

# The Geosciences in Europe's Urban Sustainability: Lessons from Glasgow and Beyond (CUSP)

## Persistent organic pollutants (PAH, PCB, TPH) in freshwater, urban tributary and estuarine surface sediments of the River Clyde, Scotland, UK

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**ABSTRACT:** Surface sediments from a 160-km stretch of the River Clyde, Scotland, were analysed for persistent organic pollutants to investigate distribution, source and environmental effect. Glasgow's urban tributaries polyaromatic hydrocarbons (PAH) ranged from 2.3 to 4226 mg kg<sup>-1</sup>, total petroleum hydrocarbons (TPH) 72 to 37879 mg kg<sup>-1</sup> and polychlorinated biphenyls (PCB) 3 to 809 µg kg<sup>-1</sup>, which were more polluted than the upper River Clyde PAH that ranged from 0.1 to 42 mg kg<sup>-1</sup>, TPH 3 to 260 mg kg<sup>-1</sup> and PCB 2 to 147 µg kg<sup>-1</sup>. Intermediate values of the inner Clyde estuary PAH ranging from 0.6 to 30 mg kg<sup>-1</sup>, and PCB ranging from 5 to 130 µg kg<sup>-1</sup>, were attributed to point sources and sediment transfer from the urban tributaries. Comparison with sediment quality criteria suggested possible adverse effects on aquatic biota. PAH isomeric ratios confirmed a pyrolytic source throughout the Clyde and benzo[*a*]pyrene/benzo[*g,h,i*]perylene ratios >0.6 confirmed that upper, urban and estuarine domains all to a lesser or greater extent accumulated PAH from traffic emissions. The degree of chlorination determined from PCB homologues differed in each of the three domains, suggesting variable source or that the process aerobic/anaerobic degradation varied in each of the three domains. The anthropogenic impact of the city of Glasgow can be quantified in that the urban tributary sediment mean values were 60 (PAH), 33 (TPH) and 11 (PCB) times higher than the rural upper Clyde counterpart.

**KEY WORDS:** Anthropocene, benzo[*a*]pyrene, contamination, Glasgow, polyaromatic hydrocarbon, polychlorinated biphenyl, total petroleum hydrocarbon.

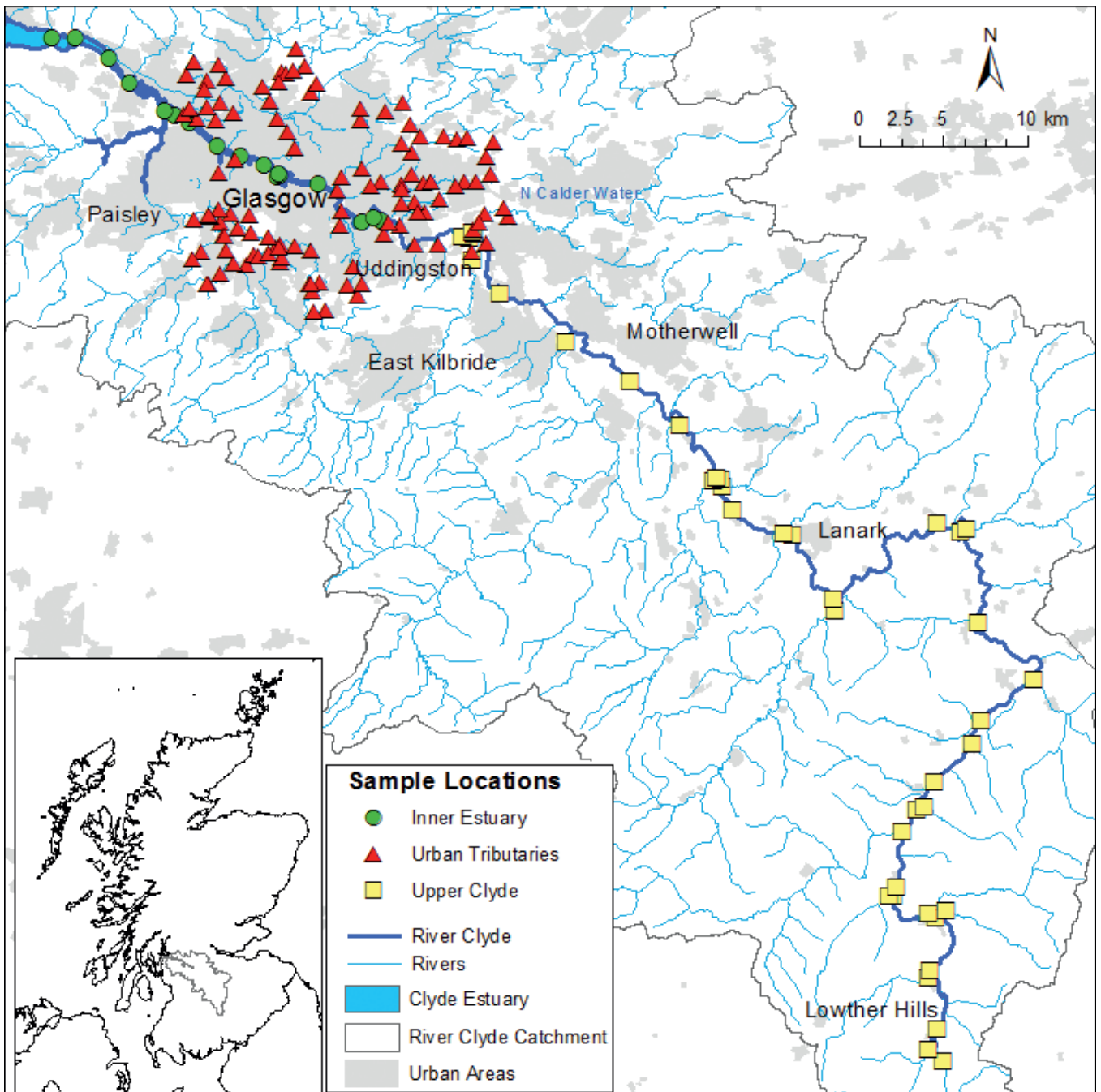
The River Clyde catchment drains an area of approximately 3100 km<sup>2</sup> stretching from the Lowther Hills in the Scottish Borders to the Clyde estuary on the west coast of Scotland (Fig. 1). The catchment is predominantly rural, comprising moorland hill terrain in its upper headwaters and agricultural land in the middle reaches. In contrast, the lower Clyde is urbanised with one of the UK's foremost historical industrial centres, the city of Glasgow situated close to the tidal limit. Glasgow grew rapidly from a small ecclesiastical centre in the 1600s to become a major industrial powerhouse by the early 20th Century. Much of this development resulted from a combination of excellent transport/shipping links centred on the River Clyde and coal and iron mineral resources located in close proximity, which fuelled engineering and metal-processing activities during the Industrial Revolution. During the latter half of the 20th Century, heavy industry and coal-fired power generation declined (Browne *et al.* 1986). Over more recent decades, care has been taken to minimise chemical and metal pollution from industries along the Clyde corridor. However, several studies focussed on the Clyde estuary

have observed persistent organic pollutants (POPs) in sediments and ascribed these to sources such as, but not limited to, landfill sites, legal sewage discharge and shipping and road run-off (Vane *et al.* 2010). Additionally, persistent organic pollution from past industrial activity that is retained in surface and near-surface sediments from former industries such as power stations and oil refineries, which were essential for the development of Glasgow and were located in close proximity to the River Clyde, can still be a long-term environmental threat due, in part, to sediment remobilisation, reworking and chemical recalcitrance (Hursthouse *et al.* 1994; Edgar *et al.* 2006; Vane *et al.* 2007a, 2010, 2011).

POPs such as polyaromatic hydrocarbons (PAH), total petroleum hydrocarbons (TPH) and polychlorinated biphenyls (PCB) are associated with a variety of industrial activities such as coal burning, gas works, shipping and power generation as well as incineration, demolition and made-ground including road-surface dusts (Yang *et al.* 1991; Vane *et al.* 2014).

The main PAH in soils and near-surface sediments may be ascribed to either petrogenic sources (from petroleum source)





**Figure 1** Location of the River Clyde sediment samples from the upper Clyde (yellow squares), urban tributaries (red triangles) and inner estuary (green circles). Geoscience data, BGS © NERC. Contains Ordnance Survey data © Crown Copyright and database rights 2016.

or from pyrolytic origin (from incomplete combustion of carbon-containing materials as wood, coal and petroleum), or a combination of the two. Previous studies have measured PAH concentration, predominately in Clyde estuary sediments, and concluded that they are useful indicators of current and former industrial activity in this system (Hursthouse *et al.* 1994; Rogers 2002; Vane *et al.* 2007a, 2011). Vane *et al.* (2007a) found that the PAH concentrations of 11 samples from the inner Clyde estuary were comparable to other European estuaries whose environments are highly industrialised. Based on isomeric ratios of the different PAH, they estimated that the majority of the PAH had a pyrolytic source. This was in agreement with results reported by other studies from the Clyde estuary (Rogers 2002) and two Clyde tributaries (Wilson *et al.* 2005). By contrast, analysis of sediment cores from sites

in the outer estuary revealed that most of the PAH had a petroleum and petroleum combustion origin (Vane *et al.* 2011). This was explained by the closer proximity of inner estuary samples to former domestic and industrial coal-burning sources, while the samples located further out in the estuary were more influenced by unburnt fuel emissions from shipping and traffic together with petroleum product spills and historic discharges from local industries (Vane *et al.* 2007a, 2011).

TPH are a ubiquitous compound class observed in low concentrations in pristine riverine/estuarine sediments and at much higher concentrations in urbanised areas as a consequence of industrial discharges, spills and shipping activities (Guo *et al.* 2011; Vane *et al.* 2011). When analysed together, TPH and PAH concentrations facilitate the identification of changes in the use of different fuel sources (e.g., coal versus

oil). Analysis of sediment cores from the River Clyde estuary revealed that the peak of TPH concentrations occurred at shallower depths than the total PAH, reflecting the earlier use of coal and later use of oil as a fuel source (Vane *et al.* 2011). Low TPH concentrations were measured during pre-industrial and in modern non-polluted sediments. The onset of environmentally significant concentrations of TPH did not occur until after ca.1915 and started to decrease from 1980s to present. This latest decrease in TPH concentrations is commensurate with both a decrease in industrial activities and an increase in environmental legislation, awareness and enforcement.

