Marine Pollution Bulletin 175 (2022) 113340

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Contrasting sewage, emerging and persistent organic pollutants in sediment cores from the River Thames estuary, London, England, UK

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ARTICLE INFO

Keywords:
Anthropocene
Contamination
Pharmaceuticals
Black carbon (BC)
Polycyclic aromatic hydrocarbons (PAH)
Petroleum hydrocarbons (TPH)

ABSTRACT

Sedimentary organic pollution in the urban reaches of the Thames estuary is changing from fossil fuel hydrocarbons to emerging synthetic chemicals. De-industrialisation of London was assessed in three cores from Chiswick (Ait/Eyot) mud island using pharmaceuticals, faecal sterols, hydrocarbons (TPH, PAH), Black Carbon (BC) and organotins (TBT). These ranked in the order; BC 7590-30219 mg/kg, mean 16,000 mg/kg > TPH 770–4301, mean 1316 mg/kg > $^{\Sigma 16}$PAH 6.93–107.64, mean 36.46 mg/kg > coprostanol 0.0091–0.42 mg/kg, mean of 0.146 mg/kg > pharmaceuticals 2.4–84.8 μg/kg, mean 25 μg/kg. Hydrocarbons co-varied down-profile revealing rise (1940s), peak (1950s -1960s) and fall (1980s) and an overall 3 to 25-fold decrease. In contrast, antibiotics, anti-inflammatory (ibuprofen, paracetamol) and hormone (17β-estradiol) increased 3 to 50-fold toward surface paralleling increasing use (1970s-2018). The anti-epileptics, carbamazepine and epox-carbamazepine showed appreciable down-core mobility. Faecal sterols confirmed non-systematic incorporation of treated sewage. Comparison to UK sediment quality guidelines indicate exceedance of AL2 for PAH whereas TBT was below AL1.

1. Introduction

The majority of the world's most economically and strategically important cities are situated on river estuaries. Urban centres such as New York City (Hudson-Arthur Kill), London (Thames), Guangzhou (Pearl River), Kolkata (Ganges) and Antwerp (Scheldt) have thrived due to their ability to supply and receive manufactured goods and agricultural produce as well as physically connect people. However, their sustainable growth over decades to millennia requires management of the estuaries sediments in order to maintain shipping channels and ports, sustain fisheries, support wetlands for recreation and natural flood protection as well as disperse and dilute waste effluent from industries and its inhabitants (Vane et al., 2020a; Vane et al., 2019).

London (England, UK) is an exemplar estuarine city that expanded rapidly from about 1 M inhabitants in 1801 to 6 M 1901, to 8 M in 1939 and stabilised to its current 2020 population of ~10 M. The tidal Thames flows in an easterly direction bisecting central London and thereafter discharges into the southern North Sea. It has a catchment area of 14,000 km^2 and the tidal portion of the river is approximately 110 km long, with a width that varies from 55 m at Brentford to 270 m at Tower Bridge, and reaching a maximum of 8 km at Shoeburyness to Sheerness. The tidal portion of the river serves as a key transport route for Greater London, historically one of the most populous cities in the world. Intertidal foreshore and continuously submersed channel (bed) sediments of the River Thames estuary have been previously assessed for a wide range of pollutants including trace metals (e.g. Hg, Cu, Ag), organochlorines (polychlorinated biphenyl (PCB)), flame retardants (polybrominated diphenylether (PBDE)), organobutyltins (TBTs), phosphorus and plastics in order to maintain navigation and port activities, support emplacement of engineering infrastructure as well as identify ecosystem and human health risks (Ganci et al., 2019; Khan et al., 2015; Morritt et al., 2014; Murray et al., 2011; Pope and Langston, 2011; Scrimshaw and Lester, 1997; Tye et al., 2018; Vane et al., 2015; Vane et al., 2020b). These studies mainly report lateral changes along the river-estuary salinity gradient or utilise sediment cores from saltmarshes situated in the outer Thames to identify changes with depth. However, recent examination of cores from intertidal mud-islands situated within the urban London reaches report the rise and fall of a range of metal contaminants commensurate with shifts in historical use due in part to uniform grain-size distribution. Taken together these factors provide an improved understanding of the balance between supply and incorporation of anthropogenic chemicals and toxicity, as well as

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https://doi.org/10.1016/j.marpolbul.2022.113340
Received 6 December 2021; Received in revised form 7 January 2022; Accepted 8 January 2022

revealing the modifying effects of other natural estuarine processes such as salting-out and natural organic matter source (Vane et al., 2020b).

In this study we assess non-volatile total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAH), black carbon (BC) from wood, coal, oil-burning, faecal sterols from sewage effluent, organobutyltins (banned biocides), as well as emerging synthetic chemicals (pharmaceuticals and a hormone) in order to provide a broader understanding of sediment quality, clarify associations and provide insights as to whether current coverage of legacy contaminants is sufficient given numerous reports of emerging contaminants in fresh, tidal and coastal waters.

2. Methods

2.1. Core collection and preparation

Three sediment cores (A-C) were collected along an axial transect (51 29 13.4 N, 14 48.18 W to 51 29 17.1 N, 14 41.64 W) Chiswick Ait (Eyot/Island), London, England on 28 March 2018 (Fig. 1). At each site a clear polycarbonate tube (120 cm length, 6 cm I·D) fitted with a stainless-steel basket catcher was pushed into the sediment and recovered. Upon return to the laboratory each core was sectioned continuously at 5 cm between 0 and 20 cm and 10 cm between 20 and 60 cm and each of the 24 depth intervals freeze-dried, sieved to pass 2 mm sieve and ground in an agate ball-mill (Vane et al., 2020b).

2.2. Black carbon (BC)

In summary, sediments (n = 24) were subject to a two-step procedure consisting of an aqueous extraction to remove inorganic carbon and organic carbon and a thermal treatment stage used to remove traces of IC (inorganic carbon) and OC (organic carbon). The remaining residue was quantified for total carbon (TC) and the carbon that is resistant to aqueous extraction and thermal treatment, defined as BC. For each aqueous extraction, 2 g of sediment were sequentially treated with 25 mL: 2 × NaOH (1 M), 1 × 70 mass % HNO_3, 6 × 1 M NaOH, 1 × 1 mass % HCl, and 2 × 18 Ω water. Samples were sonicated for 15 min at 40 °C, centrifuged 3000 rpm for 15 min and the supernatant decanted and residue dried (100 ± 5 °C, 1.5 h) and weighed. Thermal treatment was performed on 0.5–1.0 g of the aqueous extracted sediment by heating in a furnace at 340 °C 5 h. Total organic carbon (TOC) was determined on samples treated with HCl (5.7 mol L) to remove IC, dried at 100 ± 5 °C for 1 h using an Elementar Vario Max C analyser. TC was estimated using the same method but without acidification, TIC was calculated by difference ((i.e. TC) TOC = TIC). Procedural blanks were below instrumental response threshold. The limit of quantification for TOC for a typical 300-mg sample was 0.18%. The marine reference material Baltimore Harbor, (MD), USA, sediment NIST 1941b has (non-certified) BC of ~7 to 10 mg/g using CTO-375 method we obtained a similar slightly higher value of 10.29 mg/g (n = 3) using modified CTO method (Hammes et al., 2007; Rawlins et al., 2008; Vane et al., 2021).

2.3. Total petroleum hydrocarbons (TPH)

Sediments (2 g) were extracted with dichloromethane/acetone (1:1 v/v) by accelerated solvent extraction (ASE, Dionex-300). Extracts were reduced to dryness and reconstituted in 1 mL of toluene and TPH determined by thin-layer chromatography-flame ionization detection (Chromarods-S III - Iatroscan Mk6) calibrated for saturate hydrocarbons using pristine and aromatic hydrocarbons using triphenylene (Vane et al., 2011; Vane et al., 2019). TPH concentration was calculated by summation of the saturate and aromatic hydrocarbons (Shantha and Napolitano, 1998; Volkman and Nichols, 1991) (Supplementary 2.3).

2.4. Polycyclic aromatic hydrocarbons (PAH)

Sediments (1 g) were spiked with deuterated standards, extracted using an ASE and PAH isolated for GC/MS analysis (Supplementary 2.4). PAHs concentrations were determined using a Thermo Scientific Trace 1300 GC coupled to a Thermo Scientific TSQ9000 triple quadropole MS operating in single ion monitoring (SIM) mode (ionization energy 70 eV). Sample application (1 μL) was by PTV injection operated in splitless

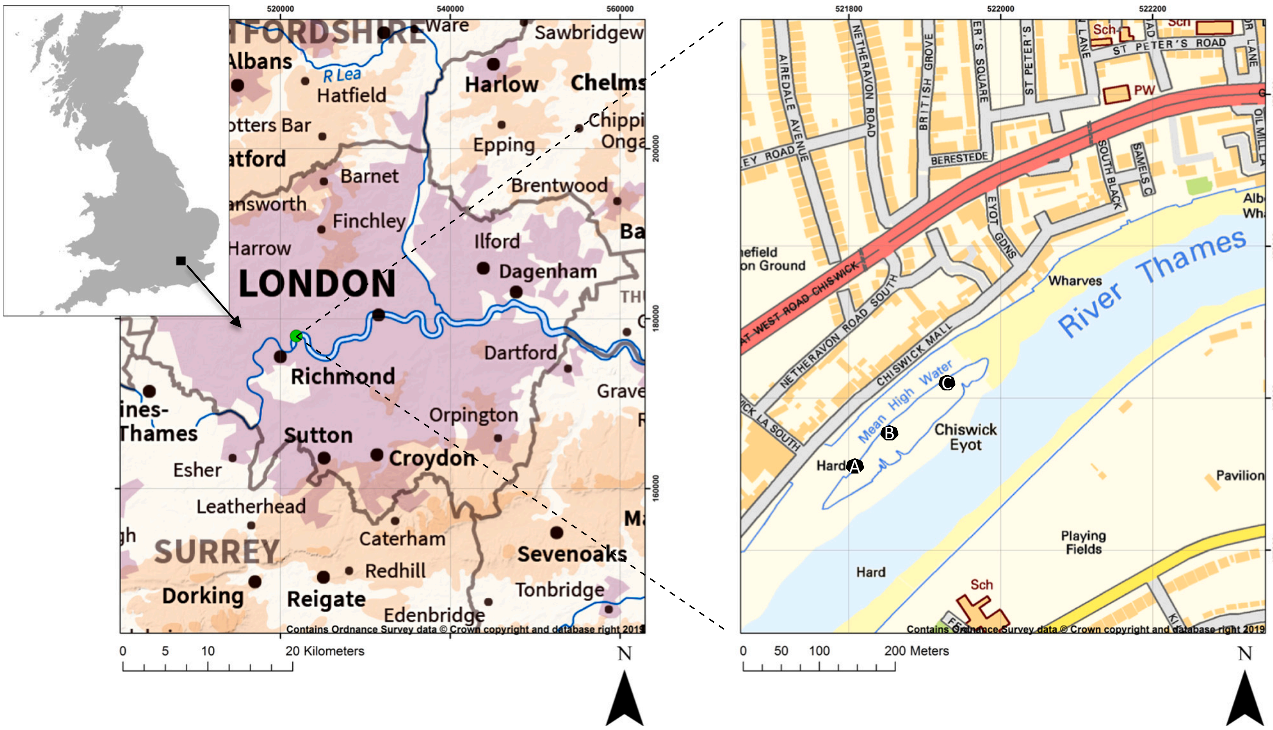

Fig. 1. Study area and core locations on Chiswick Ait/Eyot, River Thames, London, England, UK.

