Baseline

Grain size and organic carbon controls polyaromatic hydrocarbons (PAH), mercury (Hg) and toxicity of surface sediments in the River Conwy Estuary, Wales, UK

Christopher H. Vane[a,*], Alexander W. Kim[a], Joseph F. Emmings[a], Gren H. Turner[a], Vicky Moss-Hayes[a], Jack A. Lort[a], Peter J. Williams[b]

[a] British Geological Survey, Keyworth, Nottingham NG12 5GG, UK
[b] British Geological Survey, Crowmarsh Gifford, Wallingford, Oxfordshire OX10 8BB, UK

ABSTRACT

The Conwy estuary was evaluated for sediment quality. Microtox bioassay revealed 38 of 39 sites were non-toxic. Hg ranged from 0.001 to 0.153 $\mu g\ kg^{-1}$, mean 0.026 $mg\ kg^{-1}$, $\Sigma16$ PAH from 18 to 1578 $\mu g\ kg^{-1}$, mean 269 $\mu g\ kg^{-1}$, $\Sigma22$ PAH, 18 to 1871 $\mu g\ kg^{-1}$ mean to 312 $\mu g\ kg^{-1}$, two sites had high perylene relative to ΣPAH. $\Sigma22$PAH correlated positively with TOC, clay and silt (R^2 0.89, 0.92, 0.90) and negatively with sand. Multivariate statistics, delineated four spatial (site) and five variable (measurements) clusters. Spatial clustering relates to sediment grain size, in response to hydrodynamic processes in estuary; fine (clay to silt) sized sediments exhibit the highest Hg and PAH content, because these components partitioned into the fine fraction. Comparison to national and international environmental standards suggests Hg and PAH content of Conwy sediments are unlikely to harm ecology or transfer up into the human food chain.

Estuaries are dynamic environments in which sedimentation is driven by the interplay of geomorphology, tectonics and fluvial-tidal processes as well as variety of human interventions such as engineering and river catchment management. Consequently, estuaries can act as permanent or transient stores of sedimentary pollution, prior to re-mobilisation and transport out to adjacent shelf sea (Ridgway and Shimmield, 2002). The UK's urban-industrial estuaries such as the Thames (London) and Clyde (Glasgow), Mersey (Liverpool) and Humber (Hull) have benefited from chemical pollutant assessments to assist in the sustainable management of sediment resources and compliance to national legislation and international agreements (Jones et al., 2019; Lee and Cundy, 2001; Vane et al., 2020b). In contrast, information on organic chemistry and toxicity within rural UK estuaries, such as the Conwy is lacking.

The River Conwy (Afon Conwy) is a 55 km-long exemplar rural-agricultural catchment (590 km km^2) (Emmett et al., 2016). Land-use-cover comprises of blanket bog, moorland, semi-natural woodland and coniferous forests, as well as agricultural land (diary, beef and sheep). Consequently, the Conwy is a centre for tourism but is ranked at a low to intermediate position of the national productivity gradient (Emmett et al., 2016; Maskell et al., 2013). The tidal reaches of the river (final 16 km) are flanked by agricultural pasture and a variety of protected habitats such as reedbeds, saltmarshes, mudflats including the Conwy RSPB reserve at Llandudno Junction. The lower reaches host; 1) the historic towns of Conwy (west bank), famous for its waterfront world heritage medieval Castle, built in 1289 CE by King Edward 1st, and; 2) the Llandudno Junction /Deganwy area (east bank). These towns are linked via Conwy Railway bridge (1849), and a tunnel for vehicles (1991; Fig. 1). The narrow outlet of the estuary contains the culturally important Conwy Bay and Estuary Mussel Fishery, which has harvested *Mytilus* for over 500 years. Whilst data exists on the heavy metal content in suspended particulates, waters and suspended faecal wastes, very little is known about the distribution of organic pollutants in bed sediments (Elderfield et al., 1979; Mudge and Norris, 1997; Perkins et al., 2014; Zhou et al., 2003). This study was undertaken to fill this information gap with the potential to be a background (control) against which other UK estuaries may be assessed.

Surface sediments from the active channel of the tidal River Conwy were collected on August 1st 2017 using a 2 L van Veen grab deployed from the vessel 'Four Reasons' (Fig. 1). The position of each site was recorded using a handheld Garmin GPSMAP 64 s ± 6 m. At each site, the sediment (0 to ~10 cm) from three grab deployments were combined, sealed in a polyethylene bag (5.7 L) and stored in an ice box (~0 °C) for 3 h (Supplementary data 1). A subsample of ~120 g (wet

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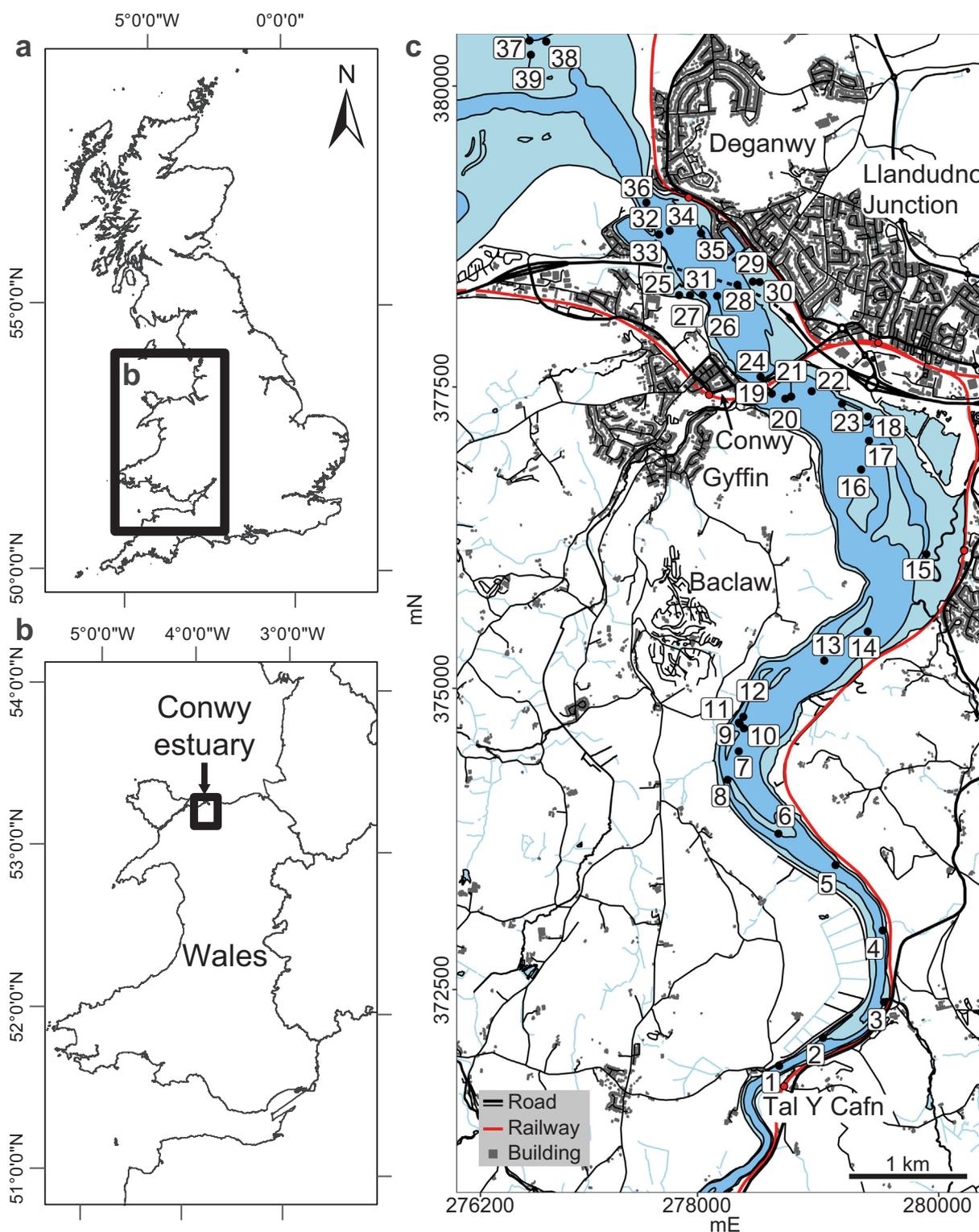
Fig. 1. Location of surface sediment sites in the River Conwy Estuary, Wales, UK. (a–b) outline of Britain, Wales and the Conwy Estuary study area (WGS84 geographic coordinates). (c) Sample locations on the Conwy Estuary (British National Grid projection). Contains Ordnance Survey data © Crown Copyright and database rights.

