Chemical signatures of the Anthropocene in the Clyde estuary, UK: sediment-hosted Pb, \(^{207}/^{206}\)Pb, total petroleum hydrocarbon, polyaromatic hydrocarbon and polychlorinated biphenyl pollution records

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The sediment concentrations of total petroleum hydrocarbons (TPHs), polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), Pb and \(^{207}/^{206}\)Pb isotope ratios were measured in seven cores from the middle Clyde estuary (Scotland, UK) with an aim of tracking the late Anthropocene. Concentrations of TPHs ranged from 34 to 4386 mg kg\(^{-1}\), total PAHs from 19 to 16163 mg kg\(^{-1}\) and total PCBs between less than 4.3 to 1217 mg kg\(^{-1}\). Inventories, distributions and isomeric ratios of the organic pollutants were used to reconstruct pollutant histories. Pre-Industrial Revolution and modern non-polluted sediments were characterized by low TPH and PAH values as well as high relative abundance of biogenic-sourced phenanthrene and naphthalene. The increasing industrialization 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 PAHs mirrored the lessening of coal use and increasing reliance on petroleum fuels from about the 1950s. Thereafter, declining hydrocarbon pollution was followed by the onset (1950s), peak (1965–1977) and decline (post-1980s) in total PCB concentrations. Lead concentrations ranged from 6 to 631 mg kg\(^{-1}\), while \(^{207}/^{206}\)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.

Keywords: Clyde estuary; pollution; total petroleum hydrocarbon; polychlorinated biphenyl; polyaromatic hydrocarbon; \(^{207}/^{206}\)Pb

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

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One contribution of 13 to a Theme Issue ‘The Anthropocene: a new epoch of geological time’.
Age, Glasgow’s industrial growth accelerated in the eighteenth and nineteenth centuries to such an extent that it was known as the second city of the British Empire. Notable Clydeside industries of the nineteenth and twentieth centuries included ship-building, textiles, chemical production as well as coal and ironstone mining [1]. Today, the Clyde still builds military ships at Govan and Scouthead, however, manufacturing is now mainly linked to light when compared with heavy industry. Consequently, the river Clyde, which flows through Glasgow City, has received pollution from the onset of the Industrial Revolution (ca AD 1770) up to the present day [2–4].

The environmental persistence of organic pollutant groups such as total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) ranges from hours through decades to centuries. When used together, non-volatile TPH and PAH compounds facilitate the reconstruction of different phases of development based upon changing fuel sources and use of chemicals [5–7]. There are four broad sources of PAHs, 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 [8]. In most industrially impacted environments, petrogenic and pyrolytic PAH sources predominate, and these have different parent PAH distributions that permit sediments contaminated with crude oil and petrol to be distinguished from combustion sources, such as coal burning and vehicular combustion emissions [3,9,10]. 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 PCBs and/or brominated flame retardants (polybrominated diphenyl ethers, PBDEs), can be used not only to trace changing industries but also to potentially provide chronological information based upon varying product formulation histories [4].

In general, multiple analyses of anthropogenic organic chemicals are required not only to 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 $^{207}/^{206}$Pb as well as radioactive isotopes such as $^{137}$Cs [11–14]. In Britain, vegetation archives that mainly record atmospheric Pb pollution show that $^{207}/^{206}$Pb values remained at about 0.85 through the nineteenth century and increased from 1920 owing to the use of leaded petrol and overseas industrial lead [15,16]. Maximal $^{207}/^{206}$Pb values of 0.89 are observed in the 1980s and then declined once leaded petrol was banned. These archives allow the construction of $^{207}/^{206}$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 (PAHs, PCBs, TPHs) and lead concentrations as well as $^{207}/^{206}$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 urbanization of the Clyde estuary.

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2. Material and methods

(a) Sampling and sample preparation

Seven sediment cores were collected in duplicate (A and B) in June 2004 and April 2006 (figure 1). Sampling sites in the estuary were accessed by a Griffon 2000TD hovercraft in 2004 and on foot in 2006 using predetermined Global Positioning System (GPS) coordinates to accurately locate each position. Clear polycarbonate tubes were manually driven into the exposed sediment and extracted to recover the core material. The British Geological Survey (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), 55/-05/702 (station 6) and 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. [14]. Sub-samples for lead analysis were similarly freeze-dried and ground to a fine powder in agate to minimize contamination.

