03	43.20	25.55	24.54	12.57	129.9
7	K. George V Dock	4.43	7.50	12.31	8.31	7.82	3.22	4.17	0.00	43.33	15.75	23.18	19.18	35.96	0.93	95.0
8	Yoker Burn	1.51	1.11	1.54	1.49	0.88	2.64	2.07	3.04	12.77	2.07	3.67	2.55	7.45	3.61	19.4
9	Duntocher Burn	4.42	4.91	7.56	5.06	5.12	6.09	4.28	0.00	33.02	7.33	14.46	10.47	14.18	0.02	46.5
10	Erskine	2.72	1.21	3.14	2.39	1.35	1.18	1.28	0.00	10.55	1.26	2.83	3.88	3.01	2.27	13.3
11	Milton	0.31	n.d.	n.d.	1.36	0.79	1.54	1.09	0.21	4.99	0.20	1.33	2.31	6.44	2.16	12.5
CRM, LGC 6113			15.1	13.2	24.5	26.4	40.8	41.8	30.4	178.10						
Std. Dev. values, CRM, LGC 6113			2.54	1.69	0.14	7.73	6.80	9.42	5.27	19.25						
Certified values, CRM, LGC 6113			14 (± 3)	11 (± 3)	23 (± 6)	28 (± 9)	42 (± 1)	43 (± 1)	29 (± 8)	none given						

n.d. : Not determined (below detectable limit)

Table 5Organotin concentrations (μg as Sn / g dry wt) in Clyde sediments

Station	Name	Tributyltin chloride (TBT)
1	Cunningar	n.d.
2	Dalmarnock Rail Br.	n.d.
3	Upper Harbour	0.41
4	Lower Harbour	n.d.
5	Princes Dock	interference
6	Merklands	interference
7	King George V Dock	0.49
8	Yoker Burn	n.d.
9	Duntocher Burn	0.61
10	Erskine	n.d.
11	Milton	n.d.
	PACS 2	1.15 (± 0.11)
	Certified values of PACS 2	0.98 (± 0.13)

Interference could not be detected due to high matrix interferences masking organotin peaks.

n.d. Not detected (below detectable limit $0.15 \mu\text{g}$ as Sn/g dry weight)

Fig 1. Sampling locations of surface sediments collected from the inner Clyde Estuary, UK.

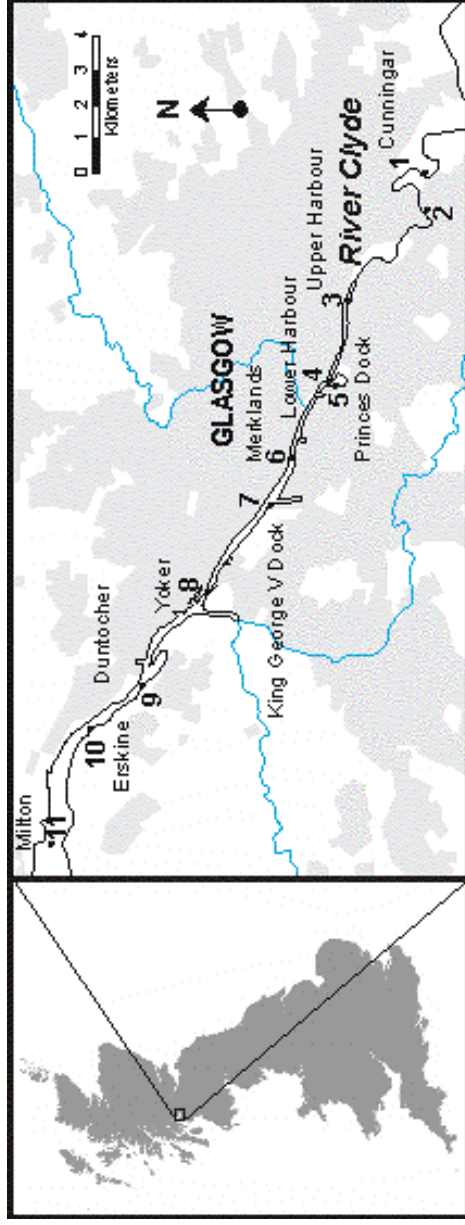


Fig 2. Total PAHs concentration ($\mu\text{g}/\text{kg}$) *versus* total organic carbon, TOC (% w/w)

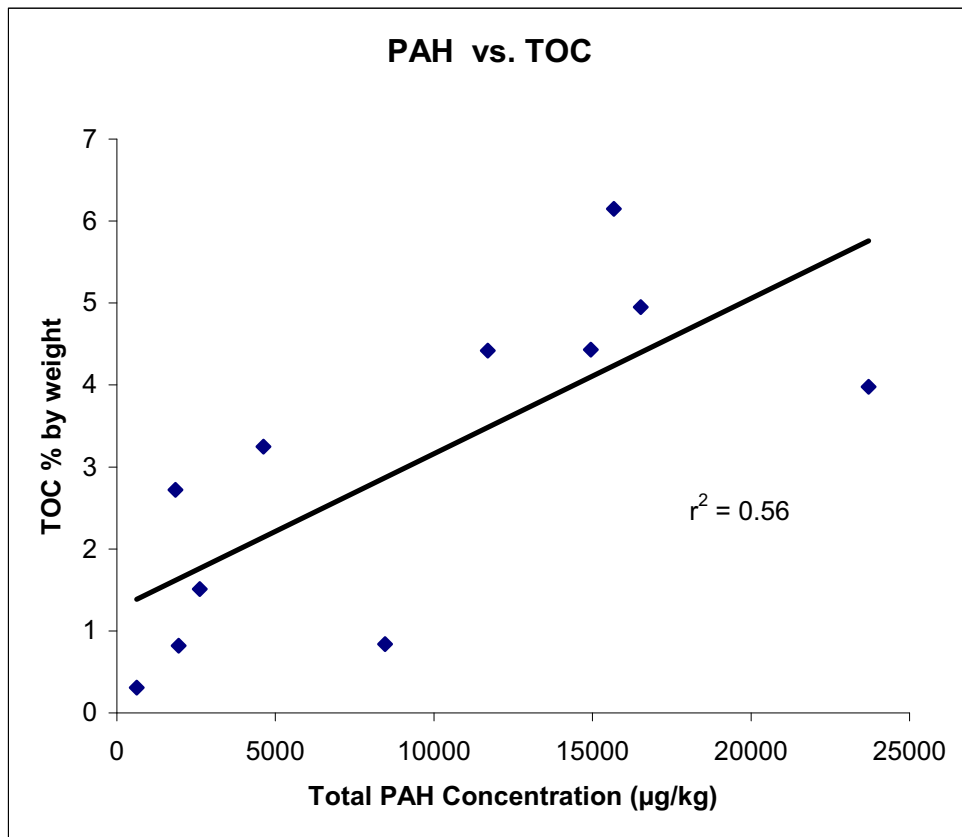


Fig 3. PAH isomeric ratios plot for stations 1 - 11

