

Chemical Signatures of the Anthropocene in the Clyde Estuary, UK: Sediment hosted Pb, $^{207/206}\text{Pb}$, Total Petroleum Hydrocarbons (TPH), Polyaromatic Hydrocarbon (PAH) and Polychlorinated Biphenyl (PCB) Pollution Records

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Abstract: The sediment concentrations of Total Hydrocarbon (TPH), Polyaromatic Hydrocarbon (PAH) Polychlorinated Biphenyl (PCB), Pb and $^{207/206}\text{Pb}$ isotope ratios, were measured in seven cores from the middle Clyde estuary (Scotland, UK) with the aim of tracking the late Anthropocene. Concentrations of TPH ranged from 34 to 4386 mg/kg, total PAH from 19 to 16163 $\mu\text{g}/\text{kg}$ and total PCB between <4.3 to 1217 $\mu\text{g}/\text{kg}$. Inventories, distributions and isomeric ratios of the organic pollutants were used to reconstruct pollutant histories. Pre-industrial revolution and modern non-polluted sediments were characterised by low TPH and PAH values as well as high relative abundance of biogenic sourced phenanthrene and naphthalene. The increasing industrialisation of the Clyde gave rise to elevated PAH concentrations and PAH isomeric ratios characteristic of both grass/wood/coal and petroleum and combustion (specifically petroleum combustion). Overall, PAHs had the longest history of any of the organic contaminants. Increasing TPH concentrations and a concomitant decline in PAH mirrored the lessening of coal use and increasing reliance on petroleum fuels from ~1950s. Thereafter, declining hydrocarbon pollution was followed by the onset (1950s) peak (1965-77) and decline (post 1980s) in total PCB concentrations. Lead concentrations ranged from 6 to 631 mg/kg whilst $^{207/206}\text{Pb}$ isotope ratios spanned 0.838-0.876 indicative of various proportions of “background”, British ore/coal and Broken Hill type petrol/industrial lead. A chronology was established using published Pb isotope data for aerosol derived Pb and applied to the cores.

1. Introduction

The Clyde Estuary, (Scotland, UK) occupies a catchment that includes the major city of Glasgow as well as the outlying towns of Dumbarton, Clydebank, Renfrew, Paisley, Greenock and Port Glasgow. A settlement since the Bronze age, Glasgow’s industrial growth accelerated in the 18th and 19th C to such an extent that it was known as the second city of the British Empire. Notable Clydeside industries of the 19th and 20th centuries included shipbuilding, textiles, chemical production as well as coal and ironstone mining (Reed 1999). Today, the Clyde still builds military ships at Govan and Scoutstoun, however, manufacturing is now mainly linked to light as compared to

heavy industry. Consequently, the river Clyde which flows through Glasgow city has received pollution from the onset of the industrial revolution (*ca* 1770 AD) up to the present day (Edgar et al. 2006; Vane et al. 2007a; Vane et al. 2010).

The environmental persistence of organic pollutant groups such as total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAH) and polychlorinated chlorinated biphenyls (PCB) ranges from hours to decades to centuries. When used in together non-volatile TPH and PAH compounds facilitate the reconstruction of different phases of development based upon changing fuel sources and use of chemicals (Meyers 2003; Vane et al. 2007b; White et al. 2005). There are four broad sources of PAH namely, biogenic, geogenic, petrogenic and pyrolytic. These can be distinguished using parent and alkylated PAH distributions as well as parent PAH isomeric ratios, which are controlled by the temperature and duration of formation (Yunker et al. 2002). In most industrially impacted environments petrogenic and pyrolytic PAH sources predominate and these have different parent PAH distributions which permit sediments contaminated with crude oil and petrol to be distinguished from combustion sources such as coal burning and vehicular combustion emissions (Huntley et al. 1995; Iannuzzi et al. 2005; Vane et al. 2007a). The known history of initial production, peak production and banning of a particular group of environmentally persistent organic compounds, which have no known natural sources, such as PCB and or brominated flame retardants (PBDE) can be used to not only trace changing industries but also potentially provide chronological information based upon varying product formulation histories (Vane et al. 2010). In general, multiple analyses of anthropogenic organic chemicals are required to not only build a complete picture of urban /industrial activities but also to avoid and account for the well known complicating effects of molecular diffusion, post-depositional transformation mediated by microbes, bioturbation and variable sediment accumulation rates.

Alternative means of tracking human-induced environmental change in industrial estuaries include the use of heavy metal concentrations and isotope ratios e.g. Pb, and $^{207/206}\text{Pb}$ as well as radioactive isotopes such as ^{137}Cs (Fox et al. 1999; Plater et al. 1998; Ridgway et al. 2003; Vane et al. 2009). In Britain, vegetation archives which mainly record atmospheric Pb pollution show that $^{207/206}\text{Pb}$ values remained at about 0.85 through the 19th century and increased from 1920 due to the use of leaded petrol and overseas industrial lead (Bacon et al. 1996; Farmer et al. 2002). Maximal $^{207/206}\text{Pb}$ values of 0.89 are observed in the 1980's and then declined once leaded petrol was banned. These archives allow the construction of $^{207/206}\text{Pb}$ chronologies that may be used in collaboration with conventional ^{210}Pb dating, or instead when this proves problematic.

In this paper we present the results of chemical signatures in sediment cores from the Clyde estuary of organic pollutants (PAH, PCB, TPH) and lead concentrations as well as $^{207/206}\text{Pb}$ isotope ratios. The principal aim was to establish whether sediment contamination profiles could be used to identify the late Anthropocene and track changing industrial activities and increasing urbanisation of the Clyde estuary.

2. Materials and Methods

2.1 Sampling and sample preparation

Seven sediment cores collected in duplicate (A & B) in June 2004 and April 2006 (Fig. 1). Sampling sites in the estuary were accessed by a Griffon 2000TD hovercraft in 2004 and on foot in 2006 using pre-determined GPS co-ordinates to accurately locate each position. Clear polycarbonate tubes were manually driven into the exposed sediment and extracted to recover the core material. The BGS core codes were 55/-05/04-06-15 (station 1), 55/-05/700 (Station 2), 55/-05/04-06-12 (Station 3), 55/-05/718 (Station 4), 55/-05/712 (Station 5) and 55/-05/702 (Station 6), 55/-05/714 (station 7). Upon return to the laboratory each core was cut in half and sub-sampled. Sediments for organic analyses were freeze-dried and prepared as reported in Vane et al. 2009. Sub-samples for lead analysis were similarly freeze dried and ground to a fine powder in agate to minimise contamination.

2.2 Total organic carbon and non-volatile hydrocarbons

Total organic carbon (TOC) content was determined using an 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%. Non-volatile hydrocarbons (Total Petroleum Hydrocarbons (TPH)) were determined as reported in Vane *et al.*, (2009). Briefly sediments were extracted with, dichloromethane (DCM) / acetone (1:1 v/v) mixture using an accelerated solvent extraction (ASE 200 Dionex) system. Saturated and aromatic hydrocarbons were determined using by an Iatroscan Mk6s instrument fitted with a flame ionization detector (FID).

2.3 Polychlorinated Biphenyls (PCBs)

The method used to extract and determine PCB congeners was based on that described in Vane et al., 2007a. In summary, sediments were extracted with hexane/acetone (1:1v/v) in an ASE 200 (Dionex) and washed with conc. H₂SO₄. PCB congeners were separated from other compound classes using a florsil/sodium sulphate column and the *n*-hexane eluent subject to liquid-liquid extraction using dimethylsulphoxide (2 × 12 ml) and de-ionised water (25 ml) prior to extraction with *n*-hexane. The *n*-hexane extracts volume was reduced to 5 ml, passed through anhydrous sodium sulphate (1g) and reduced to 100 µl. Combined gas chromatography-mass spectrometry (GC-MS) was performed on a Carlo Erba Mega 500 series GC directly coupled to a Varian 1200L triple quadrupole mass spectrometer.

2.4 Polycyclic aromatic hydrocarbons (PAHs)

Sediments (5g) were extracted with 25 ml of a 1:1 v/v mix of acetonitrile and tetrahydrofuran (THF) in an ultrasonic bath (Camlab, 300W) for 45 minutes at 50°C. Samples were stored in the dark (2 h), to permit some clarification of the supernatant, before taking a 2 ml aliquot and filtering with a 0.2 µm in-line syringe filter (25 mm dia. - Nylon 66). Filtered sample extracts were injected into the HPLC system (Waters 600E) via a 5 µl sample loop (Rheodyne). Separation of 17 PAHs was achieved within 40 mins by gradient programming the eluent. PAH detection was accomplished employing a scanning fluorescence detector (Waters 474). The

following PAH abbreviations are used throughout: Naph=naphthalene; Ace=acenaphthene; Fluor=fluorine; 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.

2.5. Total lead concentrations and lead isotope ratio determinations

For each sample, 0.25 g of powdered sediment was dissolved by a HF/HClO₄/HNO₃ mixed concentrated acid attack in Savillex™ PFA vials. Once taken to dryness the sample material was redissolved in 2mls of 1M HBr. The Pb was separated using an anion exchange chromatography column (Dowex AG1-X8 resin) pre-cleaned and conditioned with 1M HBr. The separated lead was dried to remove the acid and the test portion redissolved in 1% HNO₃. On the day of analysis samples were diluted using 1% HNO₃ and spiked with thallium. Pb and isotope ratio determinations were made using a quadrupole ICP-MS instrument (Thermo PQ ExCell) fitted with either a conventional glass concentric nebuliser or a Cetac Aridus 2 desolvating nebuliser system. The 2sd precision for the BCR-2 reference material, which has a total lead concentration of 11 mg/kg was $^{207/206}\text{Pb} = 0.0012$, $^{208/206}\text{Pb} = 0.0042$, based on n=5 replicates. The BCR-2 reference material is a basalt rock from the Columbia River and was produced and certified by the U.S. Geological Survey. This was chosen as the BGS long-term quality control for lead isotope ratio analysis as it has proved to be one of the few geological/environmental materials that is highly homogeneous with modern reliable certificated isotope values at background lead concentrations. Data (raw isotope intensity count rates) were processed off-line using Microsoft Excel spreadsheets. The processing consisted of: (i) removal of background including $^{204}\text{Hg}^+$ interference on $^{204}\text{Pb}^+$ in proportion to $^{202}\text{Hg}^+$ response; (ii) calculation of isotope ratios; (iii) determination of mass bias correction factor from defined isotope ratios of thallium (de Laeter et al. 2009) or SRM981 (Thirlwell 2002); (iv) application of mass bias factors derived from SRM981 using external standard -sample-standard bracketing; (v) optional further internal mass bias correction using $^{205/203}\text{Tl}$ ratio. During the current study the use of Tl as an internal measure of mass bias was not found to be necessary and external correction based on SRM981 was used.

3. Results and discussion

3.1 Lead concentrations

Total lead and lead isotope ratio determinations were made on depth increments from 7 cores (Station numbers: 1B, 2A, 4A, 4B, 5A, 6A, 7A) with two cores (4A & 4B) being duplicates but with 4B having a greater resolution of depth increments (Fig. 2). The cores varied significantly in concentration ranges with Station 7A being the least contaminated (6-24 mg/kg) and Station 1B being the most contaminated (26-631 mg/kg). The range of concentration values for the duplicate cores at Station 4 (360-35 & 377-23 mg/kg) are in excellent agreement considering the choice of different depth increments. The general trend was for both the maximum and minimum concentrations to decrease from the inner to the outer estuary. The median values also follow this trend with the exception that the mid-channel cores at Station 4 were

anomalously high. The median rather than the mean was chosen to report due to the non-normal data distribution.

If the median concentration Pb (63 mg/kg) for all the cores is compared against mean data for other UK river estuaries, as summarised in Spencer (2002), it is found to be less than the Humber (127) and Forth (89), similar to the Medway (67) and Thames (63) but greater than the Solway (25) and the estimated natural background (20). This suggests the Clyde sediments are typical of a river that has flowed through the industrial heart of an urban conurbation.