(b) 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 limit of quantification (LOQ) reported for a typical 300mg sample was 0.18 per cent. Non-volatile hydrocarbons (TPHs) were determined as reported in Vane et al. [14]. Briefly, sediments were extracted with dichloromethane/acetone (1:1 v/v) mixture using an accelerated solvent extraction (ASE 200 Dionex) system. Saturated and aromatic hydrocarbons were determined by using an Iatroscan Mk6s instrument fitted with a flame ionization detector.

(c) Polychlorinated biphenyls

The method used to extract and determine PCB congeners was based on that described in Vane et al. [3]. In summary, sediments were extracted with hexane/acetone (1:1 v/v) in an ASE 200 (Dionex) and washed with concentrated
H$_2$SO$_4$. 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 dimethysulphoxide (2 × 12 ml) and de-ionized water (25 ml) prior to extraction with $n$-hexane. The $n$-hexane extracts volume was reduced to 5 ml, passed through anhydrous sodium sulphate (1 g) 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.

(d) Polycyclic aromatic hydrocarbons

Sediments (5 g) were extracted with 25 ml of a 1 : 1 v/v mix of acetonitrile and tetrahydrofuran in an ultrasonic bath (Camlab, 300W) for 45 min 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 diameter, nylon 66). Filtered sample extracts were injected into the high-performance liquid chromatography (HPLC) system (Waters 600E) via a 5 µl sample loop (Rheodyne). Separation of 17 PAHs was achieved within 40 min 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, fluorene; Phen, phenanthrene; Anth, anthracene; Fanth, fluoranthene; Pyr, pyrene; BaA, benz[a]anthracene; Chrys, chrysene; BbF, benzo[b]fluoranthene; BkF, benzo[k]fluoranthene; BaP, benz[a]pyrene; DBA, dibenz[a,h]anthracene; BghiP, benzo[g,h,i]perylene; IP, indeno[1,2,3-c,d]pyrene.

(e) Total lead concentrations and lead isotope ratio determinations

For each sample, 0.25 g of powdered sediment was dissolved by an HF/HClO$_4$/HNO$_3$ mixed concentrated acid attack in Savillex PFA vials. Once taken to dryness, the sample material was redissolved in 2 ml of 1 M HBr. The Pb was separated using an anion exchange chromatography column (Dowex AG1-X8 resin) pre-cleaned and conditioned with 1 M HBr. The separated lead was dried to remove the acid and the test portion redissolved in 1 per cent HNO$_3$. On the day of analysis, samples were diluted using 1 per cent HNO$_3$ and spiked with thallium. Pb and isotope ratio determinations were made using a quadrupole inductively coupled plasma–mass spectrometry (ICP-MS) instrument (Thermo PQ ExCell) fitted with either a conventional glass concentric nebulizer or a Cetac Aridus 2 desolvating nebulizer system. The 2 s.d. precision for the BCR-2 reference material, which has a total lead concentration of 11 mg kg$^{-1}$, was $^{207/206}$Pb = 0.0012, $^{208/206}$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 US 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 offline using Microsoft Excel spreadsheets. The processing consisted of: (i) removal of background including $^{204}$Hg$^+$ interference on $^{204}$Pb$^+$ in proportion to $^{202}$Hg$^+$ response, (ii) calculation of isotope ratios, (iii) determination of mass bias correction factor.

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from defined isotope ratios of thallium [17] or SRM981 [18], (iv) application of mass bias factors derived from SRM981 using external standard–sample–standard bracketing, and (v) optional further internal mass bias correction using 205/203Tl 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

(a) Lead concentrations

Total lead and lead isotope ratio determinations were made on depth increments from seven cores (station numbers: 1B, 2A, 4A, 4B, 5A, 6A, 7A) with two cores (4A and 4B) being duplicates but with 4B having a greater resolution of depth increments (figure 2).