Other organic pollutants of anthropogenic origin commonly found in riverine/estuarine sediments are PCBs. They have been analysed in Clyde estuary sediments by a few studies that reported an association between the distribution of these compounds in the sediments and the presence of local industrial activities (Edgar *et al.* 1999, 2003; Vane *et al.* 2007a, 2011). Although all the sites analysed by these studies showed the presence of PCB, the total concentration of these compounds in most of the samples did not reach the threshold for probable effect concentrations (PEC;  $676 \mu\text{g kg}^{-1}$ ) defined by MacDonald *et al.* (2000). This suggested that the PCB contamination in the sediments was not likely to adversely affect sediment-dwelling organisms.

As stated above, previous studies focused mainly on the analyses of POPs from the Clyde estuary. The objective of this study is to gain a better understanding of the distribution, source and fate of POPs in the entire River Clyde system by examining sediment PAH, TPH and PCB concentrations along its length, including the upper reaches of the Clyde, the Glasgow urban area and the estuary. The results are used to evaluate the potential toxicological impacts of the POPs on the local environment.

## 1. Method

### 1.1. Sample collection and preparation

The data presented here are based upon two existing sediment datasets for (i) the Clyde inner estuary (Vane *et al.* 2007a) and (ii) urban tributaries draining into the River Clyde from the Glasgow area (Fordyce *et al.* 2004). In addition, a new dataset of sediment samples from the upper Clyde was collected for this study to provide information on POPs concentrations in the largely rural environment upstream of Glasgow. The upper Clyde and inner estuary samples are river sediment samples (160 km river-inner estuary transect), while the majority of the urban tributary dataset were collected from small streams (<3 m across). The sample collection methods for these three areas are described in the following sections.

**1.1.1. Inner estuary and urban tributary sediment samples.** Inner estuary surface sediment samples (0–20 cm) were collected between October and February 2003 at 17 sites in the Clyde inner estuary (Fig. 1) using either a stainless steel Van Veen or Day grab. After each deployment–collection cycle, the grab was cleaned with bottled tap water to avoid contamination from the previous site. Samples were wrapped in aluminium foil and sealed in polyethylene bags for transport to shore where they were immediately stored in a freezer (Jones *et al.* 2004; Vane *et al.* 2007a). Urban tributary sediment samples (Fig. 1) were collected every km of stream length on all tributaries draining into the River Clyde within the Glasgow City Council area in June 2003. A total of 116 sediment samples were retrieved from the active water channel using a stainless steel trowel. Samples were stored in pre-cleaned 500 mL glass jars fitted with screw caps lined with aluminium foil. They

were kept in cool boxes following collection and frozen on return to the field base (Fordyce *et al.* 2004).

**1.1.2. Upper Clyde sediment samples.** In October 2010, 40 sediment samples were collected from the upper reaches of the River Clyde, upstream of Glasgow to its headwaters (Fig. 1). The material was taken from the active water channel using a steel trowel, removing any bulky organic matter and large stones before collection into a Rilsan sampling bag. Collected sediments were kept in cool boxes (4 °C) and were frozen on return to the field base. Upon return to the laboratory, each sample was freeze-dried, disaggregated, passed through a brass sieve with an aperture of 2 mm and milled to approximately <40  $\mu\text{m}$ . This method was chosen as a statistically robust method for high precision and accuracy PAH quantification (Bearcock *et al.* 2011; Beriro *et al.* 2014).

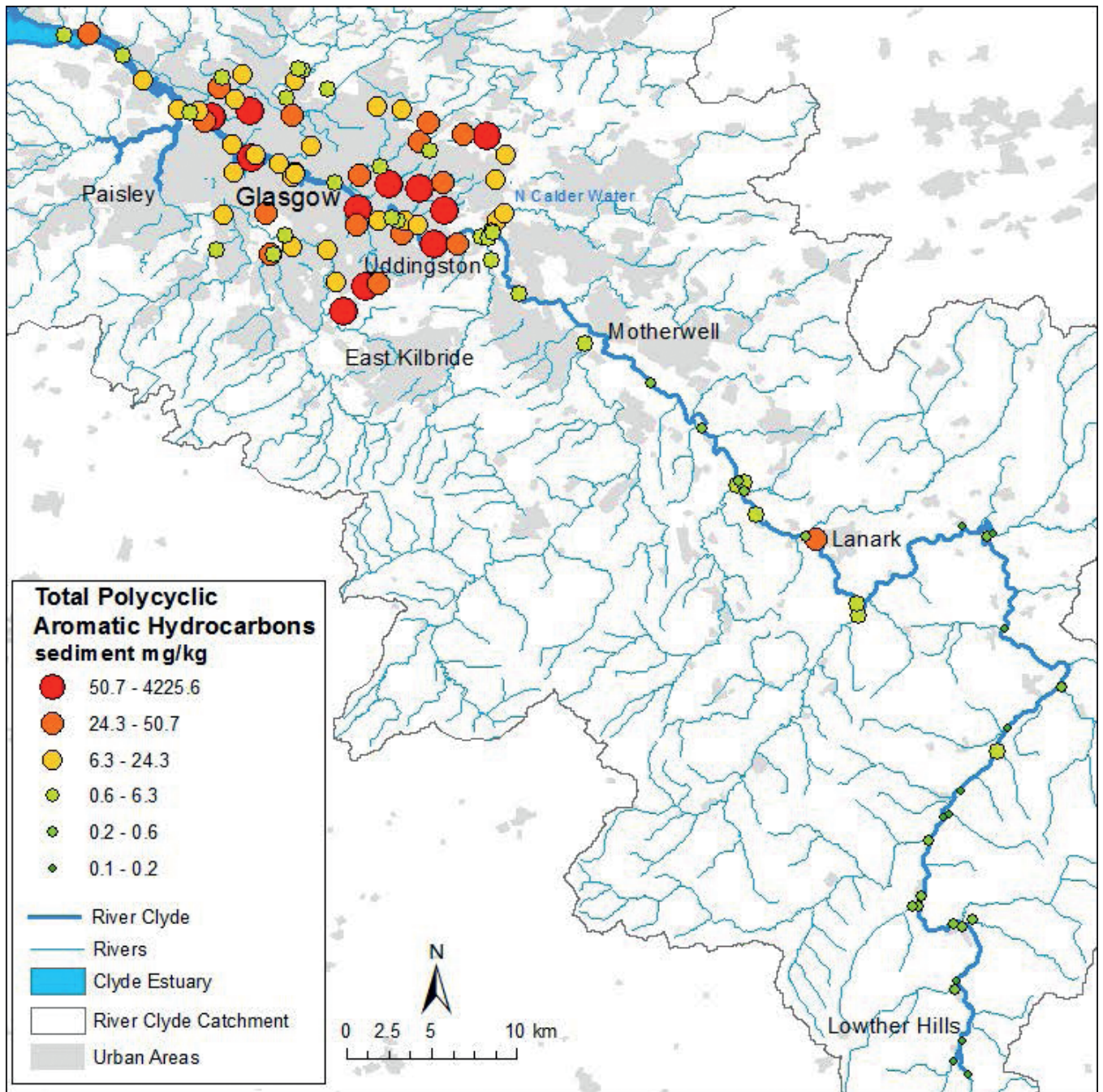
### 1.2. Sample analysis

All samples were analysed for total organic carbon (TOC;  $n = 173$ ) and a smaller subset comprising the urban tributary and upper Clyde sediments were analysed for TPH ( $n = 153$ ). Some samples of the inner estuary, urban estuary and upper Clyde were evaluated for PAH ( $n = 109$ ) and a smaller subset selected for PCB ( $n = 72$ ).

**1.2.1. Total organic carbon (TOC).** TOC content (% wt/wt) was measured using an identical method to that previously published (Vane *et al.* 2009). Briefly, TOC was measured on 300 mg of sediment using an Elemental VarioMax C, N analyser after acidification with hydrochloric acid (HCl). The limits of quantification were 0.18 % (wt/wt).

**1.2.2. Polyaromatic hydrocarbon (PAH) analysis.** PAH analysis was carried out on all the inner estuary and upper Clyde sediment samples. A subset of 52 urban tributary samples were selected for PAH analysis on the basis of higher TOC results and on the locations of likely sources of contamination (Fordyce *et al.* 2004). Samples were spiked with internal standards: naphthalene- $\text{d}_8$ , biphenyl- $\text{d}_{10}$ , phenanthrene- $\text{d}_{10}$ , pyrene- $\text{d}_{10}$ , benzo[*a*]anthracene- $\text{d}_{10}$ , benzo[*a*]pyrene- $\text{d}_{12}$  and benzo[*g,h,i*]perylene- $\text{d}_{12}$ . They were extracted using an accelerated solvent extraction (ASE) system with dichloromethane/acetone 1:1 v/v at 100 °C and 2000 psi and after being reduced in volume, the extract was transferred to a solid phase extraction (SPE) cartridge (Varian, Bond Elute TPH w.500 mg  $\text{Na}_2\text{SO}_4$ , 1 g sorbent, 3 mL reservoir volume). The first fraction was eluted with pentane. The second fraction, which contained the PAH, was eluted with hexane/iso-propanol (97:3 v/v), spiked with an extraction efficiency standard: methylanthracene- $\text{d}_{10}$  and chrysene- $\text{d}_{12}$  and reduced in volume.

Concentrations of PAH were measured using a Varian 3800 gas chromatograph (GC) coupled to a Varian 1200L triple quadrupole mass spectrometer (MS) operating in full scan mode (ionisation energy 70 eV, mass range 47–500 amu). The GC was fitted with an Agilent capillary column (DB-35 ms Ultra Inert, 30 m length, 0.25 mm internal diameter (i.d.), 0.25  $\mu\text{m}$  film thickness). The oven temperature program was 60 °C (isothermal for 1 min) to 320 °C (isothermal for 10 min) at 6 °C  $\text{min}^{-1}$ . 1  $\mu\text{L}$  was injected at 280 °C in splitless mode for 0.7 min, split 1:20 thereafter. Helium carrier gas was 1  $\text{mL min}^{-1}$ . The PAH limits of detection (calculated as five times the background peak height of a pure standard normalised to a typical 1 g of sample) ranged from 1.45 to 50.07  $\mu\text{g kg}^{-1}$ . Quality control was achieved by determining PAHs in the CRM, NRCHS-5 Harbour Sediment and in a candidate soil from an inter-laboratory proficiency study, Contest 58.3c (LGC, Bury, UK) every nine samples. A procedural blank was analysed every 17 samples to ensure batch-to-batch quality.