mode (1:10, 60 °C to 300 °C for 2 min at 14.5 °C/s). The GC was fitted with a Varian Select PAH column (30 m length × 0.25 mm i.d. × 0.1 μm film thickness). The GC oven-temperature programme was 70 °C (2 min. isothermal) to 180 °C at 85 °C/min. to 230 °C at 2.7 °C/min (7 min. isothermal) to 280 °C at 28 °C/min. (10 min. isothermal) to 350 °C at 14 °C/min (8 min. isothermal). Helium was used as the carrier gas (2 mL/min). Sample of reference material (NIST-1944: New York/New Jersey Waterway) 1 g (dry wt.) were inter-dispersed throughout ASE and GCMS runs for quality control (Supplementary 2.4).

2.5. *Pharmaceuticals and hormones*

Sediments (2 g dry wt.) were spiked with surrogate standards extracted using an ASE and isolated using SPE (supplementary). Each sample (100 μL) was injected into a triple-stage quadrupole (TSQ) Quantiva mass spectrometer (MS) coupled to an uHPLC Acella fitted with a guard column GOLD (3 m, 10 × 2.1 mm) and Hypersil Gold column (50 × 2.1 mm 1.9 μm) held at 40 °C with a flow rate of 0.3 mL/min. Detection and quantification were based on precursor and product ions of the 17 analytes using a 7 level calibration. A commercially certified reference material was unavailable, so spiked river sediment samples were used as QC material. Blanks and QC material were run every 10 samples to determine instrument background signal and performance (Supplementary 2.5).

2.6. *Sewage from faecal stanols and sterols*

Sediments (4 g dry wt.) were spiked with deuterated standards, extracted using ASE and cleaned/isolated using SPE (Supplementary). Faecal marker compounds were determined by gas chromatography–mass spectrometry (GC–MS-MS) using a Thermo Scientific Trace 1300-TSQ9000 triple quadropole MS in single ion monitoring (SIM) mode (ionization energy 70 eV). Sample application (1 μL) was by PTV injection, splitless mode (1:20, 150 °C to 310 °C for 2 min at 14.5 °C/s). The GC was fitted with a Agilent DB-5MS capillary column (30 m length × 0.25 mm i.d. × 0.10 μm film thickness). The GC oven-temperature programme was 60 °C (1 min. isothermal) to 200 °C at 20 °C/min. to 300 °C at 4.0 °C/min (5 min. isothermal). Helium was used as the carrier gas (1 mL/min). A 6-level calibration from 0.17 to 9.00 μg/μL was performed using: 5α-cholestane, coprostanol, 5β-epicoprostanol, coprostan-3-one, cholesterol, 5α-cholestanol, campesterol, stigmasterol, β-sitosterol, fucosterol, and stigmastanol. Retention times and characteristic ions were established for epicholestanol, 5β-brassicastanol, 5β-lichestanol, 5β-epibrassicastanol, 5β-campestanol, 5α-epicampestanol, 5β-epicampestanol, 5β-stigmastanol, brassicasterol, lichesterol, 5β-epistigmastanol, ergosterol, ethylcoprostanol, 5α-ergostanol, steliasterol, campestanol, ethylepicoprostanol and ambrien (Harrault et al., 2019; Kemp et al., 2021; Rowland et al., 2020; Vane et al., 2010). Tentative identification of cholest-3-ene, (5β), lupeol and glutinol was achieved using full-scan mode.

2.7. *Organotin*

Organotin determinations were performed at SOCOTEC laboratories, Burton on-Trent. Thames sediment was digested with HCl and MeOH and extracted into toluene. Extracts were derivatized using sodium tetraethylborate (STEB) and elemental sulphur removed from the sample using copper/silica clean-up. Concentrations of monobutyl-, dibutyl- and tributyltin (MBT, DBT, TBT) were measured using a Agilent 7890B GC coupled to a Agilent GCMS 5977 Turbo MS System fitted with a Rxi-5Sil MS Capillary GC 30 m × 0.25 mm, 0.25 μm + 10 m IntegraGuard. The GC oven ramped from 80 to 300 °C and the detector temperature was 230 °C with helium used as a carrier gas. Organo-tins were quantified by comparing the responses against a calibration curve made up of six standards for each of the target analytes. The limits of detection were ~0.005 μg/g, procedural blanks yielded values <0.001 μg/g. Quality assurance was established using certified reference material BCR 646, a fresh water sediment containing organobutyltin compounds TBT 480 ± 80, DBT 770 ± 90, MBT 610 ± 120 μg/g dry wt.

2.8. *Chronology*

The chronology presented herein is taken from the recent publication by Vane et al. (2020b) which used Pb isotope ratio ($^{207/206}$Pb) and caesium (^{137}Cs) activity in combination with peak trace metal and polychlorinated biphenyl (PCB) concentrations to understand historical event age-depth relationships at the same location (Supplementary 2.8). Of the cores assessed, core A yielded the most nuanced and consistent chronology, these dates are therefore presented in Fig. 2 (green text y axis). However, before proceeding it is important to note that owing to the dynamic nature of the Thames estuary, variable incorporation-lag times and coarse sampling intervals the dates conferred throughout are approximate.

3. Results and discussion

3.1. *Trends in black carbon*

Thames sediment Black Carbon (BC) concentrations ranged from 7.52 to 30.21 mg/g with a mean of 16.00 and median of 13.56 mg/g. Inspection of BC depth profile A shows basal values 15.84 to mid-core high 30.21 mg/g to near surface fall from to 7.56 mg/g; core B showed the same profile (Fig. 2). Peak BC concentrations were displaced down-profile (~10 cm) in core C suggesting greater sedimentation accumulation rate at this site. Identification of pollution horizons of known age from trends in Cs^{137}, Pb $^{207/208}$ and PCB contaminants have been reported (Vane et al., 2020b). Based on this established chronology, sediment cores (A, B) initial rise of BC occurs at depth interval conferred a date ~1940 at 45 cm depth reaching the maximal BC at 35 cm that corresponds to mid-1950s (Vane et al., 2020b) (Fig. 2). The decrease in BC concentrations from 25 cm to 15 cm occurs gradually from the 1960s to the early 1980s which parallels a general trend to relocate power stations, situated on the inner tidal Thames, away from central London to outside of central London (e.g. Battersea 1935 to 1983 CE, Lotts Road 1905 to 1977 CE, Fulham 1901 to 1978 CE, Bankside (now Tate Modern) 1893 to 1981 CE). Also, the fall in BC concentrations from 1960s to present day may also be caused an associated switch to oil powered boilers as compared to coal from late 1950s to 1980s. This notion is further supported by comparison of BC depth-profile with available UK coal power generation input which displays a similar rise, peak and fall pattern (1930–2018) with occasional inflections (e.g. Coal Miner strike 1984–1985) (Fig. 2c). However, the decrease in BC concentrations from 35 cm (Cores A, B) and (45 cm core C) to surface is also broadly coincident with key UK environmental legislation, such as the Clean Air Acts of 1956 and 1968 which introduced smoke control areas and use of smokeless domestic fuels as well as EC directives (1982–1990 CE) that aimed to reduce road vehicle exhaust emissions. Given that the analytical method used herein cannot distinguish BC source(s), it is prudent to conclude that the near surface decrease in BC observed in all these Thames cores could be due to a combination of diminishing power generation in central London, declining domestic coal use, switch to cleaner fuels as well as other factors such as improvement of air quality due to enhanced vehicle emissions testing (Fig. 2).