The cores varied significantly in concentration ranges, with station 7A being the least contaminated (6–24 mg kg\(^{-1}\)) and station 1B being the most contaminated (26–631 mg kg\(^{-1}\)). The range of concentration values for the duplicate cores at station 4 (360–35 and 377–23 mg kg\(^{-1}\)) 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 owing to the non-normal data distribution.

If the median concentration Pb (63 mg kg\(^{-1}\)) for all the cores is compared against mean data for other UK river estuaries, as summarized in Spencer [19], 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 that 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 (figure 2), the cores split into two groups: (i) cores 2A, 5A, 6A and 7A that appear to have baseline concentrations in the deeper sections, with a discrete rise between 28 and 40 cm down and then peak in concentration between 18 and 28 cm, and (ii) cores 1B and 4B for which even the basal measurements at 90–100 cm may not be background and peak in concentration between 39 and 74 cm beneath the surface. These results suggest either the second group has a much higher sedimentation rate or the first group was subject to sediment erosion events or the Pb in the second group was more mobile and moved down-core.

(b) Lead isotope ratio determinations

A number of lead isotope ratios were determined: \(^{206}/^{204}\)Pb, \(^{207}/^{204}\)Pb, \(^{208}/^{204}\)Pb and \(^{207}/^{206}\)Pb, \(^{208}/^{206}\)Pb. The ratios to \(^{204}\)Pb were not found to be useful owing to the poorer precision in measuring this isotope by quadrupole ICP-MS. However, significant variation was found in the \(^{207}/^{206}\)Pb and \(^{208}/^{206}\)Pb ratios, with ranges 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 \(^{207}/^{206}\)Pb and \(^{208}/^{206}\)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 $^{207}/^{206}$Pb and $^{208}/^{206}$Pb ratios and two or more sources with lower but different $^{207}/^{206}$Pb and $^{208}/^{206}$Pb ratios. For comparison, potential mixing end-members have been plotted, and these include galena (PbS) ores from northern England and Scotland [20–22] and aerosols from the Isle of Man–Liverpool [23] and London [24], believed themselves to represent a mixture of petrol and industrial lead in airborne particles [16]. The anomalously high $^{207}/^{206}$Pb ratio of UK petrol lead compared with UK ore/coal lead was the result of it being

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2.15
2.14
2.13
2.12
2.11
2.10
2.09
208/206Pb
Southern Uplands
Midland Valley
Pennines
aerosol—London
station 1
station 2
station 4A
station 4B
station 5
station 6
station 7
2.08
2.07
2.06
0.83 0.84 0.85 0.86 0.87
207/206Pb
0.88 0.89 0.90 0.91

Figure 3. Pb isotope ratio correlation diagram between $^{207}/^{206}$Pb and $^{208}/^{206}$Pb for Clyde sediment cores and potential end-member sources including Scottish coal [25], Clyde area tree bark as atmospheric lead proxy [26], London aerosol [24], Liverpool and Isle of Man aerosol [23], and ore lead from the Pennines [21], Southern Uplands [22] and Midland Valley [22].

primarily derived from Broken Hill in Australia and other non-UK sources [27,28], recording a mean value of the $^{207}/^{206}$Pb ratio of 0.9294 ($\pm$0.0095; 1 s.d.; $n = 33$) 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 thorogenic ($^{208}$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 [29], 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 $^{207}/^{206}$Pb isotope ratio is considered with respect to Pb concentration (figure 4), a complex but explainable picture emerges. Four of the cores (2A, 5A, 6A and 7A) have their lowest concentrations when $^{207}/^{206}$Pb is less than 0.850, which may be taken as a pre-petrol lead industrial signature [16,30], and it is assumed that these are representative of the geogenic background lead from the Clyde catchment. The five cores closest 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 [27] and the early industrial aerosol signature.

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of 0.850. This early industrial signal resulted from both lead smelting and coal burning; Farmer et al. [25] have estimated the contribution of lead from coal to depositional flux as being 15 per cent in 1830, 36 per cent in 1887 and 59 per cent between 1913 and 1930. For these more contaminated cores, their maximum $^{207}/^{206}$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 [27] and are associated with an intermediate to high concentration 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 $^{207}/^{206}$Pb ratios, suggesting that 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 $^{207}/^{206}$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.