If the logs of Pb concentration versus depth are considered (Fig. 2), the cores split into two groups: (i) Cores 2A, 5A, 6A and 7A that appear to have base-line concentrations in the deeper sections with a discrete rise between 28-40cms down and then peak in concentration between 18-28cms; (ii) cores 1B and 4B for which even the basal measurements at 90-100cms may not be background and peak in concentration between 39-74 cms beneath the surface. These results suggest either the second group have a much higher sedimentation rate or the first group were subject to sediment erosion events or the Pb in the second group was more mobile and moved down core.

3.2 Lead isotope ratio determinations

A number of lead isotope ratios were determined $^{206/204}\text{Pb}$, $^{207/204}\text{Pb}$, $^{208/204}\text{Pb}$ and $^{207/206}\text{Pb}$, $^{208/206}\text{Pb}$. The ratios to ^{204}Pb were not found to be useful due to the poorer precision in measuring this isotope by quadrupole ICP-MS. However, significant variation was found in the $^{207/206}\text{Pb}$ and $^{208/206}\text{Pb}$ ratios with ranges from 0.8382-0.8764 and 2.078-2.124 respectively with typical uncertainties of 0.0012 and 0.0042 on individual determinations. The range of $^{207/206}\text{Pb}$ and $^{208/206}\text{Pb}$ ratios for depth increments from all cores is plotted in Figure 3. The data tend to fall along a linear array with tighter adherence for the greater ratios and a greater spread at the smaller ratios, indicative of one lead source with high values for both $^{207/206}\text{Pb}$ and $^{208/206}\text{Pb}$ ratios and two or more sources with lower but different $^{207/206}\text{Pb}$ and $^{208/206}\text{Pb}$ ratios. For comparison, potential mixing end-members have been plotted, these include galena (PbS) ores from northern England and Scotland (Barreiro 1995; Barreiro & Spiro 1997; Parnell & Swainbank 1984) and aerosols from the Isle of Man-Liverpool (Charlesworth et al. 2006) and London (Noble et al. 2008) believed themselves to represent a mixture of petrol and industrial lead in airborne particles (Farmer *et al.*, 2002). The anomalously high $^{207/206}\text{Pb}$ ratio of UK petrol lead compared to UK ore/coal lead, was the result of it being primarily derived from Broken Hill in Australia, and other non-UK sources (Sugden et al. 1993). Farmer et al. 2000 recording a mean value of $^{207/206}\text{Pb}$ ratio of 0.9294 (+/- 0.0095; 1sd n=33) between 1989 and 1998. The diagram suggests mixing of the aerosol composition, with ore lead from either local natural or industrial sources and a more thoriogenic (^{208}Pb) lead probably from natural background rocks. The “aerosol” signature may have resulted from some or all of the following: (i) direct input of airborne particulate material to the Clyde and tributaries; (ii) input and dissolution of airborne particulate material to the Clyde and tributaries or (iii) aqueous or particulate discharge from industrial-urban sources that equate to the averaging effect of an aerosol. As noted by Ellam (2010), there are certain deficiencies in such a diagram in terms of discriminating more than two lead isotope sources and the use of ^{204}Pb ratios would be preferable.

However, the extra analytical overhead of such measurements would not have been viable for the current study.

When the $^{207/206}\text{Pb}$ isotope ratio is considered with respect to Pb concentration (Fig. 4) a complex but explainable picture emerges. Four of the cores (2A, 5A, 6A and 7A) have their lowest concentrations when $^{207/206}\text{Pb}$ is less than 0.850, that may be taken as a pre-petrol lead industrial signature (Farmer et al. 2002; Weiss et al. 2002) and it is assumed these are representative of the geogenic background lead from the Clyde catchment. The five cores closest in to Glasgow (1A, 2A, 4A, 4B and 5A) have isotope signatures of 0.8521-0.8591 at their maximum lead concentration; therefore they are dominated by local lead ore, with reference to ratios of 0.8511-0.8540 from Wanlockhead (Sugden et al. 1993) and the early industrial aerosol signature of 0.850. This early industrial signal resulted from both lead smelting and coal burning; Farmer et al, (1999) having estimated the contribution of lead from coal to depositional flux as being 15% in 1830, 36% in 1887 and 59% between 1913-1930. For these more contaminated cores their maximum $^{207/206}\text{Pb}$ isotope ratios (0.8638-0.8674) are indicative of a significant proportion of petrol lead input or modern industrial lead from a non-UK Broken Hill type deposit (Sugden et al. 1993) and are associated with an intermediate to high concentrations of lead with reference to their maximum concentration. For cores 6A and 7A, those furthest from Glasgow, the highest concentrations are associated with their peak $^{207/206}\text{Pb}$ ratios suggesting the most significant proportion of the lead input is from petrol or modern industrial lead (non-UK Broken Hill type deposit). The changing nature of the $^{207/206}\text{Pb}$ isotopic signals with time and deposition is seen in Figure 2 where a common overall pattern emerges: a lower isotope ratio deeper in the cores, which then rapidly rises to a higher value and in most cases turns over and decreases in the top few centimetres of the core.

3.3 Towards a lead contaminant chronology for Clyde core material

There are a number of sources of information on long term changes of lead concentration and lead isotope ratios of contaminant inputs to the environment over time. These Scottish or UK sources primarily record atmospheric aerial deposition and include peat cores (Cloy et al. 2008; Weiss et al. 2002), lake sediment cores (Eades et al. 2002), vegetation, such as tree bark (Patrick and Farmer, 2007), moss (Farmer et al. 2002) and grass (Bacon et al. 1996). The major issues with peat or lake cores include collection from sites remote from the Clyde and accurate dating of layers. The dating of these cores has been almost exclusively by ^{210}Pb , as a radiometric technique it should give an absolute age but due to the necessity of modelling the rate of ^{210}Pb atmospheric input and assumptions therein, a greater level of uncertainty arises. However, in Scotland a unique record is available spanning nearly 200 years; *Sphagnum* moss has been collected across Scotland on known dates and archived at the Herbarium Collection of the Royal Botanical Garden, Edinburgh from 1838 till present. This archive was analysed for lead concentrations and isotope ratios, on a decadal basis by Farmer *et al*, 2002. Key dating observations on this data include a static trend in the 19th century through until ~1915 in the $^{207/206}\text{Pb}$ isotope ratio (0.853) when the ratio starts to dramatically increase with the use of leaded petrol and overseas industrial lead. The ratio peaked in the 1980s (0.893) and has since declined significantly. This peak and decline are commensurate with maximum petrol emissions in 1976 and reductions in lead in petrol in 1981, 1986 and its phasing out in 2000. This data set is generally consistent with that of Bacon *et al*, 1996 for

grass collected annually since 1860, at Rothamsted in the south of England, and analysed on a half-decadal basis. This study also observed a constant $^{207/206}\text{Pb}$ isotope ratio (0.855) but only until approximately 1880 before rising and peaking between 1980-1985 at 0.911. Bacon et al. (1996) noted that the initial rise in ratio was well in advance of the introduction of tetra-ethyl lead in petrol and an additional anomalously high ratio between 1945-1950 suggests short as well as long term changes in the use of overseas lead in industry. The data from Farmer et al (2002) and the other sources has been synthesised in Fig. 5 to give a lead isotope chronology. To this, data from Core 4B has been overlain; this core was chosen for having the best detail over a long time period. The current data was linearly scaled to give the best visual fit to the data from Farmer et al. (2002). The concurrence although not perfect suggests that in this core at least, the lead isotope ratios reflect those found from aerial deposition, that there is no apparent removal of core material and the deposition rate must have been relatively constant; therefore, in the absence of ^{137}Cs or ^{210}Pb data and accepting the possibility that due to contributions from rivers, streams or runoff there may be some delayed input, chronologies are feasible.

From this conclusion two key time periods have been added to Figure 2, the period 1835-1915 when the $^{207/206}\text{Pb}$ isotope ratio was static and 1980-1985 when the isotope ratio peaked. Any deep core values lower than the static value are assumed to represent a pre-Industrial Revolution (pre-IR = pre-1750) signal. The following specific observations were made for individual cores.

Core 1B: The time period 1980-1985 equates to a depth of 40cms; 1915 at a depth of 75 cms, which also appears to be the period of maximum lead concentration and the deepest parts of the core have an early-industrial plateau and do not reach pre-IR isotope signatures or concentrations.

Core 2A: The time period 1980-1985 equates to a depth of 5-10cms; 1915 at a depth of 32 cm, which is just before the period of maximum lead concentration and the deeper parts of the core values reach pre-IR (> 40cms); the lack of an early-industrial plateau suggests either a very slow deposition rate in this period or removal of such material by erosion. The background lead concentration is reached at a depth of 50cms.

Core 4B: The time period 1980-1985 equates to a depth of 5-10cms; 1915 at a depth of 40 cm, which is coincident with the period of maximum lead concentration and the deepest parts of the core have an early-industrial plateau and do not reach pre-IR isotope signatures or concentrations. The background lead concentration is not reached at the bottom of the core.

Core 5A: The $^{207/206}\text{Pb}$ isotope ratio never peaks or reaches the same values as the other cores suggesting recent erosion of the surface layers; the 1915 marker occurs at a depth of 40 cm, which is not coincident with the period of maximum lead concentration which occurs at a younger depth of 20cms; an early-industrial plateau is observed between 50-80 cm whilst a pre-IR isotope signature occurs at the deepest part of the core (90 cm). The background lead concentration is reached at a depth of 40cm.

Core 6A: The time period 1980-1985 equates to a depth of 18cms, which matches the period of maximum lead concentration; 1915 at a depth of 43 cms, and the deeper parts of the core reach and plateau pre-IR (> 50cms); the lack of a early-industrial plateau, the maximum lead concentration being associated with the peak isotope ratio (1980-1985) imply this site was little impacted by industrial lead but probably dominated by petrol lead as might be expected further away from Glasgow centre. The background lead concentration is reached at a depth of 45cms.

Core 7A: The time period 1980-1985 equates to a depth of 10-20cms and just after the maximum lead concentration; 1915 is at a depth of approximately 55 cm; there is no firm early-industrial plateau but 1835-1915 occurs between 55-80cm whilst below 80 is pre-IR. The very low maximum lead concentration being associated with the peak isotope ratio (1980-1985) imply this site being little impacted by industrial lead but probably influenced by petrol lead as might be expected for further away from Glasgow centre. The background lead concentration is reached at a depth of 45cm.

In summary, the cores provide a range of lead concentrations and $^{207/206}\text{Pb}$ isotope ratios reflecting a contaminant chronology back to the pre Industrial Revolution period. In most cases the last century is covered by the top 40cms of the cores. However, Core 1B from the inner-most estuary site, has the most expanded recent section, with the last century being represented by 70cm and the period from 1980-1985 onwards being 40cm. Perhaps of further note is the validity of comparing the aerosol input to *Sphagnum* moss with the water-sediment information from the Clyde. A comparison of the mass of Pb emitted by road traffic in the UK (NAEI & 2009) and the Pb concentration in Clyde water (SEPA 2009) for the period 1980-present showed remarkably good correlation, strongly supporting the use of the moss data of Farmer *et al*, 2002, at least for the most recent period.