weight) was frozen at −20 °C (24 h), freeze dried (48 h), disaggregated and sieved ≤2 mm, milled in agate ≤40 μm.

Particle size (< 1 mm) was measured using a Malvern Mastersizer 2000 (Naden et al., 2016). Each sediment was placed in a beaker with 20 mL H_2O and the suspension (0.5 mL) analysed with HydroS with pump/stir speed of 2700 rpm or HydroG with pump speed 1600 rpm.

The proportions of particles at each size class (100 groups, from 0.1 μm – 1000 μm) were calculated using the Fraunhofer model and grouped using established size term categories clay-silt-sand (Folk and Ward, 1957).

Total organic carbon (TOC % wt/wt) was determined on de-carbonated sediment using a Europa Scientific Elemental analyser, the
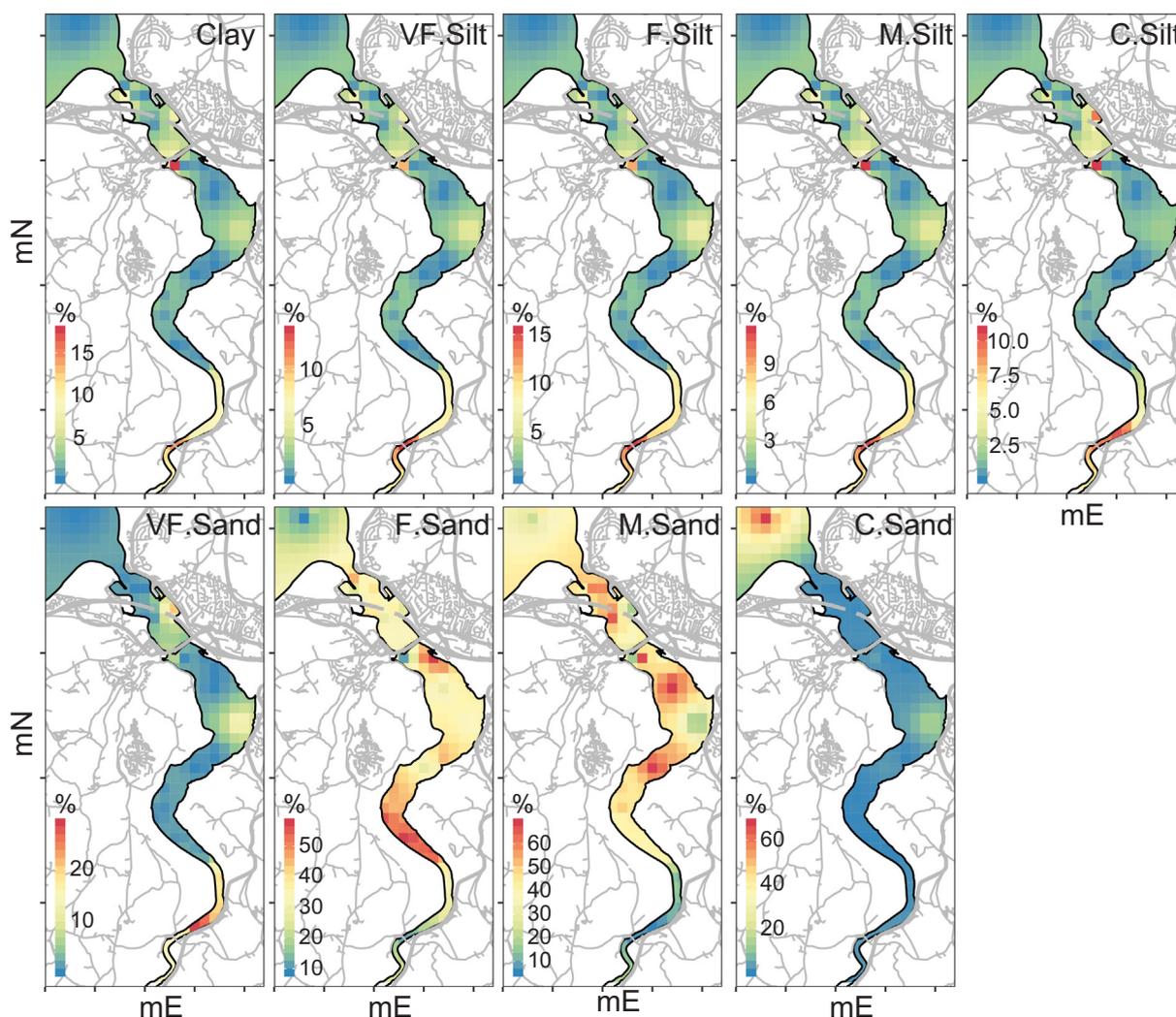
Fig. 2. Particle size of clay, silt, and sand (%) of Conwy river-estaury sediments (0 to 10 cm) (Tal Cafyn Bridge to Conwy Bay): grouped using classical grouped using established size term categories (Folk and Ward, 1957).
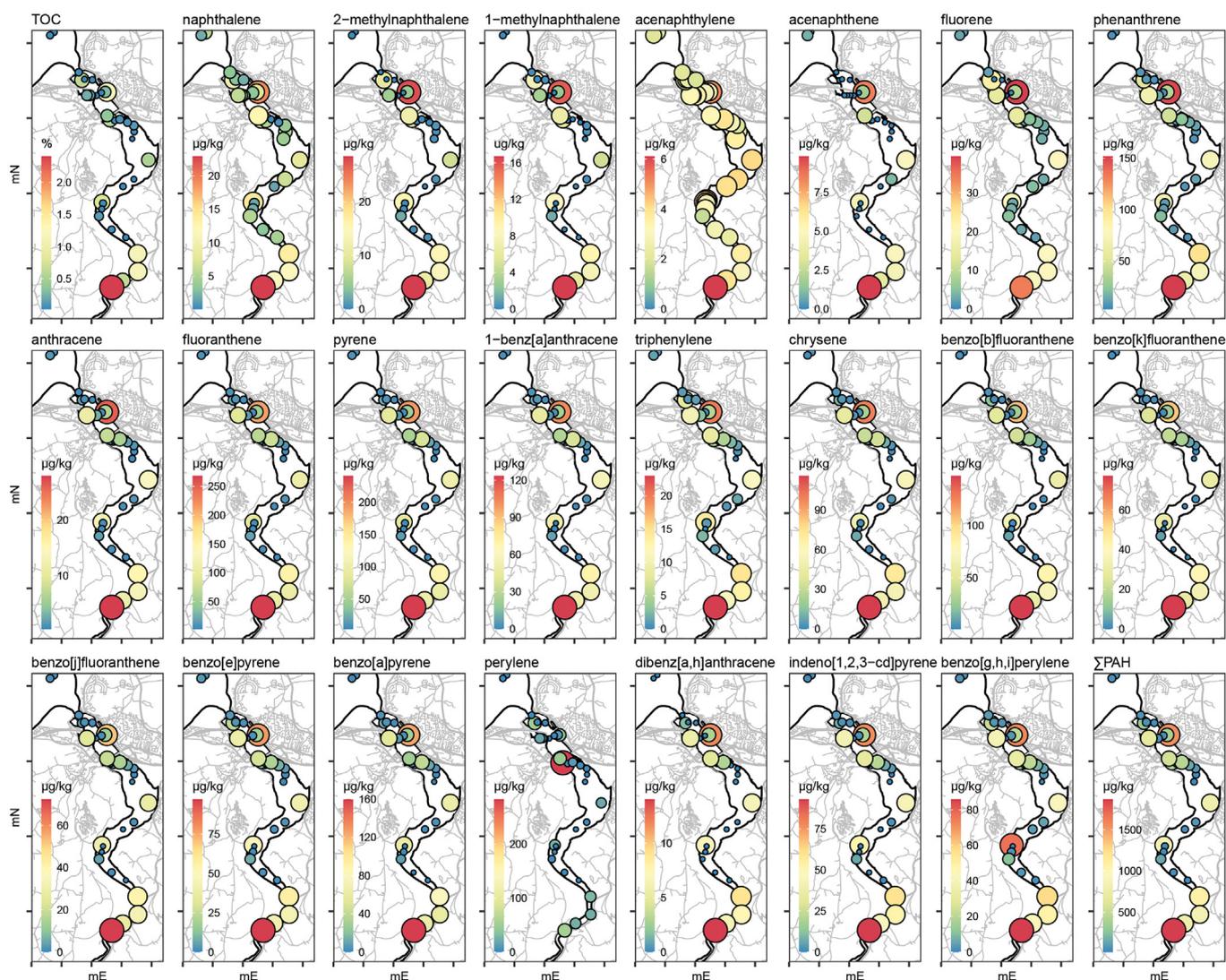Contains Ordnance Survey data © Crown Copyright and database rights.