Thames BC concentrations are similar to those given for UK urban industrial soils of Glasgow (5 to 52.5 mg/g), Stoke (1.3 to 31.6 mg/g) and Coventry (1.0 to 62.3 mg/g) as well as from a urban soils from NE England (mean of 16.8 mg/g) (Edmondson et al., 2015; Rawlins et al., 2008). But, as expected, are higher than those reported in rural UK settings of woodland (0.49 to 2.0 mg/g, mean 1.35 mg/g) and grassland (0.55 to 1.64 mg/g, mean 1.27 mg/g) (Nam et al., 2008). Conversely, the BC concentrations reported here at Chiswick are similar to London

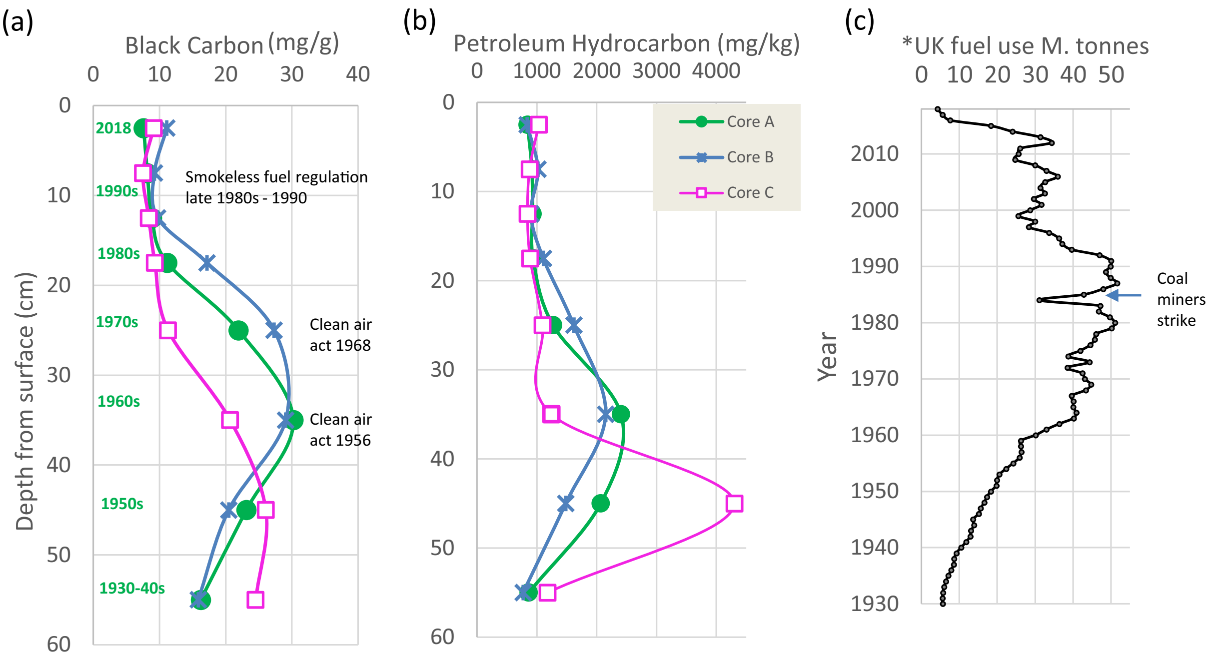

Fig. 2. Sedimentary chemical depth-profiles from inner Thames estuary: a) Black carbon (BC) concentrations (dates assigned from combined Cs^{137}, $Pb^{207/208}$, polychlorinated biphenyls records (Vane et al., 2020a, 2020b)); b) Total petroleum hydrocarbons concentrations (TPH); c) Changing UK coal and oil use 1930 to 2018.

surface soils (3.72 to 32.71 mg/g, mean 13.8 mg/g) (Vane et al., 2021). When taken together, this suggests that the inner Thames sediments contain very similar BC concentrations as London soils. Comparison to other international aquatic sediments suggest that the inner Thames estuary has higher BC concentrations which is commensurate with numerous current and historical BC producing activities in and around London as well as its location within the innermost reaches of the urban estuary as compared to outer estuary or open coastal settings (Table 1).

The high concentration of BC in Thames sediments is important as elevated BC contents have been shown to enhance the sorption of a variety of organic pollutants including PAH, PCB, pentachlorophenol, nonylphenol and chlorinated pesticides as compared to that of the % TOC in the sediment (Cheng et al., 2017; Lou et al., 2012; Yang et al., 2012). Further, measurement of ^{14}C phenanthrene in soils amended with BC incubated for 20 days suggested a decrease in bioaccessibility to microbial degradation via entrapment in nanopores (Rhodes et al., 2008). Conversely, measurement of pyrethroid insecticides in sediments amended with BC (charcoal) were found to be similar to that of the overall TOC % due to the large molecular weight and size hindering diffusion into nanopores (Yang et al., 2009).

Table 1
Comparison of sedimentary black carbon (BC) concentrations from Europe, N America and SE Asia.

Study area	Black carbon mg/g dry wt	Sample type	Reference
Thames estuary (UK)	7.52–30.22 (16.00)	Cores 1940s-2018	This study
Pearl River Delta (China)	0.4–4.6	Cores 1900s-2000	(Sun et al., 2008)
East China Sea (China)	0.13–1.52 (0.86)	Surface	(Huang et al., 2016)
Pettaquamscutt estuary (USA)	4.7–6.10	Cores 1750–1999	(Hanke et al., 2017)
Gulf Maine, Harbors (USA)	1.76–6.94	Surface	(Gustafsson and Gschwend, 1998)
Plateau Lakes (Tibet)	0.04–64.5 (15.5)	Cores, 1800s-2018	(Neupane et al., 2019)

3.2. *Trends in petroleum hydrocarbons*

In the UK, total petroleum hydrocarbons mainly occur in soils and sediments by accidental release of crude and refined oils, road run-off (e.g. vehicle engine leaks, petrol), incorporation of brownfield soils as well as discharges from ports, marine vessels and pipelines. Consequently, TPH concentrations have been shown to track industrialisation in sediments from Clyde estuary (Scotland, UK) and increase with depth in London soils; (Jones et al., 2019; Vane et al., 2011; Vane et al., 2021).

Thames sediment TPH ranged from 770 to 4301 mg/kg with mean of 1280 (core A), 1235 (core B) and 1432 mg/kg (core C) (Fig. 2). All three TPH profiles show a minima at the base (1930s–1940s) before rising to the highest concentrations of 2408 and 2150 mg/kg at 35 cm (cores A, B) and 4301 mg.kg^{-1} at 45 cm (core C) which corresponds to 1950 to mid-1960s (Fig. 2b). From these maxima the TPH concentrations then decline (1970s to 1980s) before stabilising at 12.5 to 2.5 cm depth (1990s) to concentrations of 837 to 1032 mg/kg near the surface (2018) which are similar to those values observed at the base of the core (Fig. 2b). When taken together the TPH depth profiles suggest that TPH pollution at surface (2018) has fallen to about the same as that encountered in 1930s–1940s and between 2 and 4 times lower than that in sediments conferred dates of 1950s to 1960s (Fig. 2b). As with BC concentrations, the peak of sedimentary TPH pollution appears to be broadly co-incident with peak power-generation from central London's larger decommissioned power stations (e.g. Battersea, Bankside (now Tate Modern)) as well as increased wastewater treatment capacity (e.g. Mogden STW) but are not synchronous with overall UK Fuel use data which reaches its maxima in 1987 (Fig. 2c). Conversely, the gradual decline in TPH from early 1970s and late 1980s is approximately co-incident with clean air act 1968 and use of smokeless fuel and/or decline in number of riverside industries and commercial vessels on the tideway. A survey of non-volatile TPH in urban soils collected from central London (n = 73 sites) reported lower TPH at surface (0–2 cm depth, 72 to 4673 mg/g, mean 421 mg/kg, median 298 mg/kg) compared to sub-surface (5–20 cm depth, 89–2618 mg/kg, mean 466 mg/kg, median 346 mg/kg) which is consistent with the near surface decrease displayed in the Thames sediment cores (Fig. 2b) (Vane et al., 2021). The higher TPH concentrations in these Thames sediments as compared to London soils situated in close proximity could be due to a range of factors such as; 1) TPH pollution from boats/shipping; 2) TPH from local industries/treatment works effluent discharge in close proximity to the study site and; 3) differences in rates of post-depositional decay and or mixing (soil > aquatic sediment).

Currently, no UK sediment quality guidelines (SQG) for non-volatile TPH in river-estuarine and coastal sediments exist. Evaluation of TPH SQG used in other countries reveals a wide variety of benchmarks depending on region, background values and environmental relevance as well as analytical methodology. For example, Australia and New Zealand TPH benchmarks are <280 mg/kg (no concern) and >550 mg/kg (of concern) whereas those in Nigerian sediments are <50 mg/kg to >5000 mg/kg (intervention) (Boyce and Michelsen, 1993; Simpson et al., 2013). Based on these guidelines we therefore propose that sediments at the 35 to 45 cm (>2000 mg/kg) might be of possible concern, but only if the sediment is disturbed remobilised, whereas those at other depth intervals (1000 to 1618 mg/kg) should be considered as urban background and less likely to cause adverse biological effects.

3.3. Trends and source of polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbon concentrations (Σ^{16}USEPA) ranged from 6.93 to 107.64 mg/kg with a mean value for all depth intervals of 36.46 mg/kg. Concentration depth-profiles of the both Σ^{16}PAH and individual parent PAH compounds spanning 3 to 6 ring PAHs show the same systematic decline toward the core surface, all be it with core C maxima occurring 10 cm down-profile compared to cores A and B (Fig. 3). Thames sediment PAH increased from 1930s–40s reaching a peak in early to mid-1950's before steadily declining in concentration from 1960's and 1970s as well as 1980s. All three cores show a less pronounced but nevertheless detectable decline in PAH in the upper 10 to surface (1990s to 2018) including the key human health PAH benzo[*a*]pyrene, which is commensurate with atmospheric PAH records (PM10) from London (Supplementary). Comparison of the PAH to BC and PAH to TPH concentrations reveal different profiles indicating either multiple diffuse pollution sources and or different transport mechanisms and/or depositional lag-times. The peak PAH concentration (at 45 and 55 cm) in the 1950s is probably due to widespread domestic coal burning and or coal fired power stations (e.g. Battersea, Bankside,