3.4 Variation in non-volatile hydrocarbons

The TPH profiles 1A, 2A, 3A, 4A and 6A clearly show the on-set, rise and decrease in non-volatile hydrocarbon pollution in the Clyde (Fig. 6). Comparison of the TPH to PAH profiles revealed that peak TPH concentrations occurred at shallower depths than the total PAH reflecting the earlier use of coal and later use of oil as an energy/fuel source. The decrease in TPH concentrations in the uppermost 10cm of stations 2A, 3A, 4A, 5A, 6A is commensurate with both a decrease in industrial activities as well as increased environmental legislation and awareness from the 1980's to present (Fig. 6). Using the $^{207/206}\text{Pb}$ chronology to define an approximate date of 1915 it is clear that the on-set of environmentally significant concentrations of TPH did not occur until after this date as shown at stations 1A, 4A, 5A and 6A. Comparison of the seven TPH depth profiles revealed that for 2A, 3A, 4A, 5A and 6A TPH concentrations were highest in the uppermost 30 cm whereas core 7A showed no systematic change in TPH concentrations (Fig. 6). In contrast station 1A recovered from the innermost portion of the study area showed the highest TPH values between 40-60 cm below surface (4386-2838 mg/kg) (Fig. 1 & 6). Unpolluted estuarine and coastal sediments have reported TPH concentrations of 2-10 mg/kg and this value may increase up to about 100 mg/kg in organic rich sediments which contain high concentrations of biogenically sourced *n*-alkanes derived in part from plant waxes (Readman *et al*. 2002; Vane *et al*. 2008; Volkman & Nichols 1991). Based on these criteria it appears that the entire length of core 1A is contaminated with petroleum hydrocarbons and that the 10--30 cm depth interval of cores 2A, 3A, 4A and 6A are also contaminated

whereas the TPH concentrations in cores 7A and 5A are indicative of the low concentrations sourced from natural biogenic organic matter.

3.5 Polychlorinated biphenyl contamination

Inspection of the total PCB concentration profiles showed that contamination was mainly restricted to the top (0 to ~20 cm) of each core (Fig. 6). Total PCB content ranged from <4.3 to 5797 µg/kg, these values are considerably higher than those observed in surface sediments from the inner Clyde reported at 5.2 to 129.9 µg/kg, the Mersey Estuary 36 to 1409 µg/kg and pristine coastal sites in the USA (Vane et al. 2007a; Vane et al. 2008). This near surface increase in PCB contamination was widespread throughout the study area, but was observed at greater depth at station 1A (Fig. 6). Maximum PCB concentrations at station 1A of 1217 µg/kg were observed in the middle portion of the sediment core (39-58 cm) these values thereafter decreased to the limit of quantification (<4.3 mg/kg) at the base of the core. The difference in PCB profiles at 2A, 3A, 4A, 5A and 6A as compared to 1A is best explained by differing sediment accumulation rates in the different parts of the estuary. Low concentrations of PCB were detected throughout the entire length of core 4A which was conferred a date of ~1830 on the basis of Pb^{207/206} at 90 cm. In light that PCBs were not commercially produced until 1929 it is reasonable to assume that the low but nevertheless quantifiable concentrations of PCB were due to down-profile mixing and or diffusion.

Comparison of the summed tri, tetra, penta, hexa and hepta PCB homologue groups profiles for 1A and 4A varied with increasing depth from surface (Fig. 7). Site 1A was mainly comprised of hexa and penta chlorinated homologues as was the upper portion (0-15 cm) of core 4A. At depths greater than and equal to 20 cm the dominant homologue group at site 4A switched to trichlorobiphenyls. One plausible explanation for the change in homologue distributions at site 4A could be that the industrial source(s) of PCB pollution changed. For example, use of PCBs in transformers mainly utilised Aroclor 1254 (54% Cl) which is virtually devoid of trichlorinated biphenyl where as carbonless paper production used Aroclor 1242 (42 % Cl) which is dominated by trichlorinated homologues (Frame et al. 1996). Alternatively dechlorination of highly chlorinated homologues to less chlorinated homologues has been observed in aerobic and anaerobic sediments (Borja et al. 2005). Therefore, it is also possible that the increase in trichlorinated homologues and relative decrease in hexachlorinated congeners observed in this study is due to biodegradation in the subsurface (Fig. 7).

Previous studies of dated sediment cores demonstrated that PCBs were introduced via environmental processes before the onset of production in the UK (1954) and that sedimentary storage reached a maximum in the mid to late 1960's, then gradually declined after the sales ban in 1977 (Alcock et al. 1993; Fox et al. 1999; Harrad et al. 1994; Sanders et al. 1995). In the current study elevated total PCB concentrations were observed at stations 2A, 3A, 4A and 6A the peak may therefore correspond to an approximate date of 1965 to about 1977 and notwithstanding down-core diffusion processes the initial rise in PCB concentrations above the limit of quantification (LOQ) are unlikely to predate the first world-wide commercial production in 1929.

3.6 PAH concentrations and isomer ratios

Total PAH concentration profiles showed a much longer history of industrial activity than either TPH or PCB compounds (Fig. 6). All of the cores gave significant amounts of PAH contamination at depths greater than the 1915 level based on the $^{207/206}\text{Pb}$ isotope marker, with the exception of station 6A. This finding was not unexpected given that coal, a common source of PAH, was mined in Lanarkshire, burnt by local industry and transported from the Clyde from 1800's. The total PAH profile at station 1A revealed moderate values ranging from 216 $\mu\text{g}/\text{kg}$ at a depth of 27 cm to a maximum of 16163 $\mu\text{g}/\text{kg}$ at 57 cm before decreasing to 5869 $\mu\text{g}/\text{kg}$ at the base of the core (Fig. 6a). Other stations also showed elevated total PAH concentrations, for example site 3A gave values up to 15745 $\mu\text{g}/\text{kg}$ at 8 cm beneath the surface. Recent studies of surface sediments from the inner Clyde estuary reported total PAH concentrations in the ranges 630 $\mu\text{g}/\text{kg}$ to 23,711 $\mu\text{g}/\text{kg}$ (Vane et al. 2007a) and 450 $\mu\text{g}/\text{kg}$ to 28321 $\mu\text{g}/\text{kg}$ (Rogers 2002) which broadly concur with those presented in the current study.

In an attempt to gain insights into the sources of the PAHs in the sediments, isomeric ratios were investigated. This diagnostic approach, based essentially on the relative thermodynamic stability of isomeric pairs of PAHs, has been comprehensively reviewed and refined (Yunker et al. 2002). The resulting isomeric cross plotting, adopted from that of Yunker et al., is presented in Fig. 8 and employed four sets of isomeric ratios:

$$\begin{aligned}
 1). \text{ Anth:Phen} &= \frac{[\text{Anth}]}{([\text{Anth}] + [\text{Phen}])} & 2). \text{ Fanth:Pyr} &= \frac{[\text{Fanth}]}{([\text{Fanth}] + [\text{Pyr}])} \\
 3). \text{ BaA:Chrys} &= \frac{[\text{BaA}]}{([\text{BaA}] + [\text{Chrys}])} & 4). \text{ IP:BghiP} &= \frac{[\text{IP}]}{([\text{IP}] + [\text{BghiP}])}
 \end{aligned}$$

The majority of points tended to occupy portions of the charts denoting petroleum and combustion (specifically petroleum combustion) with comparatively few occupying the grass/wood/coal combustion portions. However, it should not necessarily be inferred that grass/wood/coal combustion made no significant contribution. For instance, in a situation in which both substantial petroleum PAH and grass/wood/coal PAH occur, the resulting isomeric ratios would display values intermediate between petroleum and grass/wood/coal combustion, *i.e.* they would mainly plot in the petroleum combustion chart regions. Therefore, some caution needs to be exercised in ascribing PAH origins on the basis of isomeric ratios and these need to be considered in concert with other factors.

Core 4A: All of the points plot within the combustion/petroleum combustion portions. This would seem to imply that throughout its depth this core has received PAHs that have emanated from similar or the same sources. However, the caveat above should be borne in mind. The other cores have points that plot across the various graphical sections suggesting diverse PAH inputs over the period in which the core sediments have accumulated. In seeking to clarify the effect of the various inputs of PAHs to the cores, plots of isomeric ratios against depths were constructed (Figs. 9a & 9b). For all the ratios employed, a rise in their value indicated an increase in pyrolytic character and, conversely, a decrease in petrogenic character.

Core 1A: This core, in contrast to all the others, exhibited, from the surface to a depth of 40 cm, comparatively low levels of TOC, TPH, PAH and PCB all of which rose to maxima at greater depths (Fig. 6a & 6b). From total concentration and isotopic ratios ($^{207/206}\text{Pb}$) of lead it was possible to ascribe tentatively a date of 1986 to the sediment at 40 cm. Such a marked degree of deposition over the past 18 years (*ca.* 1986 to 2004) was not evident in any of the other cores. From 40 cm to the surface the isomeric ratios (Fig. 9) appeared to decrease as the total PAH concentration declined from 4189 $\mu\text{g}/\text{kg}$ to 348 $\mu\text{g}/\text{kg}$. This ratio-decrease implied an increasing petroleum contribution over the 18 year period and this correlated with an increase in the [BghiP]/[BaP] ratio (Fig. 10) - a parameter taken to be characteristic of road traffic sources when its value exceeds 3.14 (Creaser et al. 2007). It can be seen that from 40 cm upwards its value rose dramatically from 1.0 to reach 9.2 at the surface. None of the other cores exhibited [BghiP]/[BaP] ratios of this magnitude (for all other cores the ratio was always <3 , ranging between 0.6 to 2.8 with an average of 1.2). Probably, this late, substantial and rapid deposition of relatively uncontaminated sediment had arisen from a number of recent flood events. Were flooding responsible, then it is likely that surface material contaminated by aerial deposition and run-off PAHs from the busy nearby A82 primary-route dual carriageway would form the bulk of the deposited sediment offering a valid explanation of the above observations.

The beginning of a marked increase in PCB concentration probably signified the start of extensive PCB use and conferred a date of *ca.* 1950 on sediment at a depth of 57 cm. This depth also coincided with maximum total PAH concentration. There was a steady decline in total PAH concentration to a depth of 87 cm. Isotopic ratios ($^{207/206}\text{Pb}$) indicated that sediment at a depth of 75 cm probably dated from *ca.* 1915. Accordingly, from pre-1915 to *ca.* 1950 there was a considerable and increasing input of PAHs to the sediments. The increase in total PAH concentrations and their mixed input signatures (divergent isomeric ratios) corresponded well with dates for the zenith of Clydeside industry, particularly shipbuilding activity.

Between *ca.* 1950 and *ca.* 1986, *i.e.* between core depths of 40 cm and 57 cm respectively, total PAH concentration fell from a maximum 16163 $\mu\text{g}/\text{kg}$ to 4189 $\mu\text{g}/\text{kg}$ coinciding with the decline of the shipbuilding industry (Fig. 6). Some augmentation from road traffic sources was indicated by the rise in the [BghiP]/[BaP] ratio from 1.6 at 57 cm to 4.6 at 48 cm and 4.2 at 43 cm (Fig. 10). Meanwhile, the Fanth:Pyr ratio trended downwards, likewise suggesting a shift to more petroleum/petroleum combustion-derived PAH contributions. This was not reflected in the other three isomeric ratios however. The maximum in TPH concentration also occurred during this period and probably represents the compound influence of increasing road traffic and fuel and oil discharges/spills from local industry.

Core 2A: From examination of total concentration and isotopic ratios ($^{207/206}\text{Pb}$) of lead for this core an approximate date of 1915 may be attributed to sediment at a depth of 40 cm. Below 40 cm the total PAH concentration remained fairly constant and within the range 954 $\mu\text{g}/\text{kg}$ to 2435 $\mu\text{g}/\text{kg}$ (Fig. 6a). Up to 40 cm the isomeric ratios Anth:Phen, BaA:Chrys and IP:BghiP (if the point at 60 cm is ignored) displayed a gradual increase but this was not imitated by the Fanth:Pyr ratio which showed a gradual decrease (Fig. 9a). It may be that the rising ratios mirror the influx of industrial revolution PAHs (predominantly coal and wood combustion) up to 1915.