limits of quantification for a typical 300 mg sample was 0.1%. Total mercury (Hg) was determined by atomic absorption spectrophotometer (AAS) using a Milestone DMA-80, direct mercury analyser (MA122). Analysis of external reference materials MESS3-1 (Hg, 0.092 mg kg^{-1}) and TH2-1 (Hg, 0.620 mg kg^{-1}) yielded ± 0.01 and 0.002 mg kg^{-1} (2σ), respectively. Sediment toxicity was determined using the Microtox® solid phase test (SPT) applied to the luminescent bacterium *Aliivibrio fischeri* (strain NRRL B-1117) (Vane et al., 2020a).

PAH were measured by spiking 10 g sediment (dry weight) with deuterated (surrogate) standards. Samples, procedural blanks and certified reference materials (CRMs) were extracted using a Dionex ASE-200 with dichloromethane/acetone 1:1v/v, 100 °C at 1500 psi. The extract was transferred to a conditioned (6 mL n-hexane) SPE cartridge (Varian, Bond Elute TPH w.500 mg Na$_2$SO$_4$, 1 g sorbent, 3 mL reservoir volume). The first fraction was eluted with pentane (0.5 + 1 mL) using gravity. The second fraction which contained the PAHs was eluted with 6 mL hexane/isopropanol (97:3) v/v. The volume of eluant was reduced and internal standards added (Vane et al., 2020a). PAH were determined using a Varian 3800 gas chromatograph (GC) coupled to a Varian 1200 L triple quadrupole mass spectrometer fitted with an Agilent PAH Select column (30 m × 0.25 mm × 0.1 μm). All PAH concentrations are reported in this study are in μg kg^{-1} on a dry sediment weight basis. The marine/harbour reference material (NIST

1941b) was used to ensure PAH concentrations were within expected limits (n = 8 analysed in duplicate) (Wise et al., 2004). A comparison of the CRM certified reference PAH values revealed a good correlation to the values obtained in this study (Supplementary data 2).

The Microtox® Solid Phase Test (SPT) EC$_{50}$ values for Conwy sediments ranged from 5587 to 83,522,531 mg/L. When benchmarked against > 10,000 non-toxic, 10,000 to 5000 moderately toxic, and 5000 to 0 as acutely toxic criteria indicated that the majority (38 of the 39 sites) did not contain toxins at sufficient levels to elicit an acute biological response. (Guerra et al., 2007; Kwan and Dutka, 1995; Vane et al., 2020a) In contrast, site 19, a location close to the Conwy Rail Bridge and the historic castle, exhibited EC$_{50}$ of 5587 mg/L, a value taken to indicate moderate toxicity. Greater sediment toxicity at this location may be explained by direct anthropogenic input possibly related to materials inadvertently or deliberately discarded from the bridge. Overall, the microtox bioassay indicated that the Conwy sediments were not toxic, with one exception.