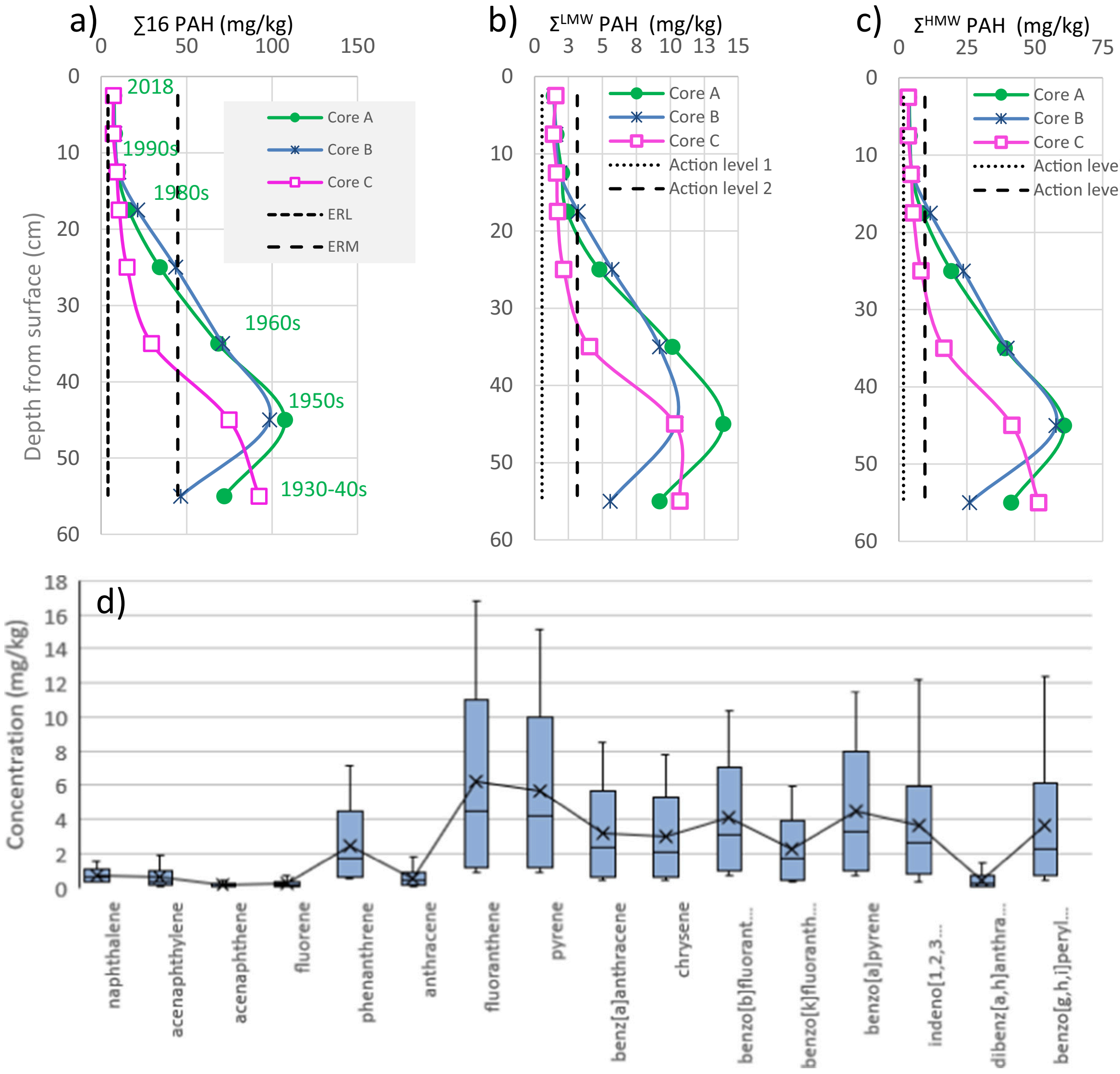

Fig. 3. Sedimentary polyaromatic hydrocarbon (PAH) depth-profiles for; a) total USEPA 16 PAH, b) low molecular weight PAH and c) high molecular weight PAH, dashed vertical lines on depth -profiles represent non-statutory marine-estuarine sediment quality guidelines, values above AL2 suggest likely effect on sediment-dwelling biota; d) Box and whisper plot for individual PAH. The boundary of the box indicates the 25th and 75th percentiles, the x and line within the box denotes the mean and median and the error bars indicate the 10th and 90th percentiles.

Fulham, Lotts Road, Stepney Bank). This notion is supported in part by historical events such as the London smog of December 1952 which killed between 4000 and 12,000 inhabitants and led to growing awareness of the link between pollution and public health culminating in new regulation legislation (clean air act 1956) which promoted the use of smokeless fuels (Bell et al., 2004).

Source apportionment using parent PAH ratios provides a broad indication of the main aromatic hydrocarbon inputs in river-estuaries (Boehm et al., 2018; Budzinski et al., 1997; Vane et al., 2011). Inspection of Ph:An/Fl:Py bi-plot suggests a combustion source (Supplementary 3.3). Whereas, the slightly more nuanced evaluation using B[*a*]A:Ch/Fl:Py and B[*a*]A:B[*a*]P/Fl:Py bi-plots suggest PAH combustion sources from coal, industrial processing (carbonisation, coke and tar) and vehicle exhaust (Supplementary 3.3).

PAHs were negatively correlated with TOC (%) (Core-A R^2 0.03, Core-B R^2 0.62, Core-C R^2 0.2) but were positively correlated to BC (Core-A R^2 0.6, Core-B R^2 0.50, Core-C R^2 0.85) (Supplementary 3.3). The clear correspondence between PAH and BC in the Thames sediment cores may be due to an identical combustion source (co-emission) and/or sorption of PAH onto BC (e.g. soot) surfaces and/or trapping within BC occlusions (Accardi-Dey and Gschwend, 2002; Cornelissen and Gustafsson, 2004; Koelmans et al., 2006). Overall, the strong association between PAH to BC supports the view that in many urban soils and sediments BC exerts a stronger control on sorption of organic pollutants, such as PAH, than the overall TOC (Accardi-Dey and Gschwend, 2002; Vane et al., 2021). The negative PAH to TOC is caused by the higher TOC (>4–10%) in the upper~20 cm of each core.

3.4. Polyaromatic hydrocarbons sediment quality

Thames sediment PAH were compared to consensus guideline values effects on marine and estuarine sediment dwelling biota using effects range low (ERL) and effects range median (ERM) criteria (Fig. 3 and supplementary 3.3)(Long et al., 1995). Sediments from the base to mid core (55 to 35 cm depth) exceeded ERL (44.79 mg/kg) suggesting the likelihood of adverse effects, whereas sediments from 25 cm to surface were between ERL (4.02 mg/kg) and ERM which cannot be taken to indicate either likely or unlikely effect (Fig. 3 and Supplementary 3.3). Benchmarking of individual parent PAH such as fluorene, phenanthrene, anthracene, pyrene, benz[*a*]anthracene, indenol[1,2,3-*cd*]pyrene and benza[*a*]pyrene revealed the same exceedance of ERL in the deeper intervals and concentrations that decrease between ERL and ERM values in the upper intervals (Supplementary 3.3). In contrast, the lowest molecular weight PAH naphthalene did not exceed ERM at any depth interval but did exceed ERL.

In the UK, new marine management action levels (AL) for dredge and disposal at sea are currently under review for a range of pollutants including PAH (Mason et al., 2020). Owing to variations in physico-chemical properties PAH low molecular (LMW) and high molecular weight (HMW) have been separated in the revised criteria to enable a more nuanced evaluation so that ΣPAH^{LMW} (naphthalene, acenaphthene, fluorene, anthracene, C1- naphthalenes, acenaphthylene, phenanthrene) give AL1 0.55 mg/kg and AL2 3.16 mg/kg and ΣPAH^{HMW} (fluoranthene, pyrene, benz[*a*]anthracene, chrysene, benzo[*a*]pyrene, dibenz[*a,h*]anthracene) give AL1 1.7 mg/kg and AL2 9.6 mg/kg (Mason et al., 2020). Based on these proposed benchmarks all near surface sediments <20 cm depth, decrease between AL1 and AL2 for both ΣPAH^{LMW} and ΣPAH^{HMW} which suggest further assessment action is required and exceedance of AL2 at >35 cm depth for both ΣPAH^{LMW} and ΣPAH^{HMW} suggest these deeper more contaminated depth intervals are possibly unsuitable for disposal at sea (Fig. 3 and Supplementary 3.3).

3.5. Sewage marker compounds

Faecal sterols are an established chemical markers for sewage in river, estuarine and marine environments that facilitate tracking plumes, mapping dump sites and in some instances permit source identification and/or extent of sewage treatment (Goodfellow et al., 1977; Hatcher and McGillivary, 1979; Leeming et al., 1996; Vane et al., 2010). Untreated human faeces contain high concentrations of coprostanol compared to most other animal faeces and environmentally altered or treated sewage yields a higher concentrations of epi-coprostanol and or ethylcoprostanol (Grimalt et al., 1990; Mudge and Ball, 2006; Pratt et al., 2008). In contrast, the precursor compound cholesterol is ubiquitous and inputs from plant biomass or ruminant animal dung and maybe identified on the basis of elevated stigmasterol and β-sitosterol relative to other faecal sterols.

In this study (Fig. 4), concentrations of the human faecal marker compound coprostanol ranged from 0.0091 to 0.42 mg/kg with a mean of 0.146 mg/kg median 0.122 mg/kg and epicoprostanol ranged from 0.007 to 0.018 mg/kg. Coprostanol values <0.10 mg/kg are reported to indicate no sewage input whereas values >0.10 mg/kg may indicate sewage contamination (Cabral et al., 2019). Using these rather conservative criteria 17 of the 19 sediment intervals at Chiswick contain sewage. Both depth profiles (Cores A, B) increased from base of the core to a peak at 35 cm (1960s) and then declined before increasing from 10 cm to surface 2.5 cm. Conversely, the plant and/or herbivore markers, sitosterol and stigmasterol were invariant from base of the core up to 20 cm depth and then increased to surface which is probably due to increasing incorporation of plant organic matter (e.g. particulates/stem debris) in the upper intervals (Fig. 4). Consequently, the Σ^{19} sterols depth-profile show features common to both human sewage and plant sterol/herbivore sources.

Diagnostic sterol ratios such as coprostanol: cholesterol and coprostanol/(coprostanol + cholestenol) offer a complimentary approach to tracking sewage input in estuaries and coastal environments as compared to using a single concentration by minimising, sediment dilution, grain-size and TOC sorption and source mixing effects (Grimalt et al., 1990). In this study, the coprostanol: cholesterol ratio exceeded the 0.2 threshold value in all three cores which supports continuous, but variable, deposition of sewage from 1930s–40s to 2018. In contrast, only 10 sediments out of 21 exceeded the coprostanol/(coprostanol + cholestenol) 0.7 threshold (Fig. 4). Also, inspection of the epicoprostanol/coprostanol: coprostanol/cholesterol plot suggests that the faecal matter had undergone extensive sewage treatment (Fig. 4), which is to be expected since Chiswick Ait is situated 8 km upstream of the discharge point of Mogden STW, that receives and treats waste water from 2 M people living in North and West London. Combined concentration profiles and source ratios indicate that sediments from Chiswick Ait contain moderate amounts of treated sewage.