Thereafter, from 1915 onwards there was a rapid increase in the ratios of Anth:Phen, BaA:Chrys, and to some extent of IP:BghiP, all attaining maxima at about 30 cm and it was observed that total PAH concentration also followed this pattern. These ratios all began to subside substantially after 20 cm, as did the total PAHs, and on the basis of the PCB evidence (*i.e.* start of extensive PCB use) a date of *ca.* 1950 may be assigned to sediment at this depth. Given that the peak in PCB concentration marks the cessation of its large-scale usage, then a date of *ca.* 1977, may be accorded sediment at a depth of 8 cm. At this depth and above the total PAH concentration diminished achieving its lowest value (592 $\mu\text{g}/\text{kg}$) throughout the core just below the surface at 3 cm. From about 10 cm to the surface, and with total PAH concentration low, the isomeric ratio behaviour was erratic. The rise of total PAH and TPH concentrations in the sediments after 1915 may possibly reflect the increasing use of fuel oil (bunker fuel) as a replacement for coal in ship propulsion (Dear & Kemp 2006). In addition, this would have been supplemented by the emplacement of riverside petroleum refineries and the increasing use of petroleum by industries and transport in general. It will be noted that in the latter stages of the period the TPH concentration remained high whilst the total PAH concentration began to wane (Fig. 6) probably as a consequence of lessening coal use and increasing reliance on petroleum fuels. Certainly, all the points, for the isomeric ratios in the period 1915 (40 cm) to 1977 (8 cm), plot in regions defined by the Yunker et al. criteria as characteristic of petroleum and its combustion (Fig. 9). Thus, Anth:Phen – combustion region; Fanth:Pyr – petroleum region; BaA:Chrys – combustion region; and IP:BghiP – petroleum and petroleum combustion regions.

Core 3A: Unfortunately, for dating purposes, no lead analysis (*i.e.* total concentration and isotopic ratios) had been conducted on this core. Nevertheless, the PCB concentration plot (Fig. 6a) made it possible to conjecture that at 13 cm beneath the surface lay sediment deposited at the start of extensive PCB usage, conferring a date of *ca.* 1950. Total PAH concentration remained relatively constant from 84 cm to 40 cm (ranging between 233 $\mu\text{g}/\text{kg}$ and 356 $\mu\text{g}/\text{kg}$) as did three of the isomeric ratios (Fig. 9a), Anth:Phen 0.07-0.15 (petroleum/combustion border), BaA:Chrys 0.15-0.20 (petroleum) & IP:BghiP 0.11-0.22 (petroleum/petroleum combustion). The Fanth:Pyr ratio showed an overall downward trend and ranged from 0.15-0.36 (petroleum/petroleum combustion). These low total concentrations in tandem with a strong non-pyrolitic component probably signified a background PAH composition comprising, in the main, aeolian deposition, *i.e.* from anthropogenic and natural combustion sources (Jaward et al. 2004) together with a substantial biogenic PAH input (Wilcke 2007). The contrast between this background composition and a combustion-contaminated composition can be illustrated by comparison of the PAH distribution at 52.5 cm (total PAHs concentration 371 $\mu\text{g}/\text{kg}$) with that at 17 cm (total PAHs concentration 11297 $\mu\text{g}/\text{kg}$) as shown in Figure 11. The numerals above each PAH plot refer to their relative abundance. The relative abundances of the biogenically-generated PAHs, *i.e.* naphthalene, phenanthrene and perylene (Wilcke 2007) are much greater in the sediment at 52.5 cm compared with sediment at 17 cm. Furthermore, the effect of difference in concentrations of isomer pairs upon the diagnostic isomeric ratios can be appreciated, (*e.g.* at 17 cm Fanth and Pyr have comparable concentrations leading to Fanth:Pyr ratio \sim 0.5 but at 52.5 cm [Fanth] < [Pyr] yielding a Fanth:Pyr ratio \sim 0.15 and similarly for BaA:Chrys and for IP:BghiP). Sediments deeper than 40 cm, therefore, probably pre-date significant industry.

Above 40 cm there began an increase in total PAH concentration probably denoting the onset of the Clyde's industrial activities (Fig. 6a). Significant correlations between isomeric ratios and total PAH concentration emerged (Anth:Phen $r^2 = 0.567$, Fanth:Pyr $r^2 = 0.620$, BaA:Chrys $r^2 = 0.676$, IP:BghiP $r^2 = 0.379$). Thus, as total PAH concentration increased so generally did the allied isomeric ratios signifying that the increase was attributable to combustion-related processes. This was supported by the prevalence of the pyrolytic PAHs, *i.e.* Fanth, Pyr, BaA, Chrys, BbF, BaP, BghiP and IP (McCready et al. 2000), in the PAH distribution for the sediment at 17 cm (Fig. 11).

Core 4A: Data on total concentration and isotopic ratios ($^{207/206}\text{Pb}$) of lead for this core made it possible to ascribe dates to sediment of *ca.* 1985 to that at 5 cm depth, *ca.* 1925 to that at 29 cm, *ca.* 1915 to that at 36 cm and *ca.* 1835 to that at 88 cm (Fig. 6a). Thus, from the early industrial revolution it can be seen that there was a steady rise in total PAH concentrations from 1241 $\mu\text{g}/\text{kg}$ at 96 cm depth to a maximum of 14932 $\mu\text{g}/\text{kg}$ at 32 cm, *i.e.* at *ca.* 1920 (Fig. 6a). There was also, during this period a rise in the isomeric ratios for Anth:Phen, BaA:Chrys and IP:BghiP signifying the pyrolytic nature of the PAH increase (Fig 9b). However, none of the ratios were high enough to achieve grass/wood/coal combustion status although doubtless such would have made a major contribution. As mentioned earlier, the lack of prominence of this may be attributable to the effect of a pronounced petrogenic contribution on the isomeric ratios of a grass/wood/coal contribution, *i.e.* producing an intermediate petroleum combustion value. Thereafter, from *ca.* 1920 (32 cm) to *ca.* 1985 (5 cm) there was a steady diminution in total PAH concentration. At *ca.* 1920 (32 cm) the TPH concentration began to increase rapidly and reached a peak at 19 cm depth. Given that it was at this depth that PCBs began their increase then a date of *ca.* 1950 would seem appropriate for the TPH maximum (Fig 6a). This maximum some 30 years after that of the total PAH concentration probably reflected diminishing coal use, as the Clyde industrial slump became entrenched, and the rise of petroleum fuels as a major source of PAH. This was supported by the decreasing isomeric ratios of Anth:Phen and BaA:Chrys over this period. In fact, the behaviour of the Anth:Phen ratio more or less faithfully tracked that of the total PAH concentration throughout the core and a significant correlation between the two emerged when plotted ($r^2 = 0.574$).

Core 5A: It is possible from lead isotopic data to attribute an approximate date of *ca.* 1915 to sediment at 50 cm depth. A perceptible rise in total PAH concentration appeared to occur at about 68 cm depth and possibly related to the effect of the industrial revolution. The curve for total PAH concentration and that for TOC were distinctly similar with the two maxima on both plots coinciding (Fig. 6b). Elevated levels of PAH were maintained until a depth of 14 cm. The TPH curve again seemed to convey an increased use of petroleum during the later period of elevated PAH concentrations. Isomeric ratio plots remained virtually constant with depth (Fig. 9b), except for the IP:BghiP ratio which appeared to track the period of elevated PAHs but with an inverse relation, (*i.e.* it began to decrease when the total PAH concentration began to rise at 68 cm and increased as the PAH diminished from 22 cm upwards). This counter-intuitively implied increasing petrogenicity from *ca.* 1915 with increasing pyrogenicity in more modern times, contrary to the TPH evidence. All Anth:Phen ratios were close to the petroleum - combustion border at 0.1. All Fanth:Pyr ratios were close to the petroleum combustion - grass/wood/coal combustion border at 0.5. All BaA:Chrys ratios (except one) were above 0.35, *i.e.*

combustion. All IP:BghiP ratios plotted either in the petroleum or petroleum combustion areas.

Core 6A: It was only in this core that TPH, PAH and PCB maximum concentrations were coincident these peaks additionally corresponding with the smaller of two maxima in the TOC plot (Fig. 6b). This could perhaps indicate a lack of industrial PAH contamination of the sediment deposited at this location, which was situated on the mud-banks between the less industrial, suburban area of Port Glasgow and rural Finlaystone. Lead concentrations and isotope ratios ($^{207/206}\text{Pb}$) suggested a date of *ca.* 1986 for sediment at 18 cm depth and *ca.* 1915 at 45 cm depth. The PCB peak indicated *ca.* 1977 for 18 cm with an approximate date of 1950 for sediment at 23 cm.

Core 7A: This core, taken furthest downstream, was the least PAH-contaminated of all the cores with total PAH concentrations that varied between 19 $\mu\text{g}/\text{kg}$ and 205 $\mu\text{g}/\text{kg}$ (Fig. 6b). As with the deeper parts of core 3A, the PAH levels in this core were essentially background and, although in this core perylene was not determined, the distributions of PAHs were akin to those shown occurring at 52.5 cm depth in core 3A (Fig. 11). and all were characterised by high relative abundances of naphthalene and phenanthrene suggesting an appreciable natural biogenic PAH contribution (Wilcke 2007). Dating was difficult with data from lead concentrations and isotope ratios ($^{207/206}\text{Pb}$) not yielding any great precision. Thus, sediment with a date of *ca.* 1986 could only be defined as occurring somewhere between 15 cm and 28 cm depth. A date of *ca.* 1915 could tentatively be assigned to sediment at about 65 cm depth. The isomeric ratios remained essentially static throughout the core for BaA:Chrys, Fanth:Pyr, IP:BghiP - except that the latter two ratios showed a sharp and inexplicable rise at 5 cm (Fig. 9b). In marked contrast the Anth:Phen ratio displayed a peak that coincided with the peak in total PAH concentration. The increase in this ratio with the concomitant rise in total PAH concentration signified a period of combustion-related PAH input to the sediment. At their maximum the values of the ratio were only marginally above 0.1 (*i.e.* there were two points, both 0.11, that plotted in the combustion zone the rest were in the petroleum zone). Fanth:Pyr ratios were mostly <0.4 (petroleum zone), with only two points >0.4, *i.e.* 0.41 (petroleum combustion) at 46 cm and 0.60 (grass/wood/coal combustion) at 5 cm. BaA: Chrys ratios were all at the 0.35 combustion - mixed sources interface and varied between 0.32 to 0.38. Values for the IP:BghiP ratio were all between 0.2 to 0.5, *i.e.* petroleum combustion. On balance the data indicated a predominant petroleum/petroleum combustion PAH input to which a contribution from road traffic contribution was insignificant, *i.e.* [BghiP]/[BaP] ratio was <3 throughout core. The probability was, therefore, that the major PAH input arose from shipping emissions and petroleum-utilising riverside industries.

Taking an overview of the PAH source ascription for the cores, based on the examination of isomeric ratios in combination with core chronology (from total lead, lead isotopes and PCBs), total concentrations of organic species (PAH, TPH and PCBs) and TOC measurements, it has been possible to draw some conclusions regarding the provenance of PAHs in the sediment cores. Evidence has been elicited for the impact of road traffic *via* a criterion for the non-isomeric [BghiP]/[BaP] ratio. Although isomeric ratios can provide information on the burning of grass, wood and coal, distinct from that arising from petroleum combustion, the need to exercise caution in a situation where there is a strong petrogenic PAH contribution was noted.

That said, in certain instances the isomeric ratios were of sufficient magnitude to permit a grass/wood coal combustion attribution and this typically accompanied dating that hinted at the influence of industry and/or the industrial revolution. In cores that exhibited low total PAH concentrations, and following consideration of PAH distribution patterns, it was in some cases possible to detect the effect of biogenic PAHs. In some instances certain isomeric ratios with depth were closely followed by the total PAH concentration, *e.g.* Fanth:Pyr in core 1A, Anth:Phen in cores 4A & 7A *etc.* but in other cases they were not. Overall, in most cases the study of isomeric ratios with depth was able to furnish at least some useful insights.

4. Conclusions

We applied a geochemical approach using Pb, ^{206/207}Pb, TPH, PCB and PAH to investigate the changing industrial and urban environment within the Clyde estuary over the past ~250 years. The combination of organic pollutants, Pb contamination and Pb isotopic data within seven sediment cores facilitated the reconstruction of the main environmental changes that occurred at the local and regional scale as well as a pollutant inferred geochronology.