(c) 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 [30,31], lake sediment cores [32] and vegetation, such as tree bark [26], moss [16] and grass [15]. 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 $^{210}\text{Pb}$; as a radiometric technique, it should give an absolute age but, owing to the necessity of modelling the rate of $^{210}\text{Pb}$ 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.* [16]. Key dating observations on these data include a static trend in the nineteenth century through until approximately 1915 in the $^{207}/^{206}\text{Pb}$ isotope ratio (0.853), when the ratio starts to increase dramatically 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 and 1986 and its phasing out in 2000. This dataset is generally consistent with that of Bacon *et al.* [15] 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 and 1985 at 0.911. Bacon *et al.* [15] noted that the initial rise in ratio was well in advance of the introduction of tetraethyl lead in petrol, and an additional anomalously high ratio between 1945 and 1950 suggests short- as well as long-term changes in the use of overseas lead in industry. The data from Farmer *et al.* [16] and the other sources have been synthesized in figure 5 to give a lead isotope chronology. To this, data from core 4B have been overlain; this core was chosen for having the best detail over a long time period. The current data were linearly scaled to give the best visual fit to the data from Farmer *et al.* [16]. 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 that the deposition rate must have been relatively constant; therefore, in the absence of $^{137}\text{Cs}$ or $^{210}\text{Pb}$ data and accepting the possibility that due to contributions from rivers, streams or run-off 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 40 cm; 1915 at a depth of 75 cm, 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 5–10 cm; 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 (greater than 40 cm); 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 50 cm.
Core 4B. The time period 1980–1985 equates to a depth of 5–10 cm; 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 $^{207}/^{206}$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 that occurs at a younger depth of 20 cm; an early industrial plateau is observed between 50 and 80 cm while 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 40 cm.

Core 6A. The time period 1980–1985 equates to a depth of 18 cm, which matches the period of maximum lead concentration; 1915 at a depth of 43 cm, and the deeper parts of the core reach and plateau pre-IR (greater than 50 cm); the lack of an early industrial plateau, the maximum lead concentration being associated with the peak isotope ratio (1980–1985), implies that 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 45 cm.

Core 7A. The time period 1980–1985 equates to a depth of 10–20 cm 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

Figure 5. A composite historical $^{207}/^{206}$Pb isotope profile of Scottish moss [16] with additional time-resolved data for Scottish peat [30,31,33] and lake sediment [32] compared with an example core log from the Clyde estuary. Filled circles, core 4B; filled squares, Scottish moss.
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and 80 cm while below 80 is pre-IR. The very low maximum lead concentration associated with the peak isotope ratio (1980–1985) implies that this site was little impacted by industrial lead but was probably influenced by petrol lead, as might be expected for being further away from Glasgow centre. The background lead concentration is reached at a depth of 45 cm.

In summary, the cores provide a range of lead concentrations and $^{207}/^{206}$Pb isotope ratios, reflecting a contaminant chronology back to the pre-IR period. In most cases, the last century is covered by the top 40 cm of the cores. However, core 1B from the innermost estuary site has the most expanded recent section, with the last century being represented by 70 cm and the period from 1980 to 1985 onwards being 40 cm. 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 [34] and the Pb concentration in Clyde water [35] for the period 1980 to present showed remarkably good correlation, strongly supporting the use of the moss data of Farmer et al. [16], at least for the most recent period.

(d) Variation in non-volatile hydrocarbons

The TPH profiles 1A, 2A, 3A, 4A and 6A clearly show the onset, rise and decrease in non-volatile hydrocarbon pollution in the Clyde (figure 6). Comparison of the TPH with PAH profiles revealed that peak TPH concentrations occurred at shallower depths than the total PAH, reflecting the earlier use of coal and the later use of oil as an energy/fuel source. The decrease in TPH concentrations in the uppermost 10 cm of stations 2A, 3A, 4A, 5A and 6A is commensurate with both a decrease in industrial activities and increased environmental legislation and awareness from the 1980s to present (figure 6). Using the $^{207}/^{206}$Pb chronology to define an approximate date of 1915, it is clear that the onset 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 (figure 6). In contrast, station 1A recovered from the innermost portion of the study area showed the highest TPH values between 40 and 60 cm below surface (4386–2838 mg kg$^{-1}$) (figures 1 and 6). Unpolluted estuarine and coastal sediments have reported TPH concentrations of 2–10 mg kg$^{-1}$, and this value may increase up to about 100 mg kg$^{-1}$ in organic-rich sediments that contain high concentrations of biogenically sourced $n$-alkanes derived in part from plant waxes [36–38]. Based on these criteria, it appears that the entire length of core 1A is contaminated with petroleum hydrocarbons and that the 10 cm to approximately 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.