3.6. Pharmaceuticals

Pharmaceuticals and their metabolites are mainly discharged into urban river-estuary sediments via effluents from sewage treatment plants (STPs), industrial and hospital wastewaters. Modelled pharmaceutical removal rates during sewage treatment processes such as biodegradation, sorption to sludge, and stripping to air are 70 to 98% efficient which leads to on-going re-release of pharmaceuticals (2–30%) in STP effluent that can transfer to bed and foreshore sediments (Jones et al., 2002). Owing to lack of baseline data and appropriate ecotoxicological evidence such as that used to assess legacy contaminants (e.g. PAH, PCB, TBT, trace metals), pharmaceuticals are not currently considered within the suite of pollutants required for marine management such as sediment dredge and disposal at sea operations in the UK. Consequently, this baseline data is needed, to establish background concentrations particularly for urban estuaries which receive appreciable amounts of waste water effluent and are also frequently dredged for navigation.

In this current study (Fig. 5), carbamazepine and its metabolite epoxicarbamazepine were present at all depth intervals (100% frequency of detection (FD)) whereas the antibiotics chlarithromycin and

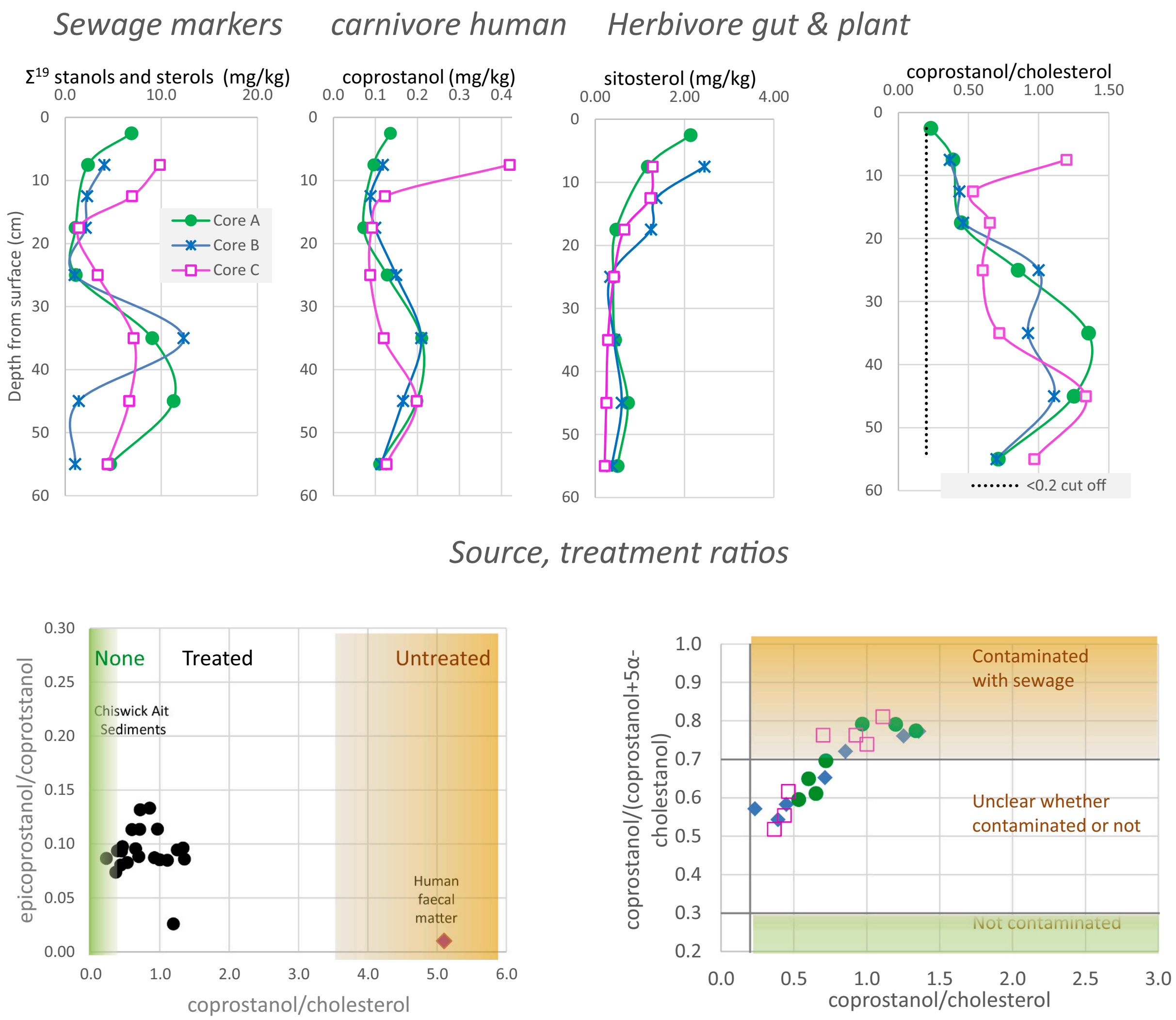

Fig. 4. Sewage marker compound depth-profiles and source apportionment/treatment bi-plot, Thames estuary, Chiswick Ait, London, England, UK.

azithromycin had 50% FD each, ibuprofen and estradiol showed a FD of 42% and acetaminophen (paracetomol) was only present at the top of core A (4% FD). The other pharmaceuticals (salbutamol, atenolol, caffeine, ifosfamide, cyclophosphamide, erythromycin, sertraline, progesterone, estriol and estrone) were either not present or below detection limits. Total pharmaceuticals ranged from 2.4 μg/kg at the bottom of core A, to maximal concentrations of 84.8 μg/kg at the top (surface) of core C confirming increasing contamination within inner tidal Thames with time. The antibiotics, namely chlarithromycin and azithromycin ranged from 0.02 to 12.80 μg/kg, mean 2.16 μg/kg and 0.05 to 12.28 μg/kg, mean 2.86 μg/kg respectively (Fig. 5). The hormone 17β-estradiol ranged from 4.21 to 17.47 μg/kg, mean 10.53 μg/kg and the pain relief/anti-inflammatory drug ibuprofen ranged from 3.30 to 12.99 μg/kg, mean 7.66 ng/g. The highest concentrations were from the antiepileptic, carbamazepine 2.36 to 30.85 μg/kg, mean 13.59 μg/kg whereas concentrations of its metabolite epoxicarbamazepine ranged from 0.06 to 1.54 μg/kg, mean 0.61 ng/g. Comparably high carbamazepine concentrations (10 to 46.5 μg/kg) have been reported for sediments collected in close proximity to a sewage discharge site on the River Medway, Kent, UK; which confirmed its recalcitrance to environmental degradation and sewage treatment (Zhou and Broodbank, 2014). In contrast, measurement of 17β-estradiol from the Rivers Uck and Ouse, UK reported low values of <0.5 to 4 μg/kg suggesting relatively higher inputs here in the Thames.

Total pharmaceuticals were moderately correlated to TOC (R^2 = 0.44) and weakly correlated to human sewage marker coprostanol (R^2 = 0.0139) but were strongly associated with the plant sterol markers sitosterol (R^2 = 0.65) and stigmasterol (R^2 = 0.81). However, it seems unlikely that the correspondence is directly causative and the association is probably best explained by an-overall increase in plant organic matter particulates near surface (0 to 17.5 cm depth).

Inspection of the antibiotics, clarithromycin and azithromycin depth profiles reveal a sharp increase in concentrations from 7.5 cm to surface, the on-set of which closely matches the known market release date in UK of 1991 (Fig. 5) (Currie et al., 2014). The occurrence of clarithromycin and azithromycin concentrations (0.22 to 0.82 μg/kg) at depths 12.5 and 17.5 cm (1980s) suggests either minor environmental release prior to full production or possibly minor mobility or both. Conversely, ibuprofen was not detected at 1969 being its official market date (Halford et al., 2012) but occurred some 10 cm up-profile in sediments conferred a date of 1980s. Ibuprofen, then increased from 17.5 cm depth (Cores A, C) to the surface, tracking increasing use from 1980s to present day (2018). 17β-estradiol profile also begins from 1980s, the period it was widely used orally (Martin et al., 1972) and varied in a non-systematic manner from 17.5 cm to surface (4.20 to 17.47 μg/kg) (Fig. 5). The antiepileptics, carbamazepine and its metabolite epoxycarbamazipine were found at all depth intervals even those preceding market date of 1965 and discovery date of 1953 (Tolou-Ghamari et al., 2013). The occurrence of carbamazepine at all depth intervals may be explained by its moderate mobility in soils and sediments (K_{oc} values