- 1) Comparison of the TPH, PAH and PCB concentration profiles and ratios showed how relatively pristine Clyde sediments were contaminated by man's evolving industrial and urban activities. Five of the seven cores recorded the rise, peak and decline of coal usage in the Clyde. Thereafter increasing petroleum pollution from fuel oil (shipping) and petroleum refinery sources was tracked followed by more modern pollution from chlorinated industrial chemicals (PCBs).
- 2) Organic pollutants were observed at concentrations which were typical of highly industrialised estuary and are considered environmentally significant *i.e.* maximum TPH at 4386 mg/kg, maximum total PAH at 16163 µg/kg mg/kg and maximum total PCB at 1217 µg/kg . In contrast pre-industrial sediments were identified on the basis of low total PAH concentrations together with high relative abundances of biogenic PAHs naphthalene and phenanthrene.
- 3) The predominant feature of the PAH isomeric cross plots, was the significance of petroleum-based activities on PAH inputs to the cores, *i.e.* petroleum combustion and unburnt fuel emissions from shipping, traffic *etc.* together with petroleum product spills and discharges from local industry and refineries. Interestingly, this contrasts with our earlier study of the Inner Clyde, where the majority of the samples plotted in the combustion – grass/wood/coal combustion region (Vane et al. 2007a). This difference was thought to be due to the much greater proximity of coal-burning sources, domestic and industrial, for the samples from the Inner Clyde. The benefit of isomeric ratio with depth plots over the isomeric cross plots was that, in concert with chronological data, they shed light on the magnitude and dating of the inputs. Frequently, this could be substantiated by correlation with total PAH and TPH determinations.

- 4) Notwithstanding the complexities of pre and post depositional processes, organic pollutants may have some utility in establishing estuarine sedimentary chronology. For example, the PCB concentration profiles from stations 1A, 2A, 3A and 4A showed a clear rise fall and decline which may broadly indicate 1950's, 1965-77 and post-1980 respectively. Similarly peak coal production in the Clyde (1915) and therefore peak PAH concentration appeared to be coincident and followed by increasing petroleum hydrocarbon (TPH) concentrations some 30 years later.
- 5) The cores studied demonstrated variable Pb concentrations and isotope ratios with depth. The changing pattern of lead isotope ratios in the cores was matched with those from other well dated records such as that from aerosol deposition on moss (Farmer et al, 2002). Key changes in ratio are known to have occurred at specific times including: c1915 the introduction of non UK Broken Hill type lead for petrol and subsequent major industrial products; 1980-1985 due to a reduction in petrol lead and c1750 the beginning of the industrial revolution and major the input of lead into aerosols, due to both smelting and coal burning. These have been used to place putative dates on core depth intervals and allow a contaminant chronology to be established.
- 6) This study has shown that there are numerous chemical markers within UK estuarine sediments that retain sufficient information to enable geologists to identify the late Anthropocene. Chemical fingerprints of past industrial heritage have evolved through the coal, petroleum and electrical ages. In the Clyde the boundary between pre and post industrial revolution is signalled by a change from low to high PAH concentrations as well as a switch from biogenic to coal sourced PAH. Furthermore, commercially produced industrial chemicals such as PCBs maybe utilised to mark other Anthropocene subdivisions-for instance the "electrical age" 1950s-1980s. However, it should be borne in mind that different regions of the world have experienced industrialisation and the resulting environmental contamination at different times. Thus any attempt to utilise a chemical marker approach has to be underpinned by an understanding of which pollutants are transported globally as well as local and regional historical knowledge of industry and urbanisation.

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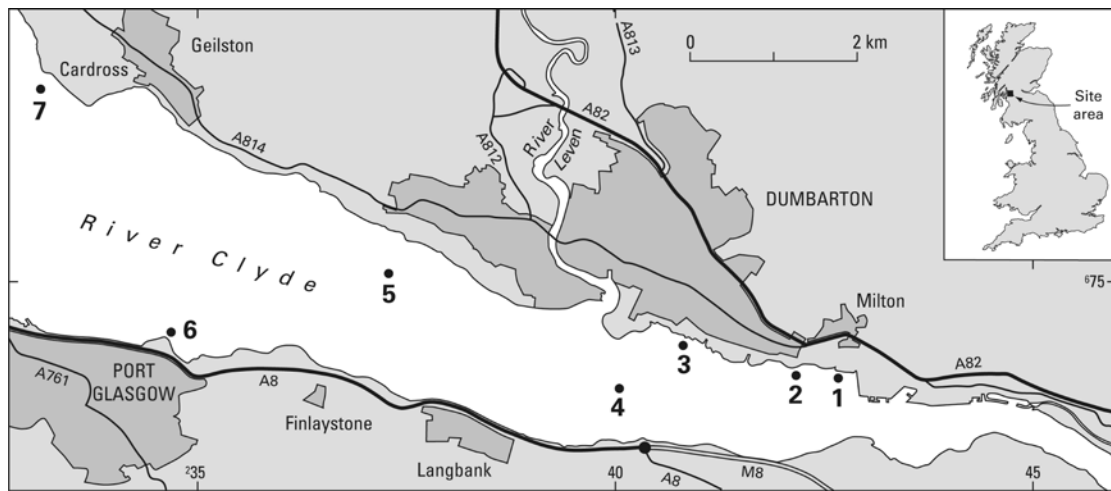


Figure 1. Location of the sampling sites in the Clyde Estuary, UK.

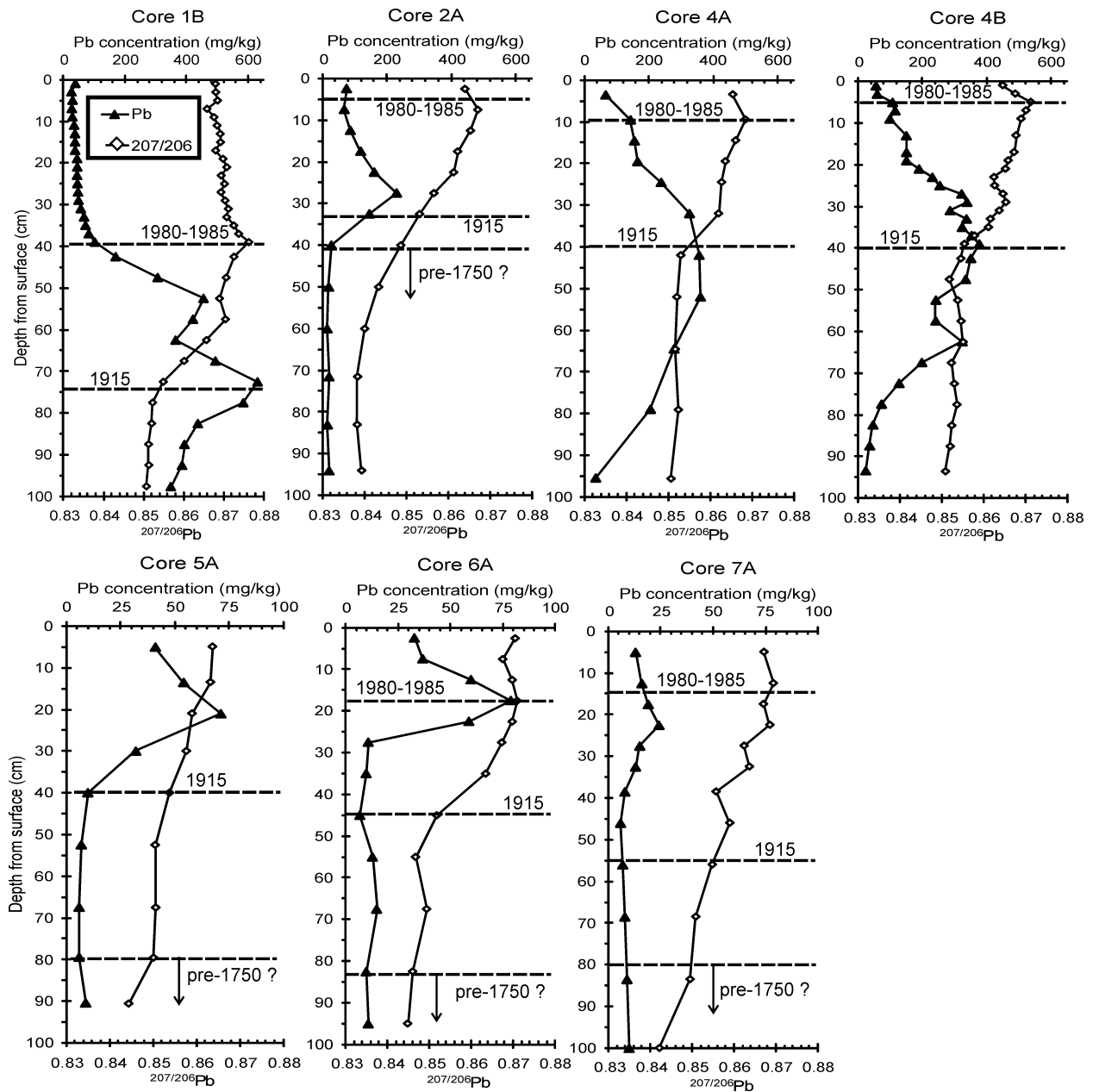


Figure 2. Down-profile changes in Pb concentration and $^{207}/^{206}\text{Pb}$ and interpreted dates in sediments from the Clyde Estuary. Note the decrease in concentration scale in the outer estuary cores.

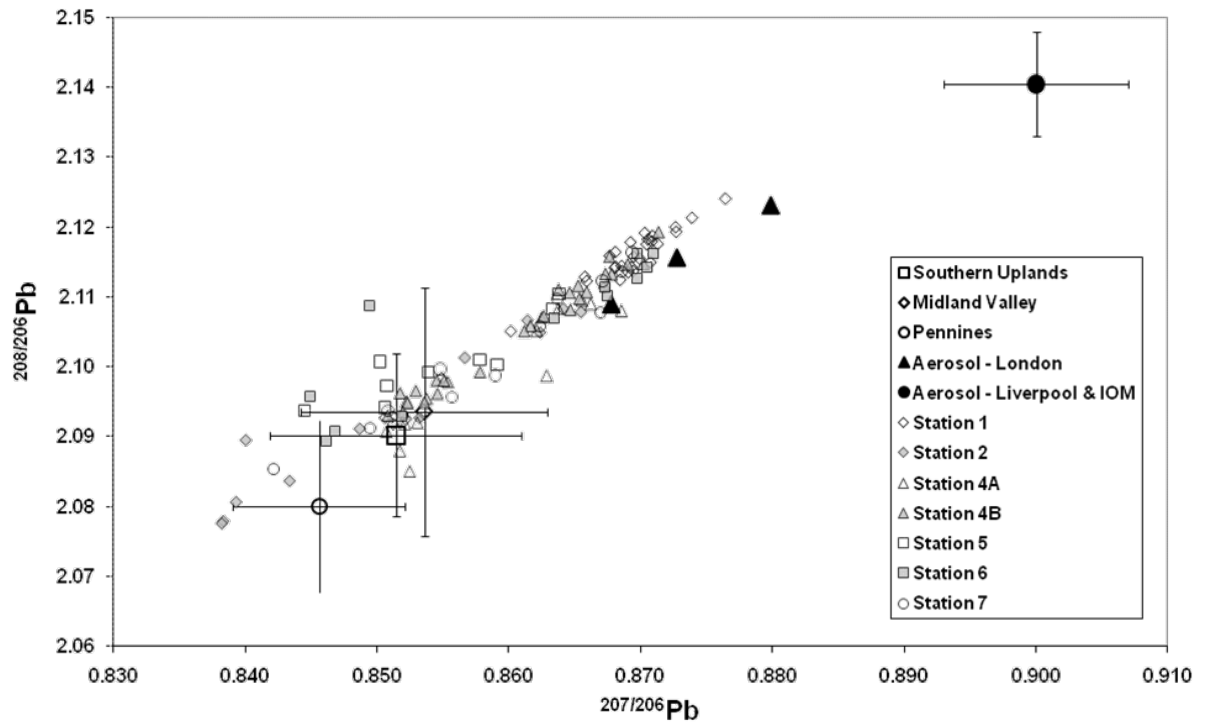


Figure 3. Pb isotope ratio correlation diagram between $^{207/206}\text{Pb}$ vs $^{208/206}\text{Pb}$ for Clyde sediment cores and potential end-member sources.