(e) Polychlorinated biphenyl contamination

Inspection of the total PCB concentration profiles showed that contamination was mainly restricted to the top (0 to approx. 20 cm) of each core (figure 6). Total PCB content ranged from less than 4.3 to 5797 μg kg$^{-1}$; these values are
considerably higher than those observed in surface sediments from the inner Clyde reported at 5.2–129.9 \( \mu \text{g kg}^{-1} \), the Mersey estuary 36–1409 \( \mu \text{g kg}^{-1} \) and pristine coastal sites in the USA \([3,37]\). This near-surface increase in PCB contamination was widespread throughout the study area, but was observed at a greater depth at station 1A (figure 6). Maximum PCB concentrations at station 1A of 1217 \( \mu \text{g kg}^{-1} \) were observed in the middle portion of the sediment core (39–58 cm), and these values thereafter decreased to the LOQ (less than 4.3 mg kg\(^{-1}\)) at the base of the core. The difference in PCB profiles at 2A, 3A, 4A, 5A and 6A as compared with 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 approximately 1830 on the basis of \( ^{207/206} \text{Pb} \) 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 group profiles for 1A and 4A varied with increasing depth from surface (figure 7). Site 1A was mainly composed of hexa- and pentachlorinated 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 used Aroclor 1254 (54% Cl), which is virtually devoid of trichlorinated biphenyl, whereas carbonless paper production used Aroclor 1242 (42% Cl), which is dominated by trichlorinated homologues [39]. Alternatively, dechlorination of highly chlorinated homologues to less chlorinated homologues has been observed in aerobic and anaerobic sediments [40]. 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 (figure 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-
late 1960s, then gradually declined after the sales ban in 1977 [11,41–43]. In the current study, elevated total PCB concentrations were observed at stations 2A, 3A, 4A and 6A, and 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 LOQ is unlikely to pre-date the first worldwide commercial production in 1929.

(f) PAH concentrations and isomer ratios

Total PAH concentration profiles showed a much longer history of industrial activity than either TPH or PCB compounds (figure 6). All of the cores gave significant amounts of PAH contamination at depths greater than the 1915 level based on the $^{207}/^{206}$Pb isotope marker, with the exception of station 6A. This finding was not unexpected given that coal, a common source of PAHs, was mined in Lanarkshire, burnt by the local industry and transported from

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the Clyde from the 1800s. The total PAH profile at station 1A revealed moderate values ranging from 216 $\mu$g kg$^{-1}$ at a depth of 27 cm to a maximum of 16163 $\mu$g kg$^{-1}$ at 57 cm before decreasing to 5869 $\mu$g kg$^{-1}$ at the base of the core (figure 6a). Other stations also showed elevated total PAH concentrations; for example, site 3A gave values up to 15745 $\mu$g kg$^{-1}$ at 8 cm beneath the surface. Recent studies of surface sediments from the inner Clyde estuary reported total PAH concentrations in the ranges 630–23711 $\mu$g kg$^{-1}$ [3] and 450–28321 $\mu$g kg$^{-1}$ [44], 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 [8]. The resulting isomeric cross-plotting, adopted from that of Yunker et al. [8], is presented in figure 8 and employed four sets of isomeric ratios:

- Anth : Phen = [Anth]/([Anth] + [Phen]);
- Fanth : Pyr = [Fanth]/([Fanth] + [Pyr]);
- BaA : Chrys = [BaA]/([BaA] + [Chrys]); and
- IP : BghiP = [IP]/([IP] + [BghiP]).