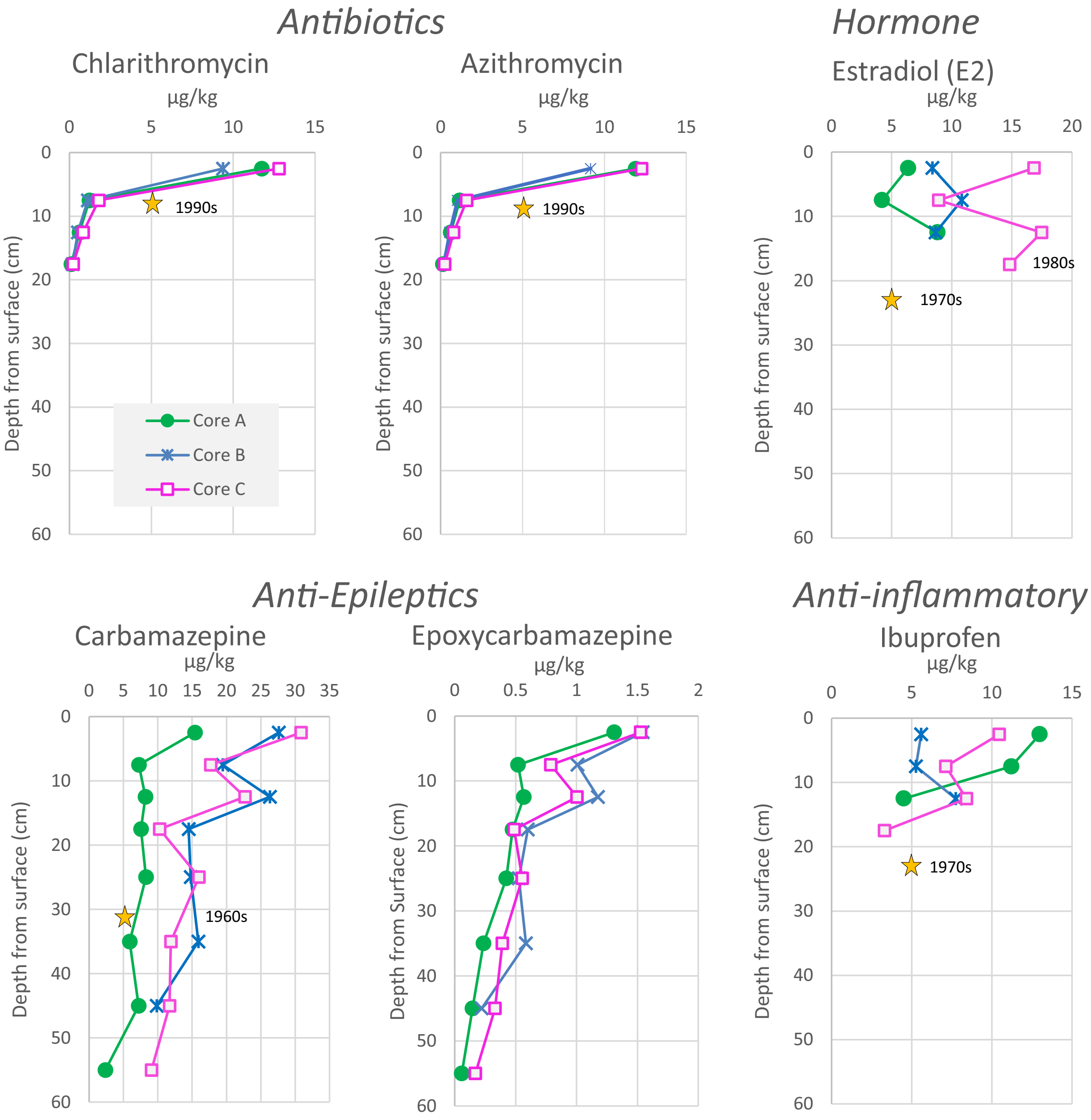

Fig. 5. Increasing sedimentary pharmaceutical concentrations in the Thames estuary, Chiswick Ait, London, England, UK.

often below 200 L.Kg^{-1}) together with its high persistence in the environment and low degradability during sewage treatment (Loffker et al., 2005). However, the close correspondence of the other pharmaceuticals and other organic contaminants (e.g. BC, TPH, PAH, TBT) to the conferred dates (Cs^{137}, Pb$^{206/207}$, PCB) indicates appreciable mobility, which in-turn confounds carbamazepine and epoxycarbamazipine use in approximate of dating sediments in the inner Thames.

3.7. *Depth trends in organotins*

Organotins are legacy toxic and endocrine disrupting contaminants of coastal sediments and river-estuaries which occur via leaching and flaking from antifouling paints applied to boat hulls and manufactured products including stabilizers added to polyvinyl chloride (PVC) as well as wood preservatives. Tributyl-tin (TBT) the main active compound can degrade to dibutyltin (DBT) and monobutyltin (MBT) which favour partitioning from water to sediment (Langston and Pope, 1995). Organotins were first used as antifouling agents in 1960s and due to their effectiveness saw increased usage throughout the 1970s. However, a series of field observations coupled with laboratory trials demonstrated that exposure to TBT negatively affected community structure, health and reproduction of a broad range of marine biota including commercially and ecologically important dog whelks, gastropods and bivalves (Langston and Pope, 1995; Waite et al., 1991). Therefore, in the UK the use of TBT was banned for boats smaller than 25 m length in 1987 and this was further extended to large vessels from 2003/2008 as part of EU legislation.

Sediment TBT concentrations in the Thames ranged from <0.005 to 0.85 mg/kg with a mean of 0.026 mg/kg (all core depth intervals) (Fig. 6). Inspection of the TBT depth-profiles reveal on-set, rise, peak and slight fall in $\sum$TBT with maximum TBT values reached at 17.5 cm cores A, B (Fig. 6a and 25 cm core C (Fig. 6b). Previous evaluation of Cs^{137}, Pb $^{207/208}$ and total PCB records suggest that the maximal TBT concentrations conferred a date of mid 1980s (Vane et al., 2020b). In the UK TBT biocide use and successive bans are well documented and proceeded in the following order; 1) 1960s low use, limited manufacture:2) 1970 to 1975 increasing use; 3) 1975 to 1986 maximum usage (pre-ban); 4) 1986 to post-ban of use on small (<25 m) vessels; 5) 2003 to 2008 ban all vessels. These changes in production and legislation are tracked in the pollutant profiles (Fig. 6); for example, sediment interval(s) conferred a date of mid-1980s are broadly coincident with peak $\sum$TBT. However, the presence of organotins at the surface (0–5 and 5–10 cm)

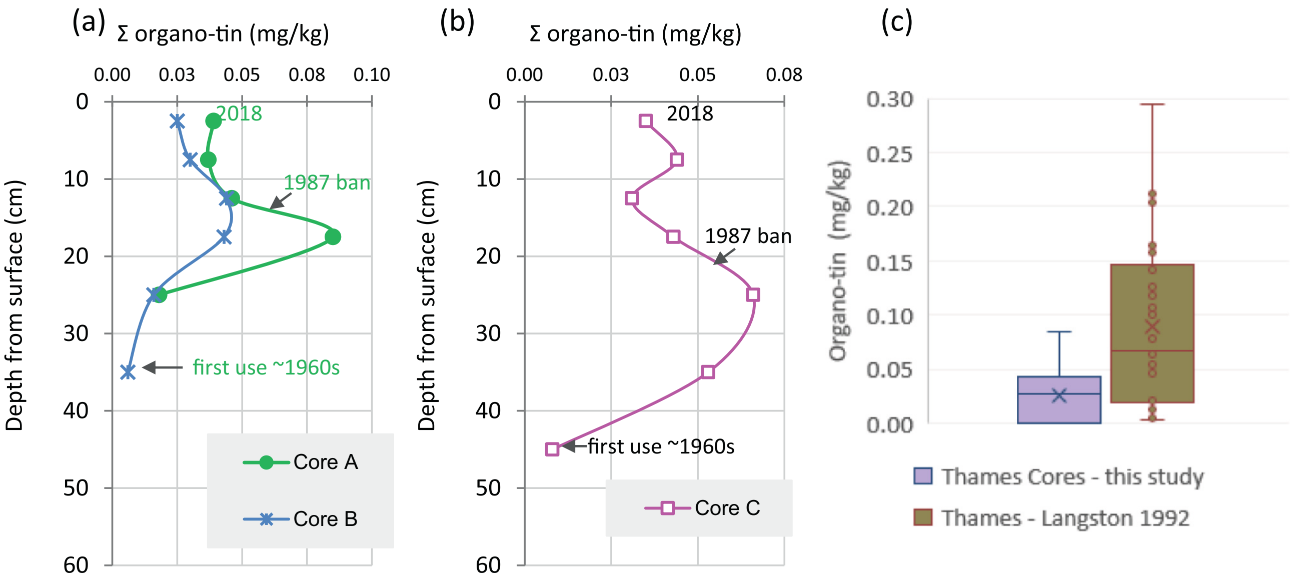

Fig. 6. Organotin concentration sediment depth-profiles, Thames estuary, Chiswick Ait, London, England, UK.

some 32 years after they were banned from application to small craft of <25 m length, suggests either long term persistence, possibly due to sorption protection offered by the fine silt and clay sediments and/or possibly a local unknown point-source origin. Comparison of TBT to earlier surveys of the inner Thames in 1997 (0.029 to 0.112 mg/kg, mean of 0.065 mg/kg) and upper-middle Thames ranged from 0.0732 to 0.1098 mg/kg with a mean 0.09028 mg/kg does however confirm an overall decrease in Thames organo-tins (Fig. 6c) (Harino et al., 2003; Langston et al., 2000; Pope and Langston, 2011).

River-estuarine surface sediment values in the UK typically range from 0.005 to 0.5 mg/kg dry weight (Bryan and Langston, 1992; Langston et al., 2012). For example organotin concentrations from Poole Harbour sediments (SE England) ranged from 0.0019 to 1.05 mg/kg (n = 16) with TBT varying from 0.009 to 0.517 and DBT from 0.007 to 0.573 mg/kg (Bryan and Langston, 1992). Similarly, TBT concentrations in estuaries and coastal water sediments in Denmark 1998–2004 ranged from 0.0012 to 0.16 mg/kg with the highest yields recorded in more restricted bays and fjords. Therefore, based on these comparisons, the TBT concentrations in this study are typical of other river-estuarine and coastal sediments.

Non-statutory sediment quality guidelines primarily used for the tidal river management and dredging licence applications in England for TBT and its decay products (TBT + MBT+ DBT) are Action level 1, ≥0.1 mg/kg and Action level 2, ≥1 mg/kg. These marine environment quality triggers are then used with complementary data to indicate whether further investigations are necessary or, if unsuitable, for disposal at sea. In this study, none of sediments exceeded either AL trigger values, suggesting that the TBT held in the sediment at Chiswick is unlikely to cause harm to ecology or humans nor strongly influence a dredging licensing or tideway management decision.

4. Conclusions

1) This study shows that organic pollution accumulating in urban sediments of the inner Thames estuary has changed since the de-industrialisation of London, as shown by a decline in compound classes (BC, TPH, PAH) sourced from raw or processed/heated fossil fuels and a rise at the near surface of both legacy and synthetic emerging contaminants (pharmaceuticals and hormones). Two of the cores (A, B) showed very similar multi-contaminant depth/time-trends whereas in core (C) peak events from all contaminants were shifted down (~10 cm) which we attribute to variations in sediment accumulation rate as a consequence of position in the tidal frame and inlet distance. Notwithstanding complications in sediment accumulation rates, market to sediment incorporation lag times and post depositional degradation and transport, the organic pollutants in these shallow sediment cores provide an excellent means to evaluate sewage treatment and discharge practices and the effectiveness of urban/regional and environmental regulation over years to decades.