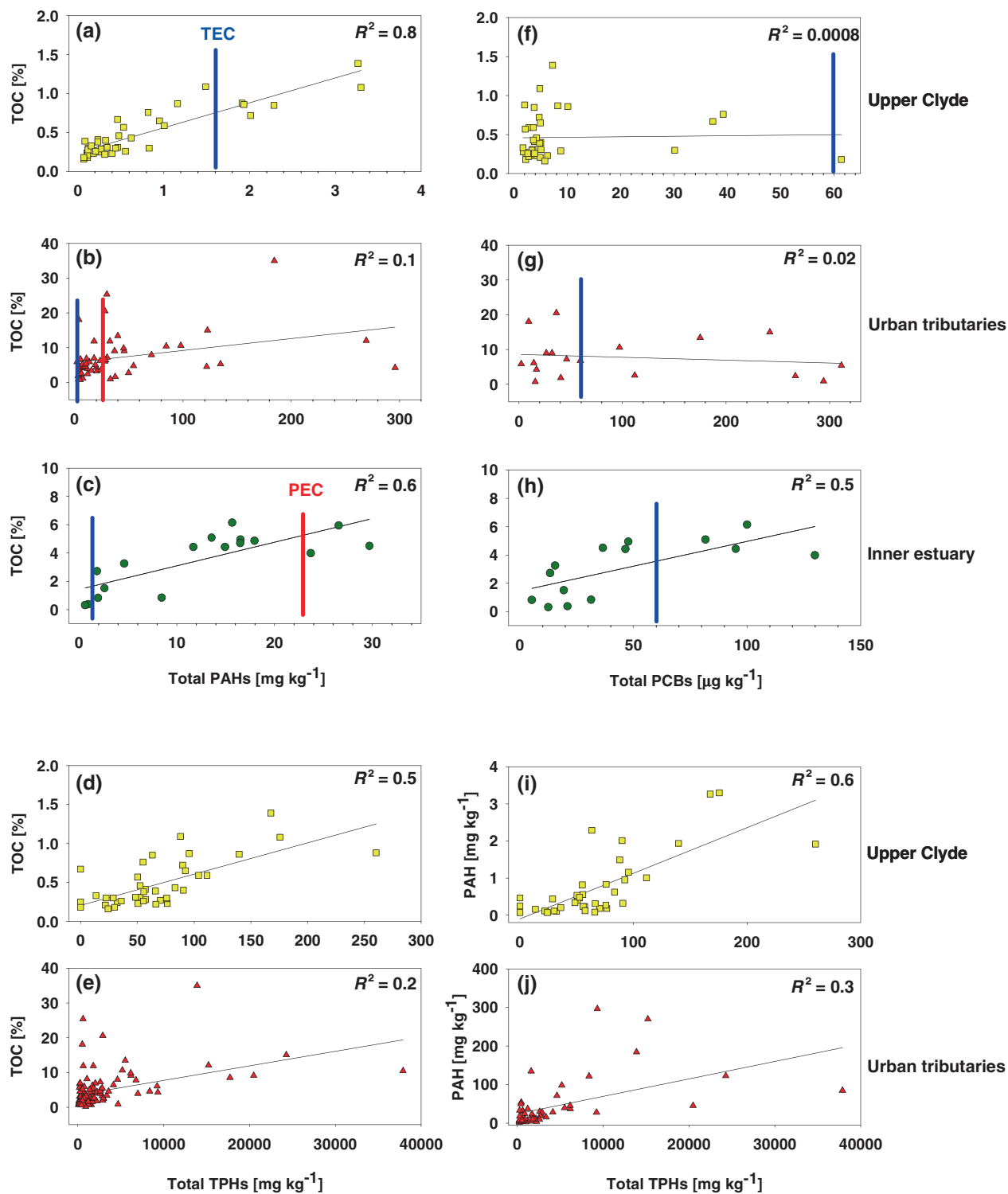
**Figure 2** Total PAH concentrations in sediments of the River Clyde, UK. Geoscience data, BGS © NERC. Contains Ordnance Survey data © Crown Copyright and database rights 2016.

**1.2.3. Total petroleum hydrocarbons (TPH) analysis.** Each sediment sample was extracted using the ASE 200, Dionex. The ASE conditions were: dichloromethane/acetone (1:1 v/v) at 100 °C and 2000 psi. Extracts were dried using a TurboVap at 30 °C and reconstituted in 1 mL of toluene. An aliquot was spotted on to silica rod (Chromarods-S III) and the rods developed for 21 min using *n*-hexane and 8 min with toluene. The concentration of saturated and aromatic hydrocarbons was determined using an Iatroscan Mk6 s instrument (Vane *et al.* 2008). This was calibrated for saturate hydrocarbons using pristine and aromatic hydrocarbons using triphenylene. The limit of quantification (LoQ) for total non-volatile hydrocarbons was 3 mg kg<sup>-1</sup>.

**1.2.4. Polychlorinated biphenyl (PCB) analysis.** Sediments were spiked with PCB 19, 34, 62, 119, 131, 147 and 173 and extracted with hexane/acetone 1:1 v/v followed by the addition of concentrated H<sub>2</sub>SO<sub>4</sub> (Vane *et al.* 2007b, 2011). The

hexane extract was reduced and cleaned using the same SPE method as for PAH and spiked with PCB 29 and 157 and reduced. Concentrations of PCB were measured using a Varian 1200L triple quadrupole mass spectrometer (GC/MS). The MS was operated in selected ion mode (*m/z* 71, 220, 256, 258, 292, 326, 328, 360, 362, 394, 396) with a scan time of 0.5 s. Congener profile distributions for tri to hepta-chlorinated biphenyls were determined using five separate individual relative response factors for each congener group. A standard consisting of 2 × 5 individual PCB based on first and last eluting congener was used to define the 'retention time window' for each group. The sum of these five groups is  $\sum^{\text{tri-hepta}} \text{PCB}$  and  $\sum^7 \text{PCB}$  comprised congeners 28, 52, 101, 118, 153, 138, 180. The individual congener limit of detection was 0.5 ng g<sup>-1</sup>.

**1.2.5. Data presentation.** Correlations between TOC and the organic pollutants were assessed using linear regression plots. Likely sources of POPs were determined on the basis of

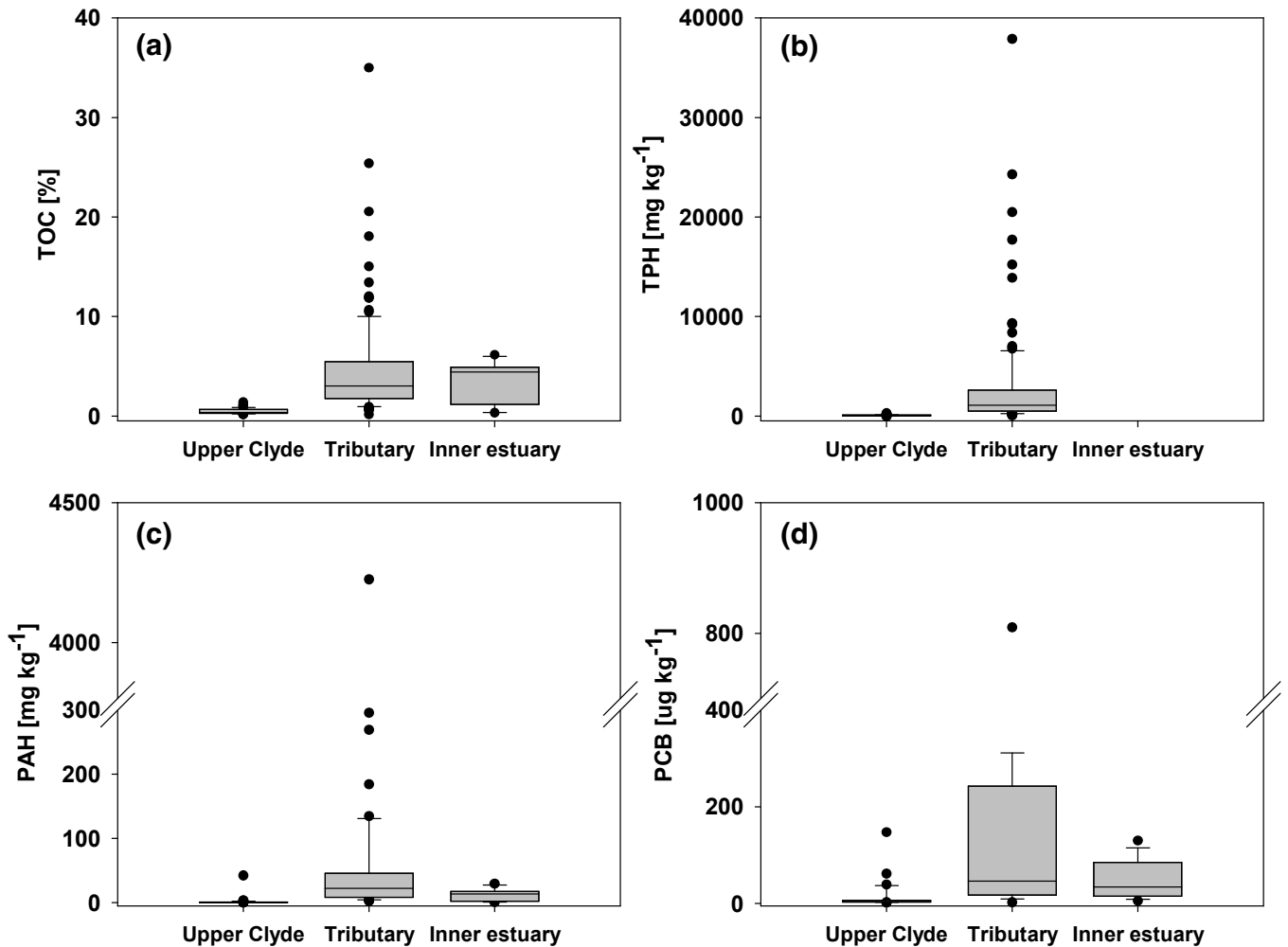


**Figure 3** Correlation between TOC, PAH, TPH and PCB concentrations in the upper Clyde (yellow squares), urban tributaries (red triangles) and inner estuary (green circles). Blue lines represent the ecological sediment-quality guideline threshold effect concentration. Red lines represent the probable effect concentration. (a) TOC versus PAH Upper Clyde; (b) TOC versus PAH Urban tributaries; (c) TOC versus PAH Inner estuary; (d) TOC versus TPH Upper Clyde; (e) TOC versus TPH Urban tributaries; (f) TOC versus PCB Upper Clyde; (g) TOC versus PCB Urban tributaries; (h) TOC versus PCB Inner estuary; (i) PAH versus TPH Upper Clyde; (j) PAH versus TPH Urban tributaries. Abbreviations: TEC = threshold effect concentration; PEC = probable effect concentration; TOC = total organic carbon; TPH = total petroleum hydrocarbons; PAH = polyaromatic hydrocarbons; PCB = polychlorinated biphenyls.