Total Hg ranged from 0.0004 to 0.153 mg kg^{-1} (mean 0.026 mg kg^{-1}, median 0.007 mg kg^{-1}), which are some of lowest concentrations in a UK estuary (Supplementary data 3). From a marine management sediment quality standpoint, primarily used for to assist in the issue of licences to dredge which in encompasses disposal of dredge at sea, all sediments are within the lower bounds of non-statutory

Fig. 3. Concentration of 22 polycyclic aromatic hydrocarcarbons (Σ22 PAH) and total organic carbon (TOC %) in surface (~0–10 cm depth) sediments of the Conwy estuary.
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legislative action Level 1 criteria (0.0 to 0.29 mg kg^{-1}), and none between 1 and 2 criteria (0.29 to < 0.3 mg kg^{-1}) or the higher action Level 2 criteria (> 0.3 mg kg^{-1}). Confirming that the sediments could, on the basis of Hg content, be disposed at sea (with no further action necessary). The highest Hg of 0.153 mg kg^{-1} (site 1) was observed close to the tidal limit suggesting deposition of particulates from the upstream catchment, and/or changing physical-chemical upstream conditions. For example, 'salting out' processes can lead to accumulation of trace metals in bed sediments at the point of salt-fresh water mixing (Supplementary data 3) (Vane et al., 2015).

Comparison with the major urban-industrial estuaries of the UK such as the Thames, Tyne, Mersey and Clyde, as well as sites in SE Asia, Europe and USA, indicates that the Conwy estuary contains 3 to 50 times less Hg. This supports the notion that river-estuarine sediment quality is influenced more by the type, proximity and intensity of industrial activity as compared to duration of human occupation. Given that total Hg in river-estuarine sediments is a combination of anthropogenic Hg hosted in industrial slag, vehicular exhausts, sewage effluent, coal particles, incineration/power site dusts augmented by background of geogenic sources, we suggest surface sediments of the Conwy have received low anthropogenic Hg. This finding is not unexpected given that the Conwy catchment (watershed) is partially

located in Snowdonia National Park, an area protected from significant industrialisation/urban development.

Total organic carbon (TOC %) ranged from 0.03% to 2.40% with a mean 0.30% and median of 0.06%. Particle size data for the 39 sites showed that the majority of sediments, comprise a mixture of fine and medium sands, whilst those from the outermost open-sea sites Conwy Bay (37–39) were coarse and medium sands (Fig. 2). In contrast, particles from some sections of the mid and inner river-estuary are relatively fine; typically clay (10%), silt (60%) and sand (30%) (Fig. 2). The most plausible explanation for the switch to finer grained sediments (e.g. sites 16–20 and 24–26) is that it either represents soil eroded from the adjacent and unembanked agricultural fields, in-wash from lower order tributaries or alternatively this fine sediment could possibly have been transported and deposited from higher in the catchment.

Sedimentary Σ16 PAH ranged from 18 to 1578 μg kg^{-1}(dry weight), with a mean 269 μg kg^{-1} and median of 67 μg kg^{-1} (Fig. 3). Addition of 2-methylnaphthalene, 1-methylnapthalene, triphenylene, benzo[j] fluoranthene, benzo[e]pyrene and perylene to the PAH inventory (Σ22 PAH), yielded only slightly higher amounts 18 to 1871 μg kg^{-1} mean to 312 μg kg^{-1} and median of 70 μg kg^{-1} reflecting minor contribution to overall PAH content (Fig. 3). Inner estuary sites, down-stream of Tal-y-Cafyn Bridge (sites 1 to 4) exhibited the highest PAH concentrations
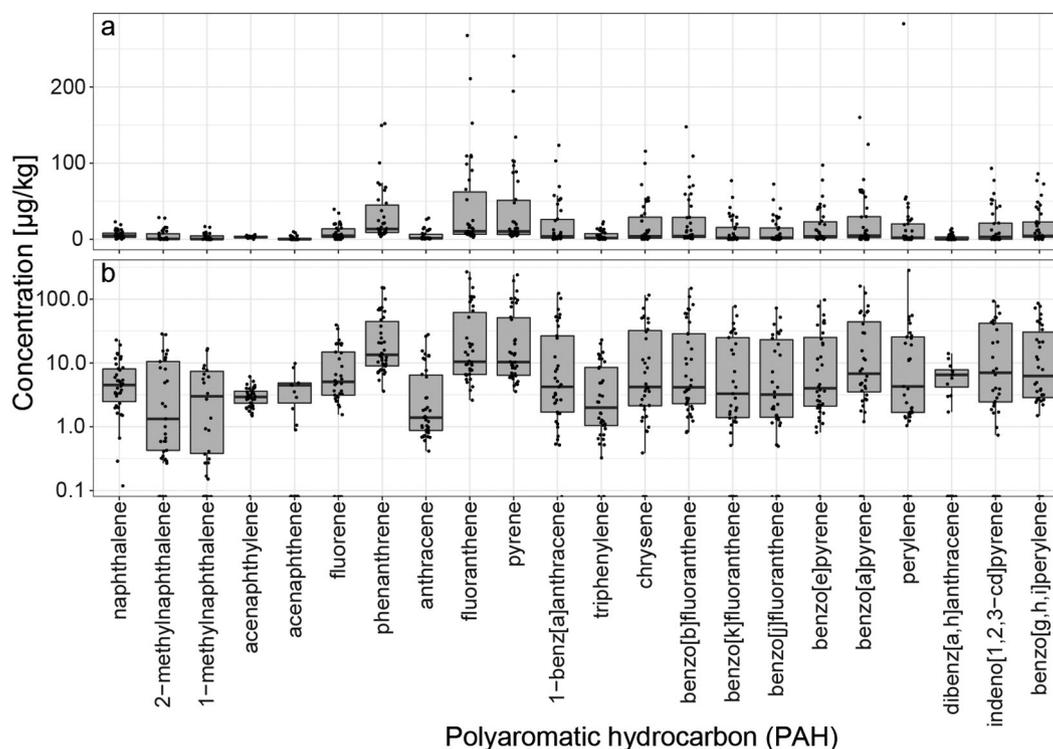
Fig. 4. Box-plot distribution of individual polycyclic aromatic hydrocarbon (Σ22 PAH) concentration for Conwy estuary (Tal Cafyn Bridge to Conwy Bay) (*n* = 38). The plot shows the upper and lower quartile boxes and median value (horizontal line), on a linear (a) and logarithmic (b) scale.