2) The contribution of common antibiotic, anti-inflammatory and anti-epileptic pharmaceuticals has increased since their introduction to the market (late 1960s to 1990s) such that antibiotics have increased 50-fold and anti-inflammatory and anti-epileptics 3-fold. This rise is commensurate with published prescription records as well as the modifying effects of sewage treatment which reduce influent concentrations by 70 to 96%. Antimicrobial resistance (AMR) has been identified as one of the top 10 global public health threats facing humanity, therefore the clear increase in Thames sediment regime is of concern as this could contribute to AMR in the UK (WHO, 1998). However, owing to the paucity of data there are no regulatory requirements for pharmaceuticals in UK sediments, therefore we propose that surface sediment (0–5 cm) concentrations of chlarithromycin, azithromycin, 11 μg/kg, carbamazepine, 25 μg/kg and ibuprofen 10 μg/kg could be used alongside other data to inform future legislation and contribute to the setting of background values. Although it is entirely reasonable to assume that sewage effluent is the main source of pharmaceuticals in the Thames we did not find a strong correlation with key human sewage compound coprostanol but did find a strong correlation with plant sterols (which are found in animal dung as well as natural plant sources); however, it is unclear whether this correlation is causative or coincidental. The presence of anti-epileptics, carbamazepine and epoxcarbamazepine at depths conferred a date 1940s suggests appreciable down-core mobility which in-turn calls into question its utility as chemical dating tool.

3) Hydrocarbon pollution profiles (TPH, PAH) co-varied with a systematic rise (1940s), peak (1950s-late 1960s) and fall (1970s–1990s) that maybe ascribed to historical decline in London's waterside industries, changes in power generation (capacity, fuel type), and housing, domestic coal burning as well as broader improvements in river management and environmental regulation/legislation in and around London. We show that since peak pollution of PAH in the 1960s their concentrations have declined 25-fold whereas TPH concentrations have only decreased 3-fold. This difference in the extent of decline between hydrocarbon compound classes is probably due to the former originating

from power generation, waste from manufactured gas-works and domestic coal burning, whereas TPH is sourced from more general (mixed) urban sources and or post depositional alteration in the sediment matrix. These changes broadly track regulation such as clean air acts of 1958, 1968 and replacement of coal with smokeless fuels in late 1980s. From a river-estuary management standpoint the presence of PAH at about 100 mg/kg >35 cm depth below surface, which is over twice UK SQG action level is of concern, particularly given that Chiswick Ait is subject to erosion due to increasing flooding. The situation is less clear for the upper 0 to 35 cm interval, which gave PAH that decrease between AL1 and AL2 and would trigger further investigation for dredging licensing. The close comparability of these Thames sediment cores (Σ^{16}PAH 6.93 mg/kg to 107.64 mg/kg, mean 36.46 mg/kg) to that recently reported for London soils (Σ^{16}PAH 1.64 to 421.23 mg/kg mean 47.99 mg/kg) is probably best explained by supply source/supply, modest amount of mineral dilution and the presence of high concentrations of black carbon which acts as a sorbent for hydrophobic organic contaminants.

4) Despite being banned from use more than 30 years ago TBTs remain ever present in Thames estuary sediments due to their widespread use as anti-fouling agents in paints applied to shipping prior to 1987. Although TBT profiles show a clear rise, peak and partial fall at surface, concentrations are approximately 50 times below the UK non-statutory SQG which in turn confirms they are not of concern and demonstrates their effectiveness of local (tidal Thames), national and global regulation/legislation (UN-EP, 2009).

CRediT authorship contribution statement

Christopher Vane: Conceptualization, Field Collection, Analyses, Primary Writing; **Alexander Kim**: Analyses, Secondary Writing.; **Raquel Lopes dos Santos**: Analyses, Secondary Writing.; **Vicky Moss-Hayes**, Analyses.

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.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.marpolbul.2022.113340.

References

Accardi-Dey, A., Gschwend, P.M., 2002. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. Environ. Sci. Technol. 36 (1), 21–29.

Bell, M.L., Davis, D.L., Fletcher, T., 2004. A retrospective assessment of mortality from the London smog episode of 1952: the role of influenza and pollution. Environ. Health Perspect. 112 (1), 6–8.

Boehm, P.D., Pietari, J., Cook, L.L., Saba, T., 2018. Improving rigor in polycyclic aromatic hydrocarbon source fingerprinting. Environ. Forensic 19 (3), 172–184. https://doi.org/10.1080/15275922.2018.1474287.

Boyce, C.P., Michelsen, T.C., 1993. Cleanup standards for petroleum hydrocarbons. Part 2. Case study comparisons of site-specific cleanup standards with generic TPH standards. J. Soil Contam. 2 (3), 265–280.

Bryan, G.W., Langston, W.J., 1992. Bioavailability, accumulation and effects of heavy-metals in sediments with special reference to the United Kingdom estuaries- a review. Environ. Pollut. 76 (2), 89–131.

Budzinski, H., Jones, I., Bellocq, J., Pierard, C., Garrigues, P., 1997. Evaluation of sediment contamination by polycyclic aromatic hydrocarbons in the gironde estuary. Mar. Chem. 58 (1–2), 85–97.

Cabral, A.C., Wilhelm, M.M., Figueira, R.C.L., Martins, C.C., 2019. Tracking the historical sewage input in south american subtropical estuarine systems based on faecal sterols and bulk organic matter stable isotopes (δ13C and δ15N). Sci. Total Environ. 655, 855–864.

Cheng, G., Sun, M., Ge, X., Xu, X., Lin, Q., Lou, L., 2017. Exploration of biodegradation mechanisms of black carbon-bound nonylphenol in black carbon-amended sediment. Environ. Pollut. 231, 752–760.

Cornelissen, G., Gustafsson, O., 2004. Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and native sorbates. Environ. Sci. Technol. 38 (1), 148–155.

Currie, C.J., Berni, E., Jenkins-Jones, S., Poole, C.D., Ouwens, M., Driessen, S., de Voogd, H., Butler, C.C., Morgan, C.L., 2014. Antibiotic treatment failure in four common infections in UK primary care 1991–2012: longitudinal analysis. BMJ [Br. Med. J.] 349, g5493.

Edmondson, J.L., Stott, I., Potter, J., Lopez-Capel, E., Manning, D.A.C., Gaston, K.J., Leake, J.R., 2015. Black carbon contribution to organic carbon stocks in urban soil. Environ. Sci. Technol. 49 (14), 8339–8346.

Ganci, A.P., Vane, C.H., Abdallah, M.A.-E., Moehring, T., S, H., 2019. Legacy PBDEs and NBFRs in sediments of the tidal River Thames using liquid chromatography coupled to a high resolution accurate mass Orbitrap mass spectrometer. Sci. Total Environ. 658, 1355–1366.

Goodfellow, R.M., Cardoso, J., Eglinton, G., Dawson, J.P., Best, G.A., 1977. A faecal sterol survey in the Clyde estuary. Mar. Pollut. Bull. 8 (12), 272–276.

Grimalt, J.O., Fernandez, P., Bayona, J.M., Albaiges, J., 1990. Assesment of fecal sterols and ketones as indicators of urban sewage inputs to coastal waters. Environ. Sci. Technol. 24, 357–363.

Gustafsson, Ö., Gschwend, P.M., 1998. The Flux of Black Carbon to Surface Sediments on the New England Continental Shelf. Geochim. Cosmochim. Acta 62 (3), 465–472.

Halford, G.M., Lordkipanidzé, M., Watson, S.P., 2012. 50th anniversary of the discovery of ibuprofen: an interview with dr Stewart Adams. Platelets 23 (6), 415–422.

Hammes, K., Schmidt, W.I., Smernik, R.J., Currie, L.A., Ball, W.P., Nguyen, T.H., Louchouarn, P., Houel, S., Gustafsson, O., Elmquist, M., Cornelissen, G., Skjemstad, J., Masiello, C.A., Song, J.A., Peng, P., Mitra, S., Dunn, J.C., Hatcher, P. G., Hockaday, W.C., Smith, D.M., Hartkopf-Fröder, C., Böhmer, A., Lüer, B., Huebert, B.J., Amelung, W., Brodowski, S., Huang, L., Zhang, W., Gschwend, P.M., Flores-Cervantes, D.X., Largeau, C., Rouzaud, J.N., Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F.J., Gonzalez-Perez, J.A., de la Rosa, J.M., Manning, D.A.C., Ding, L., López-CapeL, E., 2007. Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. Glob. Biogeochem. Cycles 21 (3016), 1–18.

Hanke, U.M., Reddy, C.M., Braun, A.L.L., Coppola, A.I., Haghipour, N., McIntyre, C.P., Wacker, L., Xu, L., McNichol, A.P., Abiven, S., Schmidt, M.W.I., Eglinton, T.I., 2017. What on Earth Have We Been Burning? Deciphering Sedimentary Records of Pyrogenic Carbon. Environ. Sci. Technol. 51 (21), 12972–12980.

Harino, H., O'Hara, S.C.M., Burt, G.R., Chesman, B.S., Pope, N.D., Langston, W.J., 2003. Organotin compounds in Mersey and Thames estuaries a decade after UK TBT legislation. J. Mar. Biol. Assoc. U. K. 83 (1), 11–22.

Harrault, L., Milek, K., Jardé, E., Jeanneau, L., Derrien, M., Anderson, D.G., 2019. Faecal biomarkers can distinguish specific mammalian species in modern and past environments. PLOS ONE 14 (2), e0211119.

Hatcher, P.G., McGillivary, P.A., 1979. Sewage contamination in the New York bight. Coprostanol as an indicator. Environ. Sci. Technol. 13 (10), 1225–1229.

Huang, L., Zhang, J., Wu, Y., Wang, J., 2016. Distribution and preservation of black carbon in the East China Sea sediments: Perspectives on carbon cycling at continental margins. Deep-Sea Res. II: Top. Stud. Oceanogr. 124, 43–52.

Jones, O.A.H., Voulvoulis, N., Lester, J.N., 2002. Aquatic environmental assessment of the top 25 english prescription pharmaceuticals. Water Res. 36 (20), 5013–5022.

Jones, D., Vane, C.H., Lass-Evans, S., Chenery, S., Lister, B., Cave, M., Wilkinson, I., 2019. Geochemistry and related studies of Clyde estuary sediments. Earth Environ. Sci. Trans. R. Soc. Edinb. 108 (2–3), 269–288.

Kemp, A.C., Vane, C.H., Kim, A.W., Dutton, C.L., Subalusky, A.L., Kemp, S.K., Parnell, A. C., 2021. Fecal steroids as a potential tool for conservation paleobiology in East Africa. Biodivers. Conserv. https://doi.org/10.1007/s10531-021-02328-y.