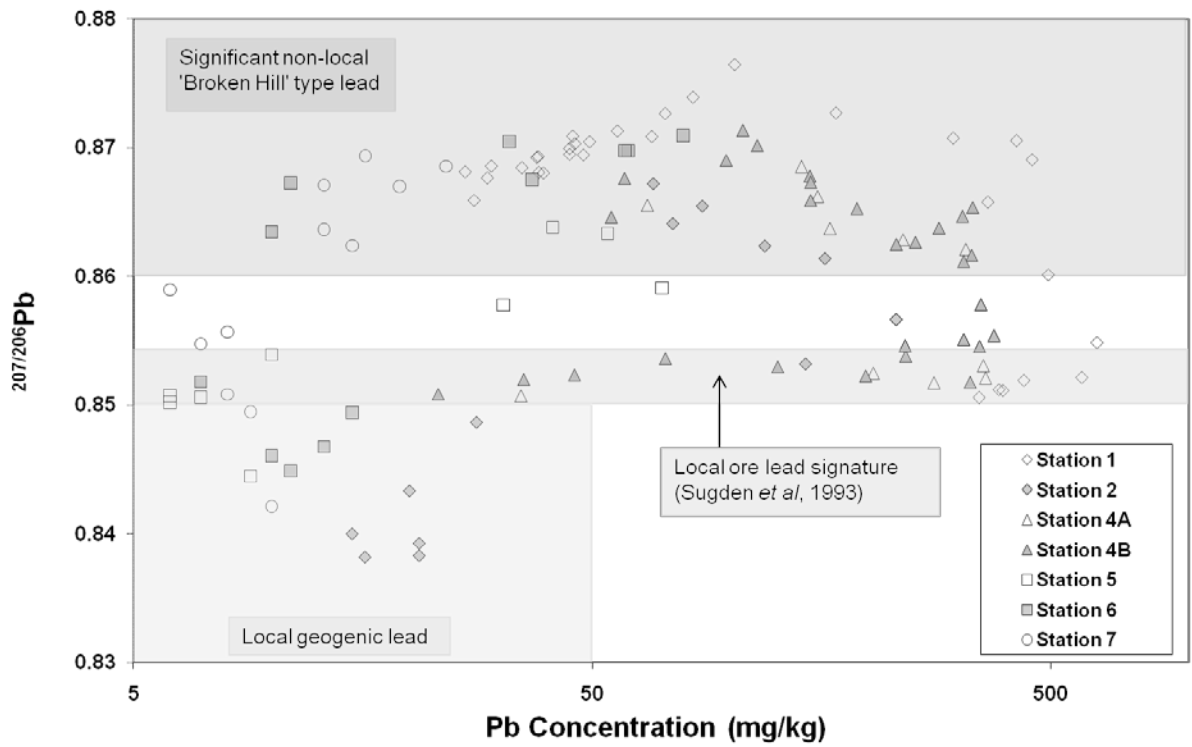


Figure 4. Cross plot of Pb concentration vs $^{207/206}\text{Pb}$ for Clyde sediment cores, likely sources; local ore, Broken Hill (Aus) and local geogenic Pb are highlighted.

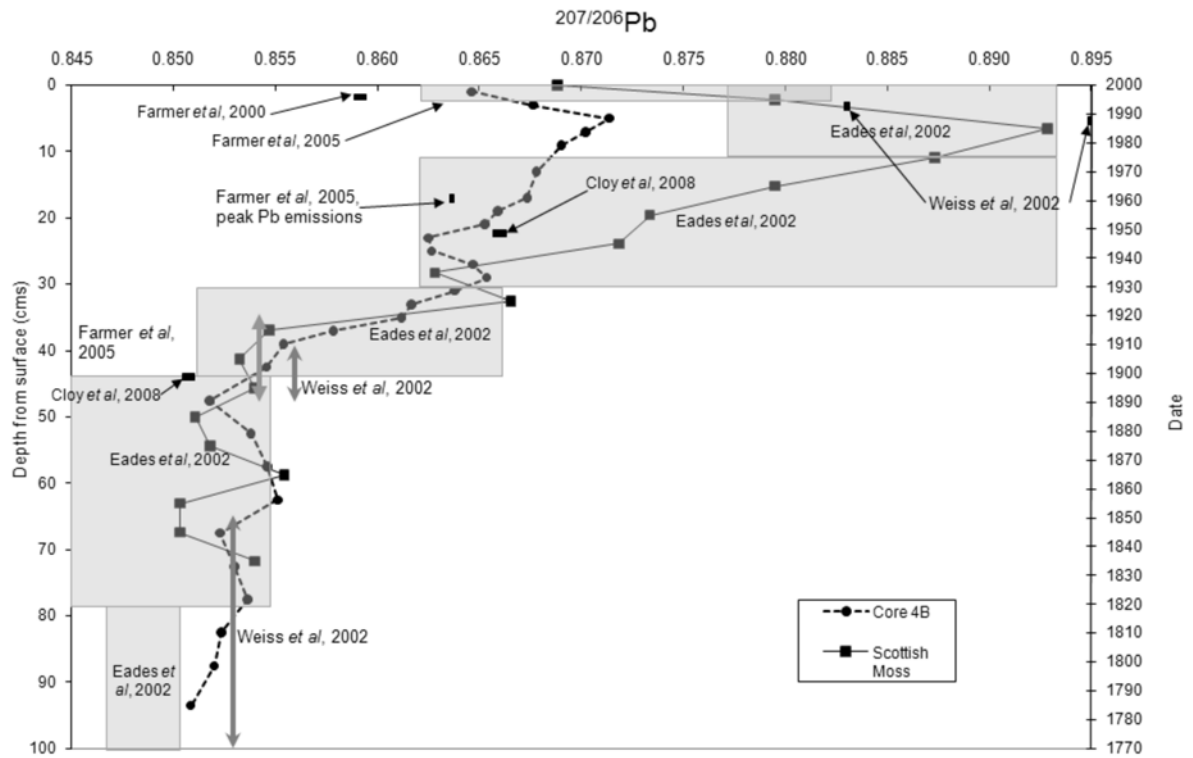


Figure 5. A composite historical Pb isotope profile (Scottish Moss) compared to an example core log from the Clyde estuary.

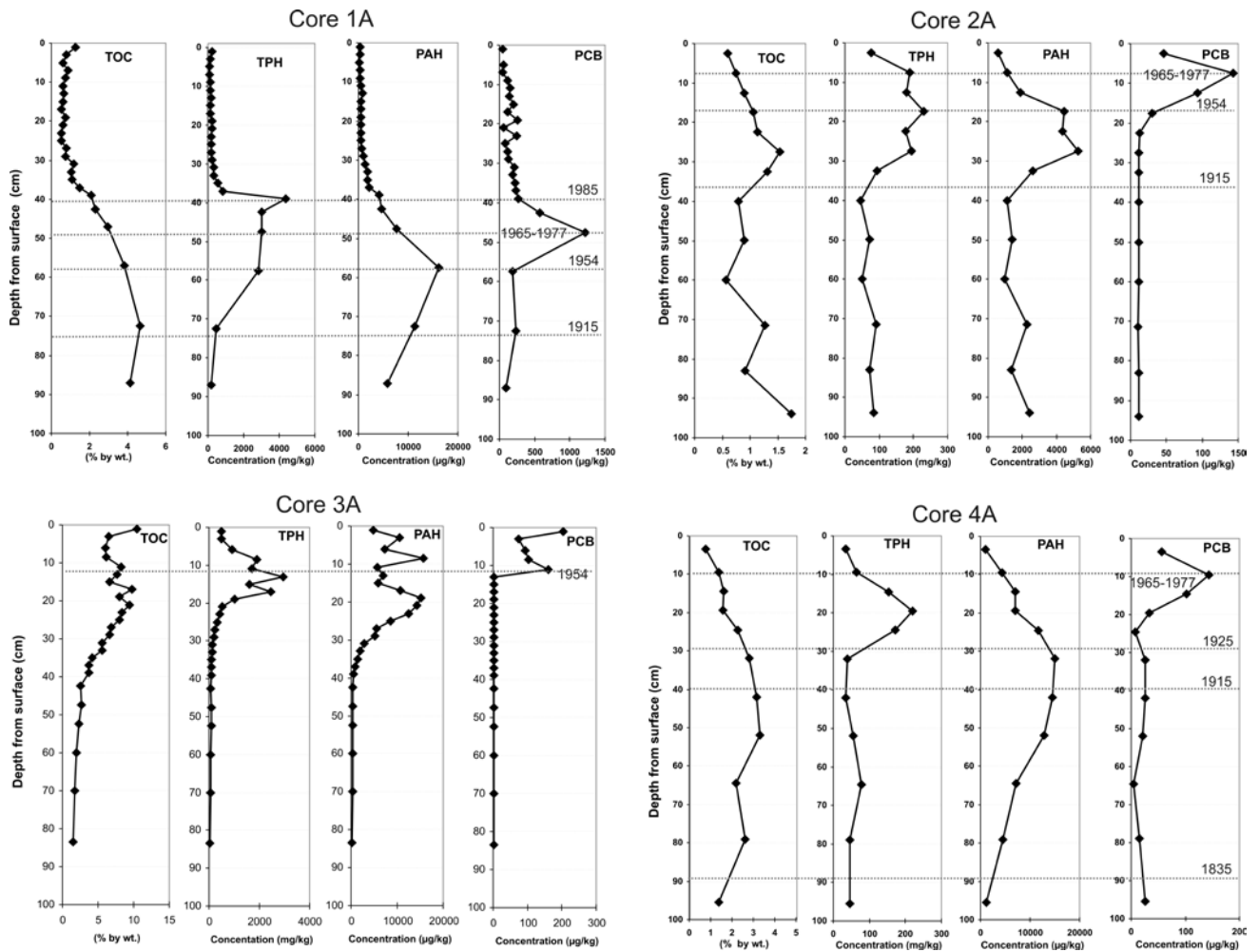


Figure 6a. Organic contaminant depth profiles (Cores 1-4) of sediments from Clyde Estuary. Abbreviations: TOC = Total organic carbon; TPH= Total Petroleum Hydrocarbon; PAH= Polyaromatic Hydrocarbon; PCB=Polychlorinated Biphenyl. Rationale for dates: 1750= pre-Industrial from ^{207/206} Pb; 1915= peak coal production; 1954= onset of PCB production in UK; 1965-77= peak PCB production; 1985 from peak ^{207/206} Pb values.