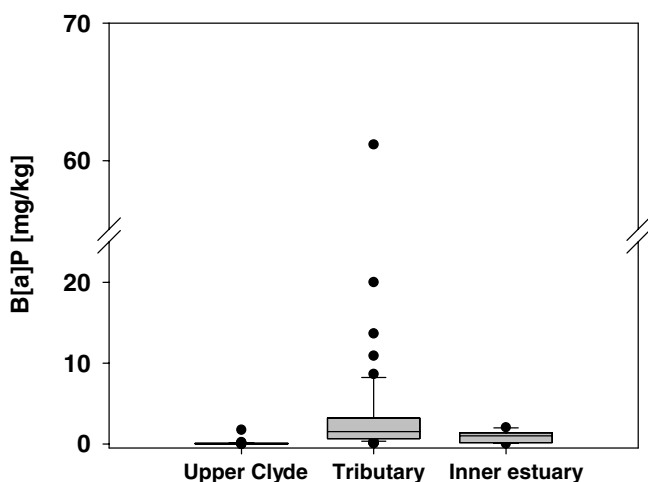
isometric ratio plots (Vane *et al.* 2008, 2011). Maps showing the distribution of POPs in the samples (Annex I) in the River Clyde catchment were generated using the graduated symbol function in a geographic information system (ArcMap10.1, Environmental Systems Research Institute, ESRI®).

## 2. Results and discussion

The main groups of POPs (TPH, PAH and PCB) were quantified in 173 sediment samples from the River Clyde system. The samples were collected from three domains: the upper-freshwater Clyde, the urban tributaries of Glasgow and the inner estuary (Fig. 1).



**Figure 4** Box and whisker plots of (a) TOC, (b) TPH, (c) PAH and (d) PCB concentrations in sediments from the three geographic domains across the Clyde River estuary. The boundary of the box indicates the 25th and 75th percentiles, the line within the box marks the median and error bars indicate the 10th and 90th percentiles. Dots indicate outlying points.



**Figure 5** Benzo[a]pyrene concentrations along a 160-km land-to-sea transect spanning upper freshwater–rural Clyde, Glasgow’s urban tributaries and the inner Clyde estuary. Outliers (solid dots), highest and lowest non-outliers (upper and lower whisker limits) and upper and lower quartiles (box limits).

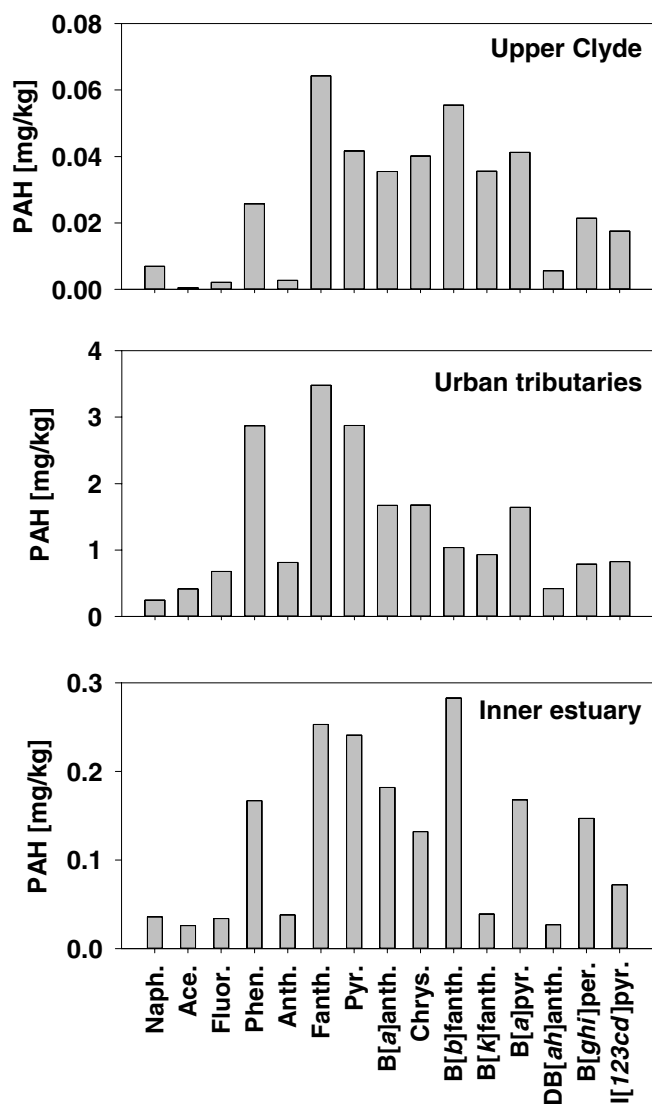
### 2.1. PAH concentrations and distribution

The sum of 15 USEPA PAH concentrations was measured in a total of 109 sites (Figs 2–4). Sediments from the upper Clyde had the lowest PAH concentrations of the three fluvial domains, ranging from 0.1 to 3.3 mg kg<sup>-1</sup>. However, one sample collected

in the town of Lanark, adjacent to a sewage works, contained 42 mg kg<sup>-1</sup> PAH (Fig. 2). The near ten-fold increase in PAH concentration (relative to other upper Clyde sites) and close spatial proximity to a sewerage treatment works (STW) suggests that this may either be due to sorption of pre-existing PAH to organic-rich STW effluent or, alternatively, could be due to the STW effluent itself containing elevated amounts of PAH. A similar anthropogenic organic carbon overprinting within portions of the tidal Thames influenced by London’s main STW situated at Crossness and Beckton, has been recently reported using changes in proportions of glycerol dialkyl glycerol tetraethers compounds (Lopes dos Santos & Vane 2016). On balance, the site at Lanark was anomalous relative to the rest of the upper Clyde sediments and was excluded from the correlations on Fig. 3a.

Sediments from the urban tributary domain had the highest PAH concentrations, ranging from 2.3 to 4226 mg kg<sup>-1</sup> (Fig. 4c). The latter site (proximal to a known bus oil spill site) was anomalous relative to the rest of the urban tributaries dataset (maximum 296 mg kg<sup>-1</sup>) and was also removed from Fig. 2b as it would distort the correlation. The inner estuary sediment PAH values ranged from 0.6 to 30 mg kg<sup>-1</sup> (Figs 2, 3c, 4c). As expected, the lowest concentrations were associated with the rural upper reaches of the Clyde, many km upstream of Glasgow urban centre and associated satellite towns (Fig. 2).

Inspection of the concentration of benzo[a]pyrene (BaP), one of the most toxic of the parent PAH from the three fluvial domains of the Clyde, also confirms the total PAH



**Figure 6** Typical PAH profile of sediments from the upper Clyde, urban tributaries and inner estuary. PAH = polyaromatic hydrocarbons.

concentrations, following a pattern of urban tributary > inner estuary > upper Clyde (Fig. 5). The higher concentrations of total PAH observed in the urban tributaries probably reflects: (1) close proximity to multiple industrial/traffic/urban pollution source(s); (2) less sediment dilution and mixing in these systems; and (3) general anoxic burial conditions, which enhances preservation and limits enzymatic microbial degradation of many organic compounds and biopolymers.

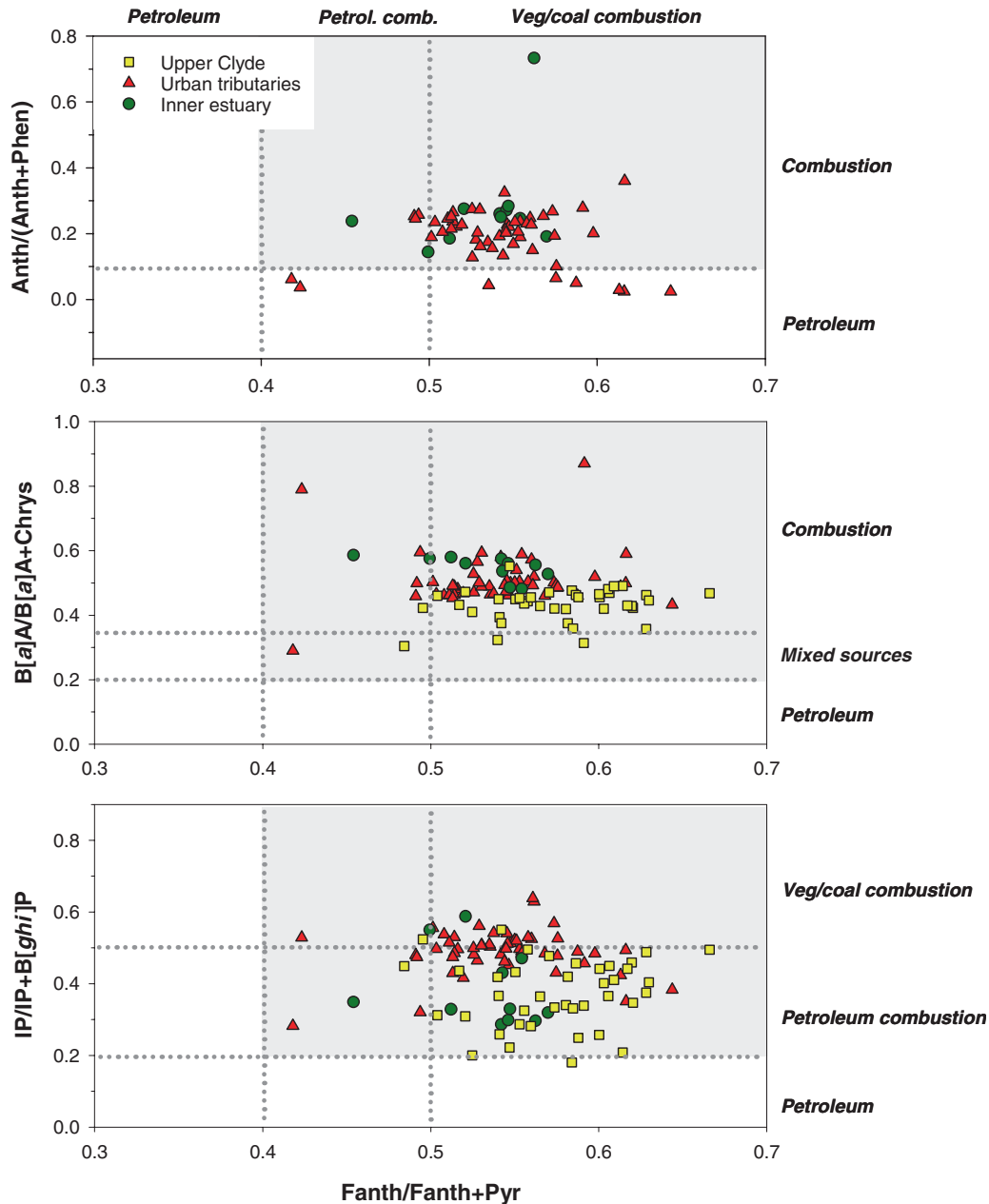
The elevated PAH concentrations in the inner estuary demonstrates the impact that polluted inputs from the urban tributaries have on sediment quality in the Clyde relative to the rural upper reaches. However, PAH concentrations are lower in the inner estuary than in the urban tributaries, probably because the estuary is further from the main pollution inputs and also subject to dilution with cleaner sediment from other sources such as the outer Clyde. The total PAH concentrations in the River Clyde were comparable to those previously reported in other studies of UK estuaries. For instance, sediments from the Mersey, Tyne and Tees estuaries showed concentrations ranging 0.2–43 mg kg<sup>-1</sup> (Woodhead *et al.* 1999; Rogers 2002; Vane *et al.* 2007b) that were similar to the concentrations in the inner estuary, upper Clyde and the majority of urban tributary samples. However, some PAH concentrations in the urban tributary sediments were much higher. Wilson *et al.* (2005) analysed POPs in selected Scottish urban rivers and