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 PAHs and grass/wood/coal PAHs 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 (figure 9a,b). 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, TPHs, PAHs and PCBs, all of which rose to maxima at greater depths (figure 6a,b). From total concentration and isotopic ratios ($^{207}/^{206}$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 1986–2004) was not evident in any of the other cores. From 40 cm to the surface, the isomeric ratios (figure 9) appeared to decrease as the total PAH concentration declined from 4189 to 348 $\mu$g kg$^{-1}$. This ratio decrease...
Figure 8. PAH isomeric cross-plot of sediments from the Clyde estuary for the determination of PAH origin. Abbreviations: Anth, anthracene; Phen, phenanthrene; BaA, benz[a]anthracene; Chrys, chrysene; IP, indeno[1,2,3-c,d]pyrene; BghiP, benzo[g,h,i]perylene. Filled diamonds, 1A; filled triangles, 2A; open squares, 3A; cross symbols, 4A; filled squares, 5A; open diamonds, 6A; open triangles, 7A.
PAH isomer ratios criteria [8]

- Anth/(Anth+Phen)  
  >0.1  combustion  
  <0.1  petroleum  

- Fanth/(Fanth+Pyr)  
  >0.5  grass/wood/coal combustion  
  0.5–0.4  petroleum combustion  
  <0.4  petroleum  

- BaA/(BaA+Chrys)  
  >0.35  combustion  
  0.35–0.2  mixed sources  
  <0.2  petroleum  

- IP/(IP+BghiP)  
  >0.5  grass/wood/coal combustion  
  0.5–0.2  petroleum combustion  
  <0.2  petroleum  

Figure 9. Variation in PAH isomeric ratios with depth for Clyde cores. Filled diamonds, Fanth/(Fanth+Pyr); open squares, Anth/(Anth+Phen); open triangles, BaA/(BaA+Chrys); filled triangles, IP/(IP+BghiP).
implied an increasing petroleum contribution over the 18-year period, and this correlated with an increase in the [BghiP]/[BaP] ratio (figure 10)—a parameter taken to be characteristic of road traffic sources when its value exceeds 3.14 [45]. 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 less than 3, ranging between 0.6 and 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 the sediment at a depth of 57 cm. This depth also coincided with maximum total PAH concentration. There was a steady decline in the total PAH concentration to a depth of 87 cm. Isotopic ratios ($^{207/206}$Pb) indicated that the 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 ship-building activity.

Between ca 1950 and ca 1986, i.e. between core depths of 40 and 57 cm, respectively, total PAH concentration fell from a maximum 16163 to 4189 μg kg$^{-1}$, coinciding with the decline of the ship-building industry (figure 6). Some
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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 (figure 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 ($^{207}/^{206}$Pb) of lead for this core, an approximate date of 1915 may be attributed to the sediment at a depth of 40 cm. Below 40 cm, the total PAH concentration remained fairly constant and within the range 954–2435 μg kg$^{-1}$ (figure 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 (figure 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, 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 the 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 to the sediment at a depth of 8 cm. At this depth and above, the total PAH concentration diminished, achieving its lowest value (592 μg kg$^{-1}$) 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 [46]. 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 while the total PAH concentration began to wane (figure 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. [8] criteria as characteristic of petroleum and its combustion (figure 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 (figure 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 to 40 cm (ranging between 233 and 356 μg kg$^{-1}$) as did three of the isomeric ratios (figure 9a), Anth : Phen 0.07–0.15 (petroleum/combustion border), BaA : Chrys 0.15–0.20 (petroleum)
Figure 11. Intra-core variations in PAH distribution patterns. (a) Depth 17 cm is indicative of mainly combustion sources, whereas (b) the distribution at 52.5 cm has high biogenically generated PAHs such as naphthalene (Naph), phenanthrene (Phen) and perylene (Pery).

and IP:BghiP 0.11–0.22 (petroleum/petroleum combustion). The Fanth:Pyr ratio showed an overall downward trend and ranged from 0.15 to 0.36 (petroleum/petroleum combustion). These low total concentrations in tandem with a strong non-pyrolytic component probably signified a background PAH composition comprising, in the main, aeolian deposition, i.e. from anthropogenic and natural combustion sources [47], together with a substantial biogenic PAH input [48]. 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 PAH concentration 371 \( \mu g \text{kg}^{-1} \)) with that at 17 cm (total PAH concentration 11,297 \( \mu g \text{kg}^{-1} \)) 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 [48], are much greater in the sediment at 52.5 cm compared with the 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 approx. 0.5 but at 52.5 cm [Fanth] < [Pyr] yielding a Fanth:Pyr ratio approx. 0.15 and similarly for BaA:Chry 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 (figure 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 [49], in the PAH distribution for the sediment at 17 cm (figure 11).