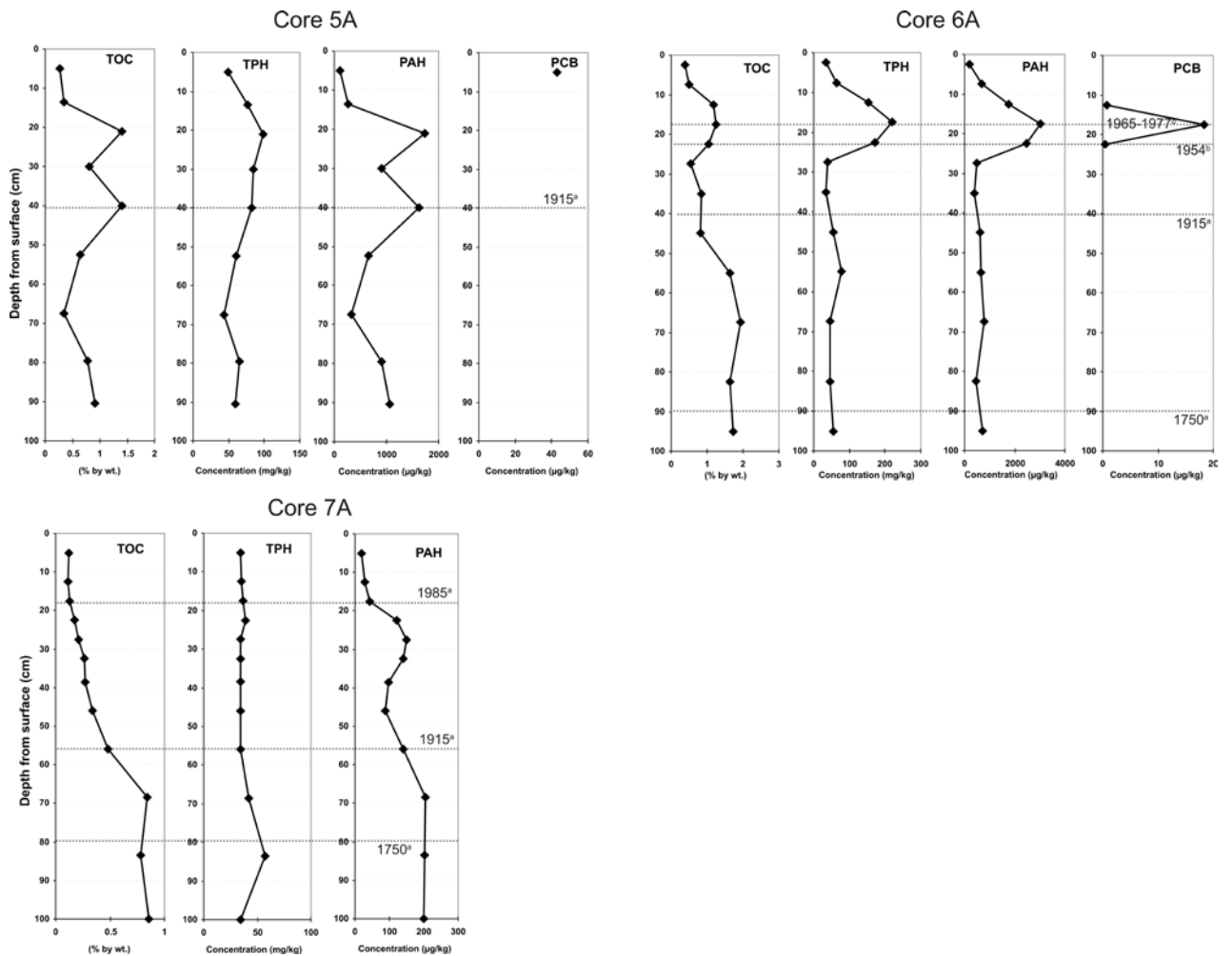


Figure 6b. Organic contaminant depth profiles (Cores 5-7) of sediments from Clyde Estuary. Abbreviations: TOC= Total organic carbon; TPH= Total Petroleum Hydrocarbon; PAH= Polyaromatic Hydrocarbon; PCB= Polychlorinated Biphenyl. PCB concentration data not shown for core 7A due to interferences. Rationale for dates: 1750= pre-Industrial from ^{207/206}Pb; 1915= peak coal production; 1954= onset of PCB production in UK; 1965-77= peak PCB production; 1985= from peak ^{207/206}Pb values.

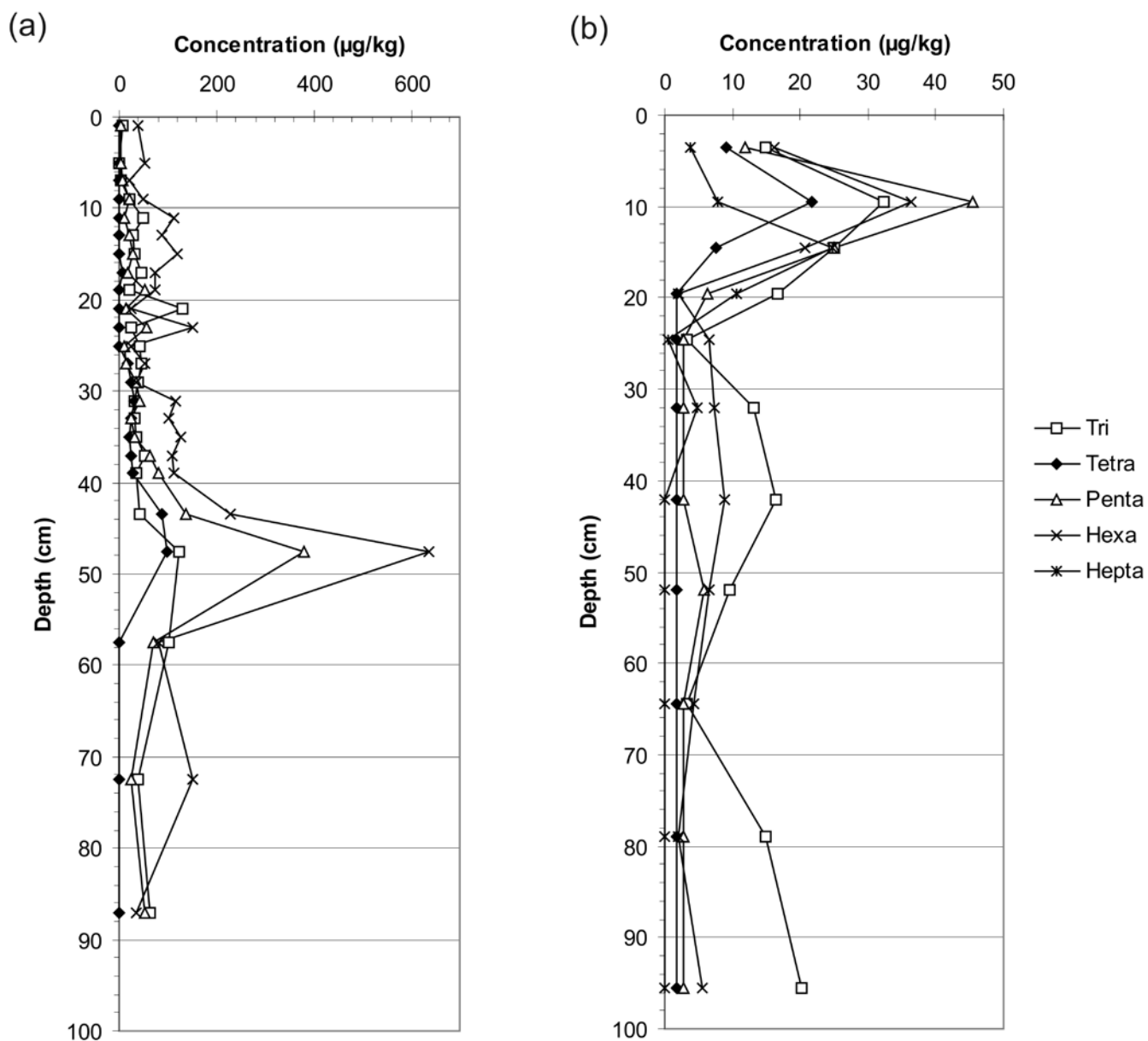


Figure 7. Depth profiles of summed PCB homologue groups at sites (a) 1A and (b) 4A. Abbreviations: Σ trichlorinated; tetra= Σ tetrachlorinated; Penta= Σ pentachlorinated; Hexa= Σ hexachlorinated; Hepta= Σ heptachlorinated congeners.

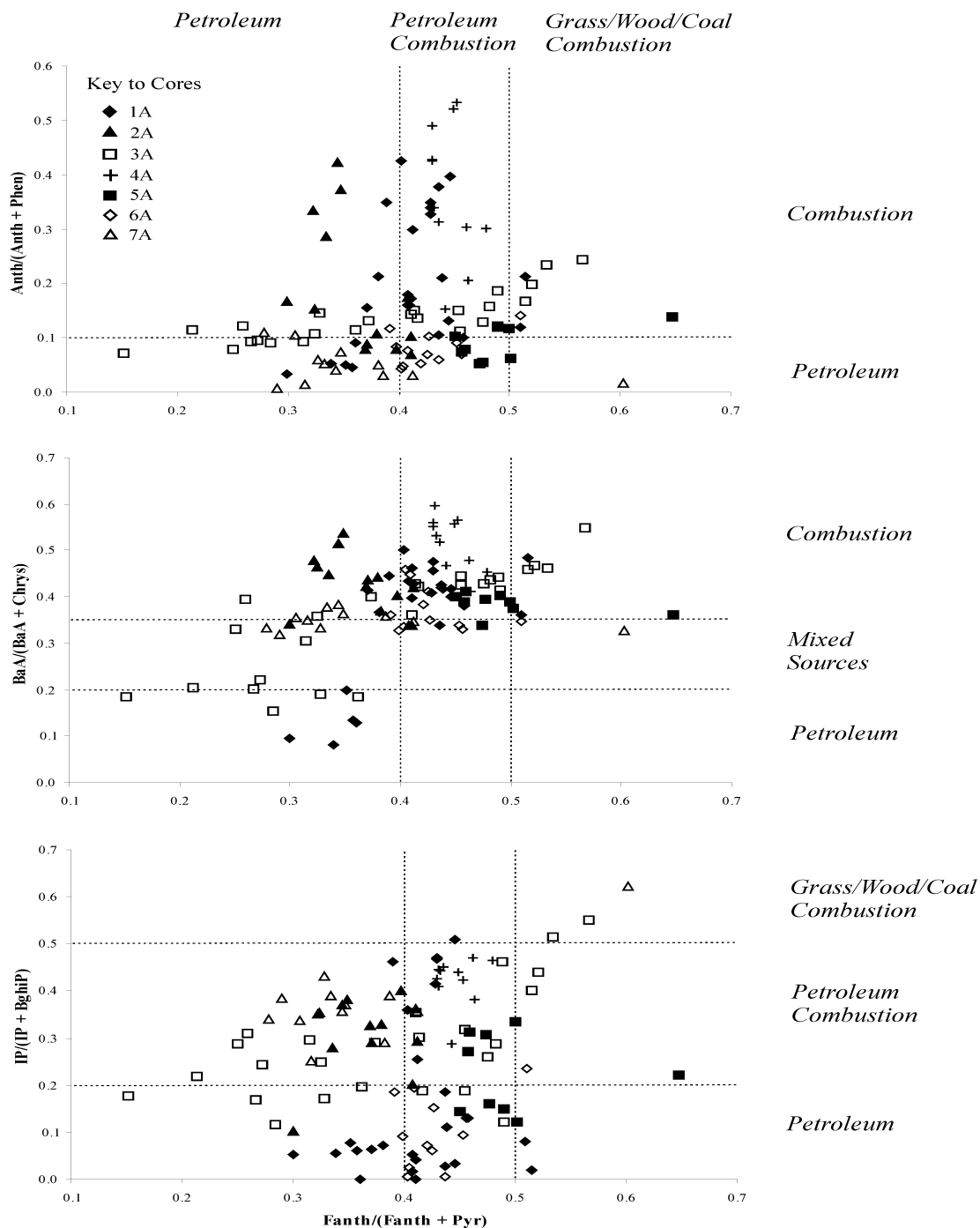


Figure 8. PAH isomeric cross-plot of sediments from Clyde Estuary for the determination of PAH origin. Abbreviations: Anth=Anthracene; Phen=Phenanthrene; BaA=Benz[a]anthracene; Chrys=Chrysene; IP=Indenol[1,2,3-*cd*]pyrene; BghiP=Benzo[*ghi*]perylene.