found values of total PAH concentration up to 52 mg kg<sup>-1</sup>. Similarly, analysis of the distribution of PAHs in the River Seine, France, found maximum concentrations of 60 mg kg<sup>-1</sup> (Ollivon *et al.* 1995). Ten of the urban tributary samples exceeded these values and were considerably more polluted than these urban rivers in Scotland and France. Of these, oil pollution was present at five of the sites and three of the samples were collected from industrial locations. Therefore, the higher concentrations reflect the fact that urban sediments and the surrounding soils act as sinks for historic and current industrial POPs pollution including oil/petroleum spills, slag materials from the former use of coal as an industrial fuel, degradation of tar-based road coverings and increased surface run-off containing traffic pollutants.

PAH are commonly associated with organic matter in sediments, and increased organic matter derived from the cross-contamination of sewerage networks can also have a detrimental impact on urban sediment quality (Selbig *et al.* 2013). In this current work, a positive correlation exists between TOC content and PAH concentration for the samples of the upper Clyde and inner estuary ( $R^2 = 0.8$  and 0.6, respectively; Fig. 3a, c). This possibly reflects the adsorption of PAH to the natural organic matter in the sediments in agreement with the results of other studies (Vane *et al.* 2007a, 2007b). On the other hand, urban tributary sediment PAH values show a weak correlation ( $R^2 = 0.1$ ) with the TOC (Fig. 3b). This lack of correspondence between PAH and TOC is explained by some of the urban samples that were collected in semi-natural marshy/peat areas and have high natural TOC (e.g., 10–20%) and/or that soils and sediments receiving highly polluted wastes sometimes show weak correlation due to the consumption of organic coatings (active sorption sites) on mineral surfaces. Hence, overall, the greater variety of TOC and PAH sources in the urban area probably masks the correlation that might otherwise be observed between them.

The distribution of individual parent PAH compounds showed minor differences between the three areas (upper Clyde, urban tributaries and inner estuary; Fig. 6). Overall, the pattern corresponded to PAH assemblages that result from high-temperature combustion processes (McCready *et al.* 2000). This is characterised by an abundance of high molecular weight (HMW) PAH with 4–7 rings with predominance of fluoranthene, pyrene, benzo[b]fluoranthene and benzo[a]anthracene. Phenanthrene, the most thermodynamically stable of the three-ring PAH, was also present in all sites but it is an indicator of a petrogenic origin when found in high concentrations (Budzinski *et al.* 1997). The urban tributary domain showed the largest variation in PAH distributions in comparison to the other sites; this suggested either a wide variety of PAH sources and associated mixing, or may also be attributable to less weathering/biodegradation in the urban domain as compared to fluvial-estuarine domains due to rapid burial and incorporation in the sediment. For instance, a few urban tributary samples contained a greater proportion of the low molecular weight (LMW) PAH (naphthalene, acenaphthene, fluorene, phenanthrene, anthracene) suggesting input of PAH from a petrogenic origin (Budzinski *et al.* 1997; Vane *et al.* 2007b).

**2.1.1. Use of PAH ratios to infer possible sources.** To better assess the variations in the molecular weight of the PAH in the sediments, the ratio LMW/HMW (Brown & Peake 2006) was applied to identify potential sources of the PAH. Almost all the samples in this study had a ratio <1, suggesting a combustion origin. Only six urban tributary sediments showed a LMW/HMW >1, suggesting a petrogenic origin. These sediments may be influenced by some oil input. In fact, in two



**Figure 7** PAH isomeric ratio plot for samples from the upper Clyde (yellow squares), urban tributaries (red triangles) and inner estuary (green circles).

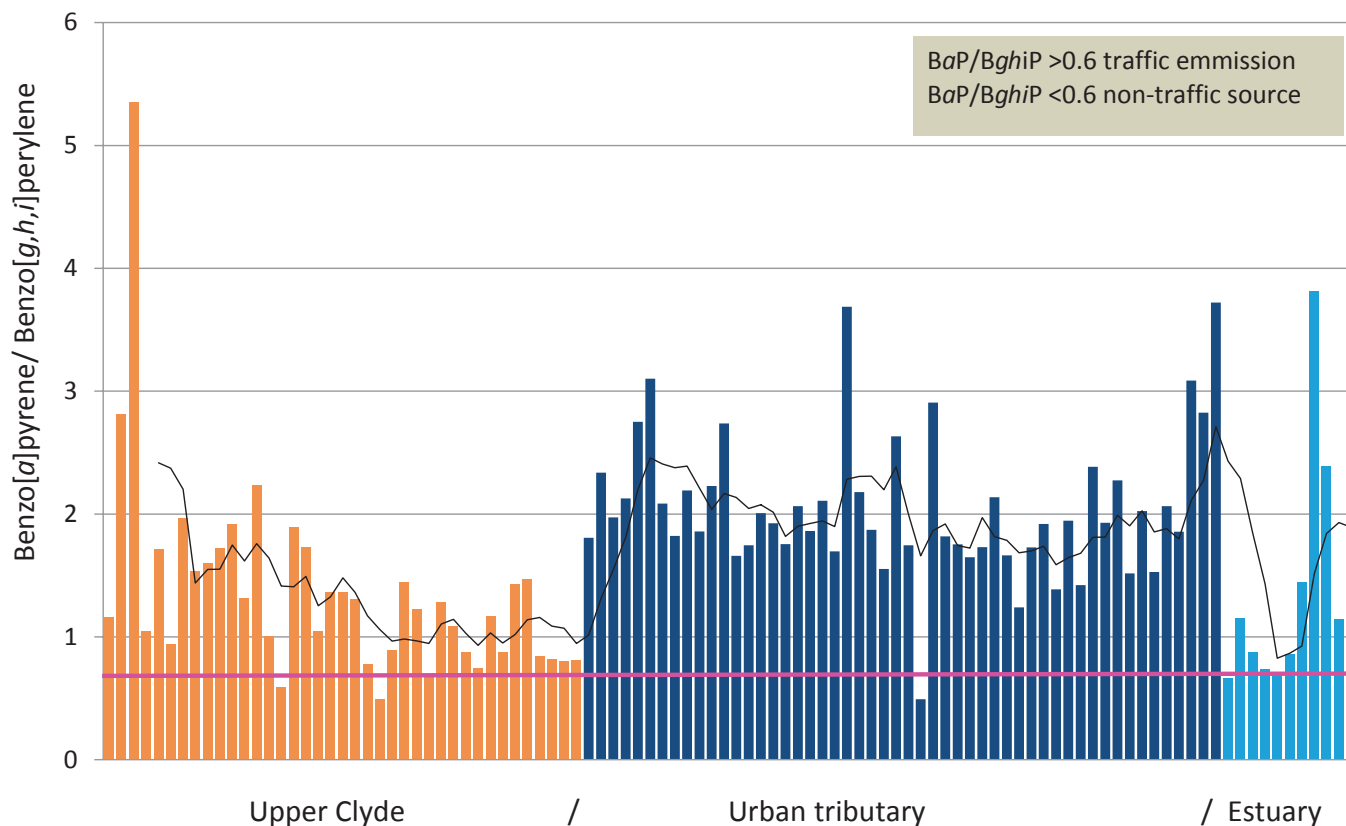
of these samples, oil contamination was visible at the time of sampling.

A more common approach to identify the sources of PAH is the use of diagnostic ratios of selected parent PAH (Readman *et al.* 2002; Yunker *et al.* 2002; Vane *et al.* 2007a, b; Tobiszewski & Namiesnik 2012). This approach is based on the analyses of PAH isomers with different degrees of thermodynamic stability, allowing the determination of the processes producing them. The application of these ratios can produce different results (Tobiszewski & Namiesnik 2012). Therefore, they are usually assessed graphically using a combination of two ratios to facilitate a more reliable estimate of sedimentary PAH source(s). Fig. 7 shows the application of four ratios used to estimate PAH sources in this study. The upper plot displays the ratios between phenanthrene and anthracene versus fluoranthene and pyrene. The results for most of the sediments confirm a pyrolytic PAH origin (shaded area). However, some of the upper Clyde and the urban tributary sediments have borderline petroleum values. Given the rural setting of the upper Clyde sediments, it is expected that PAH in this area largely derive from combustion, including burning of vegeta-

tion, as compared to direct spill of petroleum origin (Vane *et al.* 2013). Concentrations of anthracene for most of the samples of the upper Clyde were extremely low (at or below LoQ), which confounds use within isomeric bi-plots for source apportionment (Fig. 7). The middle plot (Fig. 7) shows the ratios between benzo[*a*]anthracene and chrysene as compared to fluoranthene and pyrene. It suggests a combustion origin for PAH for the majority of the samples and none of the samples showed an exclusively petroleum origin. Finally, the bottom plot (Fig. 7) showing the ratios between indeno[1,2,3-*c,d*]pyrene and benzo[*g,h,i*]perylene (BghiP) as compared to fluoranthene and pyrene, also signifies a pyrolytic origin for all the samples. Taken together, the isomeric and the LMW/HMW ratios indicate a pyrolytic PAH source in the Clyde sediments with a dominance of petroleum combustion in the upper Clyde and inner estuary, while most of the urban samples are on the border between petroleum and coal combustion as both will have been important in the urban domain.