Core 4A. Data on total concentration and isotopic ratios ($^{207}$/206Pb) of lead for this core made it possible to ascribe dates to the 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 (figure 6a). Thus, from the early Industrial Revolution, it can be seen that there was a steady rise in total PAH concentrations from 1241 $\mu$g kg$^{-1}$ at 96 cm depth to a maximum of 14932 $\mu$g kg$^{-1}$ at 32 cm, i.e. at ca 1920 (figure 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 (figure 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 (figure 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 PAHs. 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 the 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 (figure 6b). Elevated levels of PAHs 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 (figure 9b), except for the IP:BghiP ratio that 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 counterintuitively 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 (figure 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 $^{207}/^{206}$Pb suggested a date of ca 1986 for the 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 the 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 and 205 mg kg$^{-1}$ (figure 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 (figure 11), and all were characterized by high relative abundances of naphthalene and phenanthrene, suggesting an appreciable natural biogenic PAH contribution [48]. Dating was difficult, with data from lead concentrations and isotope ratios $^{207}/^{206}$Pb not yielding any great precision. Thus, the sediment with a date of ca 1986 could only be defined as occurring somewhere between 15 and 28 cm depth. A date of ca 1915 could tentatively be assigned to the sediment at about 65 cm depth. The isomeric ratios remained essentially static throughout the core for BaA:Chrys, Fanth:Pyr and IP:BghiP—except that the latter two ratios showed a sharp and inexplicable rise at 5 cm (figure 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 less than 0.4 (petroleum zone), with only two points greater than 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 and 0.38. Values for the IP:BghiP ratio were all between 0.2 and 0.5, i.e. petroleum combustion. On balance, the data indicated a predominant petroleum/petroleum combustion PAH input to which the contribution from road traffic was insignificant, i.e. [BghiP]/[BaP] ratio was less than 3 throughout the core. The probability was, therefore, that the major PAH input arose from shipping emissions and petroleum-using 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 (PAHs, TPHs 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 and 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, TPHs, PCBs and PAHs to investigate the changing industrial and urban environment within the Clyde estuary over the past approximately 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.

— 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).

— Organic pollutants were observed at concentrations that were typical of a highly industrialized estuary and are considered environmentally significant, i.e. maximum TPHs at 4386 mg kg$^{-1}$, maximum total PAHs at 16 163 μg kg$^{-1}$ and maximum total PCBs at 1217 μg kg$^{-1}$. In contrast, pre-industrial sediments were identified on the basis of low total PAH concentrations together with high relative abundances of the biogenic PAHs naphthalene and phenanthrene.

— 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 [3]. 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.

— 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 the 1950s, 1965–1977 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.

— 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 [16]. Key changes in ratio are known to have occurred at specific times including: ca 1915, the introduction of non-UK Broken Hill-type lead for petrol and subsequent major industrial products; 1980–1985, owing to a reduction in petrol lead; and ca 1750, the beginning of the Industrial Revolution and the major 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.

— 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 PAHs. Furthermore, commercially produced industrial chemicals such as PCBs may be used to mark other Anthropocene sub-divisions—for instance the ‘electrical age’ 1950s–1980s. However, it should be borne in mind that different regions of the world have experienced industrialization and the resulting environmental contamination at different times. Thus, any attempt to use 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 urbanization.

John Farmer and Andrew Hursthouse are thanked for thorough and constructive reviews of the manuscript. The authors are indebted to Griffon Hovercraft Ltd as well as all BGS staff involved in sample collection. This paper is a contribution to the British Geological Survey’s cross-cutting Clyde-Urban Super-Project (CUSP) and is published by permission of the Executive Director, British Geological Survey.

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