Σ22 PAH, 804 to 1871 μg kg^{-1}. In addition, several sites adjacent to Conwy and Llandudno Junction (sites 22–32) exhibited higher PAH, typically > 300 μg kg^{-1}, and rising to a maxima of 1541 μg kg^{-1} at site 30 (Fig. 3). In contrast, the most offshore Conwy Bay sites 36 to 39 had low Σ^{16} PAH of < 100 μg kg^{-1}. Inspection of the lateral distribution of benzo[*a*]pyrene, one of the most toxic of the parent PAH, used as a surrogate chemical marker for genotoxic organic compounds, revealed a similar spatial pattern to that of the Σ16 or Σ22 PAH (Safe, 1998). Benzo[*a*]pyrene content is high in the upper estuary (78 to 160 μg kg^{-1}), highly variable in the mid estuary (1 to 124 μg kg^{-1}) and low in the outer estuary (~2 to 4 μg kg^{-1}) (Fig. 3) (Cave et al., 2015; Vane et al., 2020a). The PAH distribution profile of Conwy sediments show a minor contribution of low molecular weight PAH (2–3 ring), and major contributions from higher molecular weight PAH (4–6 ring) dominated by fluroanthene, pyrene, benzo[*a*]pyrene, phenanthrene, benzo[*b*]fluroanthene and benzo[*a*]anthracene (Fig. 4). The rise in PAH concentrations observed in the latter middle reaches are likely due to greater proximity to anthropogenic activity (Llansanffraid, Glan Conwy, Landudno Junction, Deganwy and Conwy) emanating either as road run-off and/or combusted particulates from vehicles or possibly the railway tracks (Figs. 1 and 3). Also, the middle portion of the river-estuary is spanned by three closely spaced bridges namely, Conwy-suspension Bridge, Road Bridge and Rail Bridge and underlain by the Conwy tunnel which may influence sediment and tidal flow processes and therefore indirectly affect accumulation of sedimentary PAH.

The five ring compound perylene is one of the predominant PAHs in upland UK vegetation (10 to 18%) and soils (3 to 5%) but reported in lower amounts in UK urban soils and sediments (≤3%)(Vane et al., 2014; Vane et al., 2013). In the Conwy, the perylene concentration was low and ranged from < 1.0 to 55.5 μg kg^{-1} such that it contributed ~3% ΣPAH (Fig. 3). In contrast, site 19 contained 283 μg kg^{-1} perylene, comprising 63% of the total PAH Σ22 (Fig. 5). Unusually high concentrations of perylene that are poorly correlated to other PAH have been widely reported in lakes and coastal sediments since the 1980s (Venkatesan, 1988). Perylene has also been shown to be a product of

fungal decay of wood in the rhizosphere such that it can serve as a marker for soil erosion and subsequent aquatic deposition (Grice et al., 2009; Hanke et al., 2019). Precursor compounds, perylene-quinones from ectomycorrhizal fungi found in boreal, temperate and sub-tropical woodland soils are deoxygenated during sedimentary burial to yield perylene (Hanke et al., 2019). Therefore, the elevated perylene concentration at site 19 may be explained by erosion and deposition of woodland soils containing perylene-quinone precursor compounds. However, it's also prudent to consider that whilst an eroded soil source fits current theory, the fact that it was only observed at one site seems at odds with what must be a ubiquitous catchment scale biogeochemical process. Thus, in this instance an unknown/unproven anthropogenic source seems more plausible (e.g. decomposition of chemical dyes which contain perylene backbone). Although perylene is not considered to be as toxic to humans compared to benzo[*a*]pyrene or other key PAH such as dibenz[*a,h*]anthracene, the causative connection to the low EC$_{50}$, which infers moderate toxicity observed at the same site seems entirely plausible (Safe, 1998). For example, evaluation of perylene toxicity on benthic bacteria and macrofauna such shrimps (*Corophium multisetosum*) in an estuarine environment toxicity assay revealed statistically significant negative effects on the survival, growth and number of pregnant females (Cunha et al., 2006). Further, exposure of *Salmonella typhimurium* to PAH suggested that perylene caused mutagenic activity a lower concentration than benzo[*a*]pyrene (O'Donovan, 1990). Triphenylene, the four ring PAH found in low amounts in coal tars, cigarette smoke and vehicular exhaust is rarely reported in marine environmental pollution studies in the UK due to co-elution with chrysene on standard GC columns and similarities in mass spectra. We observed triphenylene at concentrations ranging from 0.33 up to 22.98 μg kg^{-1} with a mean of 4.68 μg kg^{-1} and median of 1.49 μg kg^{-1}.

PAH concentration (Σ22) exhibits a strong positive correlation with TOC (R^2, 0.89) (Supplementary data 4) This relationship is likely due to sorption of PAH to natural organic matter (humic substances coating mineral surfaces), or possibly black carbon including coal particles
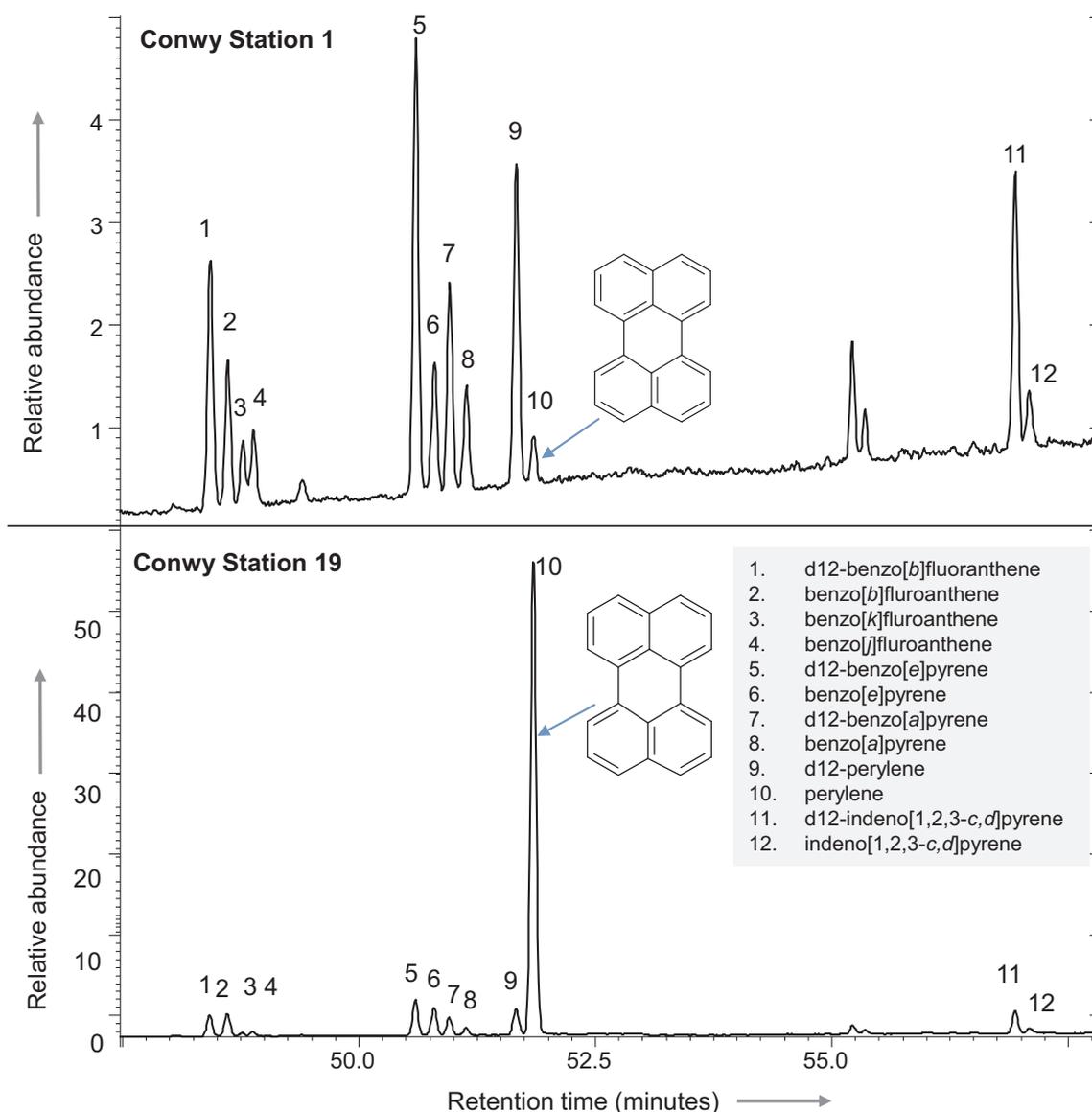
Fig. 5. Patial chromatogram (from triple quadropole GC/MS) showing high perylene concentration at site 19 (close to Conwy Castle) as compared to more typical relative abundance at site 1 (Tal-Cafyn). Positions of sites shown Fig. 1.