Previous studies have used the non-isomeric ratio of BaP/BghiP to infer vehicular emission PAH (Katsoyiannis *et al.* 2007; Tobiszewski & Namiesnik 2012) where values >0.6





**Figure 8** Benzo[a]pyrene/Benzo[g,h,i]perylene along a 160-km land-to-sea transect of the River Clyde.

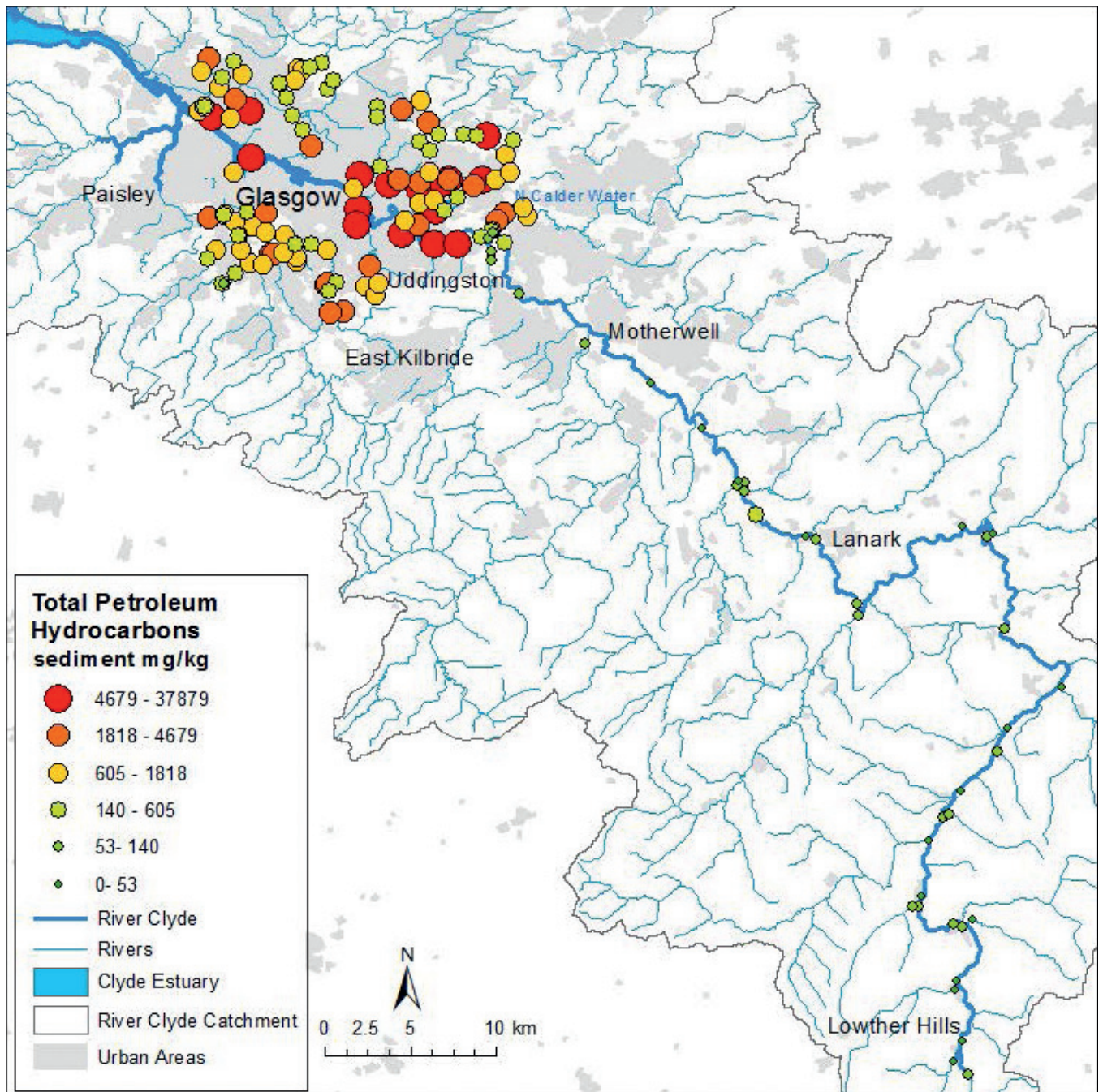
infer traffic exhaust emissions and  $<0.6$  to infer non-traffic PAH source (Mi *et al.* 2000; Lim *et al.* 2007). Inspection of Fig. 8 shows that the majority of sites have  $BaP/BghiP$  ratios  $>0.6$ , which suggests all three domains – namely, upper, urban tributary and estuarine – are, to a lesser or greater extent, receiving PAH generated from traffic emissions, either from transport of diesel and/or unleaded vehicle exhaust particulates transported either in water as road run-off or by aerial deposition, or both. The incorporation of PAH derived from petrol and diesel vehicular exhaust into surface sediments is not entirely surprising in the urban (Glasgow) and estuarine reaches of the River Clyde since these domains are flanked by numerous major motorways such as the M82, M74 and M8. However, the exceedance of the  $BaP/BghiP >0.6$  traffic exhaust source criteria in the upper Clyde rural-reaches probably signifies that either minor roads located alongside or in close proximity to the Clyde contribute to fluvial sedimentary PAH pollution or that there is a diffuse (atmospheric) traffic emission source. Alternatively, it is possible that some other factor confounds the diagnostic use of the  $BaP/BghiP$  ratio in the upper Clyde. For example, the managed burning of moorland vegetation in Yorkshire, UK (e.g., heather and associated species), reported PAH concentrations which yield  $BaP/BghiP$  of up to 1.6 (Vane *et al.* 2013). Therefore, caution does need to be exercised when applying  $BaP/BghiP$  as a marker for vehicular emissions in moorland settings because even small amounts of burnt heather could potentially increase the  $BaP/BghiP$  values to such an extent that they exceed the 0.6 value and are then easily misinterpreted.

## 2.2. TPH concentrations and distribution

Sedimentary TPH concentrations in the upper Clyde ranged from  $<3$  mg to  $260$  mg  $kg^{-1}$  with a mean of  $68$  mg  $kg^{-1}$  (Figs 4b, 9). These values are similar to those reported from undisturbed sediments from mangroves of southern China

(mean  $58$  mg  $kg^{-1}$ ) and barrier island river inlets of New Jersey, USA (mean  $231$  mg  $kg^{-1}$ ) (Vane *et al.* 2008, 2009 and references therein). This comparison confirms the general TPH criteria of  $<100$  mg  $kg^{-1}$ , which is taken to indicate natural sources of TPH (e.g., algae, plant waxes) as compared to  $100$  to  $<500$  mg  $kg^{-1}$  indicating low anthropogenic petroleum hydrocarbon input and  $>500$  mg  $kg^{-1}$  for sites receiving appreciable anthropogenic petroleum pollution.

In contrast, tributaries TPH from the urban domain (Glasgow) ranged from  $72$  to  $37879$  mg  $kg^{-1}$  with a mean  $2779$  mg  $kg^{-1}$ . Of these, 86 sites were above  $>500$  mg  $kg^{-1}$  criteria (significant petroleum inputs) and 26 were between the  $100$  to  $500$  mg  $kg^{-1}$  banding, suggesting low but discernible anthropogenic petroleum hydrocarbon pollution, with the exception of one site, which was  $<100$  mg  $kg^{-1}$ , suggesting mainly natural background. The concentrations encountered in the urban tributaries of Glasgow are higher than that reported from historical sediment cores of the Clyde estuary (maximum  $4386$  mg  $kg^{-1}$ ; Vane *et al.* 2011) and sites from Southampton estuary (maximum  $3100$  mg  $kg^{-1}$ ; Knap *et al.* 1982). This probably reflects closer proximity to pollution sources in the urban domain and less associated dilution by mineral matter. The latter hypothesis being, in part, confirmed by the highest TPH concentration recorded in the urban samples ( $37879$  mg  $kg^{-1}$ ) due to oil contamination at the sample site. Interestingly, a parallel onshore study (this issue) of TPH from urban Glasgow soils (5–10 cm depth interval;  $n = 82$ ) had lower concentrations from  $40$  to  $2505$  mg  $kg^{-1}$  (mean  $353$  mg  $kg^{-1}$ ) (Kim *et al.* 2018). Therefore, on balance, it may be inferred that Glasgow's urban tributaries have a higher amount of TPH than soils because they receive multiple direct discharges of waste and road run-off containing TPH, and that this loading is preserved and accumulates in the surface sediment, whereas the soils are subject to generally lower PAH loadings and have decreased PAH preservation potential due to factors such as weathering,