Khan, S.N., Vane, C.H., Horton, B.P., Hillier, C., Riding, J.B., Kendrick, C., 2015. The application of δ13C, TOC and C/N geochemistry to reconstruct Holocene relative sea levels and paleoenvironments in the Thames Estuary, UK. J. Quat. Sci. 30 (5), 417–433.

Koelmans, A.A., Jonker, M.T.O., Cornelissen, G., Bucheli, T.D., Van Noort, P.C.M., Gustafsson, O., 2006. Black carbon: the reverse of its dark side. Chemosphere 63 (3), 365–377.

Langston, W.J., Pope, N.D., 1995. Determinants of TBT adsorption and desorption in estuarine sediments. Mar. Pollut. Bull. 31 (1–3), 32–43.

Langston, W.J., Gibbs, P.E., Pascoe, P.L., Chesman, B.S., Burt, G.R., Pope, N.D., J, M., 2000. Tributyltin (TBT) Impact in the Thames Estuary, NERC.

Langston, W.J., O'Hara, S., Pope, N.D., Davey, M., Shortridge, E., Imamura, M., Harino, H., Kim, A., Vane, C.H., 2012. Bioaccumulation surveillance in Milford Haven waterway. Environ. Monit. Assess. 184 (1), 289–311.

Leeming, R., Ball, A., Ashbolt, N., Nichols, P., 1996. Using faecal sterols from humans and animals to distinguish faecal pollution in recieving waters. Water Res. 30 (12), 2893–2900.

Loffker, D., Rombke, J., Meller, M., Ternes, T.A., 2005. Environmental fate of pharmaceuticals in water/sediment systems. Environ. Sci. Technol. 39 (14), 5209–5218.

Long, E.R., MacDonald, D.D., Smith, S.L., Calder, F.D., 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine estuarine sediments. Environ. Manag. 19 (1), 81–97.

Lou, L., Luo, L., Yang, Q., Cheng, G., Xun, B., Xu, X., Chen, Y., 2012. Release of pentachlorophenol from black carbon-inclusive sediments under different environmental conditions. Chemosphere 88 (5), 598–604.

Mason, C., Lonsdale, J., Vivian, C., Griffith, A., Warford, L., Hynes, C., Barber, J., Sheahan, D., Bersuder, P., Bakir, A., 2020. Review of Action Levels Used for Assessing Dredging and Disposal Marine Licences. Centre for Environment Fisheries and Aquaculture.

Morritt, D., Stefanoudis, P.V., Pearce, D., Crimmen, O.A., Clark, P.F., 2014. Plastic in the Thames: a river runs through it. Mar. Pollut. Bull. 78 (1–2), 196–200.

Mudge, S.M., Ball, A.S., 2006. Sewage. In: Morrison, R.D., Murphey, B.L. (Eds.), Environmental Forensics, Contaminant Specific Guide. Elsevier, Amsterdam, pp. 36–53.

Murray, D., Dempsey, P., Lloyd, P., 2011. Copper in the Thames estuary in relation to the special protection areas. Hydrobiologia 672, 39–47.

Nam, J.J., Gustafsson, O., Kurt-Karakus, P., Breivik, K., Steinnes, E., Jones, K.C., 2008. Relationships between organic matter, black carbon and persistent organic pollutants in european background soils: implications for sources and environmental fate. Environ. Pollut. 156 (3), 809–817.

Neupane, B., Kang, S., Chen, P., Zhang, Y., Ram, K., Rupakheti, D., Tripathee, L., Sharma, C.M., Cong, Z., Li, C., Hou, J., Xu, M., Thapa, P., 2019. Historical Black Carbon Reconstruction from the Lake Sediments of the Himalayan–Tibetan Plateau. Environ. Sci. Technol. 53 (10), 5641–5651.

Pope, N.D., Langston, W.J., 2011. Sources, distribution and temporal variability of trace metals in the Thames estuary. Hydrobiologia 672, 49–68.

Pratt, C., Warnken, J., Leeming, R., Arthur, M.J., Grice, D.I., 2008. Degradation and responses of coprostanol and selected sterol biomarkers in sediments to a simulated major sewage pollution event: a microcosm experiment under sub-tropical estuarine conditions. Org. Geochem. 39 (3), 353–369.

Rawlins, B.G., Vane, C.H., Kim, A.W., Tye, A.M., Kemp, S.J., Bellamy, P.H., 2008. Methods for estimating types of soil organic carbon and their application to surveys of UK urban areas. Soil Use Manag. 24 (1), 47–59.

Rhodes, A.H., Carlin, A., Semple, K.T., 2008. Impact of black carbon in the extraction and mineralization of phenanthrene in soil. Environ. Sci. Technol. 42 (3), 740–745.

Rowland, S.J., Sutton, P.A., von der Lühe, B., Volkman, J.K., Vane, C.H., Ingram, S.N., Dunn, C., Claridge, D., 2020. Ambrein: a minor, but common constituent of mammalian faeces? Nat. Prod. Res. 1–6.

Scrimshaw, M.D., Lester, J.N., 1997. Estimates of the inputs of polychlorinated biphenyls and organochlorine insecticides to the River Thames derived from the sediment record. Philos. Trans. R. Soc. Lond. A 355, 189–212.

Shantha, N.C., Napolitano, G.E., 1998. Lipid analysis using thin-layer chromatography and the Iatroscan. In: Hamilton, R.J. (Ed.), Lipid Analysis in Oils and Fats. Springer US, Boston, MA, pp. 1–33.

Simpson, S.L., Batley, G.E., Charlton, A.A., 2013. Revision of the ANZECC/ARMCANZ Sediment Quality Gudielines. CSIRO, Lucas Heights, NSW Australia.

Sun, X., Peng, P.a., Song, J., Zhang, G., Hu, J., 2008. Sedimentary record of black carbon in the Pearl River estuary and adjacent northern South China Sea. Appl. Geochem. 23 (12), 3464–3472.

Tolou-Ghamari, Z., Zare, M., Habibabadi, J.M., Najafi, M.R., 2013. A quick review of carbamazepine pharmacokinetics in epilepsy from 1953 to 2012. J. Res. Med. Sci. 18 (Suppl. 1), S81–S85.

Tye, M.A., Rushton, J., Vane, C.H., 2018. Distribution and speciation of phosphorus in foreshore sediments of the Thames estuary. Mar. Pollut. Bull. 127, 182–197.

UN-EP, 2009. In: Rotterdam Convention-Decision Guidance Document-Tributyltin Compounds, Rotterdam, Netherlands, p. 29.

Vane, C.H., Kim, A.W., McGowan, S., Leng, M.J., Heaton, T.H.E., Kendrick, C.P., Coombs, P., Yang, H., Swann, G.E.A., 2010. Sedimentary records of sewage pollution using faecal markers in contrasting peri-urban shallow lakes. Sci. Total Environ. 409 (2), 345–356.

Vane, C.H., Chenery, S.R., Harrison, I., Kim, A.W., Moss-Hayes, V.M., Jones, D.G., 2011. Chemical signatures of the anthropocene in the Clyde estuary, UK: sediment-hosted pb, 207/206Pb, total petroleum hydrocarbons, polyaromatic hydrocarbon and polychlorinated biphenyl pollution records. Phil. Trans. R. Soc. A 369, 1085–1111.

Vane, C.H., Beriro, D.J., Turner, G.H., 2015. Rise and fall of mercury (Hg) pollution in sediment cores of the Thames estuary, London, UK. Earth Environ. Sci. Trans. R. Soc. Edinb. 105 (4), 285–296.

Vane, C.H., Lopes, D.S., Kim, A.W., Moss-Hayes, V., Fordyce, F.M., Bearcock, J.M., R.A, 2019. Peristent organic pollutants (PAH, PCB, TPH) in freshwater, urban tributary and estuarine surface sediments of the River Clyde, Scotland, UK. Earth Environ. Sci. Trans. R. Soc. Edinb. 108 (2-3)), 299–314.

Vane, C.H., Kim, A.W., Moss-Hayes, V., Turner, G., Mills, K., Chenery, S.R., Barlow, T.S., Kemp, A.C., Engelhart, S.E., Hill, T.D., Horton, B.P., Brain, M., 2020a. Organic pollutants, heavy metals and toxicity in oil spill impacted salt marsh sediment cores, Staten Island, New York City, USA. Mar. Pollut. Bull. 151, 110721.

Vane, C.H., Turner, G.H., Chenery, S.R., Richardson, M., Cave, M.R., Terrington, R., Gowing, C.J.B., Moss-Hayes, V., 2020b. Trends in heavy metals, polychlorinated biphenyls and toxicity from sediment cores of the inner river Thames estuary, London, UK. Environ Sci Process Impacts 22, 364–380.

Vane, C.H., Kim, A.W., Beriro, D., Cave, M.R., Lowe, S.R., Lopes dos Santos, R., Ferrari, A.M.P.J., Colins, C., Nathanail, C.P., Moss-Hayes, V., 2021. Persistent organic pollutants in urban soils of Central London, England, UK: measurement and spatial modelling of black carbon (BC), petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB). Adv. Environ. Eng. Res. 2 (2), 1–42.

Volkman, J.K., Nichols, P.D., 1991. Applications of thin layer chromatography-flame ionization detection to the analysis of lipids and pollutants in marine and environmental samples. J. Planar Chromatogr. 4, 19–26.

Waite, M.E., Waldock, M.J., Thain, J.E., Smith, D.J., Milton, S.M., 1991. Reductions in TBT concentrations in UK estuaries following legislation in 1986 and 1987. Mar. Environ. Res. 32 (1–4), 89–111.

WHO, 1998. Guidelines for drinking-water quality. In: Addendum to Vol. 2. Health Criteria and Other Supporting Information Geneva, 2nd ed.

Yang, Y., Hunter, W., Tao, S., Gan, J., 2009. Effects of black carbon on pyrethroid availability in sediment. J. Agric. Food Chem. 57 (1), 232–238.

Yang, W., Lampert, D., Zhao, N., Reible, D., Chen, W., 2012. Link between black carbon and resistant desorption of PAHs on soil and sediment. J. Soils Sediments 12 (5), 713–723.

Zhou, J., Broodbank, N., 2014. Sediment-water interactions of pharmaceutical residues in the river environment. Water Res. 48, 61–70.