Table 1

Comparison of sedimentary PAH concentrations of the Conwy estuary to international marine sediment quality benchmarks. With one exception all sites PAH content suggest good ecological status (e.g. within < Background (BAC) and < Effects Range Low (ERL)).

Polyaromatic hydrocarbon	< BAC ($\mu g\ kg^{-1}$)	No. sites < BAC	< ERL ($\mu g\ kg^{-1}$)	No. sites > BAC to < ERL	No. sites ≥ ERL
Naphthalene	8	28	160	10	0
Phenanthrene	32	26	240	12	0
Anthracene	5	27	85	11	0
Pyrene	24	27	665	11	0
Chrysene	20	27	384	11	0
Benzo[a]pyrene	30	29	430	9	0
Benzo[g,h,i]perylene	80	37	85	0	1
Indeno[1,2,3-cd]pyrene	103	38	240	0	0

which also contain PAH (Bucheli et al., 2004; Hedges and Keil, 1999; Lohmann et al., 2005; Stout and Emsbo-Mattingly, 2008; Ukalska-Jaruga et al., 2018). The strong correspondence of PAH to TOC has been previously shown in sediment cores from the Mersey estuary where a variable PAH to TOC correlation (R^2 of 0.5) was attributed to a PAH association with wind-blown soot fraction (Vane et al., 2007). The relationship between PAH and sediment grain-size (% clay, silt, sand) was similarly clear, with silt (R^2 0.90) and clay (R^2 0.92) content showing a strong positive correlation and sand content being negatively correlated (Supplementary data 4). The positive correlation maybe explained by PAH being partitioned/adsorbed to the organics coating clay/silts 'or' directly to clay minerals. However, it should also be borne in mind that the relationship may be driven by other factors, for example, organic matter might behave in a hydrodynamically similar manner to the clay fraction; thus, the correlation between PAH and clays may not be necessarily causual.

On a national basis (UK), the mean concentrations and ranges of PAH for the Conwy rank below those reported for major urban industrial estuaries in the UK such as the Mersey (626 to 3776 $\mu g\ kg^{-1}$), Clyde (630 to 23,711 $\mu g\ kg^{-1}$), Humber (598 to 3372 $\mu g\ kg^{-1}$) and Tyne (260 to 43,470 $\mu g\ kg^{-1}$) (Vane et al., 2007; Vane et al., 2019;
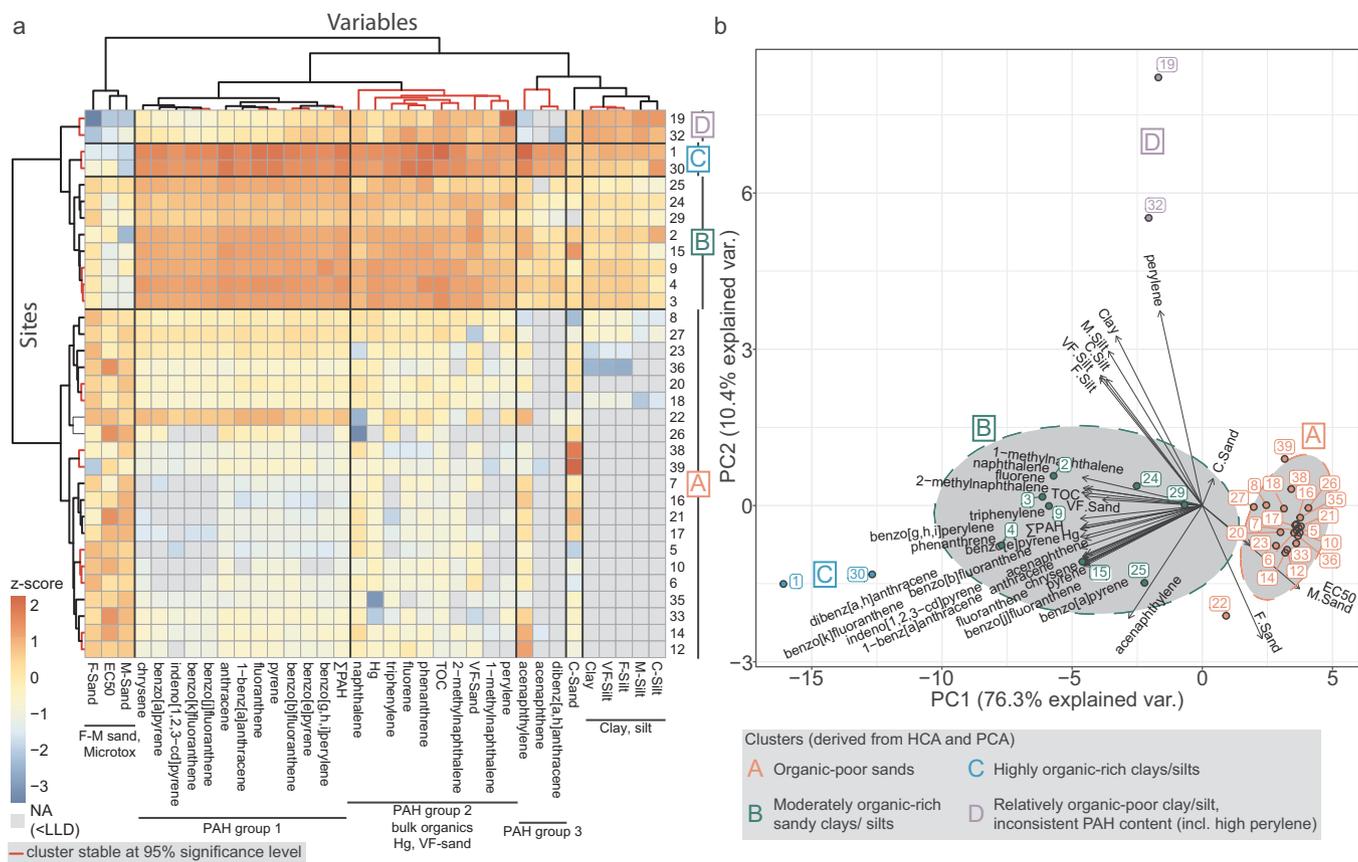
Fig. 6. (a) Hierarchical cluster analysis (HCA) for sites (y axis) and measurements (x axis). (b) Biplot for principal components 1 and 2, including verification of clusters derived from the HCA in (a). Clusters A and B are delineated with a 95% probability ellipse. See text for methods and discussion.