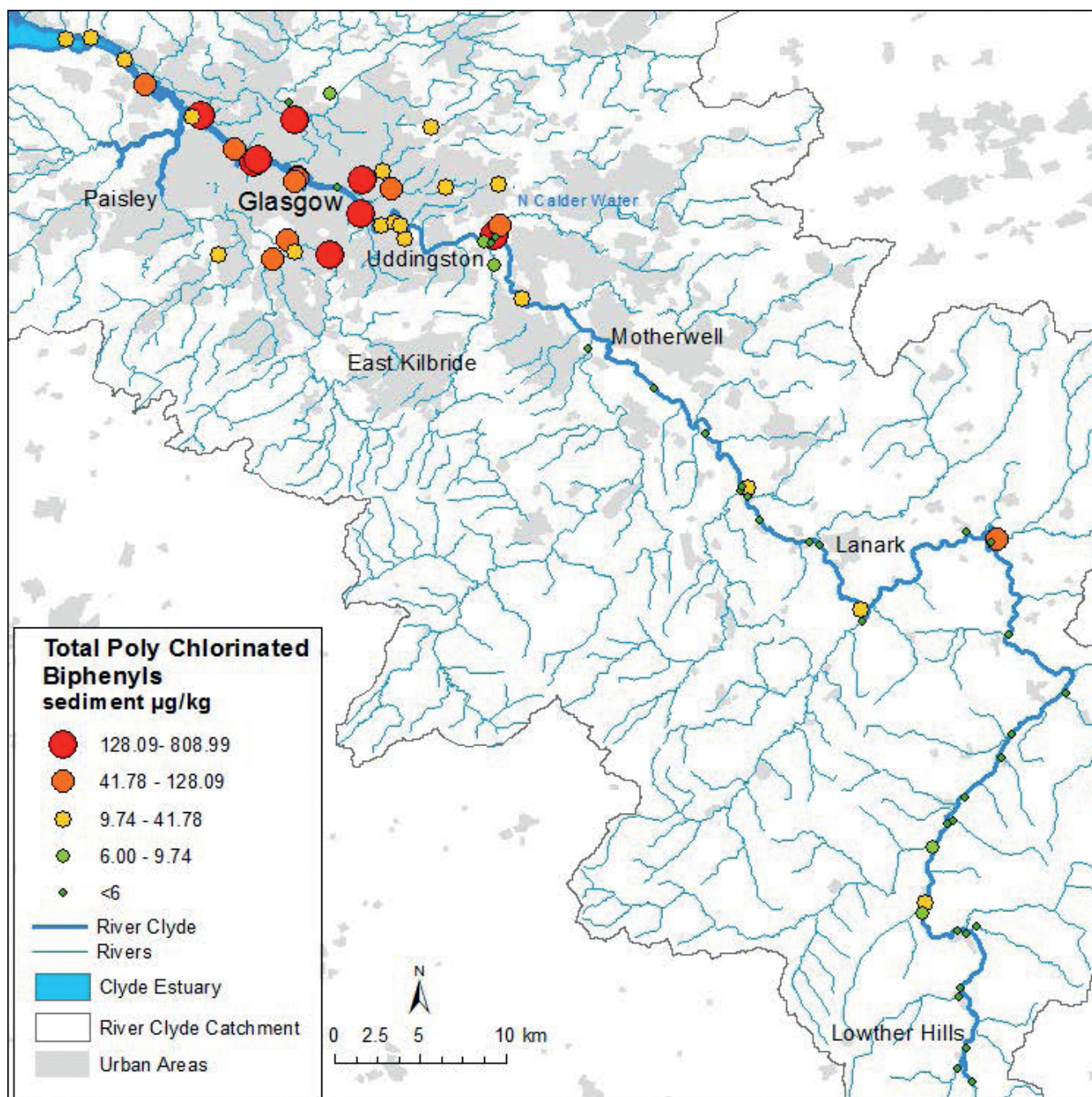
**Figure 9** Total (non-volatile) petroleum hydrocarbon concentrations in sediments of the River Clyde, UK. Geoscience data, BGS © NERC. Contains Ordnance Survey data © Crown Copyright and database rights 2016.

microbial decomposition and photo-degradation. From a global perspective, the TPH values shown here for urban tributary samples are fairly high and are comparable to those reported in soils subject to oil contamination (e.g., Liu *et al.* 2011).

Examination of the TPH and TOC bi-plots for upper Clyde and urban tributary samples showed a stronger correlation of  $R^2 = 0.5$  compared to  $R^2 = 0.2$ , respectively (Fig. 3e), and, similarly, the correlation between TPH and PAH in the upper Clyde sediments ( $R^2 = 0.6$ , Fig. 3i) was stronger than in the urban tributary sediments ( $R^2 = 0.3$ , Fig. 3j). This weak correlation between TPH and PAH in the urban tributaries suggests that the TPH may have other sources besides petroleum; for instance, urban samples that have high TPH but low PAH due to industrial (e.g., paper mills and processing) and sewage waste effluent that could account for higher organic material but not necessarily higher PAH.

### 2.3. PCB concentrations and distribution

Total PCB were analysed in 72 sediments collected from three domains (freshwater/urban/inner estuary) within the River Clyde catchment (Fig. 10). Total concentrations (e.g., summed tri-, tetra-, penta-, hexa- and hepta-chlorinated congeners) ranged from 2 to 61  $\mu\text{g kg}^{-1}$  (mean of 12  $\mu\text{g kg}^{-1}$ ) in sediments from the upper Clyde (Figs 3f, 4d). However, one sample from the North Calder Water tributary junction in Uddingston contained 147  $\mu\text{g kg}^{-1}$  PCB. This site showed much higher concentrations relative to the rest of the upper Clyde and was excluded from the correlations presented in Fig. 3f. In sediments from the inner estuary, PCB concentrations ranged from 5 to 130  $\mu\text{g kg}^{-1}$  and a mean of 46  $\mu\text{g kg}^{-1}$  (Figs 3h, 4d). Sediments from the urban tributaries were the most polluted, with PCB concentrations ranging from 3 to 310  $\mu\text{g kg}^{-1}$  and a mean of 137  $\mu\text{g kg}^{-1}$  (Figs 3g, 4d). Again, one sample from a site with a known history of industrial and oil pollution

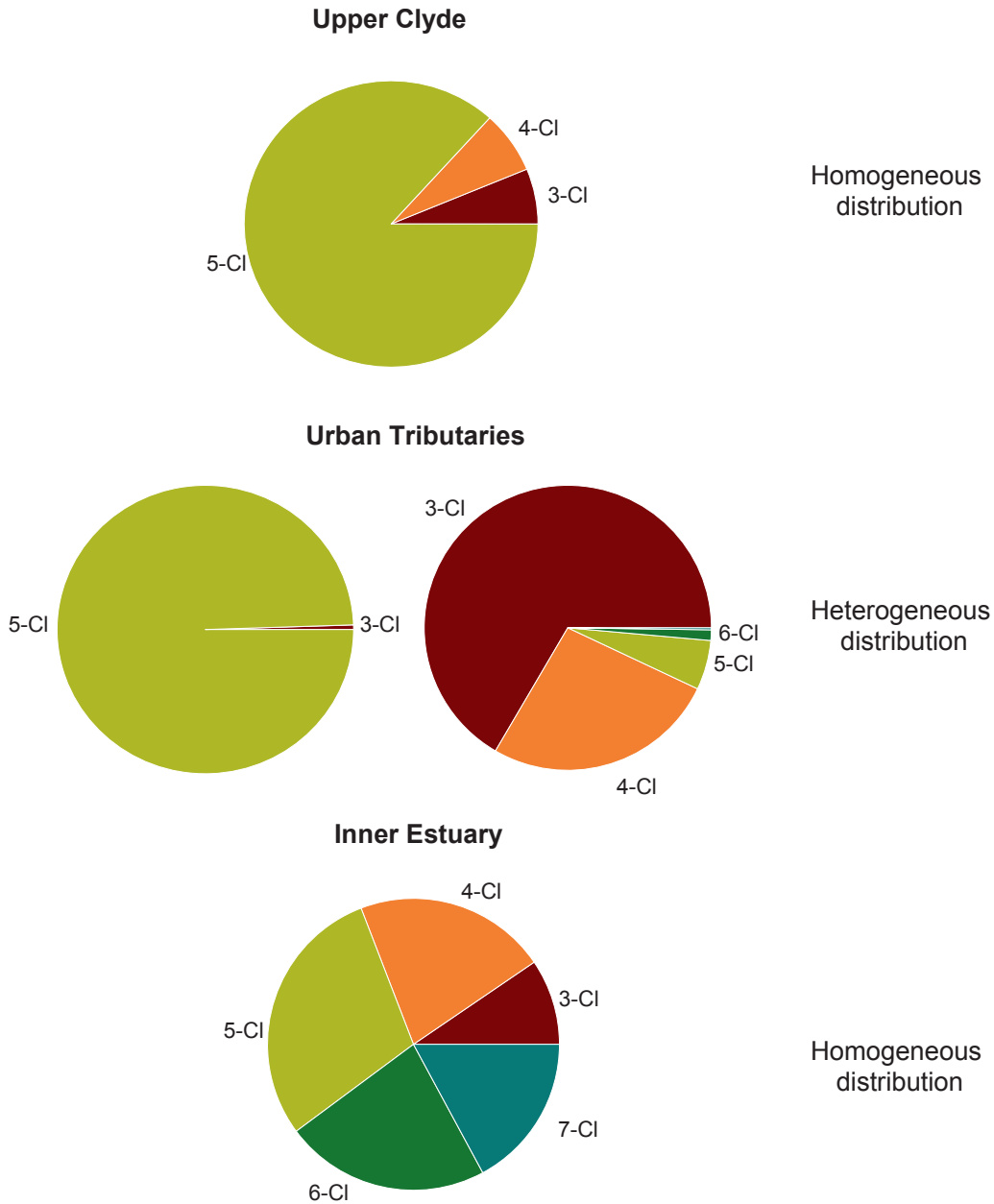


**Figure 10** Total PCB concentrations in sediments of the River Clyde, UK. Geoscience data, BGS © NERC. Contains Ordnance Survey data © Crown Copyright and database rights 2016.

contained unusually high concentrations of  $809 \mu\text{g kg}^{-1}$  and was, therefore, excluded from the correlations of Fig. 3g. Similar to the TOC, TPH and PAH concentrations (Fig. 4a–c), sediments from the upper Clyde had lower amounts of PCB with higher values in the inner estuary and highest contents in the urban tributaries. The range of PCB concentrations from the three domains are in broad agreement with previous studies on sediments from the Mersey and Clyde estuaries ( $30\text{--}1409 \mu\text{g kg}^{-1}$ ; Edgar *et al.* 1999, 2003; Vane *et al.* 2007a, b, 2011). The mean PCB value for the entire freshwater-estuarine Clyde system is  $52 \mu\text{g kg}^{-1}$ , which is lower than the values for Mersey estuary ( $123 \mu\text{g kg}^{-1}$ ; Vane *et al.* 2007b) but higher than those for the inner Thames estuary ( $14 \mu\text{g kg}^{-1}$ ; Scrimshaw & Lester 1995).

Total PCB concentration showed a weak correlation with the TOC in sediments from the upper Clyde and urban tribu-

taries ( $R^2 = 0.0008$  and  $0.02$ ; Fig. 3f, g) and a moderate positive correlation for the inner estuary ( $R^2 = 0.5$ ; Fig. 3h). The low correspondence between PCB and TOC in the upper Clyde samples is probably due to variable amounts of natural organic matter (e.g., humic and structural biopolymers), with high TOC entering and being deposited in the river from the rural catchment as well as a low PCB input. In contrast, the weak PCB-to-TOC correlation observed in the urban tributaries may be due, in part, to the overloading of active sites for sorption, particularly in urban samples with high PCB contents and not particularly high TOC located in sites with oil and industrial contamination. A similar lack of correlation between TOC and PCB was also found for estuarine sediments in the Mersey river (Vane *et al.* 2007b), where the authors explained this as a consequence of local PCB input from industrial point sources.



**Figure 11** Example congener distributions for upper, urban (tributaries) and inner estuary of the Clyde. The degrees of chlorination (3–7-Cl atoms) shown are consistent for the majority of sediments within upper freshwater Clyde and inner estuarine domains, but are highly variable within the urban tributaries of Glasgow.