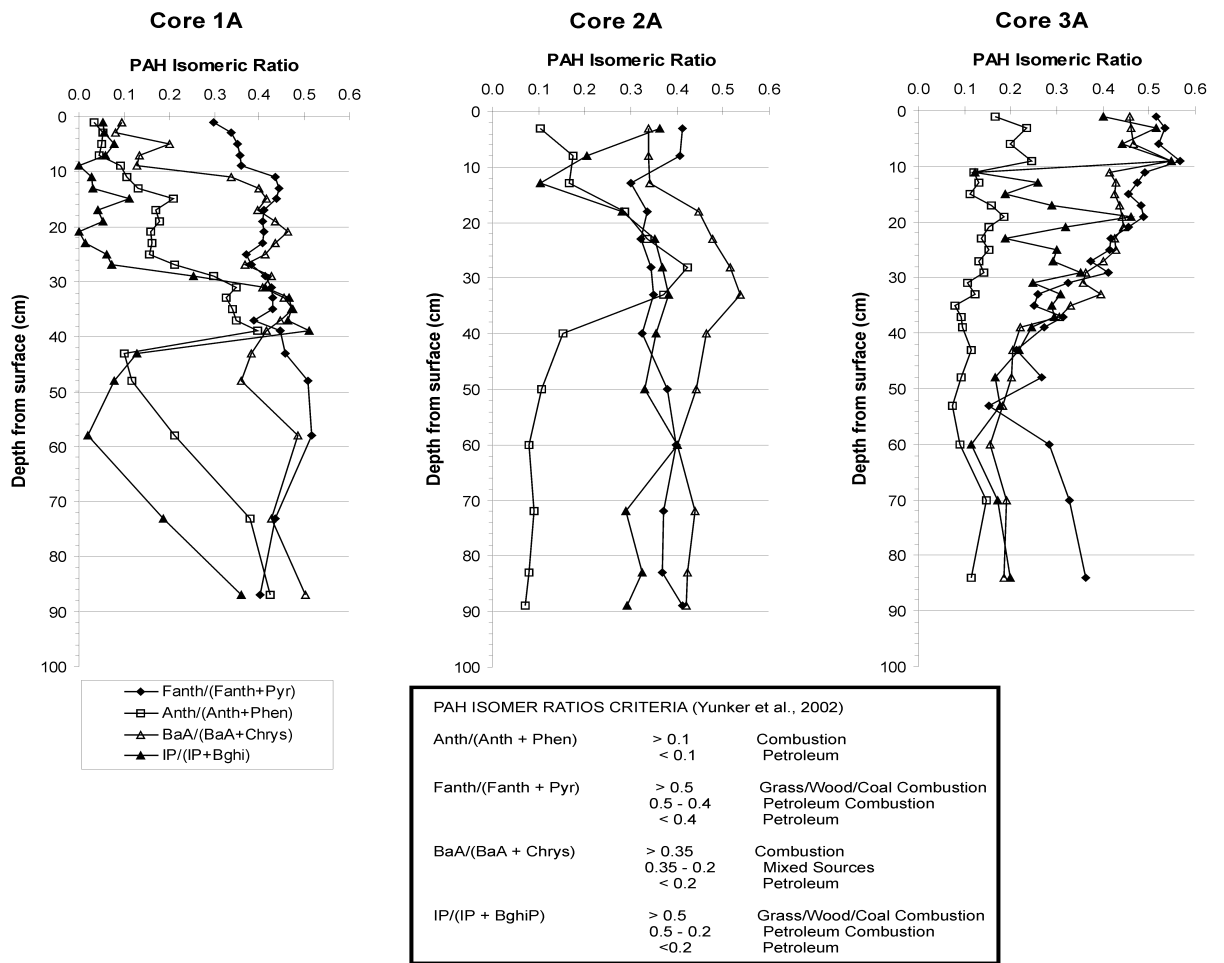


Figure 9a. Variation in PAH isomeric ratios with depth for Clyde cores 1A, 2A and 3A.

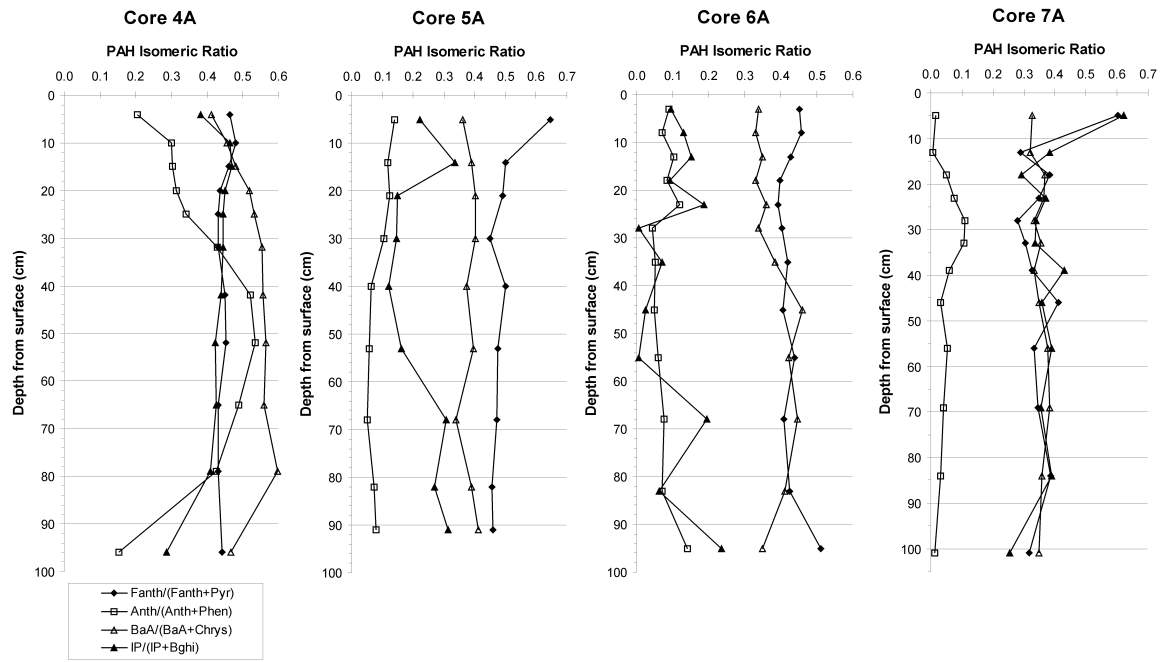


Figure 9b. Variation in PAH isomeric ratios with depth for Clyde cores

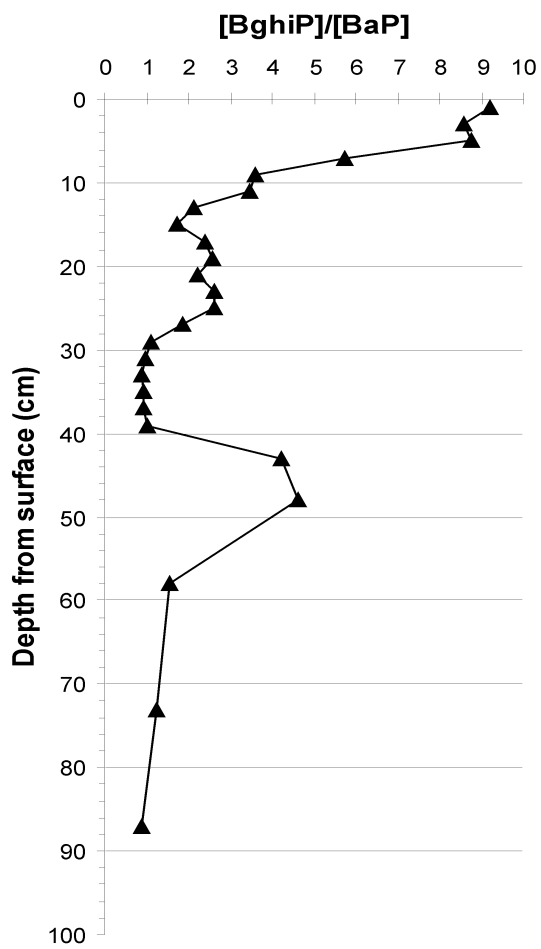


Figure 10. Ratio of [BghiP]/[BaP] versus depth in core 1A. Abbreviations: BghiP=benzo[ghi]perylene; BaP= benzo[a]pyrene.

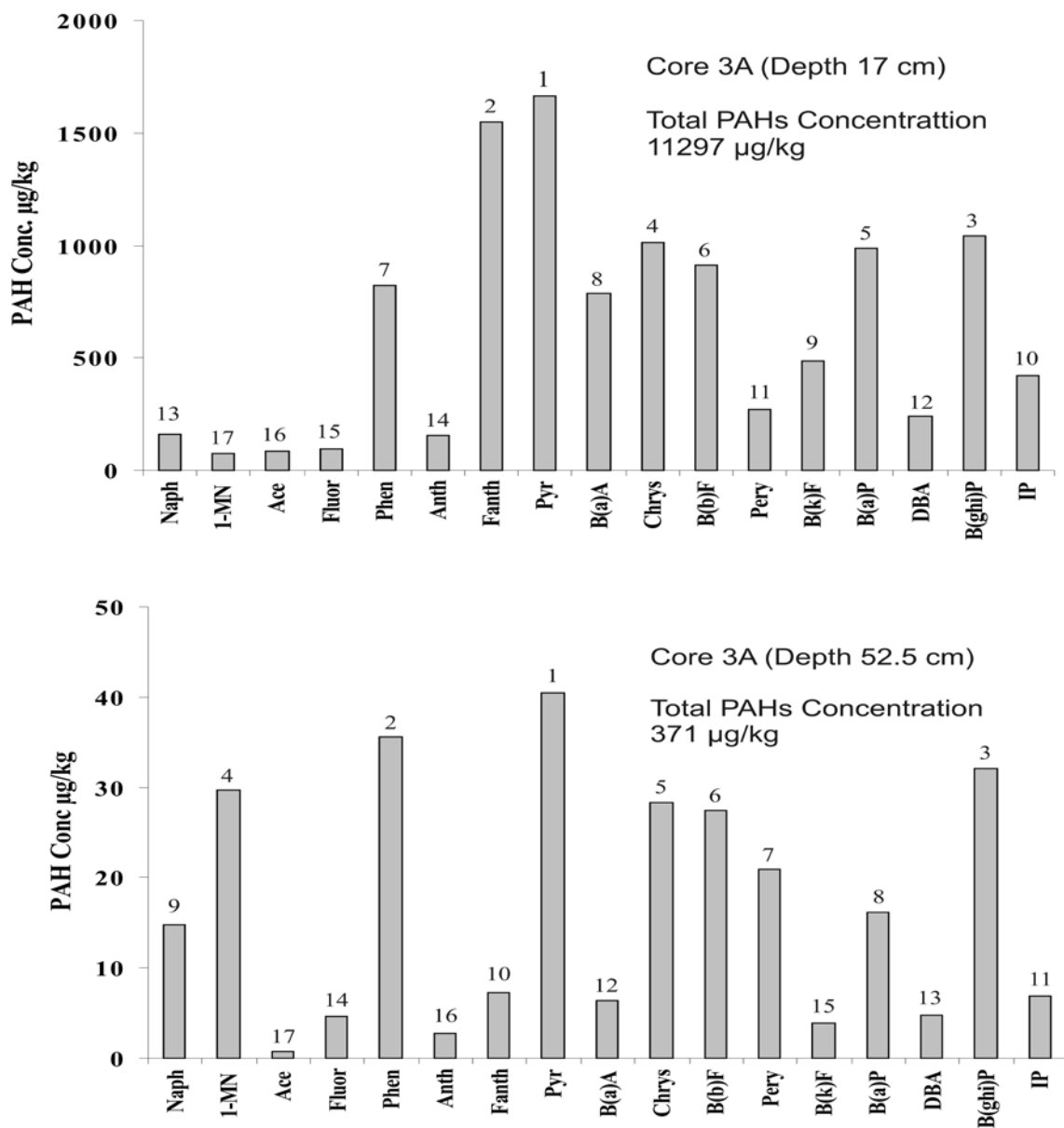


Figure 11. Intra-core variations in PAH distribution patterns. Depth 17 cm is indicative of mainly combustion sources where as the distribution at 52.5 has high biogenically-generated PAHs such as naphthalene (Naph), phenanthrene (Phen) and perylene (Pery).