Woodhead et al., 1999). However, they are similar to those reported for the more rural estuaries such as the Tweed (Σ^{14}PAH 50 µg kg^{-1}) (Woodhead et al., 1999). On an international basis, PAH contents are substantially lower than most urban industrial estuaries and are far more comparable to sections of coast considered to be fairly pristine such as Danube coastline Black Sea, Ukraine (67 to 635 µg kg^{-1} (Σ^{17}PAH)), Gironde estuary, France (4 to 853 µg kg^{-1}, mean 256 µg kg^{-1} (Σ^{14}PAH)), Barnegat Bay, USA (37 to 1696 µg kg^{-1}, mean 671 µg kg^{-1}), Benin, 80 to 1411 µg kg^{-1}, mean 487 µg kg^{-1}(Σ^{14}PAH) (Readman et al., 2002; Soclo et al., 2000; Vane et al., 2008).

In the UK, marine sediment PAH concentrations are evaluated using a combination of pre-defined OSPAR (Background concentrations (BAC)) and International Council for Exploration of the Sea (effect range low (ERL)) which mark the lower and upper thresholds of "Good Environmental Status" listed within Descriptor 8 of the Marine Strategy Framework Directive (MFSD) (Tornero and Hanke, 2018). The ERL benchmarks originated from a statistical evaluation of a concentration-effect database such that ERL is the 10th percentile and ERM is the 50th percentile of the concentrations that were toxic (Long et al., 1995). Sediments with individual contaminant concentrations > ERL may be taken to indicate a possible contamination risk. Using these criteria, the majority of sites PAH concentrations fall in the < BAC category and a few samples PAH values fall within the < ERL category. In contrast, only one site exceeded the benzo[g,h,i]perylene ERL criterion confirming the notion that the ecological threat posed by the specified PAH compounds is negligible (Table 1). Overall, comparison with non-statutory sediment quality guidelines suggests the PAH content in the Conwy is of low concern and unlikely to bioaccumulate up trophic levels and thereby cause no harm to estuarine ecology.

Data manipulation, interpolation and multivariate statistical analysis was conducted using a software package called 'R' (R Core Team,

2018). Samples were interpolated via inverse distance weighting for 200 × 200 m tiles. Hierarchical cluster analysis (HCA) was conducted on log-transformed and standardized data (z-scores). Clusters were determined for sites and variables (measurements) via the sum of squares (Ward clustering) and Euclidian distance matrix. Cluster stability was estimated using Approximately Unbiased bootstrap resampling (nboot = 10,000). Principal component analysis (PCA) was conducted on a scaled and centred (but otherwise raw) dataset.

HCA and PCA (Fig. 6) demonstrate grain size exerts a strong control on the compositional variance across sites. Interpreted hierarchical clusters by site, A-C, describe a spectrum defined by the admixture of two end-members (Fig. 6a). The majority of sampled sites represent a sand-rich and thus TOC and PAH-lean end-member (Cluster A). Cluster C represents an organic-rich end-member, defined by high Hg, relatively high toxicity, TOC, high (and typically consistent) PAH content, and high clay and silt content. Cluster B represents an intermediate between clusters A and C. Cluster D defines sample sites 19 and 32, which exhibit high clay and silt content, relatively high toxicity, and inconsistent PAH content. PCA is consistent with interpretations based on the HCA (Fig. 6b). Principal component 1 accounts for 76.3% of the variance in the dataset, and describes the spectrum between organic-poor, coarse-grained (Cluster A) and organic-rich, fine-grained (Cluster C) end-members. Principal component 2 delineates Cluster D; samples which are fine grained and exhibit inconsistent PAH content (including high perylene content). In general, this finding supports the interpretation that sedimentary PAH concentration in the tidal Conwy are highly influenced and correlated with organic matter and fine-grained sediments.

Hierarchical clustering by variables (Fig. 6) delineates at least six clusters; medium-fine sand and Microtox EC50; coarse sand; fine grains (clay and silt); and three PAH groupings. PAH group 1 includes pyrene,
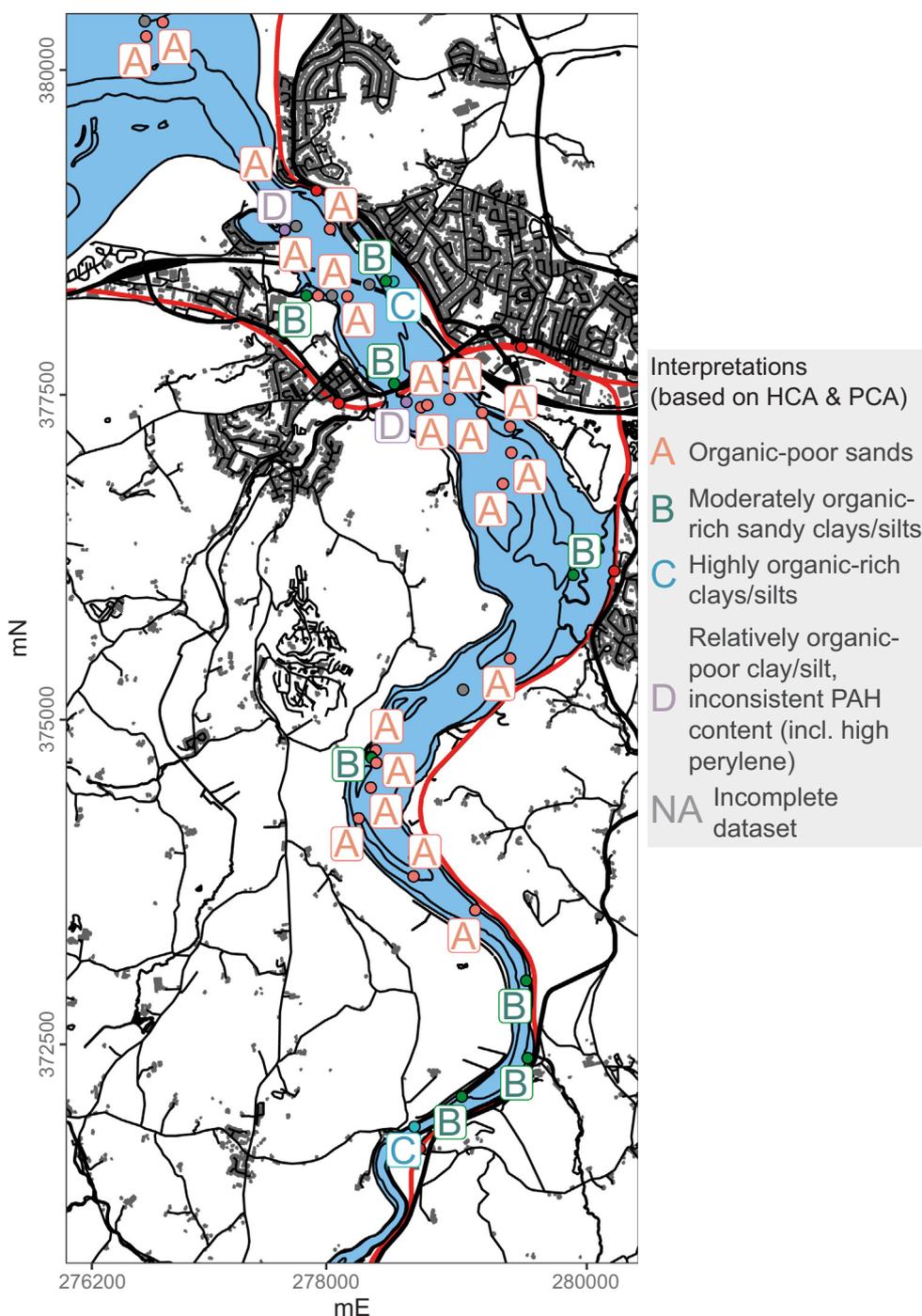
Fig. 7. Interpreted clusters, based on PCA and HCA, mapped to sites along the Conwy estuary.