Changes in the distribution of 3- to 7-chlorine (Cl) PCB homologue groups from the different environmental domains can potentially indicate shifting PCB sources and/or environmental processes (Vane *et al.* 2014, 2011). Figure 11 shows the typical homologue group profile for the rural upper, urban tributary and inner estuary. Differences between the upper/urban/estuary domains are clear (Fig. 11). For example, the upper rural Clyde sediments mainly comprise 5-Cl PCB and lower amounts of 4-Cl and 3-Cl PCB. As the upper rural Clyde has far fewer pollution sources, the PCB homologue group distribution is more homogeneous. The urban tributary sites' homologue group profiles were more variable, with some dominated almost entirely by 5-Cl PCB and others comprising mainly 3-Cl homologues and lower proportions of 4-Cl as well as minor amounts of 5- and 6-Cl (Fig. 11). The greater range of chlorination in the urban tributary sediments may be due to the wider diversity of sources (e.g., construction materials released from demolition sites (paint, caulking), electrical transformer fluids, incinerators, leaking land-fill sites) common

to the urban environment of Glasgow. In contrast, sediments from the inner estuary display a mixture spanning 3–7Cl groups in broadly similar proportions. The PCB congener profile in the inner estuary probably reflects multiple sources within the entire catchment.

It should also be borne in mind that although PCBs are classified as persistent they are not entirely inert and that different congener distributions observed in the three domains could arise, in part, from the preferential aerobic dechlorination and/or anaerobic reductive processes, or a combination of the two. However, disentangling the specific PCB decay pathways is beyond the scope of this study because: (1) it is better addressed using a compound specific isotope approach; and (2) such studies are confounded by manifold sources and a paucity of information concerning the starting formulations used. Nevertheless, the distinct distributions (Fig. 11) confirm the general notion that industrial estuaries act as sinks for original and environmentally attenuated PCB inputs (river and its tributaries) and that the sediments, therefore, contain

a full range of chlorine substitution, five homologues in approximately equal amounts, which arises because of multiple industrial inputs and also a range of microbial mediated decay processes.

#### 2.4. Evaluation of the organic pollution potential toxicological effects on the local environment

There are currently no river sediment quality guidelines (SQGs) in the UK. However, to evaluate the possible toxicological effects of sediment POPs on aquatic ecosystems in the River Clyde, concentrations in the three geographic domains were compared to the consensus-based stream-bed SQGs (MacDonald *et al.* 2000). Most of the sediments from the upper Clyde were below the PAH threshold effect concentration (TEC;  $1.6 \text{ mg kg}^{-1}$ ; Fig. 3a). A few sediments from this area were between the TEC and the PEC ( $22.8 \text{ mg kg}^{-1}$ ). In the inner estuary, most of the sediments were between the TEC and the PEC, with only three samples exceeding the PEC value (Fig. 3c). The urban tributary sediments were more polluted with the majority of samples between the TEC and the PEC, and several sediments exceeding the PEC value (Fig. 3b). This suggests that the local biota may be adversely affected by the sedimentary PAH concentration in the urban domain.

Unfortunately, no TPH threshold is stated in the consensus-based SQGs. However, as the concentrations of TPH, especially in the urban tributary sediments, are so high, it is reasonable to assume that these pollutants may be causing an adverse effect to the local biota. A study of the ecotoxicological effects of TPH on the intertidal benthic organisms off Goa reported an adverse effect to the macrobenthos exposed to a maximum concentration of  $89 \text{ mg kg}^{-1}$  TPH (Ingole *et al.* 2006). The study also reported changes in the benthos community structure as the number of species significantly decreased at these concentrations (Ingole *et al.* 2006). Although the present study concerns river sediments spanning both freshwater and estuarine (partly saline) conditions and, therefore, the environmental conditions and the biota will differ from Ingole *et al.* (2006), a stronger adverse effect of TPH on the biota is likely based on the much higher concentrations measured herein. We assert that pollution in the urban tributaries warrants further investigation, particularly if the sediment compartment is coupled to in-field bio-monitoring of bioindicator species such as that previously conducted in Milford Haven waterway (Langston *et al.* 2012).

When compared to the consensus-based SQG (MacDonald *et al.* 2000) for total PCB pollution, the majority of samples from the upper Clyde and the inner estuary are below the TEC ( $59.8 \text{ } \mu\text{g kg}^{-1}$ ; Fig. 3f, h). Only a few samples from these areas are between the TEC and the PEC, and none of the samples exceed the PEC ( $676 \text{ } \mu\text{g kg}^{-1}$ ). For the urban tributaries, 11 of the 19 samples analysed for PCB were below the TEC and the rest were between the TEC and PEC (Fig. 2g). Therefore, according to these criteria and sites examined, it is unlikely that the sedimentary PCBs are adversely altering the biota of the Clyde.

#### 2.5. Sediment quality guidelines (SQGs) for disposal at sea

Marine Scotland, a directorate of the Scottish Government responsible for the management of Scottish seas, have set non-statutory action levels for sediment PAH and PCB as part of a weight-of-evidence-based approach to the licensing for disposal of dredged material at sea. Assessment of POPs concentrations in River Clyde surface sediments using the Marine Scotland guideline (2011) showed that just five sites exceeded the total PCB Action Level 2 (AL2;  $180 \text{ mg kg}^{-1}$ ),

which may be defined as being possibly unsuitable for disposal at sea, whereas 23 sites fell between 20 and  $180 \text{ mg kg}^{-1}$ , suggesting further assessment required, and 67 sites fell below Action level 1 (AL1;  $20 \text{ mg kg}^{-1}$ ), suggesting the PCBs hosted in the sediments are of no immediate concern. Of those sites that exceeded PCB AL2, all were located within the urban tributaries (Glasgow) away from the main Clyde channel (Fig. 1).

Evaluation against the PAH benchmark ( $0.1 \text{ mg kg}^{-1}$  for the majority of individual PAH) or approximately  $1.5 \text{ mg kg}^{-1}$  (sum 15 PAH) showed that 35 sites were below AL1 (no concern) and 72 sites were above the benchmark. However, it is rather unclear what this exceedance means in terms of disposal management/site clean-up, partly because no values for the upper criterion (AL2) have been reported and also because coastal and river management typically assesses a variety of factors other than chemical concentrations, including bioassays in concert with evaluation of microbenthic community structure.

The Marine Scotland disposal guidelines report a lower AL1 of  $0.01 \text{ mg kg}^{-1}$  for dibenzo(a,h)pyrene, presumably due to its similarly high toxicity/carcinogenic activity, to BaP, a key PAH considered harmful to human health (Cave *et al.* 2010). In this current study, eight upper Clyde, 11 estuary and 47 urban tributary sites exceeded the dibenzo(a,h)pyrene AL1 value, again suggesting at the very least that further assessment is required prior to disposal/movement.

### 3. Conclusions

#### 3.1. Distribution of organic pollution

We show that surficial sediments from tributaries of Glasgow city, UK, have higher amounts of POPs (PAH, TPH, PCB) than either the freshwater reaches or inner estuarine Clyde. For example, the urban tributaries had mean sediment concentrations of  $124 \text{ mg kg}^{-1}$  for PAH,  $2279 \text{ mg kg}^{-1}$  for TPH and  $137 \text{ } \mu\text{g kg}^{-1}$  for PCB, compared to lower mean concentrations of  $2 \text{ mg kg}^{-1}$  for PAH,  $68 \text{ mg kg}^{-1}$  for TPH and  $12 \text{ } \mu\text{g kg}^{-1}$  for PCB in upper Clyde and  $12 \text{ mg kg}^{-1}$  for PAH and  $47 \text{ } \mu\text{g kg}^{-1}$  for PCB in the inner estuary. This study suggests that Glasgow city has an obvious anthropogenic organic geochemical footprint that is about 60 (PAH), 33 (TPH) and 11 (PCB) times higher, on average, than the rural upper Clyde domain. If PAH, PCB and TPH are given equal weighting in terms of environmental effect, then the overall pattern of organic pollution in the Clyde proceeds in the order urban tributaries > inner estuary > upper Clyde.

#### 3.2. Environmental health effects

A comparison of POPs concentrations to published consensus-based SQGs suggests that sediment in the urban tributaries may have an adverse effect on sensitive biota. We also observed that the majority of sites from the urban tributaries exceed the concentrations recommended for disposal at sea by Marine Scotland. However, it should be borne in mind that these sediments are not from the main channel of the River Clyde and are, therefore, not subject to maintenance and capital dredging activities that typically generate large volumes of sediment containing legacy pollutants. Individual PAH levels, as exemplified by the toxic PAH dibenzo[a,h]pyrene, were found to exceed AL1 in both urban tributary and inner estuary domains.

#### 3.3. Tracking sources of organic pollution

PAHs were observed at every site in the Clyde, confirming their widespread occurrence even in sediments from rural

headwaters. The distribution of individual PAH together with isomeric and LMW/HMW ratios confirmed pyrolytic PAH sources comprising mainly petroleum combustion PAH in the upper Clyde and inner estuarine domains. In contrast, PAH distributions and ratios suggested a mixture of petroleum and coal combustion sources in the urban tributaries. The application of BaP/BghiP >0.6 to infer traffic emissions from either diesel and or unleaded vehicle exhaust particulates suggested at face value that the entire river-estuarine continuum received vehicular PAH. However, this interpretation is not entirely proven because high BaP/BghiP values have been reported from burnt moorlands (Vane *et al.* 2013). It is, therefore, plausible that the two high BaP/BghiP values in the rural upper Clyde domain are from burning and that the values of between 0.6 and 2 actually represent a mix of both vehicular and burnt moorland vegetation sources (Fig. 8).

A comparison of the extent of PCB chlorination (% homologue groups) showed that the urban tributary sediments were more variable than the upper or estuarine Clyde. We hypothesise that this is either because (1) there are a greater variety of possible PCB sources in the urban setting, which yield a heterogeneous environmental mixture due to the many different formulations used in the original products, or that (2) the microbial and weathering processes acting on PCBs may differ in the freshwater-estuarine domains as compared to the more anoxic urban tributaries.

This study clearly demonstrates that urban tributaries are an important sink and potential source of organic contaminants. Our results imply that a comprehensive understanding of estuarine and, ultimately, coastal and marine sediment pollution chemistry in the Clyde and other UK estuaries that lie within close proximity of a major city can only be achieved by considering the manifold anthropogenic inputs from urban tributaries.

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