fluoranthene, anthracene, chrysene, indeno[1,2,3-*cd*]pyrene and all PAHs attached to a benzene ring. PAH group 2 includes naphthalene (including methylated forms), Hg, triphenylene, fluorene, phenanthrene and perylene. PAH group 3 includes acenaphthylene, acenaphthene and dibenz[*a,h*]anthracene. In terms of PAH groupings, Clusters B-C typically exhibit relatively uniform composition; whereas clusters A and D tend to exhibit increased variability. PAH consistency for sites in clusters B-C suggests 1) PAH are readily accommodated within the sediment at these sites (i.e., limited competition for sorption); 2) the PAH reservoir at these sites is relatively well-mixed; 3) residence times are similar for all PAH compounds at these sites. Increased variability between PAH groups in Cluster A suggests an environment subject to PAH input from multiple sources, coupled to

variable residence times, and perhaps related to increased competition for limited sorption sites (i.e., sand-rich grains with low surface area and unfavourable physiochemical properties for PAH fixation). Similarly, cluster D is relatively enriched in PAH group 2 (particularly perylene), depleted in PAH groups 1 and 3, and exhibits a very low TOC/clay ratio (Supplementary data 4). This shows at least one additional input or process controls PAH content in Conwy River bed sediments; potentially related to localised natural or anthropogenic input, PAH competition for fixation, selective desorption or degradation of PAH, or sampling of older and/or younger sediments that are out-of-phase with the majority of sampled sites.

Application of traditional isomeric and non-isomeric PAH ratio source apportionment bi-plots suggests mainly pyrogenic sources

(vegetation/coal/urban background) with little indication of PAH petroleum spills or crude oil (Supplementary data 5) (Tobiszewski and Namiesnik, 2012; Yunker et al., 2002). This interpretation is also supported in part by the greater amount of naphthalene as compared to 1-methylnaphthalene (parent > alkyl). However, it should be borne in mind that the ratio data are difficult to clearly interpret because many of the values plot on the borders between identifying quadrants/areas (Supplementary data 5). Inspection of the biplots with the clusters from the PCA and HCA show that Cluster B (moderately organic-rich sandy clays/silts) PAH are more likely from pyrogenic sources than for example sites from Cluster A (Organic-poor sands). Further, the non-iosmeric bi-plot also suggests that Cluster D (organic-poor clay/silt high perylene) PAH source is different. Overall, the combination of diagnostic source ratios overlain by PCA/HCA clusters suggests mixing and possibly some attenuation/affiliation of PAH according to sediment type driven by factors such as grain size and TOC (e.g. Fig. 7).

1. Conclusions

Microtox solid phase test bioassay and chemical measurement of total Hg and PAH show that Conwy estuary surface sediments (< 2 mm fraction) are unpolluted when compared to the urban-industrial estuaries of UK. Grain size analysis revealed a mainly sand dominated sediment regime with minor silts and clays. Comparison with non-statutory sediment quality criteria revealed that all sites fell below Hg action levels and the presence of PAH at concentrations 18 to 1578 μg kg^{-1} are unlikely to impact bottom feeding biota and or important cultural ecosystem services such as the mussel fishery, Conwy. The PAH compound triphenylene is rarely reported in UK pollution studies, but was observed in the Conwy at concentrations ranging from 0.3 up to 23 μg kg^{-1} suggesting that it is minor, but ever-present component of estuarine total PAH. The unusually high perylene concentrations observed close to the castle and one at the entrance to Conwy marina was unexpected and most likely linked to an unknown anthropogenic source. Whilst, other perylene sources such as degraded perylene-quinones from eroded woodland catchment soils could not be entirely discounted they are less plausible as intuitively this should be a feature to a lesser or greater extent down the entire transect.

Multivariate statistical (PCA and HCA) evaluation of chemical-toxicity-grain size data confirmed that PAH content is highly influenced by and correlated with organic matter (e.g. TOC) and fine-grained sediments (e.g. silt and clay) (R^2 ~0.90); conversely PAH content was negatively correlated with coarse sandy sediment. This approach suggested four grain size-PAH interactions, namely, organic poor sands low in PAH (Cluster A), organic rich sands/silts/clays with uniform PAH (Cluster B, C) and non-uniform (perylene) PAH (Cluster D). Based on this study there is clear evidence that estuarine pollution assessments need to consider chemical concentration data and grain size as well as organic carbon and thus counter the attenuating effects of the sediments they are found in and bound to.

CRediT authorship contribution statement

Christopher H. Vane: Conceptualization, Resources, Formal analysis, Writing - original draft.**Alexander W. Kim:**Formal analysis.**Joseph F. Emmings:**Investigation, Writing - original draft.**Gren H. Turner:**Formal analysis.**Vicky Moss-Hayes:**Formal analysis.**Jack A. Lort:**Formal analysis.**Peter J. Williams:**Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2020.111412.

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